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Operational and Environmental Consequences of Large Industrial Cooling Water Systems

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Preface

> Setting the scene and the need for integrated science for the operational and environmental consequences of large industrial cooling water systems

Industries worldwide have long used and often even abused water: it is a necessary resource but, by their activities, they have affected the quality of that water and the health of organisms inhabiting it. In particular, its major use has been as cooling water required in large amounts by power generation, steel and iron, paper and pulp and oil industries. These industries abstract water from natural water bodies in very large amounts, often up to 75 cumecs (m^3/s)—the flow rate of a moderately large river! The abstracted water often has to be treated with chemicals to combat operational problems such as biofouling and corrosion. Moreover, the withdrawal and subsequent discharge of large amounts of water may produce significant impacts on the receiving water body. Organisms, such as plankton, mobile invertebrates and finfish which may be of commercial importance, living in the discharge zone (the receiving waters) or taken in (impinged and entrained) with the cooling water are continuously subjected to a combination of mechanical, thermal and chemical stressors.

There are many ways in which, foremost, human industries affect the natural aquatic systems and, second, by which the natural systems affect human industries. We can call the first of these “operational problems”, i.e. the way in which the natural aquatic system may hinder production by a plant, and the second “environmental problems” whereby the health of the system, in some way, has been reduced. For example, for the generation of power using oil, gas, coal or nuclear sources we have built power plants adjacent to water bodies where that water is used for direct cooling. Those power plants can be regarded as having a behaviour within their environmental systems and so that behaviour requires to be understood. In turn, the natural system also has a behaviour and so it is also important to understand that behaviour and the way it affects the natural system. Coupled with these is the need for a good scientific understanding of the ecology of the aquatic system, the hydrodynamics of the system, and the management and socio-economic system within which the power plant operates. The latter, therefore, includes the costs of tackling any problems caused *on* the plant by marine organisms (biofouling) and caused by the plant on the marine system. Hence, there is the need for a synthesis of the operational and environmental issues relating to industrial cooling water systems.

The largest concerns for those involved in either production/operationally related or environmental-related problems concerning cooling water of these systems are,

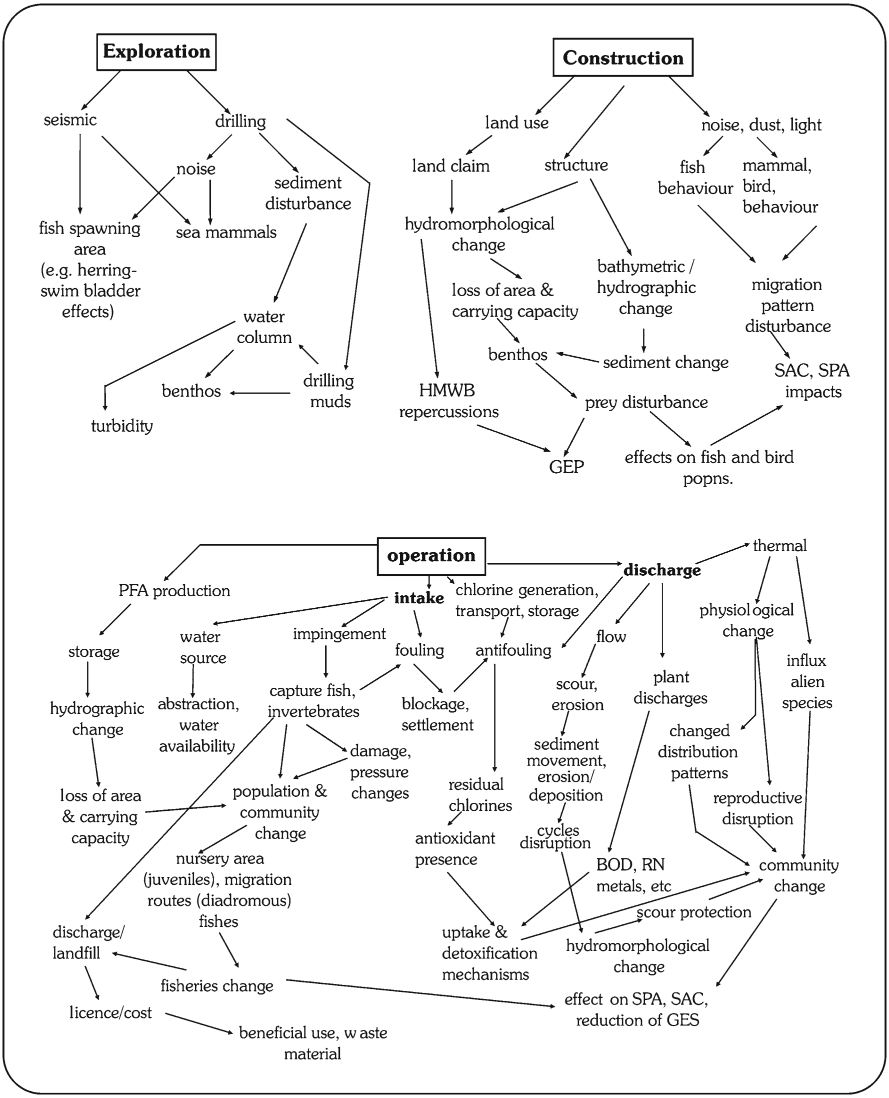

Fig. 1 Conceptual Models (Horrendograms) showing the environmental and operational aspects concerned with the exploration, construction and operation of coastal power plants (the acronyms used relate to the implementation of European Directives, see McLusky and Elliott 2004 for further details)

first, impingement, defined as the trapping of larger material such as fish and mobile invertebrates before they get the chance to pass through the plant. Second, there is entrainment or the taking into the plant of smaller organisms and the creation of surfaces for the settlement of those smaller organisms and silts thus even creating a self-sustaining system within the plant. Third, there is the fate and effects of water and materials discharged from the plant, especially any thermal plume and its constituents. In addition to heat; we may even get scouring of the seabed adjacent to the discharge. We can summarise and communicate those aspects as a set of interlinked features in a "horrendogram", i.e. a conceptual model showing all the aspects which need to be considered by operational and environmental managers concerned with industrial cooling water systems (Fig. 1).

As mentioned above, biofouling inside cooling water systems is the result of the settlement of larval organisms on the surfaces inadvertently provided by the industrial plants. A power plant needs an adequate way of monitoring its surfaces not least because of the reduction in plant efficiency or the need to determine if any antifouling measures have been successful. Hence the cooling water system has to be designed in relation to the magnitude of the fouling pressure and that design itself needs to minimise the fouling or produce an easier solution to the problem once it has occurred.

There is a known sequence of fouling, whereby surfaces are prepared by slimes and micro-organisms, yeasts etc. which could both increase corrosion, so-called MIC (microbially influenced corrosion), and also makes them mimic normal settlement surfaces; in essence the industrial concrete and metal surfaces acting as a hard substratum similar to the rocky shore. There then follows a defined sequence of colonisation, with each organism having a preferred set of conditions. For example, barnacles prefer fast flowing waters and thus clean surfaces with only a microbial slime layer, whereas mussels may prefer slower, more turbulent systems and so will colonise after other organisms have already settled. Hence, there is the need for a good understanding of the biology of the fouling organisms and the way in which antifouling measures can control each taxon. An intimate knowledge of the biology of the fouling organisms is required. For example barnacles require a neighbour to be adjacent because of their mode of reproduction involving internal fertilisation. Hence, there is the need to understand the fundamental issues and mechanisms of microbial fouling and corrosion and thus understand microbial as well as macrobial systems.

The control of biofouling by chemical means, usually summarised as "chlorination" and other control methods in industrial cooling water systems is a major issue for environmental and operational managers. The accepted means of controlling fouling is by adding biocides, very often oxidising (halogenated) compounds. These may be added as liquid (sodium hypochlorite), transported into the plant by lorries, or the chlorine may be produced on-site in specific Electro-Chlorination Plants (ECPs) where the biocide is generated by electrolysis of seawater prior to reinjection. Hence, there is the need for a good understanding of chlorination chemistry and the resultant ecotoxicology of the marine cooling water systems (e.g. Taylor 2006). Once chlorination is in operation, then the production of organic halogenated by-products, e.g. trihalomethanes, chloroform, bromoform, etc., in addition to the oxidising residuals can create environmental concerns in the receiving waters. Given the costs of biofouling treatment, yet again affecting the economic viability of the operation, power plants require technological and economically beneficial solutions to biofouling and biocorrosion control as well as environmentally sustainable solutions. For example, by adjusting the timing and magnitude of chlorination, whether as a pulse or as continuous dosing, in relation to the peak times of settlement by fouling organisms, a more cost effective and optimal solution can be produced.

The use of biocides is in itself a difficult environmental choice because of chlorinated by-product formation where some of the products are listed chemicals which may be prohibited for discharge. There is then the requirement for ecotoxicological assessments to determine the scale of those potential problems. Therefore, alternative methods of cooling are often sought. A rather old-fashioned method is to heat up the intake/outlet conduits, by plant internal recirculation, where the design of the plant allows it for heating up the water, the so-called thermoshock method. New advanced technological methods include the use of "BioBullets" composed of a toxic compound coated with an attractive nutrient for bivalves on micro scale.

In addition to the operational problems caused by entrainment, operational and environmental managers are required to address environmental concerns relating to the organisms entrained, by definition those sufficiently small to get through the initial screens, often with a mesh of 1 cm^2, and then into the body of the power plant. Hence, this includes the permanent members of the plankton, the holoplankton, and also the dispersing stages of marine organisms, the meroplankton including those of fishes (the ichtyoplankton). While there may be billions of such organisms in the water column and their populations may be spatially and temporally variable, it is still necessary to detect whether the cooling water intake is having an effect. However, that inherent variability, what may be called noise in the system, makes it difficult to detect an effect, the signal within the so-called signal-noise ratio.

Following its passage through condensers inside power plants, the discharge of the cooling water then has the potential for changing the characteristics of the receiving waters. As mentioned above, this may include the introduction of chlorinated by-products but also, and most noticeably, raising the temperature and in which case those waters become suitable for colonisation by any organisms (invaders) adapted to the conditions. For example, the clam *Corbicula* uses outlet channels in winter time as refuge for surviving and, in Southampton Water (UK) a population of the invasive clam *Mercenaria mercenaria* has become established near a power plant discharge. Thus invasive species have implications for industrial cooling water systems, which provide changed conditions in the receiving waters, for example by raising the temperature, and then those waters become suitable for colonisation by any organisms which can tolerate the conditions. Invasive species such as the zebra mussel *Dreissena polymorpha* have become a nuisance by settling inside cooling water systems in large numbers.

After passage through the industrial plant, the cooling water discharge often produces a thermal plume, in which the water may be 7–10°C higher than ambient. The characteristics and behaviour of that plume, for example, in either attracting organisms or moving over areas of nature conservation importance, become causes for concern. Of course, if the plume is then entrained by the cooling water intake, then this is a production problem for the plant which can reduce its efficiency. The resultant thermal plume may affect habitats depending on the thermal tolerances of the organisms and in cases where the receiving areas are of nature conservation importance then this could lead to breaching of environmental and conservation regulations. For example, many power plants are in estuaries which include large intertidal areas which support internationally important populations of wading birds and juvenile fishes (McLusky and Elliott 2004). Any effects of the plume on either the invertebrate prey or predators of those sites thus become a cause for concern to be addressed by environmental and operational managers. For example, given that many organisms have temperature thresholds which determine times of spawning increases of temperature could lead to warm-water spawners breeding earlier and cold-water spawners delaying their reproduction.

Perhaps the most high-profile effect of power plants and that which attracts most adverse press coverage is fish impingement, the ability of the plant to suck in fish and mobile invertebrates (and weeds and garbage). Indeed this problem may reach such proportions that we can describe power plants as "stationary trawlers"! The extent of this depends on fish populations in the area, their migrations particularly onshore or for breeding and at times such as the winter when the power plant and its cooling system may be working at a maximum (Elliott and Hemingway 2002). In addition to this being a potential problem for the natural populations in the source water areas, this is also a production problem for the power plant as the impinged fish have to be either returned to the waters, often dead and thus creating both an organic discharge from the plant and public relations problem of having dead fish washed up near the plant, or disposed of to landfill, in itself a costly exercise given that the biological material is highly organic and thus has the potential to affect watercourses. In some countries, disposal to landfill is taxed and thus expensive for the power plant. Hence, there is the need to assess the technologies dealing with impingement and disposal of impinged material and for countries to learn from one another.

As indicated above, there is the need to determine the behaviour of the power plant and any materials emanating from it within a context of the natural system. A knowledge of this behaviour will be required as a background to cooling water discharge guidelines in each country. Such guidelines may follow the "monitoring, modelling and management" framework—indeed, business would emphasise that you cannot manage a problem unless you can measure it and you cannot predict the effects of doing something unless you can model it. Recent advances in numerical modelling, such as through advanced 3D modelling are therefore important in this context. There is the need to use numerical modelling to determine the behaviour of the plume and thus the probability that it will affect certain areas around the plant and in the receiving waters. There is also the need to measure impingement and entrainment and, where possible, to model these as a way of providing predictive support to the designers and managers of cooling water systems.

It is axiomatic that any human activity which has the potential to adversely affect the natural environment requires permissions. This lies within a legal and administrative framework, thus including discharge consents, permits, licences and authorisations and environmental assessments, and requires environmental protection agencies, nature conservation bodies and ministries of the environment to enact and police these. Within political blocs such as the European Union, such laws and regulations may be at a local, regional, national and European level (including the Water Framework Directive, the Habitats and Species Directive and the Integrated Pollution Prevention and Control Directive, e.g. Apitz et al. 2006). Some of these are mirrored by the US Clean Water Act and corresponding legislation in many other countries. Countries are also obliged to follow international obligations such as the need to protect systems sustainably under the Convention for Biological Diversity or the UN Conference on Environment and Development. Of course these follow from the political will in any state to decide if the environmental consequences are sufficient to outweigh the industrial and social advantages. This regulatory and political context is what we may call environmental governance such that industries such as power plants operate within what is called a PEST environment, which includes the prevailing political, economic, societal and technological regime.

Hence by taking together all of the above aspects, we can emphasise that we need sustainable solutions to the problems created by placing cooling water systems in natural environments. More importantly, as discussed above, those solutions are required to be sustainable and hence we take the view that for them to be sustainable they have to fulfil "*the 7-tenets*"—that our actions should be:

- Environmentally/ecologically sustainable
- Technologically feasible
- Economically viable
- Socially desirable/tolerable
- Legally permissible
- Administratively achievable and
- Politically expedient (Mee et al. 2008)

Each of these aspects requires good and adequate science upon which both operational (production) management and environmental management can be based. The science has to be fit-for-purpose, not least because it is expensive and also the consequences of unforeseen events may also be expensive. We need the science to prioritise our need for knowledge—to separate the "nice to know" from the "need to know" and to determine the cost-benefit of the work (i.e. what "bang do we get for a buck"). We need to understand the sequence of understanding (now, mid, long term), our ability to do it (now, mid, long term) and the applicability of the knowledge (single- or multiple site specificity). We need to be sure of our basic understanding—do we have conceptual models leading to hypothesis generation and testing leading to what if? and so what? questions; what are the effects of power plants on marine/estuarine environment and vice versa; what is the impact on dominant processes, structure and functioning—understanding the reliance, resistance, recovery, hysteresis, etc. of natural systems; do these aspects affect the carrying capacity of systems—is the carrying capacity reduced for the biota and other human activities and exceeded for human activity such as power generation, and finally can we understand the operational and environmental consequences of cooling water discharges against what we may call the "exogenic unmanaged pressures" such as climate change.

All of this requires adequate monitoring (including surveillance monitoring, compliance/condition monitoring, investigative/diagnostic monitoring—see Gray and Elliott 2009) and an understanding of the relative roles and adequacy of survey, experimental and modelling approaches—especially to understand critical elements on temporal and spatial scales (in the near and far field/time). We can learn from elsewhere and thus quantify the level of certainty and uncertainty (what we know and what we don't know ("do we know what we don't know"?)—hence the need for "Gap Analysis"). We then, of course, need to use this science in management (and vice versa) by determining measures for mitigation/amelioration/compensation (the latter of system/habitats/components/users/uses), of defining standards/objectives/indicators and their use/value/applicability. Most importantly, we need to carry out impact assessments, especially related to legislative requirements, but above all ensure that our ability to produce "economic goods and services", such as industry and power generation, can be maintained while at the same time protecting "ecological goods and services".

This preface shows the enormity of our task but we have much background information on which to build. Previously, there have been attempts to address the operational issues related to industrial cooling water systems with primary emphasis on biofouling and its control. Likewise, there have been some attempts to highlight environmental issues arising out of cooling water intake and discharge. However, there has been no attempt to comprehensively address the two issues together, even though they are inextricably linked. This volume aims to integrate two aspects and present the state-of-the-art knowledge, by bringing together key researchers, each of whom has been active in this area over recent decades.

England, UK Michael Elliott

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Contents

Chapter 1
Operational and Environmental Issues Relating to Industrial Cooling Water Systems: An Overview

Vayalam P. Venugopalan, Sanjeevi Rajagopal, and Henk A. Jenner

1 Introduction

Water is acknowledged to be one of the most essential commodities for almost all kinds of industrial activity. Among the various industrial uses of water, its use as a heat removal fluid is of foremost importance. Thermoelectric generation, which is but one of the several industries that use water, accounts for more than 50% of all such use. The industrial use of water, especially in rapidly developing countries, is expected to grow further and aggravate an already precarious situation concerning availability of and demand for water. Accelerated growth in the power generation industry alone will account for a major share of this demand. A typical thermal power plant of 2,000 MWe capacity, on an average, needs cooling water at the rate of 65 m^3/s; the requirement would be about 50% more in the case of a nuclear power plant (Langford 1990). Most of this water is used for low-energy steam condensation.

The cooling water circuit of an electrical power plant can be of either cooling tower-aided recirculating or once-through type. In a once-through system, the water is used for cooling just once, after which it is discharged back into the source water body. On the other hand, in a recirculating system, a captive volume of water is repeatedly reused for heat removal. In a typical power plant (nuclear or fossil fuel-powered), electricity is generated by boiling high purity water to produce high

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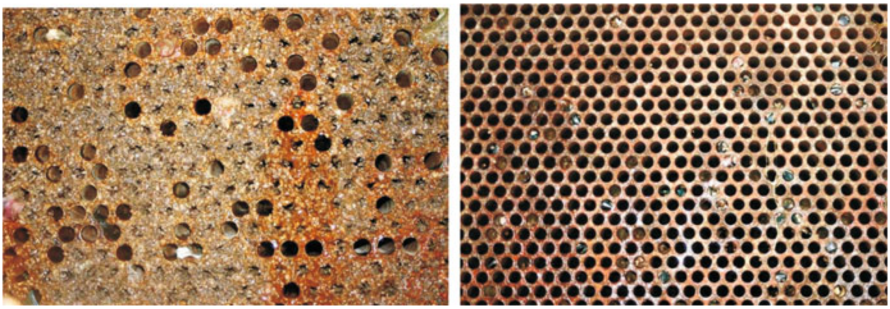

Fig. 1.1 Biofouling on condenser tube sheet heavily fouled (*left*) and relatively clean (*right*) of a coastal power plant

pressure steam. The steam is allowed to expand in a turbine, driving a generator and producing electricity in the process. The steam leaves the turbine and enters the condenser. The condenser has a large heat transfer surface for efficient condensation of the steam using large volumes of cooling water. The condenser removes the heat of condensation of steam and rejects it directly to the cooling water. This represents a critical step in the conversion of energy using steam cycle. Decreasing the steam pressure at the turbine exit is an important strategy for improving steam cycle efficiency. Efficient heat removal and maintenance of lower condenser pressure require good circulation of the cooling water. However, water flow through the condenser and consequent heat transfer across the heat exchanger surface are compromised by biological growth, both on the heat exchanger surfaces (e.g. condenser biofilm) and elsewhere in the cooling water circuit (e.g. macrofouling in the pre-condenser sections, intake systems, conduits, and pipelines Fig. 1.1). This constitutes an important operational problem for the utility. The economic penalties associated with heat exchanger fouling are generally of the following type: (1) increased capital costs (due to over-surfacing of heat exchangers and over-sizing of equipment like pumps and fans, provision for on-line/off-line cleaning equipment, use of specialty materials), (2) increased maintenance costs (due to increased pressure drop, chemical treatment), (3) loss of production (due to downtime or operation at reduced capacity) and (4) energy losses (due to fouling build-up on surfaces) (Bott 1995; Raghavan 1996).

2 Operational Problems

Microbial and macroscopic growth on material surfaces is a problem known to man ever since materials were put to use in the aquatic milieu. Such growth, variously described as slime, biofilm, microfouling, macrofouling and biofouling, depending on the nature of growth and technical background of the person, not only affects heat transfer properties of the surface but also can considerably impede flow and potentially jeopardize the integrity of the underlying material.

Deposition of micro-organisms on metallic surfaces can lead to an increase in the corrosion rate of these metals. This form of corrosion is called microbially influenced corrosion (MIC) (Fig. 1.2). The economic impact of MIC can be enormous. For example, downtime for large power stations is often of the order of $1,000,000 per day. In many cases, corrosion-resistant alloys have experienced rapid, through-wall penetration, when exposed to good quality water from rivers, lakes, estuaries or ponds—environments that would normally be considered benign. Power plants have been required to modify, repair, or replace such lines in their entirety. Therefore, such biological growth on material surfaces is assiduously kept at bay by operators by resorting to the use of various antifouling techniques. Repair or refurbishment costs for large nuclear service water systems can be $30,000,000 or more (Licina and Borenstein 1993; Venkatesan and Murthy 2009). Estimations show that 20% of all corrosion damage in heat exchangers is caused or influenced by micro-organisms (Flemming et al. 2009).

In general, fouling mechanisms, whether biological or non-biological, involve the following sequences: initiation of fouling, transport to the surface, attachment to the surface, removal from surface and ageing of deposit (Raghavan 1996). Biological fouling is generally initiated by the spontaneous adsorption of a layer of organic substances at the surface (Flemming 2009). As a consequence, a concentration

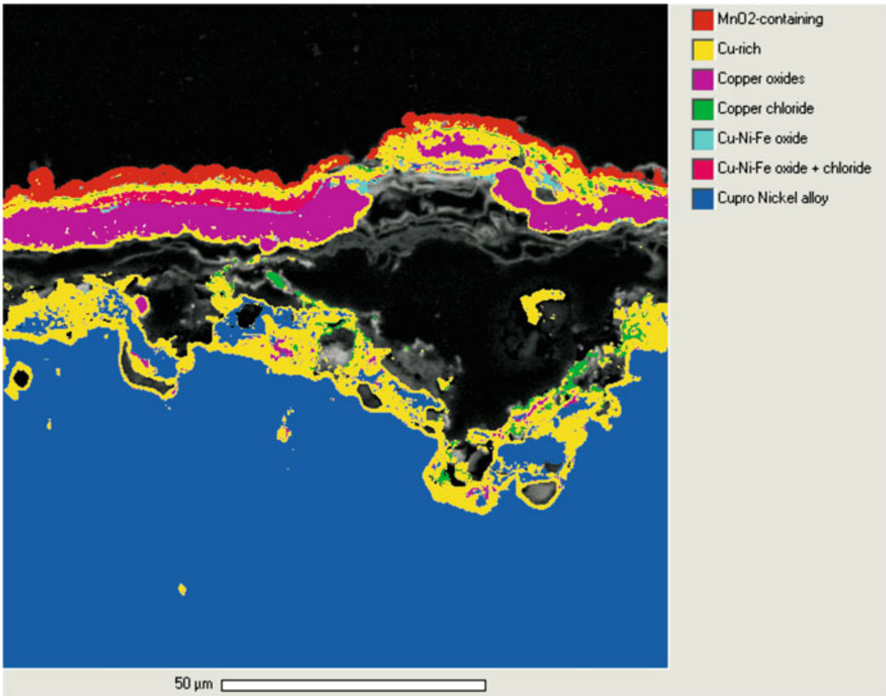

Fig. 1.2 Kemphase recording of MIC of Cu—Ni alloy tube (by courtesy of KEMA)

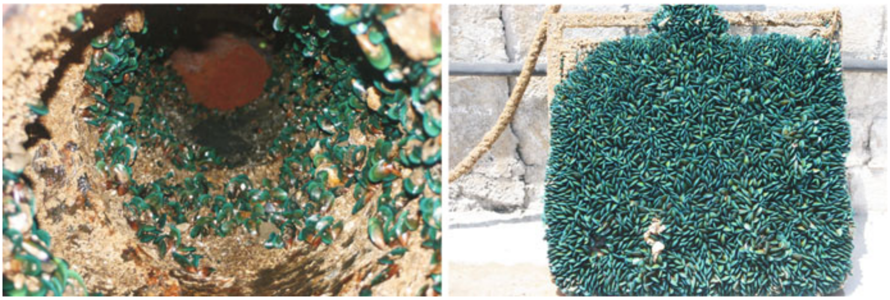

Fig. 1.3 Fouling by green mussels (*Perna viridis*) inside a seawater intake pipe (*left*) and on test coupons placed in the sea (*right*)

gradient of nutrients is generated at the solid–liquid interface and motile bacteria are chemotactically attracted to the surface, which initiates the process of surface colonization. The initial colonizers reinforce their attachment with the help of copious amounts of exopolymeric substances (Venugopalan et al. 2005). What follows is a complex process of further attachment of a diverse group of bacteria, cyanobacteria, protists, fungi and higher invertebrates. There is evidence for the important role played by chemical communication among the colonizing species, including eavesdropping by higher organisms, intent on disrupting the process (Manefield et al. 1991; Shiner et al. 2005). With the passage of time, the thin innocuous looking slime film develops into a formidable biological accretion, consisting of such diversity of organisms as hydroids, polychaetes, barnacles, mussels, oysters and ascidians. Though the number of species constituting a given biofouling community may be large, growth in industrial cooling systems tends to be dominated by just a handful of species (Venugopalan and Narasimhan 2008) (Fig. 1.3).

3 Biofouling

Biofouling in cooling water systems includes both microbial fouling (especially in condenser tubes, other heat exchangers and pipe surfaces) and macrofouling (relatively more prevalent in large diameter pipes, screens, pump chambers, etc.). There is a tendency to consider both these types of fouling together in our approach to control them. However, it must be emphasized that they need to be treated as two different but related phenomena and, accordingly, need different approaches and strategies (Mattice 1985). Microbes and macroscopic organisms tend to respond differently to biocides, and therefore, biocide type, concentration, dosing frequency and contact time need to be adjusted accordingly, in order to get best results. For example, bacteria ensconced in a polymer matrix inside a biofilm may not be affected to the same extent by chlorine as a freshly settled invertebrate larva. In the case of the former, a biodispersant may be required to be dosed to ensure that the

Fig. 1.4 Blockage of the seawater pipe at a power station by biofouling growth

biocide has access to the required target. On the other hand, an adult mussel settled inside a seawater intake pipe may not be affected by a relatively high dose of chlorine, as long as it can keep its two valves tightly shut (Jenner et al. 1998; Rajagopal et al. 1991).

The distinction between microfouling and macrofouling is important from the point of view of the economic penalties imposed by them. Microbial slime has the ability to substantially reduce heat transfer across surfaces, increase pumping costs due to its visco-elastic nature and enhance corrosion rate of the underlying metal/alloy by altering the surface electrochemical properties. Macrofouling, on the other hand, causes blockage of pipes, screens and condenser tubes. It can cause significant reduction in the seawater flow in intake tunnels and culverts by reducing the effective diameter and increasing the fluid frictional resistance (Fig. 1.4). Mussel shells lodged in condenser tubes can cause perforation of the tubes, resulting in contamination of the boiler feed water by seawater in-leakage and, ultimately, more serious problems such as boiler corrosion and turbine blade damage. Massive failure of condenser tubes caused by mussel fouling has been reported from power stations (Turnpenny and Coughlan 1992). Owing to seasonality in the reproductive behaviour of higher organisms, macrofouling severity often tends to follow a temporal pattern, which may be less conspicuous in the case of microbial fouling.

A number of factors influence the type and extent of biofouling that develops inside a system. Apart from geographical location, water temperature and local hydrobiological characteristics, system-related parameters such as flow, substratum and cooling circuit geometry play important role in the severity of the biofouling problem (Jenner et al. 1998). It is due to such differences that biofouling tends to be site-specific. Hence, management of macrofouling issues requires certain amount of finesse in one's approach and quite often it is seen that a given control strategy that works fine at a station is found wanting at a different one.

All the major fouling organisms have free swimming larval stages in their life cycle, which aid their dispersal and colonisation of new surfaces/areas. The larval size is very small (less than 1 mm in many cases) and filtration as a means of biofouling prevention is generally impractical, given the large volumes of water involved. Being endowed with fine chemosensory machinery, the larvae are capable of choosing their final place of settlement and metamorphosis with a fair degree of discretion. In fact, many larval forms are quite fastidious and continue in their swimming mode without settling until a suitable substratum is encountered (Pawlik 1992). A very pragmatic approach to biofouling control, therefore, would be to create inside the cooling circuit an environment that is inimical to competent (i.e., physiologically ready to settle) larvae, so that they do not settle but transit through the cooling water system. It may be mentioned that low-dose continuous chlorination, which is generally followed at many power stations, is based on such a rational approach (Turnpenny and Coughlan 1992). The chlorine residual is kept low (generally about 0.2–0.4 mg/L), just enough to ensure that the incoming larvae can sense the presence of chlorine, but are not killed by it. However, to be effective, the dosing needs to be carried out on a continuous basis, with no breaks in between, as long as larvae are present in the water body. Once settled, most of the fouling organisms do not have the ability to detach from the surface and move away. Apart from low-dose continuous chlorination, other dosing methods such as pulse chlorination and targeted chlorination have been developed with the objective to achieve better protection, while maintaining chlorine discharge levels within stipulated limits (Polman and Jenner 2002). Pulse chlorination exploits the behavioural idiosyncrasies of mussels, whereby mussels are made to perceive short high frequency pulses of chlorination as continuous chlorination. Using this method, it has been demonstrated that good mussel control could be achieved while the chlorine inventories are kept considerably low. Targeted chlorination employs relatively high doses to selected areas of condensers, which allows them to be treated with residuals that are normally not possible because of discharge limits. Since only a fraction of the entire tube bundle is treated, the overall discharge levels of chlorine are kept within limits.

Currently adopted antifouling measures in cooling water systems are centred on the use of injectable biocides, though some plants employ mechanical cleaning or thermal treatment as supplementary measures. Among the biocides, chlorine has come to occupy the centre stage, owing to its broad-spectrum activity, ease of use and availability. Different utilities use different forms of chlorine; mostly it is used as chlorine gas or as sodium hypochlorite. A growing number of plants find in-situ chlorine generation by electrolysis of seawater a convenient means of chlorination, as it gets rid of on-site and off-site safety issues related to transport and storage of large amounts of liquid or gaseous chlorine. In-situ generation is practiced also in the case of emerging biocides such as chlorine dioxide. Such biocides are gaining acceptance, and in coming years, one may see more and more utilities switching to them, because of advantages such as better efficacy and reduced toxic by-product formation.

As currently used antifouling strategies in cooling water systems mostly depend on injectable biocides, there is a potential for the cooling water effluents released from industrial units to cause environmental harm, depending on the biocide employed. Apart from antifouling chemicals, the condenser effluents also contain other chemicals such as anticorrosion chemicals, antiscalants and biofilm dispersants. It must be mentioned that such chemicals tend to be in use more in the case of recirculating systems. Nevertheless, condenser effluents from once-through systems also contain substances other than biocides. Examples are dissolved copper released from condenser tubes and ferrous sulphate, which is often added to protect condenser tubes made of cuprous alloys (Venkateswarlu 1996).

4 Environmental Problems

The fact that biofouling in cooling water systems is a universal phenomenon makes it imperative for all utilities to resort to biofouling control measures of one type or other. From an environmental perspective, abstraction of large volumes of water and its subsequent discharge (as a heated stream of water containing chemical additives) into a receiving water body constitutes an issue that merits careful analysis, as it can potentially harm the environment (Glasstone and Jordan 1980; Langford 1990; Bamber and Seaby 2004; Jiang et al. 2008; Chuang et al. 2009). It must be remembered that the efficiency of thermoelectric power generation through the steam cycle (<40%) is such that the process results in a large amount of waste heat being rejected into the water body acting as the heat sink. Power plants with a once-through cooling system require more water than those using the recirculating type of cooling system. Owing to dwindling freshwater resources, there is a tendency among utilities to locate new plants at coastal locations (Fig. 1.5).

Coastal electric power plants, as mentioned above, must use large quantities of seawater for condenser cooling, resulting in large amount of heat being rejected into the coastal marine environment. In addition, the effluents also contain biocides such as chlorine, added to the incoming cooling water to thwart biofouling (Schubel and Marcy 1978; Langford 1990; Choi et al. 2002; Taylor 2006). The intake system of a power plant withdraws from the source water with the associated biota and passes it through a series of mechanical devices (screens, strainers, pumps, etc.), before it is sent to the condensers. Intake systems are provided with strainers to keep large organism from entering the cooling water inlet. This causes a substantial number of fishes to get impacted onto solid structures—a phenomenon known as impingement—often leading to possible injury and death (Greenwood 2008). Moreover, a large number of small organisms, especially planktonic and weak-swimming nektonic species, pass through the strainers into the circuit—a phenomenon known as entrainment (Mayhew et al. 2000; Bamber and Seaby 2004). Entrained organisms include both holoplankton (e.g., copepods) and meroplankton (e.g., eggs and larvae of benthic invertebrates, fishes, juvenile shrimps) (Dempsey 1988; Lewis and Seegert 2000; Venugopalan 2002). These organisms are invariably subjected to a variety of physical and chemical stresses and are ultimately returned to the receiving water body along with the effluents. Apart from this, organisms (e.g., benthic organisms) living at the outfall site could be affected due to exposure to the thermal effluents/thermal plume from the plant.

Fig. 1.5 A nuclear power plant being constructed close to the seacoast. Cooling water availability is a major criterion that influences power plant siting

Temperature affects almost all properties of water, and hence, the discharge of heated effluents can potentially impact the local environment. Though warm water discharge does not affect humans directly, thermal pollution has become important due to increased general awareness regarding environmental issues and the urge to halt further ecological degradation caused by rapid expansion in energy generation. With increasing temperature, the density, viscosity, surface tension and oxygen solubility are reduced. Temperature increase can also directly affect the metabolic rate or, in extreme cases, cause the death of organisms. Apart from direct effects caused by thermal shock, chronic exposure to slightly elevated temperature can also adversely affect the organisms. Such sublethal effects on reproductive or behavioural aspects are less understood as they are far more subtle than the direct effects. Nevertheless, they are important, as they have the potential to impact the ecosystem in the long run. Studies have shown that sensitive organisms near the condenser discharge zone of a power plant may move away to safer areas, thereby affecting the species distribution (Israel et al. 2012). Sublethal effects of temperature rise may include such effects as shift in population structure and increased susceptibility to predators and parasites (Parker 1979; Langford 1990).

It is clear from the above that operation of the cooling water systems of power stations entails some environmental risks and, therefore, such operation comes under the purview of state regulatory regime. One of the environmental effects is perceived to be thermal pollution, which can be defined as degradation of water quality by any process that changes the ambient water temperature. Thermal pollution may cause direct thermal shock, changes in dissolved oxygen content of water and affect the distribution of organisms in the impacted area. Water has the unique capacity to absorb large amounts of thermal energy, entailing only minor changes in its temperature. Hence, most aquatic organisms are naturally endowed with enzyme systems that operate in a relatively narrow range of temperature. Such stenothermic organisms can be affected by sudden temperature changes that are beyond their tolerance limits. Regulatory regimes in many countries require that the cooling water discharges from power plants be designed to minimize the impact on the receiving water body in terms of thermal, chemical and mechanical effects. Accordingly, in many countries, there is provision for a mixing zone into which the discharges are let out. The spatial extent of the mixing zone varies, but the discharge criteria are enforced at the boundary of the mixing point. With regard to fish impingement, research work has shown that it is possible to design systems that return impinged fishes safely back to the receiving water body, without imparting any significant damage to them or to drive fishes away from the intake pipes before they suffer any thermal stress. Implementation of such procedures has significantly brought down fish kills caused by power plant operation (Ringger 2000).

The fouling control measures used in power plants operating in developed countries are, to a great extent, determined by the kind of discharge criteria pertaining to release of condenser effluents into receiving water bodies, and there is requirement to adopt best available techniques. The basic approach presently used universally to control biofouling in cooling water systems is to chemically treat the bulk water. Biofouling is an interfacial process, hence bulk water chemical treatment is not only wasteful but also environmentally undesirable. A rational approach, therefore, would be to release a suitable inhibitory chemical in such a way that a threshold concentration is maintained within the viscous layer close to the surface, making it unattractive to the larvae brought in by the flow and gravity. However, this is easier said than done, because maintaining a relatively high concentration close to the substratum, while leaving the bulk water free of chemicals, requires that the chemical be released from the surface itself. Paints can be used to achieve this; but paints have limited life and intake pipes and culverts of power plants are not always amenable to dewatering and repainting. An alternative is to employ surface modification. Seen from this viewpoint, foul-release coatings are an attractive option (Swain and Schultz 1996). However, as on today, their high cost and lack of experience concerning their suitability for application in cooling water systems make them poor candidates. Notwithstanding these shortcomings, it is anticipated that use of non-toxic coatings with inherent antifouling (or foul-release) properties will gain momentum in future as environmental stipulations become more and more stringent.

5 Concluding Remarks

It is generally perceived that the coming decades will see an unprecedented growth in the power generation scenario, especially in rapidly developing countries like India and China. As mentioned in previous sections, power generation through steam cycle using natural water bodies as heat sink could result in two kinds of problems—operational problems and environmental problems (Fig. 1.6). Operational problems arise because of sessile and benthic organisms extending their habitat into the cooling circuits of the power station, leading to blockage, choking and corrosion. Environmental effects result from the withdrawal and discharge of large quantity of water, which alter many of its chemical and biological characteristics. It is seen that operational and environmental issues related to cooling water systems tend to get addressed separately, though in reality they are two sides of the same coin (Venugopalan and Narasimhan 2008). There is a need to address the two issues in a comprehensive and integrated manner to ensure that utilities are able to solve the operational problems with least damage to the recipient water body.

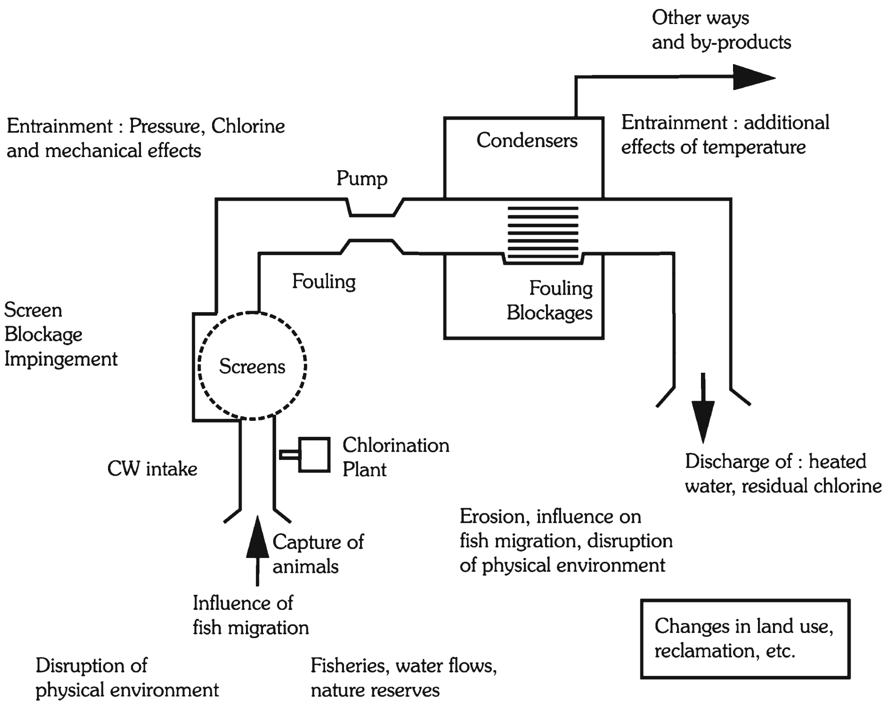

Fig. 1.6 Potential operational and environmental issues relating to the use of seawater for condenser cooling in power plants (Modified after Turnpenny and Coughlan 1992)

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Chapter 2
Biofouling in Cooling Water Intake Systems: Ecological Aspects

Sanjeevi Rajagopal and Henk A. Jenner

1 Introduction

Industrial cooling water systems employing natural aquatic systems as heat sink are prone to problems caused by the incursion of organisms into the cooling circuit. Surfaces exposed to water (fresh or saline) provide an opportunity for the settlement and growth of sessile organisms. In this chapter, we are concerned with organisms whose adult stages are characterised by macroscopic body size. This kind of biofouling, referred to as macrofouling, generally comprises of a vast diversity of organisms. According to an estimate, about 4,000 biological species are involved in the process of fouling (Crisp 1984). Moreover, this number is increasing due to expanding worldwide human activities and industrialisation. However, it is observed that in industrial cooling water systems, only a handful of species dominate the community. Mussels, barnacles, oysters and such calcareous organisms are predominantly seen. These are organisms, which in their adult lives remain permanently attached to solid surfaces. They employ planktonic larvae as propagules for expanding their territorial colonisation. The internal surfaces of cooling water systems in industrial plants generally provide ideal habitats for many such species.

Being sessile (attached to a surface), these organisms live by filtering suspended matter out of the flowing water. It is no surprise that industrial cooling water systems, which provide ideal habitat to such organisms, are densely colonised.

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Uncontrolled growth of biofouling can make normal operation of a plant extremely difficult. As just mentioned, the conditions inside the cooling water systems are ideally suitable for their survival. There is plenty of substratum on to which the larvae can attach and grow. The continuous flow of water guarantees copious supply of food and dissolved oxygen and rapid removal of waste products like ammonia. The water velocity and physical screening eliminate many of the conventional predators, which otherwise are common in the natural habitat of these organisms. Cooling system surfaces are generally not exposed to light, which precludes the growth of attached algae, potential competitors for space. On a normally lit surface, algae can quickly grow and smother the other sessile organisms. As a result of the existence of such favourable conditions, it is often seen that the growth rates of the fouling organisms growing inside the CW system are comparatively more than those of their counterparts growing outside in the natural environment (Rajagopal et al. 1998a). In this chapter, we shall try to analyse how abiotic and biotic environmental factors influence the settlement and growth of the fouling organisms and how such knowledge can be used in the mitigation of the biofouling problem.

2 Major Species of Fouling Organisms

An inventory of all the species contributing the biofouling community inside a CWS may indicate a large diversity of species. However, as mentioned earlier, the dominant species may just be a handful. The most troublesome among the macrofouling organisms are mussels. There are several species of mussels, including those found in temperate and tropical waters, while some have wide-ranging global distribution pattern (refer to Rajagopal and Van der Velde 2012 for review). In many European power stations that use coastal waters for condenser cooling, it is the common blue mussel, *Mytilus edulis,* which is the most prominent. In non-tidal low salinity waters such as the Noordzeekanaal in the Netherlands, the brackish water mussel, *Mytilopsis leucophaeata,* is found; in freshwater, the equivalent is the zebra mussel, *Dreissena polymorpha.* Other bivalve molluscs such as the Asiatic Clams *Corbicula fluminea* and *Corbicula fluminalis* are known for causing severe problems in North American and European aquatic systems (Bachmann et al. 1995; Jenner et al. 1998).

In several tropical marine power stations, mussels, barnacles and oysters have been reported to be major problem species. The green mussel *Perna viridis* is a major pest in CWS of Indian power plants (Rajagopal et al. 1996). Other mussel species such as *Perna indica* and *Brachidontes* spp. and oyster species such as *Crassostrea cuccullata* and *Pinctada margaritifera* are also commonly seen. The barnacle species include such species as *Balanus reticulatus* and *Megabalanus tintinnabulum.* Each of these species has its own characteristics in terms of reproductive ecology, settlement behaviour and response to environmental changes. Understanding of these aspects would be advantageous for those concerned with the operation and management of industrial cooling water systems.

3 Biofouling in Industrial Cooling Water Systems

Macrofoulants in industrial CWS are mostly represented by numerous species of algae, sponges, coelenterates, polychaetes, bryozoans, barnacles, amphipods, molluscs and ascidians (WHOI 1952; Costlow and Tipper 1984; Rajagopal 1997; Van der Velde et al. 2010). With regard to power plants, mussels are known to be the most problematic fouling organisms (Jenner 1980; Neitzel et al. 1984, 1986; Rajagopal 1991). Mussels can attach to virtually any solid substratum by means of their byssus threads, a bunch of proteinaceous threads produced by a specialised organ known as the foot. The cooling water system of a power station constructed with metal or concrete provides an abundance of suitable substrata for mussel settlement (Neitzel et al. 1984; Rajagopal et al. 1994). According to one estimate, the total biomass lodged inside the seawater intake tunnel of a costal power plant was about 578 tonnes (1 tonne = 1,000 kg), out of which mussels alone contributed 410 tonnes (Rajagopal et al. 1991a, 2006a).

3.1 Biofouling Problems in Power Stations

Fouling of cooling water systems by aquatic organisms is a problem of considerable economic significance to many power plants (Fischer et al. 1984; Claudi and Mackie 1994; Jenner et al. 1998; Claudi et al. 2012). Biofouling-induced problems in power plants roughly fall under four categories: (1) blockage of free flow of water in the cooling conduits and consequent mechanical damage to pumps; (2) clogging of condenser tubes; (3) reduction in heat transfer efficiency across heat exchanger surfaces and (4) acceleration of corrosion (WHOI 1952; Fischer et al. 1984; Neitzel et al. 1984; Nair 1990; Rajagopal et al. 1991a, 1991b, 1995, 2006a). The fouling also has potential to affect raw water systems including backup cooling loops provided for safety-related cooling systems in nuclear power plants (Neitzel et al. 1984). Several incidents of plant shutdown due to fouling have been reported from various parts of the world (Imbro and Gianelli 1982; Rains et al. 1984; Neitzel et al. 1986; Rajagopal 1991, 2010; Sasikumar 1991; Claudi and Mackie 1994). The number of studies on biofouling of coastal electrical power plants is few (Hoshiai 1964; Collins 1968; Board and Holmes 1972; Relini et al. 1980; Brankevich et al. 1988; Rajagopal et al. 1991a, 1991b, 1996, 2006a) and most of these studies relate to problems encountered in temperate waters. Moreover, detailed studies on the community structure of biofouling assemblages and other ecological parameters such as growth rate and settlement are lacking (Rajagopal et al. 2006b).

Mussels consume dissolved oxygen, phytoplankton and detritus from the water and release faeces, pseudofaeces and ammonia, thereby considerably altering the water quality. In turn, these changes have implications for the operation of the plant. For example, there can be problem of heavy sediment deposition in the pump chambers, caused primarily by mucus and pseudofaeces released by mussels (Venugopalan and Nair 1990). The ammonia excreted by the foulants reduces the efficacy of chlorine, by reaction with hypochlorous acid, to produce chloramines which are less effective than hypochlorous acid (Opresko 1980; Jenner et al. 1998). Presence of ammonia may cause corrosion (e.g., stress corrosion cracking) of the copper alloy-based condenser tubes. It is obvious, therefore, that biofouling must be kept to a minimum level by the judicious employment of control measures (Rajagopal et al. 2012a, b).

3.2 Ecology of Fouling Organisms

In order to develop an effective and yet environmentally sustainable antifouling strategy, a good deal of information is needed regarding the quantitative and qualitative aspects of fouling organisms. These aspects include the seasonal variations in settlement and factors controlling the development of the community (Hillman 1977; Relini 1984). The type and extent of fouling on marine structures (Table 2.1) generally vary with time, latitude, substratum, depth, water flow and distance from the shore (WHOI 1952; Barnes 1972; Smedes 1984; Venugopalan 1987; Venugopalan and Wagh 1990; Rajagopal et al. 2006a). Proper understanding of these influences can be utilised for the judicious design of cooling water systems, such that they are inherently less prone to biofouling. In our quest to understand the changes in biofouling, it is often necessary to understand the general ecology of the site. For example, factors influencing primary production in an area are extremely significant, for it signifies the trophic status of the habitat. Survival of the larvae of fouling animals depends on the amount of food available, and therefore, larval release by major fouling animals (e.g., mussels, barnacles, etc.) is often timed to coincide with phytoplankton blooms (Crisp 1984). Similarly, larval foulants may be preyed upon by larger carnivorous zooplankton, in which case, changes in the general composition of zooplankton must be taken into consideration.

3.3 The Processes of Biofouling

The first step in the fouling process in natural aquatic systems is the deposition of a conditioning film, which occurs as soon as a synthetic or engineering material is submerged in the sea (Lewin 1984). This primary event is followed by the congregation of chemotactic pioneer bacteria which, in turn, is followed by the colonisation of a variety of bacteria that produce large quantities of extracellular polymeric substances (EPS) that bind the bacteria to the surfaces (Little 1984). Further colonisation by stalked bacteria is followed by diatoms, other microalgae and protozoans, and eventually the surface film becomes highly complex with the settlement of macrofouling algae (Wahl 1989). Settlement of larvae on surfaces is known to be influenced by a variety of physical and ecological parameters such as colour and texture of the substratum, water flow, temperature, light, and presence of other

Table 2.1 Comparison of biofouling biomass (wet weight) reported from different parts of the world (depth: from 1 to 6 m; data not available)

Place	Substratum material	Biomass	Unit	References
Norfolk, Virginia, USA	–	13.2	$Kg/m^2/yr^1$	Wharton (1942)
San Diego, California, USA	–	25.0	$Kg/m^2/yr^1$	Whedon (1943)
Maine coast, USA	–	13.0	$Kg/m^2/yr^1$	WHOI (1952)
Lynn, Massachusetts, USA	Concrete	64.0	$Kg/m^2/yr^1$	WHOI (1952)
Virginia, USA	–	28.0	$Kg/m^2/yr^1$	WHOI (1952)
Palermo harbour, Sicily	–	112.9	$Kg/m^2/2\ m^1$	Riggio (1979)
Sam Mun Jai, Honk Kong	Concrete Pier	51.0	Kg/m^2	Huang (1980)
Wu Kwai Sha, Hong Kong	Concrete Pier	15.9	Kg/m^2	Huang (1980)
Ping Chau, Hong Kong	Concrete Pier	25.9	Kg/m^2	Huang (1980)
Tuticorin bay, India	Aluminium	5.0	$Kg/m^2/yr^1$	Renganathan et al. (1982)
Kalpakkam coast, India	Wood	4.5	$Kg/m^2/1\ m^1$	Karande et al. (1983)
Madras harbour, India	–	50.0	$Kg/m^2/yr^1$	Santhakumaran et al. (1983)
Trondheim, Norway	Wood	76.0	$Kg/m^2/1\ m^1$	Santhakumaran et al. (1983)
Tyrrhenian sea, Italy	Asbestos	5.1	$Kg/m^2/yr^1$	Relini (1984)
Liguria, Italy	Asbestos	16.0	$Kg/m^2/yr^1$	Relini (1984)
Cochin harbour, India	Aluminium	21.6	$Kg/m^2/6\ m^1$	Ravindran and Pillai (1984)
Cochin harbour, India	Stainless steel	20.7	$Kg/m^2/6\ m^1$	Ravindran and Pillai (1984)
Cochin harbour, India	Carbon steel	16.0	$Kg/m^2/6\ m^1$	Ravindran and Pillai (1984)
Kalpakkam coast, India	–	8.0	$Kg/m^2/yr^1$	De (1984)
Andaman, India	–	7.5	$Kg/m^2/yr^1$	De (1984)
Bombay offshore, India	–	5.5	$Kg/m^2/yr^1$	De (1984)
Bombay enclosed waters, India	–	0.2	$Kg/m^2/yr^1$	De (1984)
Ennore, India	Tiles	69.3	$Kg/m^2/yr^1$	Selvaraj (1984)
Mandovi estuary, India	Mild steel	3.9	$Kg/m^2/yr^1$	Sawant (1985)
Zuari estuary, India	Mild steel	15.1	$Kg/m^2/yr^1$	Sawant (1985)
Bombay high, India	Aluminium	8.7	$Kg/m^2/yr^1$	Venugopalan (1987)
Kalpakkam coast, India	Wood	13.5	$Kg/m^2/yr^1$	Nair et al. (1988)

(continued)

Table 2.1 (continued)

Place	Substratum material	Biomass	Unit	References
Kakinada port, India	Wood	23.4	$Kg/m^2/yr^1$	Rao and Balaji (1988)
Kakinada port, India	Glass	9.2	$Kg/m^2/yr^1$	Rao and Balaji (1988)
Kalpakkam coast, India	Wood	19.3	$Kg/m^2/yr^1$	Sasikumar et al. (1989)
Edaiyur backwaters, India	Wood	10.3	$Kg/m^2/yr^1$	Rajagopal et al. (1990)
Visakhapatnam harbour, India	–	77.6	$Kg/m^2/yr^1$	Rao (1990)
MAPS intake gates, Kalpakkam, India	Mild steel	269.2	$Kg/m^2/yr^1$	Rajagopal (1991)
MAPS intake gates, Kalpakkam, India	Mild steel	259.2	$Kg/m^2/yr^1$	Rajagopal 1991
MAPS intake gates, Kalpakkam, India	Mild steel	242.8	$Kg/m^2/yr^1$	Rajagopal (1991)
Noordzeekanaal, Netherlands	PVC	45.9	$Kg/m^2/8$ m	Rajagopal et al. (1995)
Velsen power station intake, Netherlands	PVC	126.0	$Kg/m^2/8$ m	Rajagopal et al. (1995)
MAPS forebay, Kalpakkam, India	Concrete	28.2	$Kg/m^2/yr^1$	Rajagopal (1997)
Edaiyur backwaters, India	Concrete	32.7	$Kg/m^2/yr^1$	Rajagopal (1997)
Kalpakkam coastal waters, India	Concrete	200.6	$Kg/m^2/yr^1$	Rajagopal et al. (1997)
Kalpakkam coastal waters, India	Concrete	249.9	$Kg/m^2/yr^1$	Rajagopal et al. (1997)
Kalpakkam coastal waters, India	Concrete	83.7	$Kg/m^2/yr^1$	Rajagopal et al. (1997)
Northern Beibu Gulf, China	–	23.7	$Kg/m^2/yr^1$	Yan et al. (2006)
Kalpakkam coast, India	Titanium	43.9	$Kg/m^2/8$ m	Murthy, personal comm.
Kalpakkam coast, India	Stainless steel	50.2	$Kg/m^2/8$ m	Murthy, personal comm.

organisms (Abarzua and Jakubowski 1995). However, it would be difficult to exhaustively review the influence of all parameters here and the reader is directed to the appropriate publications (refer to Costlow and Tipper 1984; Rajagopal et al. 1998b, 2006a; Claudi and Mackie 2009; Van der Velde et al. 2010 for review).

3.4 Influence of Abiotic Factors

The influence of environmental features on the settlement and progression of fouling communities is an aspect of considerable significance in the study of the fouling problem and its control. Abiotic factors such as light, temperature, salinity, turbidity, waves, tides, currents and substratum influence biofouling development (Graham and Gray 1945; Coe 1946; Kinne 1971; Rajagopal 1997; Claudi et al. 2012). Differences in the settlement pattern of sedentary benthic organisms are directly or indirectly related to seasonal changes in the physical environment, such as temperature (McDougall 1943; Southward 1958; Lewis 1963; Sutherland and Karlson 1977), salinity (Shaw 1960; Kinne 1963; Rajagopal et al. 1990, 2006b), nutrient availability (Levington 1972; Lubchenco 1978; Lubchenco and Menge 1978), light (Coleman 1933; WHOI 1952; Kinne 1971; Venugopalan 1987; Rajagopal et al. 2006a) and turbidity (Coe and Allen 1937; Fuller 1946; Sasikumar et al. 1989). The settlement pattern of fouling organisms is different between tropical and temperate conditions; the settlement tends to be continuous in the tropics and periodic in temperate areas (Barnes 1972). Relatively pronounced short-term changes in the hydrographical conditions of temperate waters have been reported as a reason for discontinuous settlement (WHOI 1952; Smedes 1984). Scheltema and Carlton (1984) stress that the differences observed in the fouling communities are not only due to geographical variations, but also due to large-scale changes within a given area. Tropical sites generally tend to be species-rich (Fig. 2.1). The influence of local hydrographical conditions on the development of fouling communities has been studied by many workers (Sutherland 1974; Sutherland and Karlson 1977; Osman 1978). Even at a given location, the faunal composition inside a CWS may be significantly different from that outside (Fig. 2.2). Depth is another important feature that determines the number of species and their biomass (Figs. 2.3 and 2.4). Sublittoral species may be predominantly observed in CWS, which has intake points placed below the low tide level (Fig. 2.5). Generally, factors that affect the rate of metabolic activity, physiological tolerance, phytoplankton productivity and larval availability can be expected to influence fouling intensity (Barnes 1957; Connell and Orias 1964; Kinne 1971; Levington 1972; Himmelman 1975; Sutherland 1981; Rajagopal 1997). Since most fouling organisms are filter feeders that depend on a continuous supply of suspended food in the water column, factors which ultimately affect the primary production can be expected to affect the fouling organisms also. Water flow is a particularly important parameter, because it ensures continuous supply of food material to the filter feeders. Because of this, one can observe enhanced growth rate of the fouling organism in the CWS, as compared to that outside (Fig. 2.6).

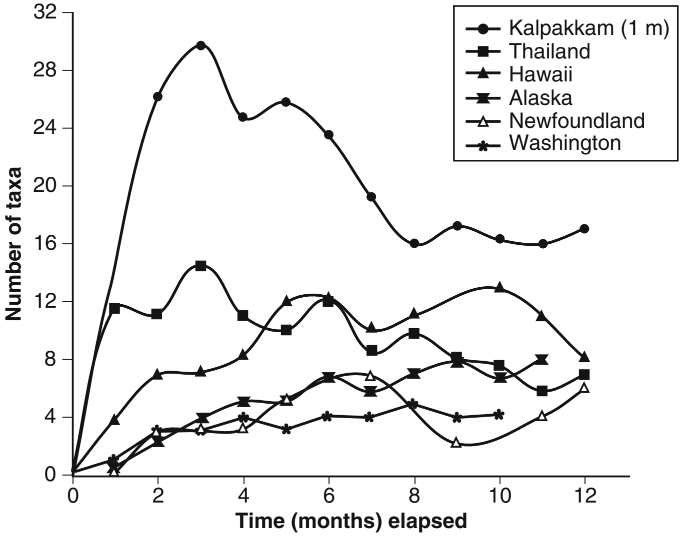

Fig. 2.1 Colonisation curves (number of taxa) on concrete panels submerged in early summer at Kalpakkam, India (Rajagopal et al. 1997) along with reported values on colonisation curves (panels submerged in spring-early summer) of Schoener et al. (1978) from Thailand, Hawaii (averages shown), Washington, Newfoundland and Alaska. (Modified after Richmond and Seed (1991) and Rajagopal et al. (1997))

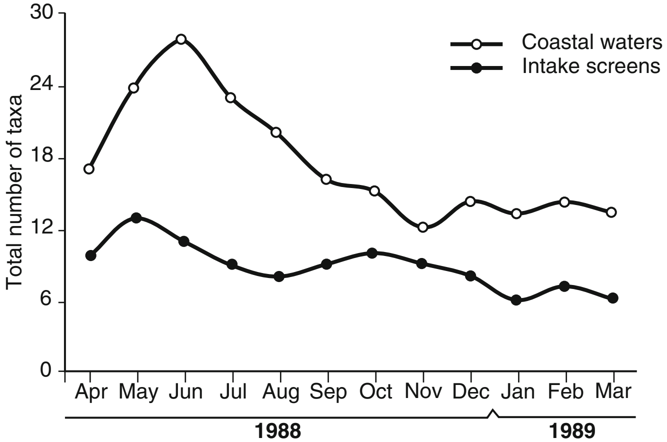

Fig. 2.2 Species diversity of the sessile community colonising concrete test blocks in Kalpakkam coastal waters (initiated in April 1988 at 1 m, 4 m and 7 m) and biomass collected from intake screens of Madras Atomic Power Station, Kalpakkam (installed in April 1988; depth - 2 m, 4 m and 6 m). Monthly mean values were calculated from three sampling depths at each station (Modified after Rajagopal et al. 1998a)

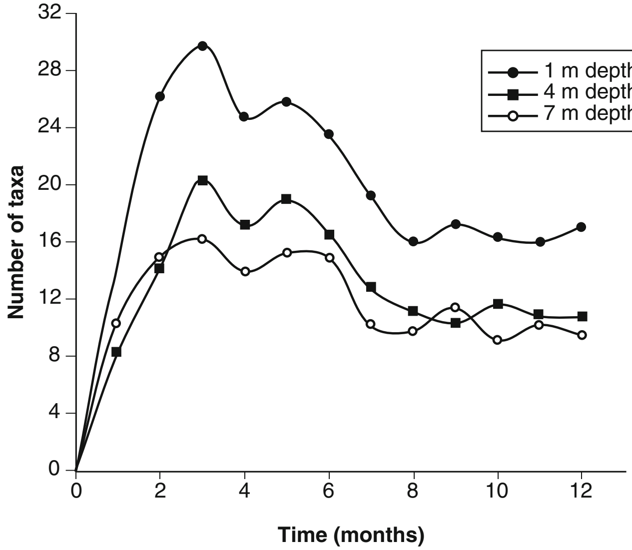

Fig. 2.3 Colonisation curves (number of taxa) on concrete panels submerged in early summer at 1 m, 4 m and 7 m depth in Kalpakkam coastal waters (Modified after Rajagopal et al. 1997)

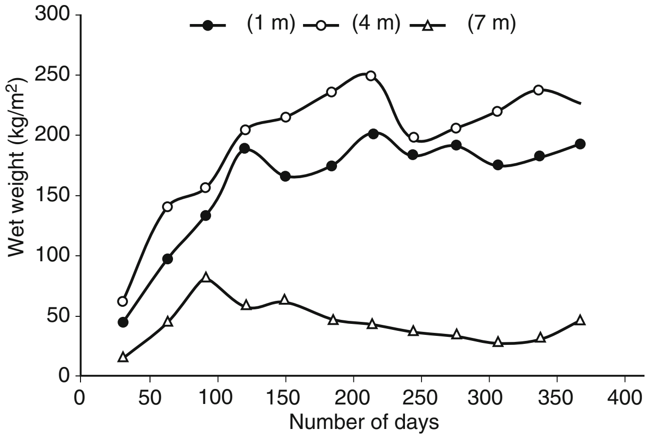

Fig. 2.4 Seasonal distribution of fouling biomass (wet weight) on long-term B-series concrete panels at 1 m, 4 m and 7 m in Kalpakkam coastal waters (Modified after Rajagopal et al. 1997)

3.5 Biotic Factors

Apart from environmental factors, there are biotic factors such as food availability (Rajagopal 1997; Rajagopal et al. 2006a), predation (Menge 1976; Sousa 1980; Rajagopal et al. 2006b), competition for space (Connell 1961, 1970; Dayton 1971;

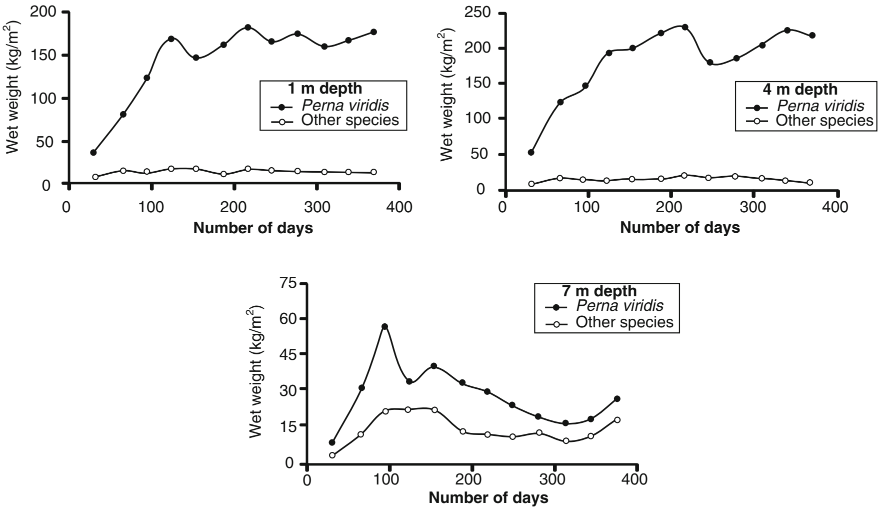

Fig. 2.5 Monthly variations of relative abundance of the green mussel *Perna viridis* on long-term B-series concrete panels at three different depths (1 m, 4 m and 7 m) in Kalpakkam coastal waters (Modified after Rajagopal et al. 1997)

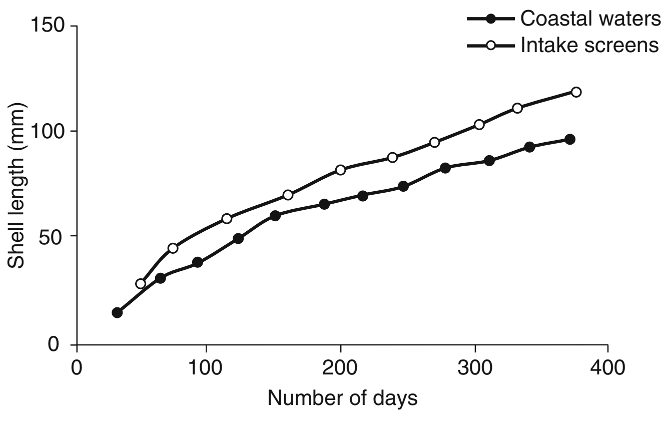

Fig. 2.6 Growth rates of mussels (*Perna viridis*) growing in Kalpakkam coastal waters and on intake screens of Madras Atomic Power Station, Kalpakkam (Modified after Rajagopal et al. 1998a)

Rajagopal et al. 2000), physical disturbance by neighbouring species (Menge 1976; Jackson 1977; Dean 1981) and differences in competitive abilities (Sutherland 1974; Buss and Jackson 1979) which play very important roles in the development of fouling community. Larvae of fouling organisms are mostly planktivorous in nature and depend on phytoplankton for their survival. It has been shown that spawning/larval release in many sessile benthic species is correlated with phytoplankton bloom, ensuring the availability of plentiful food for the developing larvae (Crisp 1984). From the viewpoint of fouling control, it is important to understand the seasonal variations in larval settlement intensity, because modern antifouling practices are directed against prevention of larval settlement rather than killing of settled organisms (please see other chapters in this book: Khalanski and Jenner 2012; Rajagopal et al. 2012b; Rajagopal and Van der Velde 2012). One of the easiest methods to study the seasonal variations in biofouling is to use test panels (or coupons) as settlement substrata and observe the changes in settlement intensity (Rajagopal et al. 1997).

3.6 Use of Test Panels to Study Seasonal Variations

Temporal changes in biofouling development can be conveniently studied using test panels (WHOI 1952; Costlow and Tipper 1984; Rajagopal et al. 1996, 2006a). With this method, it is possible to study the seasonal variations and ecological succession in sessile benthic communities and the major factors influencing such changes (Dayton 1971; Connell and Slatyer 1977; Smedes 1984).

The panel exposure strategy is explained in detail by Rajagopal et al. (1997, 1998b). Experimental blocks (20 × 20 × 20 cm) or test coupons (15 × 10 cm) of convenient size made of concrete or some other suitable material are suspended with the help of nylon ropes at different depths (e.g., 1, 4, and 7 m). The panels are categorised into short-term exposures (A-series) and long-term exposures (B and C-series). The short-term panels are suspended (duplicate or triplicate panels at each depth) and withdrawn at monthly intervals and fouling organisms are collected to follow the pattern of their seasonal settlement. The long-term panels of the B-series are all suspended (2 × 12 panels at each depth) together, but withdrawn at the rate of two every month. An exposure strategy involving short-term panels is ideal for studying seasonal larval settlement patterns. However, to follow long-term changes or succession occurring within the community, cumulative panels (B-series) are more suitable. Another set of C-series panels is suspended successively at 30-day intervals and retrieved together after one year with a view to study the climax community. Figures 2.7 and 2.8 show the type of information that could be gleaned from test panel exposure studies. Settlement periods of major fouling organisms are clearly visible from the kite diagrams plotted in the figures.

Quantitative variations in biofouling are generally expressed in terms of biomass, percentage cover, numerical density and frequency of occurrence. Lewis (1981) made a comparative study of these methods and concluded that biomass and panel coverage were better indices of fouling development than either numerical density or frequency.

The time of panel initiation and the duration of panel exposure have been reported to be important in determining the development of the fouling community observed on test panels (Dayton 1971; Dean 1981; Nandakumar 1996).

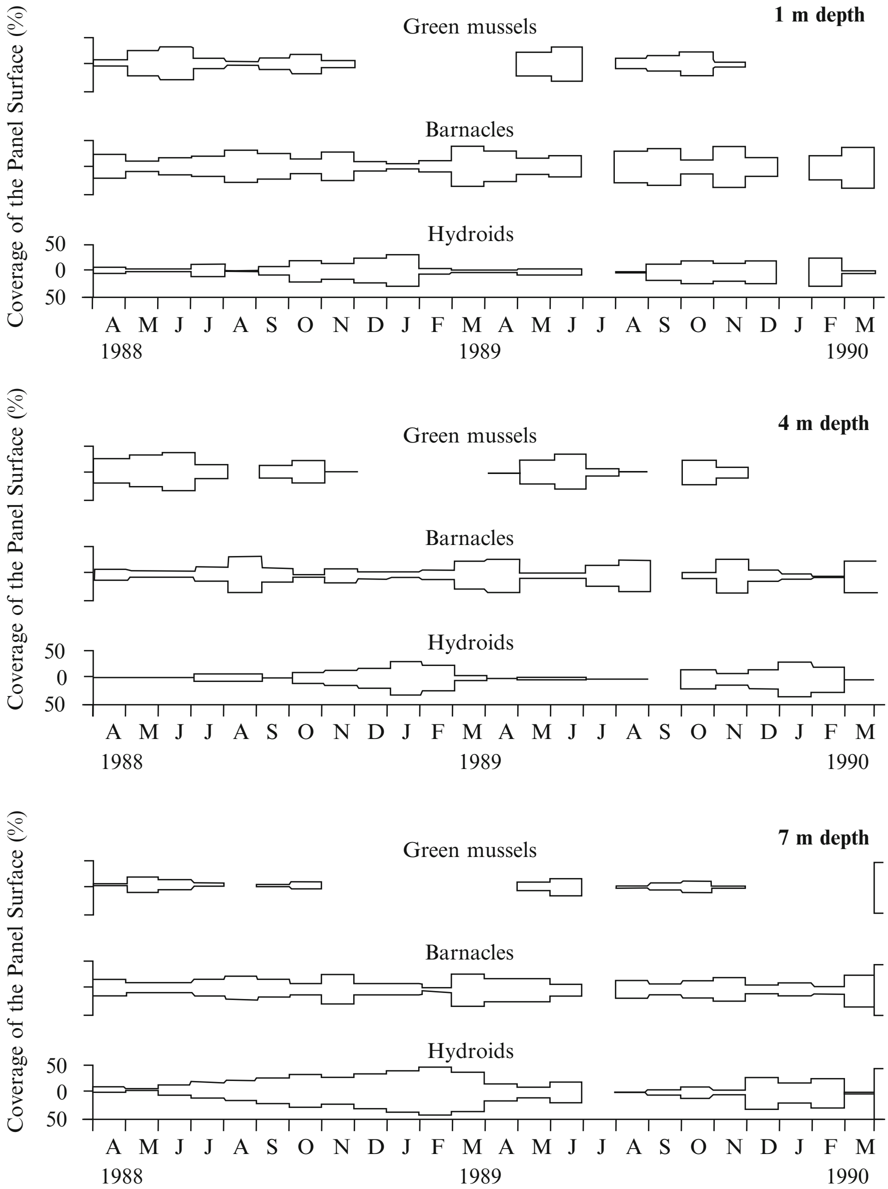

Fig. 2.7 Seasonal variations (percent coverage) in the settlement of principal fouling organisms on short-term A-series concrete panels at different depths (1 m, 4 m and 7 m) in Kalpakkam coastal waters (Modified after Rajagopal et al. 1997)

Osman (1977), Sutherland and Karlson (1977), Dean and Hurd (1980) and Smedes (1984) demonstrated the importance of initial colonisers on subsequent community development. Another important disadvantage of the test panel method is that it does not take water flow into consideration and hence may not truly represent

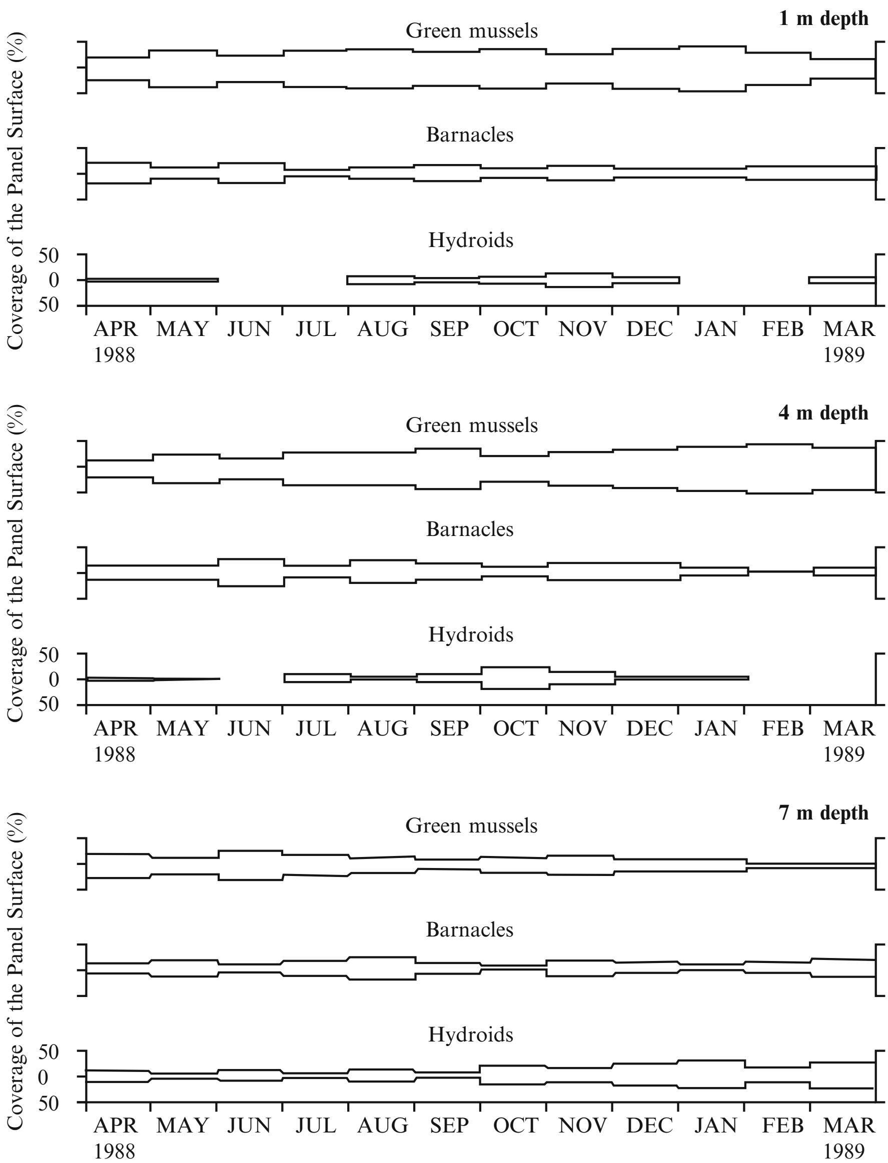

Fig. 2.8 Seasonal distribution of principal fouling organisms and their abundance (percent coverage) on long-term B-series concrete panels at three different depths (1 m, 4 m and 7 m) in Kalpakkam coastal waters (modified after Rajagopal et al. 1997)

biofouling scenario within a pipe or culvert. Nevertheless, it gives important information relating to species abundance and seasonal changes in their variation, including reproductive periods, which can be used for deciding on the control strategy to be adopted.

4 Utility of Ecological Information for Fouling Control

The characteristic that make a particular organism successful in an artificial habitat like CWS can be many. For example, the mode of attachment, ability to secure attachment under flow conditions, existence of protective shells, fast growth rate, high fecundity and ability to withstand aggressive environmental conditions (e.g., presence of biocides) are features that make some bivalves extremely important pest species (Fig. 2.9). The composition of fouling community that develops in a particular system would be related to the suite of environmental conditions present inside (e.g., type of substratum, flow conditions, presence of biocides, etc.). However, it is possible to minimise the effects of fouling by adoption of control measures based on the judicious application of the information obtained from test panel data. For example, biocide dosing strategy can be devised based on the reproductive ecology of the local species. Once the mussel settlement season is known, it is possible to use low-dose continuous chlorination (also know as exomotive chlorination) to prevent the attachment of juvenile mussels inside the CWS (Rajagopal et al. 1991a, 1996, 2006b). Moreover, one can also supplement the test panel data with real-time data obtained through the use of fouling monitors (Claudi et al. 2012).

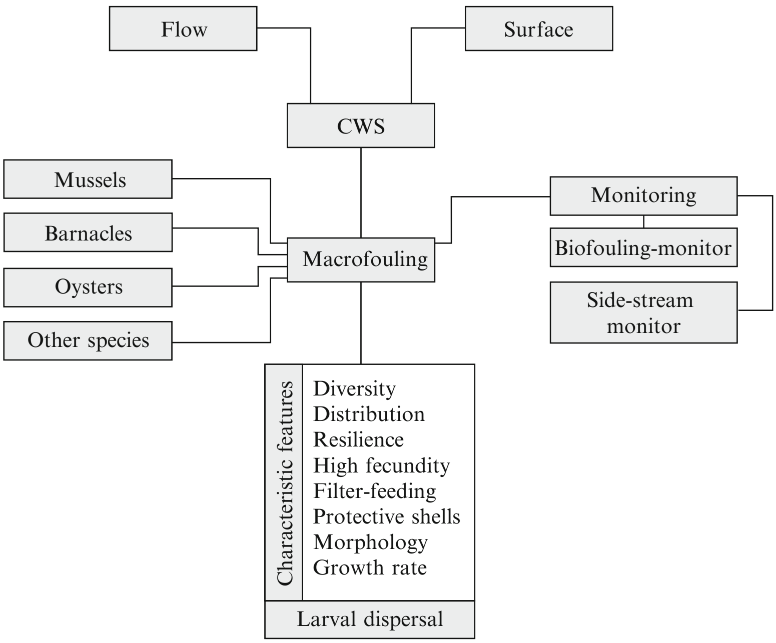

Fig. 2.9 Summative figure depicting the important features of bivalve mussels which make them successful colonisers in artificial habitat like industrial cooling water systems

5 Concluding Remarks

Biofouling in CWS follows when sessile benthic organisms residing in the adjacent coastal waters extent their habitat into it and make use of the ample substratum and other favourable conditions for rapid colonisation. Just as in the coastal waters, biotic and abiotic factors play an important role in the ecology of the organisms colonising the CWS. Understanding the interactions would be of help in devising suitable control measures to mitigate the biofouling problem. Studies using test panels and monitoring using online biofouling monitors will go a long way in understanding the dynamics of biofouling and implementation of effective control strategies.

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Chapter 3
Monitoring: the Underestimated Need in Macrofouling Control

Renata Claudi, Henk A. Jenner, and Gerald L. Mackie

1 Introduction

Most industries with once-through cooling water systems (CWS) monitor only the most basic chemical and physical parameters of the incoming raw water, if they monitor at all. They rely on operational experience and the robustness of the cooling system to cope with annual changes in ambient temperature and possibly pH. With the introduction of new macrofouling organisms (so-called exotics or alien species) into the incoming water, the need for better monitoring data (Claudi and Mackie 1994) becomes more stringent.

This chapter deals primarily with monitoring strategies designed for attached macrofoulers which possess a free swimming life stage as larvae. In fresh water (Claudi and Mackie 2009), the most important species in this category include the *Dreissenid* freshwater mussels: zebra mussel (*Dreissena polymorpha*), the quagga mussel (*Dreissenid rostriformis bugensis*), the golden mussel (*Limnoperna fortunii*) and *Mytilopsis leucophaeta*, Conrad's false mussel (also known as dark false mussel and platform mussel). In the marine environment, the main species of concern are the marine blue mussel (*Mytilus edulis*), the green mussel (*Perna viridis*) and some oyster species, such as the Japanese oyster (*Crassostrea gigas*). The above listed species are only examples of the most troublesome species; however, several other species like tube worms, e.g., *Sabellaria* species, barnacles and hydroids, can also form a severe threat to undisturbed CWS operation.

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2 Basic Principles Monitoring Set-Up

Before any facility can implement a successful program for control of these macrofoulers, they need to know the lifecycle of the macrofouling organism in their immediate geographic area, the population dynamics of this organism and the response this organism has to various control strategies. To gain this knowledge, the facility has to expand their monitoring program and interpret the data collected.

The objectives of such a monitoring program should be:

1. Determine when macrofouling organisms are present in the raw water.
2. Determine how fast the macrofouling organisms grow once they have settled.
3. Determine the density of settled population of macrofoulers at the end of a discreet time period.
4. Determine the susceptibility of the macrofouler to various control methods.

To achieve these monitoring objectives, a combination of settling plates, plankton net sampling and in-plant monitoring is generally recommended.

3 Sampling by Settlement

Settlement substrates are basically plates of solid (natural or artificial) substrate, attached to a rope and submerged in the raw water up-stream (intake area) of the industrial facility being monitored. Periodically, the plates can be removed and examined visually or the surface can be lightly scraped into a dish and the collected material is then examined under a stereomicroscope (binocular) with an ocular lens to provide up to 80× magnification. Settling plates can be made out of any number of non-toxic materials such as carbon steel, stainless steel, PVC, bricks, clay or even cement tile. For ease of sampling, a uniform size is recommended. The actual plate size will depend on the preference of the user. Plates measuring 10 by 10 cm have been frequently used as have plates of 30 by 30 cm. The thickness of the individual plate is also flexible, the most often used thickness is 0.5–1.5 cm.

As well as flat sampling plates, cylinders made of "Perspex" or PVC (diameter ca. 15 cm and a length of 25–30 cm) are commonly used in Europe. The advantage of the cylindrical settling substrate is that the inside of the cylinders generally remains undisturbed either by predators or by mechanical damage. Predator feeding by fish and mechanical damage can happen on unprotected "outside" surfaces which can affect the data collected (Fig. 3.1).

Plates or cylinders can be strung together with a rope at predetermined intervals (e.g., 1, 2, 5-m depth intervals) and suspended from a buoy or tied to an existing shoreline item such as a railing. The first plate should be at least 1 m below the surface of the water at low tide. Additional plates can follow in predetermined intervals to within 1 m from the bottom of the body of water being monitored. An anchor should be placed at the very bottom to insure the sampling plates remain vertical in

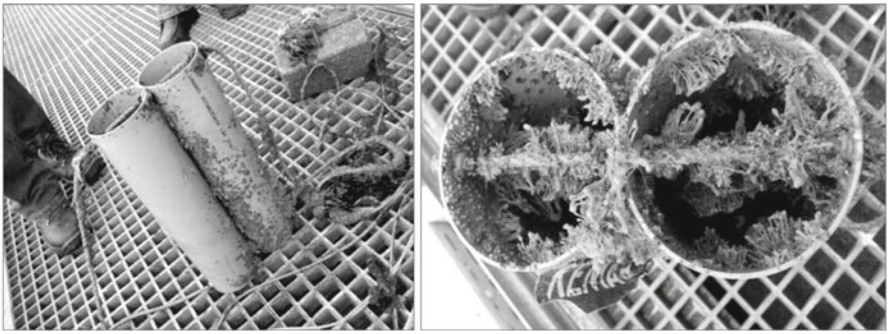

Fig. 3.1 Two-roped PVC cylinders fouled with *Tubularia*, mussel spat and barnacles

Fig. 3.2 Sampling rope exposed in seawater with first year (June–August) mussel fouling

the water column. It must be kept in mind that during a fouling season the weight gain by fouling can be considerable. At locations with known high fouling pressure, the use of only a rope (Fig. 3.2) can simplify the monitoring. Mussel spat settles preferentially in the coils of ropes.

Care should be taken not to let the sampling assembly touch any other submerged surfaces which are likely to be colonized. For example, a sampling plate which

Fig. 3.3 Sampling substrata, the one on the far right was touching a heavily colonized surface. Periodic visual observation of the sampling tools will determine if macrofouling organisms are settling at this location. Once initial settlement has been detected, the settling plates are used to determine the density of settlement

touches the face of a concrete dam already colonized will show large number of adults. This phenomenon is called translocation and is regularly observed in dreissenids. Adult mussels crowded onto a colonized surface will move to a new surface where the competition for space is low (Fig. 3.3).

Determination of settlement density is best done by having at least three identical replicates of settlement plates deployed at the same time and depth. The sampling frequency of the settling plates is flexible. The sampling can be weekly, fortnightly or monthly. After the settlement plates have been exposed for a predetermined time period, each string is lifted from the water. Both sides of each plate are scraped off and preserved in collection jars. The material collected can be either placed into pre-labeled sampling jars and preserved in 70% ethyl alcohol or 3–5% formalin for later examination or examined immediately. When diluting the alcohol or formalin, consider the water retained within the mantle cavities of the mussels.

For research purposes, the use of so-called flat culture flasks is a good option. The collected material is placed in the flasks, preserved with the addition of 3% formalin, filled up to the top and kept for years. Microscopic determination of species and numbers of spat (length 100–250 μm) can be performed by placing the flask directly under a binocular. This saves a lot of time and exhaustion equipment is not necessary.

Depending on the macrofouling organism involved and the size of the population on the sampling plate, actual number of individuals can be recorded and reported on a square meter basis if the plate size is known. Alternatively, the material collected can be recorded as wet weight or dry weight. Data from plates occupying the same depth on each of the three strings should be added together and averaged for a more statistically robust result. Once the population data are collected, as suggested above, the collected material can be examined for the presence of discrete size classes. Usually maximum shell length (tip of umbone to posterior edge of the mussel) is taken using either an ocular micrometer on a microscope for small shells, or digital calipers for large shells.

As the plates are scraped clean after each sampling period, the largest shells found on the plates during the next sampling period will have been settled for the duration of the interval between sampling. For example, if maximum growth is occurring, 1-mm-long mussels will be present after 1 week, 2-mm-long after 2 weeks and up to 4-mm-long mussel shells after 1 month. An occasional large mussel outside the expected size range could be found on the sampling plates. These mussels are usually called translocators and may have moved onto the plate from another location. They should not be included in the weekly growth calculations. The presence of more than one size class of shells in the material collected from the plates suggests multiple settling events have taken place while the settling plates have been in the water. This is also valuable information for the industrial facility. After all the plates have been scraped, the sampling string is replaced in the water column for the next sampling period.

It is very useful to measure and record ambient water temperature at each plate depth when collecting samples from the settlement plates. Having a record of the temperature at various depths could greatly help interpret settlement and growth data from the settling plates.

It may also be useful to expose additional strings of sampling plates at the same location and leave these additional strings undisturbed for a 6-to 12-month period. At the end of this period, follow the same procedure as above. These additional plates will then give you the cumulative densities of the macrofouler at each depth for the time period selected.

4 Plankton Sampling

If the macrofoulers under discussion have a planktonic life stage, collection of plankton samples may augment the data gathered by using settlement plates (Fig. 3.4).

5 Calculating the Number of Settled Juveniles per Square Meter

The area of the settlement plates (or coupons) needs to be calculated. If two sides were scraped, double the calculated area. For example, suppose the plates are 10 by 10 cm and two sides were scraped, the total area settled upon is $10 \times 10 = 100\ \text{cm}^2 \times 2$ sides $= 200\ \text{cm}^2$. Hence, if you counted 300 juveniles in 200 cm^2 area, the number per square meter is 300 juvenile/200 $\text{cm}^2 \times 10{,}000\ \text{cm}^2 = 15{,}000$ juveniles/m^2.

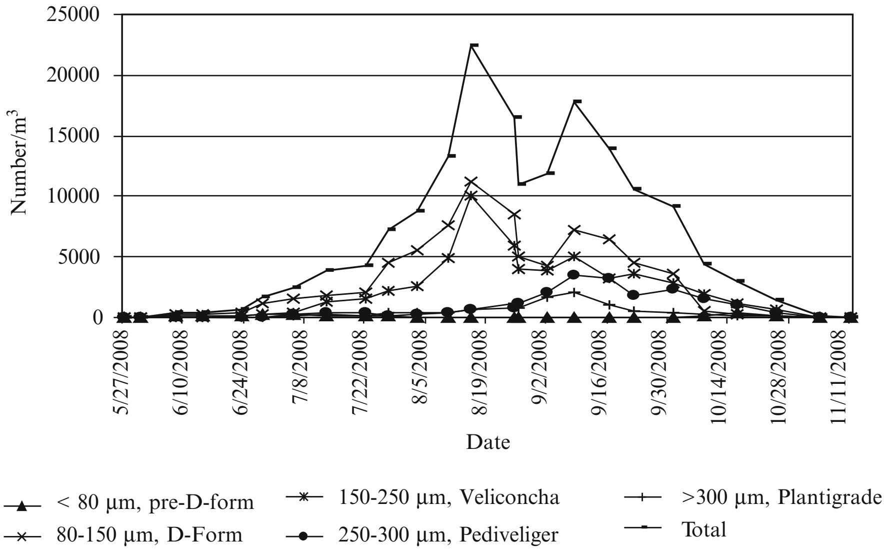

Fig. 3.4 The weekly changes in the numbers of zebra mussel larvae in five different size classes in a steel industry. A 40-µm mesh was used to filter the water samples

6 In-Plant Monitoring

To monitor the settlement of mussels within the power plant, it is recommended to use side-stream samplers. At the moment, two monitors are in worldwide use. The first is an aquarium like device commonly known as a Bio-box (Fig. 3.5). The second device is the KEMA Biofouling Monitor® (Fig. 3.6) which is a closed system. The water in this system flows upwards through four tubes into which removable fouling panels are inserted. Water is discharged via a central outlet tube which can be adjusted in height for changing flow conditions. The KEMA Biofouling Monitor® is made specific as a closed system to avoid any light input because most bivalve species are lucifugous.

Both monitors are designed to mimic the flow in the industrial piping which is in danger of fouling. The minimal flow rates in the monitor are 20–30 L/min for fresh and brackish water and 50 L/min for seawater.

A minimum of one side-stream sampling location is desirable, two locations are preferred. Suggested locations are one monitor as close to the intake of raw water as possible and a second monitor directly before the condenser or main heat exchanger near the end of the raw water system. The location at the end of the system is possible but should not be downstream of any coolers where the cooling water may reach temperatures sufficient to cause mortality in the planktonic stage of the macrofouler. If possible, the supply to the side-stream samplers should be taken from a valve (preferable a butterfly valve) located in the lower third of the diameter of the system pipe. Butterfly valves have been shown to damage the incoming spat less compared

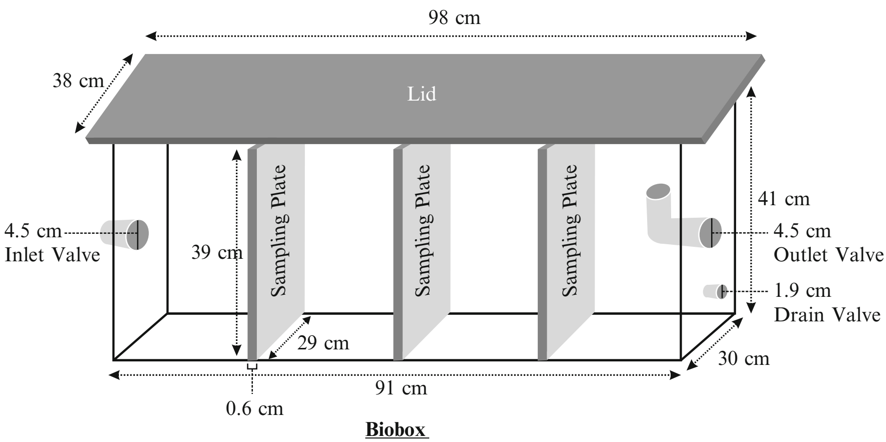

Fig. 3.5 Schematic representation of side-stream sampler commonly known as a Bio-box (refer to Claudi and Mackie 1994 for details)

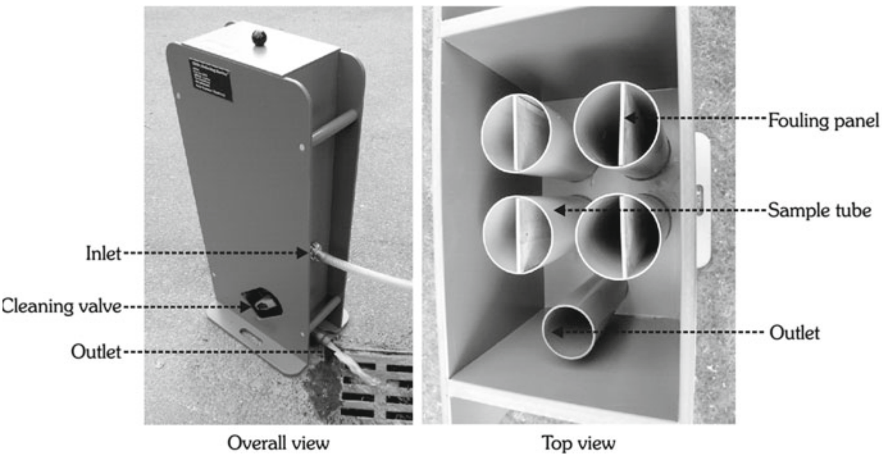

Fig. 3.6 Kema Biofouling Monitor®. The body of the monitor is made of recycled PVC. The height is 110 cm and diameter 40 cm

to membrane valves. Membrane valves have high water velocity between the membranes. This high velocity can lead to mechanical damage of the planktonic organisms. The volume of flow into the bio-monitor is regulated by a valve on the incoming water line. The water velocity through the KEMA Biofouling Monitor® is about 1 cm/s and the suggested flow through the Bio-box should be such as to achieve a retention time of 20 min. Any ready-to-settle planktonic stage in the side-stream will have an opportunity to settle in the monitors. Twenty minutes is generally the maximum time water takes to travel from the start of an industrial cooling water system to the end of it. Settlement in the bio-boxes can be monitored much

Table 3.1 Summarize the possible locations of power plants, where fouling monitoring, frequency and observations are possible

Monitoring tool	Location	Frequency	Observations
Settlement plates Size: 1 sq ft. Material: Carbon steel, stainless steel, PVC	In the incoming flow	Weekly Bi-weekly Monthly Quarterly/ bi-annually	Start of settlement Growth rate Number of settlement events Total population/time period Note: Collect water temperatures at various depth during each sampling event
Plankton tows Plankton net, 20-in. mouth, 75-µm mesh	In the incoming flow	Weekly	Presence and density of veligers % of ready-to-settle life stage
Side-stream samplers/ bio-box Sampling plates same as used for settlement plates above	Service water system	Weekly/monthly	Presence of mussels in the plant Efficacy of control

like the settlement on plates deployed outside of the plant. The monitoring interval can be determined by the user.

Water from a location on the lower portion of the system pipe will be likely to contain more planktonic life stages than supply from the upper portion of a pipe. This is because most of the plankton sediment out by gravity after they pass through a pump. The flow will become less turbulent, depending on bends in the conduits, and after circa 30–50 times the diameter of the conduit, the flow becomes more or less laminar forcing sedimentation of plankton and spat of bivalves. The sinking rate of mussel spat is about 10 mm/s at a length of 0.5 and 40 mm/s at a length of 2 mm with the valves closed. From inspection results, it is seen that sedimentation followed by smothering up in the silt layer on the bottom of conduits indeed does occur.

If macrofouling control measures are deployed in the cooling systems, the absence of macrofoulers in the bio-monitors in front of the heat exchangers or at the discharge end of a piping system (where no heat exchangers are present) would verify that the control measures are working. Conversely, if settled, live macrofoulers are found in the bio-monitors, the control measures are not working. Table 3.1 summarizes the locations, frequency and observations possible in most plants.

7 How to Use the Data Collected

The macrofoulers dealt with in this text cause multiple problems in industrial facilities. They settle in piping which carries cooling water, decreasing the flow potential in this piping, and in some cases, shells or clumps of shells can plug some components completely. Most facilities experiencing macrofouling problems will either try to prevent this settlement or periodically eliminate anything which may have settled in the piping. The data that are collected by the monitoring program described can assist industrial facilities in their decision-making process on how to best deal with macrofoulers.

7.1 Timing of Treatment for Elimination of Macrofoulers

If prevention of settlement is the aim, knowing when the settlement starts and ends will determine the start and the end of the period for a mitigation procedure. As soon as settlement is observed on the settlement plates outside the plant or in the fouling monitor in the plant, treatment to eliminate settlement in the cooling pipes should be commenced. Once new settlement is no longer observed and the previous settled organisms have disappeared, the treatment can stop.

If the treatment method chosen is to periodically eliminate any settlement in the piping, the growth rate of individual shells combined with the rate of accumulation of biomass will determine when and how often such periodic treatments may have to be administered. The size of individual shells prior to treatment should be small enough that a single shell could not block a vital part of the equipment when the macrofouler dies. The allowed accumulation of biomass should be such that the post-treatment sloughing off would not block strainers or heat exchangers and overwhelm the mechanical maintenance staff. Therefore, the data on biomass accumulation will aid in predicting the required timetable for maintenance of various systems in the plant. This would include the need for maintenance of external structures such as trash racks and rotating sieves, and at hydro power stations, spill gates or penstock gates. If heavy biomass accumulation is observed on the settling plates, these external structures may have to be cleaned more frequently.

7.2 The Length of Periodic Treatment Required Using Bio-Monitors

How long a periodic treatment has to last to remove all settlement from inside of the piping is best judged by observing macrofoulers that have settled in the bio-monitor at the end of the system. If macrofoulers have settled in the fouling monitor in sufficient numbers, it is important to observe the monitor during the periodic treatment. Depending on the treatment method chosen, the macrofoulers may disappear from the bio-monitors or die in situ. Most marine mussels die in situ during treatment with oxidizing chemicals.

Once the last individual has either exited the fouling monitor or is observed gaping and unresponsive, the treatment can be terminated. If there is low number of individuals settled in the fouling monitor prior to the start of the treatment, it is a good idea to introduce additional macrofoulers from another location into the monitor. Having a large number of individuals to observe during the treatment will give greater assurance that the treatment method is working.

7.3 Monitoring as a Way of Minimizing the Use of Chemicals During Treatment

Most macrofoulers dealt with here close their shell when exposed to oxidizing chemicals such as chlorine. After the shell is closed, it remains closed for some time before it is re-opened fully. Pulse-Chlorination®, developed by KEMA in Netherlands in the late 90s, takes advantage of this recovery time by using short successive periods of chlorination, alternated with periods without chlorine (Polman and Jenner, 2002; Jenner et al. 2003). During continuous chlorination, the bivalves close and switch from aerobic to anaerobic metabolism. By applying Pulse-Chlorination®, the bivalves have to continuously switch their metabolism from aerobic to anaerobic leading to physiological exhaustion. This leads to quicker mortality of the bivalves compared to conventional, continuous chlorination. To determine when the bivalves are ready to re-open, i.e., the recovery period has ended, the valve movements are monitored in a special valve movement monitor.

The bivalves are placed in this valve movement monitor (Fig. 3.7), and each valve of the animal has a sensor fixed to it for measuring the distance between the two valves. The monitor records the degree of opening and closing of the valves. By using the on-board dedicated computer, the valve movement pattern of the bivalves is continuously registered. In "clean" water, bivalves show a characteristic valve

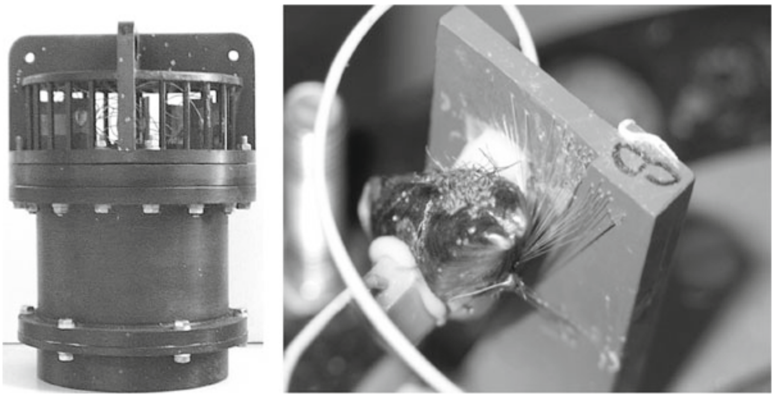

Fig. 3.7 Valve Movement Monitor®. *Left*: overview monitor. *Right*: details of mussel with sensor (note the byssus thread production)

movement pattern in which they are open most of the time and filtering. Without careful, site-specific monitoring, it is not possible to select the appropriate Pulse-Chlorination® regime. Once the specific behavior of the macrofouler in this location is established, a chlorination regime, which takes advantage of this behavior, can be implemented (Rajagopal et al. 2010). If, for example, it is established that under the particular circumstances of an industrial facility the macrofouler re-opens the shell approximately 10–20 min after exposure, the chlorine can be pulsed in 10–20 min on and 10–20 min off intervals (refer Fig. 3 of Chap. 12, Macdonald et al. 2012). The Pulse-Chlorination® regime saves on chemicals, is gentler on the receiving environment and will result in faster mortality of the macrofouler. The method is accepted as Best Available Technique (BAT) in Europe (Anon 2000).

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Chapter 4
Cooling Water System Design in Relation to Fouling Pressure

Maarten C. M. Bruijs and Henk A. Jenner

1 Introduction

In view of the many operational and environmental issues cooling water systems (CWSs) are faced with, having specific design attuned to the local ecological conditions at a specific location is crucial to prevent the implementation of costly mitigation measures after construction. Such issues are fouling by micro- and macro-organisms, jelly fish ingress and also the discharge of heated cooling water. It is, therefore, of great importance to take into account the specific ecological conditions at the location during the design phase. This chapter concerns the fouling-related issues and options to optimally design the CWS to prevent operational problems.

2 Types of Cooling Water Systems

The two main types of cooling water systems are once-through and open/closed recirculating CWS. In "once-through" systems, water is pumped from a source (e.g. a river, canal, lake, sea or estuary) and passes through the heat exchangers. In most cases, the heated water thereupon is discharged directly into surface water. Most once-through systems have large cooling capacities (>200 MW) and are used by large-scale power generators and petrochemical industries, which—for this reason—are often located close to large water bodies. Generally speaking, water quality and chemistry in a once-through system are less restrictive than in recirculating systems.

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Typical flows for large power stations amount to 30–45 m^3/s per 1,000 MWe and residence times inside the CWS typically vary between 2 and 15 min. The temperature of the cooling water at the point of discharge will generally not exceed 30°C, as this is the regulatory maximum in the Netherlands. In the biofilm on the heat exchanger, temperatures will be higher than in the bulk water, up to approximately 5°C, depending on the thickness of the biofilm and the type of material used for the heat exchanger.

In an open recirculating CWS, the cooling water circulates in an open loop. Water that has passed through the heat exchangers is returned to a cooling tower, where the temperature is lowered by evaporative cooling. The cooled water is collected in a basin, generally located under the cooling tower, from where it is pumped to the heat exchangers. The tower design can be based on natural air draft or induced draft. Water losses are caused by evaporation and drift losses from the top of the cooling tower. Because of evaporation in the tower, minerals and organics in the recirculating water concentrate to such a level that precipitation can occur, which is called "scaling". To manage the risk of scaling, and sometimes also corrosion, a certain amount of concentrated recirculating water is purged from the system. The water that is purged from the system is referred to as "blowdown". In order to compensate for water losses due to blowdown, evaporation, drift and leakages, water is added: the so-called "make-up". The make-up water flow used by an open recirculating system is 1–3% of the flow of a once-through system with the same cooling capacity. Blowdown flows generally range from 0.5 to 3 $m^3/h/MWt$, with concentration factors ranging from 4 to 1.5. Residence times vary between 1 h and 4 days. The water in a recirculating CWS can be contaminated by three different sources: (1) the air passing through the tower introduces dust, micro-organisms and exchange of gases, (2) suspended solids in the intake water and sometimes, (3) process fluids leaking from heat exchangers directly into the cooling water due to higher pressure in the process. The first source is unique to open recirculating systems, the other two also occur in once-through CWS. From an environmental viewpoint, leakages of process fluids are more problematic in once-through systems, since the cooling water here is discharged directly into the receiving water body, while in a recirculating system contaminants will be temporarily retained. In a recirculating CWS, both the cooling tower and the heat exchangers are subject to fouling processes. Fouling of the heat exchanger is generally more critical than fouling of the cooling tower, although cases of operational problems due to severely fouled cooling towers are known. Open recirculating systems are mainly used for industrial applications with a heat capacity ranging from 1 to 100 MWth, but also for power stations with larger capacities if sufficient water is not available, or if the temperature of the receiving water is too high, a situation found alongside rivers with low flows in warm summer months.

3 Cooling Water Intake

Cooling water is withdrawn from the environment via an intake structure. Regardless of the scale of the cooling water flow, any given intake system has similar arrangement of civil and mechanical systems to provide the cooling water to the station. A distinction is made between offshore and onshore intake systems.

3.1 Offshore Intake Systems

The offshore intake systems are applied at marine and estuarine locations and comprise a water tunnel which runs out from land, below the seabed, to open in relatively deep water some distance offshore. The openings of the intake are usually close to the seabed to avoid drawing in the warmer surface layers and may be equipped with some kind of concrete capping arrangement (sometimes known as the "velocity cap") to reduce abstraction from the surface layers. Such an arrangement is believed also to reduce fish ingress, by eliminating vertical water currents which fish are ill-equipped to avoid (Schuler and Larson 1974). Some form of coarse screening is always provided at this point, to prevent the entry of large items such as tree branches and fishing nets which might otherwise obstruct the CW tunnels. Offshore intakes may have no visible superstructure above the water surface, being evident only from the necessary navigation marks, or may have elaborate superstructures. The latter provide access and support cranes or other lifting gear designed for the insertion and removal of stop-logs and trash-racks during maintenance. As such mechanical equipment is remote from normal power station operations and therefore difficult and costly to maintain in a hostile salt-water environment, it is common nowadays to dispense with such elaborations.

The CW tunnel which conveys the water back to the main site is normally designed to permit a water velocity of around 1.5–3.0 m/s, to avoid sedimentation. A descending shaft below the intake opening leads to a near-horizontal tunnel, a slight uphill slope being provided to prevent air retention. At the onshore end, the tunnel opens into the floor of a forebay open to the atmosphere; the water upwells in a violent maelstrom. The tunnel arrangement functions like a manometer: flow into the forebay chamber occurs by gravity; water is drawn from the forebay chamber by the CW pumps, a hydraulic gradient is thus created across the limbs of the "manometer", causing water to flow in from the inlet.

3.2 Onshore Intake Systems

Onshore intake systems are often associated with a wharf-type structure, where deep water is found at the water margin (e.g. Thames-side power stations, UK). Alternatively, a dredged channel, often based on a pre-existing tidal creek or from a water basin such as a harbour (e.g. Gravelines (France) and Maasvlakte power stations (Netherlands)) (Parent and Monfort 1985; Bordet 1983), can be used to connect offshore waters with the onshore intake. At Gravelines, this connecting channel is 1.5 km long. From the intake entrance, water normally collects in a forebay area, in the same manner as the landward end of the offshore intake type. Thereafter, the CW systems of both intake types become comparable. Fine materials are removed by moving screen systems.

Two types of moving screens can be distinguished: band screens and drum screens. Band screens are common in older power stations but are still used in smaller power stations having a CW flow of 5 m^3/s or less. The screen comprises a continuously revolving belt of linked mesh panels. Width may be up to 4 m and the screens may be used with sump depths of up to 30 m, making them suitable for sites experiencing a large tidal range. Mesh sizes range from around 3.5–10 mm, depending on location. Water passes from outside to middle. The screen is backwashed continuously by spray jets located near the top of its travel and all the impinged material is carried, via sluices, to a trash collecting system. A fairly common screening system for sewage and industrial use, including dewatering of sewage sludge, the drum screen was introduced to overcome the large number of (moving parts) joints of bandscreens. Drum screens were introduced in the 1960s to cope with the high debris loadings found at some coastal power stations, which had been found to overload the capacity of bandscreens. As the name suggests, the screen is in the form of a large rotating drum, which may be anything up to 25 m in diameter and ranging from 1 to 5 m in width. The required diameter is determined by the CW flow of the water level. The largest diameters (up to 25 m) are used at nuclear units which require more than 40 m^3/s of cooling water (e.g. EdF stations at Gravelines, Paluel, Penly and Flammenville) or at sites where tidal range is exceptional, e.g. 15 m on the Severn Estuary in Britain. Mesh sizes are as for band screens, but the common usage in France is for 3.5 mm meshes, whereas in the UK up to 15 mm and in The Netherlands up to 10 mm are used. The smallest mesh used in power stations operated by EdF is approximately 1 mm.

4 Fouling in Cooling Water Systems

Various types of macroscopic organisms are responsible for problems in power station operation, depending on the type of natural water used for cooling. Fouling is mainly caused by organisms with a shell or hard exoskeleton, such as mussels or barnacles. Clogging problems at marine intakes are caused by drifting organisms, such as jellyfish and seaweeds or by shoals of small fishes. Similar weed problems are found at inland sites. Special problems are found in cooling towers where blue–green algae (Cyanobacteria) grow as thin sheets over the internal surface of the tower shell. When the towers are out of service, the algal sheets dry up and fall onto the droplet eliminators and then to the main packing. This causes blockage of the packing and additionally blockage of the removable screens at the exits to the tower ponds.

4.1 Micro- and Macrofouling

When the natural waters of rivers and the sea are brought in contact with man-made surfaces, such as the pipework of a cooling water circuit, then the surfaces are colonized by living organisms. This colonization takes place in an orderly pattern. Firstly, organic molecules are deposited, followed closely by the attachment of bacteria, especially those which have a pellicle and produce slime as a part of their metabolic functioning (Characklis 1981). Once these bacteria are established, the colonization of the surfaces by other organisms becomes possible. Both the bacterial slimes and the larger animals or macro-invertebrates constitute the fouling community. Clearly, the types of fouling are dependent on the geographical location of the power station and on the salinity and quality of the water. Speed of colonization depends to a large extent on the metals: titanium condenser tubes are very rapidly colonized, whereas copper alloys, cupronickel and brass, which have inherent toxicity to bacteria, are colonized at much slower rates.

Macrofouling is usually thought of as colonizing the intake pipework of direct cooled power stations and it is from the problems caused by the Blue Mussel (*Mytilus edulis*) that the interest in this subject developed. In non-tidal low salinity waters such as the Noordzeekanaal in The Netherlands, the brackish water mussel (*Mytilopsis leucophaeata*) is found and in freshwater the equivalent is the Zebra Mussel (*Dreissena polymorpha*). In addition, in North America, severe problems have been caused by another bivalve mollusc, the Asiatic Clam (*Corbicula fluminea*). During recent years, this species has been found in European rivers, the Rhine in Germany and in The Netherlands, the Moselle (CEMAGREF 1989–94), the upper Rhone (Bachman et al. 1995) and the Garonne basin (Dubois 1995) in France. The species is found at a few stations in the Netherlands along the River Rhine, on the bottom of pits and sometimes in the Taprogge ball sieve system.

4.2 Other Fouling Types

Fouling is not restricted to micro- and macrofouling, as three other types of problem may be considered in this category (Fig. 4.1). Firstly, there is the material generally known as trash, which is swept into the power station along with the cooling water. The trash consists of inert debris, seaweed, hydroids reeds, plastic bags, bits of wood and many other sorts of free-floating material and living material such as sea gooseberries (*Pleurobrachia pileus*), jellyfish and fish. These last include those types which form shoals as they migrate in the nearshore waters from which the cooling water is withdrawn, such as Sprat (*Sprattus sprattus*) and Herring (*Clupea harengus*), and those species drawn into intakes on their migratory movements into and out of estuaries and rivers like the shad (*Alosa* spp.), salmonids and eels. The rotating screens generally remove most of the trash. Any material which passes through these screens and penetrates the main and secondary cooling systems is called debris. Debris causes problems with screens and end plates in small-sized heat exchangers, most usually in the auxiliary or secondary circuits. Intake structures

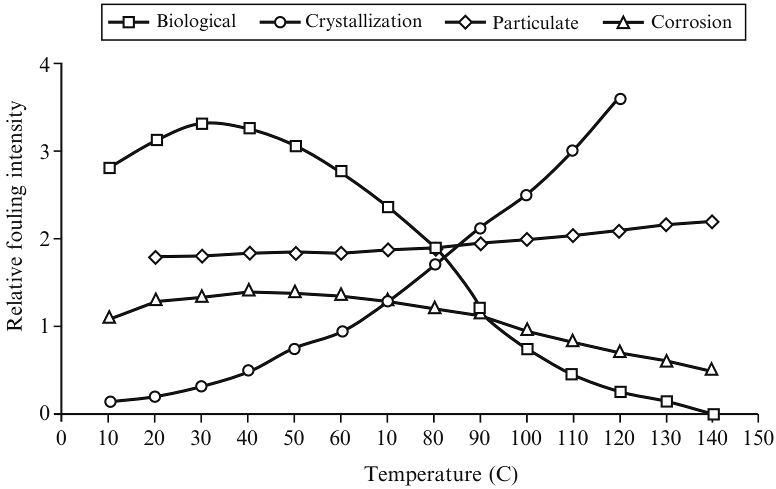

Fig. 4.1 The effects of surface temperature on relative fouling at constant flow

should be designed in such a way that entrainment of fish, debris, organic and inorganic material, including suspended matter, is kept at a minimum. Macrofilters, such as rotating filter screens, in combination with automatically cleaning trash-racks are useful to prevent larger (>5 mm) particles from entering into the CWS. The solutions to prevent ingress of fish and techniques to increase the survival of impinged fish are discussed elsewhere (Bruijs and Taylor 2012).

Secondly, in inland stations using cooling towers, there is the problem of scale formation. Scaling is the deposition of chemicals as a layer on the cooling water side of heat exchangers, which is best considered as a form of fouling because its formation resembles the processes related to those which cause biofilms to develop on the same surfaces. In particular, the quantity and quality of make-up water entering the system, the flow rates of the circulating water and the inlet and outlet temperatures of the condenser water have a strong influence on the rates of scale formation.

Thirdly, there is the problem of silt, deposited from make-up water with a high suspended solids load. This causes trouble when deposited in low flow zones, especially cooling tower ponds, and may enhance slime growth by becoming entrapped in the slime so that deposits in condenser tubes and on cooling tower packing are thicker than would be the case with bacterial slimes on their own. In some instances, it is known that silt accumulates so fast that the tower ponds become filled to the rim so the carrying capacity of the closed cooling water circuit is reduced to that of a direct cooled circuit.

5 Corrosion, Deposition and Fouling in Heat Exchangers

A CWS, irrespective of the source water used for cooling, contains many types of metals and alloys. Their interactions with fouling are almost all unique to the specific process and conditions, as shown in the many publications that discuss cooling water chemistry, deposits and corrosion failures. Heat exchanger fouling is a major economic

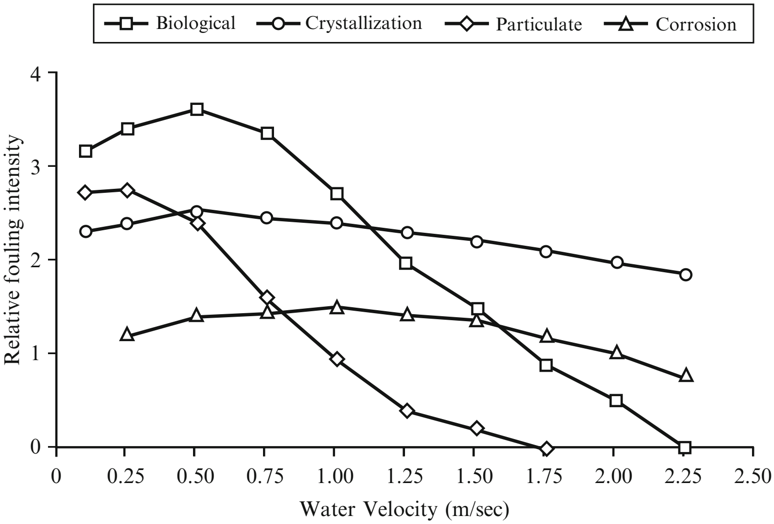

Fig. 4.2 The effects of flow on relative fouling at constant temperature

problem, and maintenance costs are estimated to account for 0.25% of the world GDP (Pugh et al. 2003). Fouling typically falls into the following discrete categories:

- Micro and macrofouling
- Particulates—silt, mud, sand, insoluble products, suspended solids, or sediment accumulation
- Crystalline-salt deposition (carbonates and sulphates of Ca, others)—salt deposition (organic/inorganic) or crystalline-ionic fouling
- Corrosion products—metals are oxidized, metal fluid reactions
- Chemical reaction-petroleum refining and polymer production interactions (these include organic fouling such as asphaltenes, coking and polymerization reactions)

Equipment is usually subject to more than one type of fouling. The mechanisms are interactive and inter-related. For example, macrofouling affects cooling water flow and thus allows more sedimentary deposits, which in turn can lead to micro-fouling and corrosion. Fouling rates are affected by both temperature and cooling water flow rate (Figs. 4.1 and 4.2).

- Crystalline fouling greatly increases with temperature
- Biological fouling decreases with temperatures above 50°C and has little to no effect at temperatures above 140°C
- Particulate fouling increases slightly with temperature but is almost constant
- Corrosion fouling decreases slightly above 50°C
- Biological fouling decreases with flow over 0.7 m/s and stops over 2.2 m/s
- Crystalline fouling slightly decreases with flow over 0.5 m/s

- Particulate fouling decreases with flow and stops above 1.7 m/s
- Corrosion fouling decreases very slightly with flows above 1.2 m/s

The extent of fouling can be determined in a variety of ways, including looking in the heat exchanger and tubes, calculating pressure drops, temperature rises, turbine backpressures or other unit efficiency measurements. The most common control method is simply cleaning when plant operations are affected. This method is not enough to minimize the cost of fuel or electricity or loss of equipment life due to tube corrosion. Performance modelling is necessary to determine optimum times for cleaning and efficiency maintenance. For this purpose, Heat Exchanger Institute (HEI) standards (Cleanliness Factor, CF), EPRI standards (Taborek and Tsou Performance Factor, PF) or Engineering Sciences Data Unit (ESDU) guide data (ESDU 2003) can be used, but most companies develop their own performance models. The simplest way to develop a model is to compare heat transfer just before and after cleaning, and then calculate the increase in efficiency due to the heat transfer gained.

6 Effects of Fouling in Cooling Water Conduits

CWSs are commonly used in industry to extract and dissipate low temperature heat from processes. Together with the cooling water, a wide range of living organisms is entrained into the CWS, which can readily colonize the available concrete, metal, wood and plastic surfaces in the heat exchangers, the cooling water conduits and the cooling tower. Growth conditions in the CWS often are ideal for sessile organisms: the steady water flow assures abundance of nutrients and oxygen, while access for predators is limited. The consequence of this is that substantial “biofouling”—defined as undesired biological growth—may take place inside the CWS. Biofouling may cause restriction of the cooling water flow, blockage of heat exchangers, increased rates of corrosion and loss of heat transfer. All these have negative environmental and economical consequences.

Biofouling is generally of two main types: macrofouling, involving organisms such as mussels, oysters, barnacles and hydroids; and microfouling or slime, consisting of a sessile microbial population, comprising slime-producing bacteria and anaerobic sulphate-reducing bacteria.

Macrofouling may cause gross blockages of pipework and culverts and so-called erosion-corrosion, when shells get caught at the entrance or inside heat exchanger tubes. Macrofouling is very much location- and water quality-specific, both in terms of quantity and species variety. A practical example: two identical units of the same coastal power station are colonised by the same macrofouling species, but over the last years biomass development has been consistently larger in one unit. Experience in Rotterdam harbour has shown that mussel fouling can disappear within a distance of a few kilometres, or from 1 year to another, due to variations in water quality and salinity levels.

Table 4.1 Hydraulic roughness values of smaller artificial concrete channels (refer Barton et al. 2008 for details)

Substratum	Minimum	Normal	Maximum
Clean concrete	0.013	0.013	0.015
Microfouled concrete	Increase roughness value with +0.01		
Macrofouled concrete	0.020–0.045[a]		

[a]Differences between clean and fouled systems

Macrofouling is generally confined to once-through CWS, although it may occur in the intake conduits of recirculating CWS. Inside recirculating CWS, however, high temperatures and the concentration of salts inhibit macrofouling growth. In marine and brackish water, macrofouling is more severe than in freshwater, with potential biomass development up to hundreds of tonnes within 2 years for an average power station of 1,000 MWe. In freshwater, this could reach a maximum of several tonnes.

Development of macrofouling in power plant CWS leads to reduced water flow due to build-up of organisms along the walls of the pipes and culverts, causing pump head pressure to drop. Hydraulic roughness values presented in Table 4.1 show the differences between clean and fouled systems. Growth eventually will lead to blockage and an unexpected trip of a 600 MW power station is estimated at EUR one million per day. Detachment of larger organisms, e.g. live mussels and empty mussel shells, can lead to blockage of small bore condenser tubes and lodged shells lead to long-term erosion-corrosion of the tubes and hence contamination of the feed water, which in turn causes corrosion of boiler tubes and turbine blades. This loss of efficiency and mechanical damage is extremely costly.

In order to define a proper roughness value for biofouled closed pipes, one must take into account the growth ratio and characteristics of mussels. Assuming that the mussel is growing 4 cm within 30 weeks, it can be said that during the growing period the pipe roughness n (Manning coefficient) can vary from 0.020 to 0.045 ($L^{-1/3} \times T$). From the above, it is obvious that the variation of the pipe roughness can lead to different velocities and flow profiles, and in case of biofouling, decrease in velocity and drop in pressure profile. Concerning the pressure drop in the whole pipe flow profile, a friction factor and a Reynolds number can be chosen, according to Colembrook (Moody diagram) for hydraulically rough walls and turbulent flow. Therefore, values above 10^4 for the Reynolds number (turbulent flow) and values higher than 0.001 for relative roughness λ (k/D) can be the case for a fouled system. The above-mentioned approximations have been made under the assumption of incompressible, steady and uniform turbulent flow in closed pipes (Douglas et al. 2001; Idelchik 1994; Barr and Wallingford 2005).

Microfouling is always the primary colonizer of surfaces in the development of biofouling and is often a precursor to the successful settlement of larger organisms. Microfouling-related problems occur both in once-through and recirculating systems. There are two types of microbial populations distinguished in a CWS: a planktonic population, with micro-organisms free in suspension; and a sessile one, with micro-organisms attached to the surfaces in a matrix of organic material forming a biofilm, or the slime layer, in which suspended solids can be caught from the cooling water. The matrix consists of extra-cellular polymers produced by the bacteria to harbour themselves and to improve their immediate environment.

For this reason, a combination of measures is taken to control biofouling. One of these is the application of a biocide: compounds added to the cooling water aiming to control growth of organisms.

It can be concluded that various types of macroscopic organisms are responsible for problems in power station operation depending on the type of natural water used for cooling. Fouling is mainly caused by organisms with shell or hard exoskeleton such as mussels and barnacles. Clogging problems at marine intakes are caused by drifting organisms, jellyfish and seaweeds or from shoals of small fishes. Similar weed problems can be found at inland sites also. In Table 4.2, some key data on water characteristics, together with fouling-related data per CWS type, are presented.

7 CWS Design and Fouling

Many design and layout features directly or indirectly affect the amount of biocide needed for adequate biofouling control in an operating CWS. Many antifouling techniques require special provisions to be integrated in the design of the CWS. Examples of these are filtering devices, mechanical cleaning devices and facilities, backwash systems, provisions for recirculation of the cooling water (for thermal treatment) or special dosing racks and dosing points. Provisions can also be of a more simple nature, for example connection points for chemical and biological monitoring devices.

7.1 Water Velocity

Water velocity and the potentially complex hydrodynamics of circuit design are important factors in the "fouling potential" of a given CWS. Settlement of larvae and the ability of settled organisms to remain on a given surface depend greatly on water velocity. Some species are well adapted to slow-running or even stagnant water, while others require strong water currents.

Water velocity varies considerably in cooling water circuits from the water intake structure to the outlet. It is low near filtering devices like travelling screens and in basins, especially cooling tower basins. It is high in pipes leading to heat exchangers and in heat exchangers. The operating regime of pumps in any given circuit must also be considered as this can cause both variations in flow rate locally and even periods of stagnation.

For organisms which settle on circuit walls, the routine renewal of water in a CWS is an extremely favourable factor as it provides a source of nutrients and dissolved oxygen. For this reason, when water velocity is not excessive, organisms

Table 4.2 Characteristics of industrial cooling water systems

Cooling water characteristics							Fouling-related data			
Type	Residence time	Water type	Intake flow (m^3/s)	Temp. of bulk (°C)	pH value	Concentration factor	Fouling problems	Biofouling organisms	Cooling water additives	Biocides used
Once-through	2–15 min	Fresh, brackish, marine	2–60	Max. 30	7–9	1	Biofouling Corrosion Scaling[a]	Macrofouling: mussels, oysters, barnacles, hydroids, amphipods, tubeworms Microfouling	Biocides	Oxidizing (NaOCl most frequently used, >90% of biocide using systems)
Open recirculating	1 h–4 days	Fresh	0.1–0.2	20–30, sometimes higher	7–9	3–5[b]	Biofouling Corrosion Scaling Pathogenesc	Microfouling Macrofouling[d]: algae bryozoa, snails	Biocides corrosion Inhibitors scaling Inhibitors dispersants[e] pH adjustment (acid)	Oxidizing (NaOCl most frequently used, >90% of the cooling water systems) Non-oxidizing
Closed recirculating	Up to 6 months	Fresh[f]	0	30–50 and higher	7–9	n.r.	Biofouling Corrosion	Microfouling: (of minor importance)	Biocides corrosion Inhibitors dispersants pH adjustment (acid)	Non-oxidizing

[a]Scaling does not frequently occur in once-through CWS, it is a more relevant problem in recirculating CWS
[b]These are typical; values as low as two (power stations) up to nine are found in practice
[c]Open recirculating CWS may harbour many human pathogens which are of concern
[d]Macrofouling can be a problem in intake conduits, but not in the recirculating CWS itself
[e]Typical concentrations are: biocide 1–50 mg/L (active compound); corrosion inhibitors 2–20 mg/L; scale control agents 2–20 mg/L; dispersants 1–10 mg/L
[f]In closed recirculating CWS, often high quality, slightly alkaline demineralised water is used

show optimum growth, generally more rapid than that of the corresponding population in the natural environment (Fig. 4.2). When the velocity exceeds a critical threshold, larvae are no longer able to settle and adults are not able to feed well. They may even become detached from the substratum. In the absence of water circulation, dissolved oxygen becomes the limiting factor and can cause mortality by asphyxia in 1–3 weeks, depending on the temperature and the organisms present.

7.2 Water Velocities in Conduits

When designing a CWS, stagnant zones and sharp curves in conduits and heat exchangers (e.g. man-holes and dead end lines) should be kept to a minimum. In the stagnant zones, biological growth thrives, because water velocities are low which favours settlement of biofouling organisms. Additionally, the mass transfer of biocides to the biofilm will be reduced if the water velocity is too low. This is especially important in once-through CWS at locations where macrofouling is an issue. Water velocities, therefore, are a very important factor in the design of cooling water conduits and heat exchangers. Low water velocities favour precipitation of debris in general and allow settlement of macrofouling. A general rule of thumb for the cooling water conduits is to keep water velocities above 2.5 m/s, to prevent settlement of macrofouling as much as possible.

7.3 Water Velocities in Fresh Water CWS

For fresh water fed once-through CWSs, the zebra mussel (*D. polymorpha*) is the most important hard shell fouling species. In natural waters, zebra mussels tolerate a wide water velocity range from 0.05 to 1.0 m/s (Leglize and Ollivier 1981). Post-veligers (<1 mm) are more sensitive to current than adults, as their attachment strength is two order of magnitude less than that of adults (Ackerman et al. 1995). This species is not found at 2 m/s, although some isolated specimens can resist 2 m/s. In several CWSs, zebra mussels are found in high numbers at velocities of 10–50 cm/s, but not in parts of the circuit where water velocity exceeds 1 m/s.

7.4 Water Velocities in Seawater CWS

For marine and estuarine water fed once-through CWSs, a variety of hard shell fouling species play an important role. Main species are mussels (*M. edulis* and *Mytilus galloprovincialis*), barnacles (*Balanus crenatus*), oysters (*Crassostrea gigas*) and hydroids (*Tubularia*). The presence of these species is considerably reduced when the mean velocity is in the range of 1.8–2.2 m/s. Table 4.3 presents an overview of biofouling development in relation to velocity at Le Havre power station (France).

Table 4.3 Biofouling development in two intake conduits at Le Havre power station units 1 and 2, as a function of mean water velocity (refer to Jenner et al. 1998 for details)

	Water chamber rotating screen	Rectangular section 5.5–11 m^2		Circular section 3.0–4.9 m^2		
	<0.5 m/s	1.4 m/s	2.0 m/s	1.8 m/s	2.2 m/s	2.9 m/s
Ascidians *Ascidiella aspersa*	Important coverage	Absence	Absence	Absence	Absence	Total absence of settled organisms and organic debris
Mussels *Mytilus edulis*	Important coverage	Total coverage of one wall 14,400/m^2	Total coverage of one wall, the other is less colonized than at 1.4 m/s	Presence on seals only	Presence on seals and some small walls	
Barnacles *Balanus improvisus*	Important coverage	Total coverage of one wall, the other is less colonized (mussels are settled on this surface)	Infrequent living barnacles	Presence on seals only	Infrequent living barnacles	
Hydroids *Tubularia*	Important coverage	Total coverage of one wall, the other is less colonized	Some mats of hydroids in decomposition	Presence on seals only	Some mats of hydroids in decomposition	
Mud and organic debris	Abundant deposits	Abundant deposits	Abundant deposits	Very little organic deposit		

Table 4.4 Water velocity as factor influencing settlement of macrofouling

Water velocity (m/s)	Comment	References
>0.1 but <1.5	Allows blue mussel and oyster larval settlement	Rajagopal et al. (2006)
1.8–2.2	Allows settlement of oysters, mussels, barnacles, hydroids in circular conduits	Jenner et al. (1998)
>3.0–>3.3	Does not detach mussels	Syrett and Coit (1983)

Table 4.5 Erosion limits: maximum design water velocities for flows inside tubes

Low carbon steel	10 ft/s	304.8 cm/s
Stainless steel	15 ft/s	457.2 cm/s
Aluminium	6 ft/s	182.9 cm/s
Copper	6 ft/s	182.9 cm/s
90–10 Cupronickel	10 ft/s	304.8 cm/s
70–30 Cupronickel	15 ft/s	457.2 cm/s
Titanium	>50 ft/s	>1,524 cm/s

7.5 *Water Velocity in Heat Exchangers*

A first approach to prevent fouling in heat exchanger is the choice of material. Materials commonly used in condensers and heat exchangers are titanium, stainless steel, carbon steel and Cu-alloys (but also nickel alloy, molybdenum alloy, duplex alloy). Biological fouling can be largely eliminated by the selection of copper-bearing alloys, such as 90–10 copper–nickel (UNS70600) or 70–30 copper–nickel (UNS71500). Generally, alloys containing copper in quantities greater than 70% are effective in minimizing biological fouling. Titanium heat exchangers have proven to be corrosion-proof, even at locations where seawater is used as a coolant, under severe fouling conditions. However, micro-organisms colonize titanium tubes much more rapidly than copper alloy heat exchangers, making it necessary to install online sponge ball cleaning system.

Some types of fouling can be controlled or minimized by using high-flow velocities (Table 4.4). If this technique is to be employed, the possibility of metal erosion should be considered as it is important to restrict the velocity and/or its duration to values consistent with the satisfactory tube life (Table 4.5). Some metals, such as titanium or stainless steel, can be quite resistant to erosion by the high velocity effluent.

In the heat exchanger tubes, velocities should be kept higher than 2.5 m/s, to ensure effective heat transfer and to prevent macrofouling settlement. Ti-tubed condensers can withstand velocities up to 3 m/s without any problem. Too high water velocities, however, introduce a risk of corrosion erosion. Critical water velocities depend very much on the type of material used (e.g. 7 m/s for carbon steel, 2 m/s for 90/10 Cu–Ni alloys). Minimum velocity to prevent sediment deposition and under deposit corrosion is 1.0 m/s.

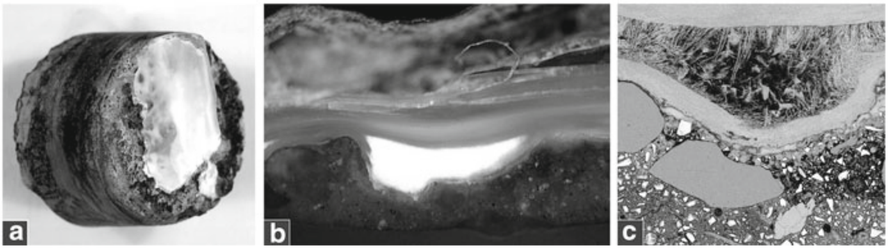

Fig. 4.3 Mode of attachment of the Japanese oyster shell to concrete: (**a**) Side view of the concrete sample, (**b**) Detail of the embedded sample, (**c**) SEM image of the oyster shell/concrete interface: concrete (*below*) and the oyster shell (*above*)

8 Application of Coatings

Most cooling water conduits are made out of concrete, although there is a tendency to apply glass fibre reinforced plastics (GRP) at new constructions. The roughness of the conduit surface walls plays an important role in the settlement of fouling. The smoother the surface, the more difficult it is for the larvae to attach to the surface. Biofouling species show a variety of strategies to attach to a surface, e.g. mussels use byssus threads, barnacles develop a basal plate that is strongly cemented on the surface and the Japanese oyster cements right shell half fully to the surface. Figure 4.3a, b show details of the attachment of Japanese oyster on concrete surface.

It is possible to treat surfaces on which biofouling develops to prevent settlement of larvae and stop the growth of settled organisms. Paints or complex multi-layer coatings can be applied at different locations in the cooling water circuit: intake conduits, screens, pipes, condenser waterboxes and condenser tube plates.

Coatings are not standard applied in cooling water intakes, mainly due to the costs involved and the fact that the coatings need to be re-applied after a certain period. However, antifouling coatings and paints are able to play an important role in the reduction of fouling settlement and growth. The application of coatings in cooling water conduits and other surfaces is well known and there are a large number of coatings specifically developed for this. They also indirectly reduce the amount of biocide needed for adequate control. Therefore, such coatings can be very cost effective.

The most promising product available for CWS at this moment are the non-toxic, fouling-release, silicone-based coatings. The coatings are usually applied in layers, although experience with a single layer has also shown good results. The silicones are physically soft and therefore susceptible to impact damage and abrasion. The development of a paint with both properties remains a challenge to the paint industry. The estimated life time of the silicone coatings that are commercially available is 4–5 years, but there are records of longer functional periods.

For the power industry, the application of coatings in CWSs, both on surfaces in the inlet structure and conduits, can provide advantages with respect to fouling control (better mitigation, less usage and discharge of biocides, as well as better pumping capacity due to less drag) and extension of the equipment lifespan. Experiments in power stations in the US showed that financial benefits (savings on cleaning, disposal and fuel costs) vastly exceeded the costs of application and reapplication.

Antifouling coatings are defined in the Biocidal Product Directive (BPD) of the European Union as: “products used to control the growth and settlement of biofouling organisms (microbes and higher forms of plant or animal species) on vessels, aquaculture equipment or other structures used in water” (EU 1998). Non-toxic, effective coatings are very suitable to prevent fouling (antifouling) or to make it easy to remove the fouling (fouling-release), by which the application of biocides can be reduced. Application of non-toxic coatings is advantageous from the viewpoint of lowering the operational costs (biocide dosing and less effects by fouling) and lowering the environmental impact.

The development of antifouling systems has a long history, but the last 10–12 years showed an increase in the focus on environmentally acceptable alternatives. The first antifouling paints used biocides to kill organisms through a leaching process using heavy metals or organo-metallic compounds, e.g. copper. In the late 1960s, a breakthrough in antifouling paints came with the development of the so-called self-polishing paints, in which organo-tin compounds were chemically bonded to a polymer base. This organo-tin compound replaced the traditional copper-containing antifouling paints, because of its excellent antifouling properties. The leaching rate of these paints is controlled because the biocide is released when seawater reacts with the surface layer of the paint. Tributyl-tin (TBT) was the most used organo-tin compound, but triphenyl-tin (TPT) was also used. However, organotins turned out to be quite toxic and persistent in the marine environment. As a result of this, the Marine Environment Protection Committee of the International Maritime Organization (IMO) has proposed a ban on the application of TBT-based antifouling paints from January 2003 and the ban of the presence of such paints on the surface of vessels from January 2008 (Yebra et al. 2004). Alternatives to organo-tin-based antifouling coatings are roughly divided into the following two-classes:

8.1 Biocidal Coatings

- Biocide-releasing coatings and booster biocides
- Self-polishing copolymer (SPC) coatings
- Coatings continuing natural products/enzymatic antifouling coatings
- Copper–nickel epoxy coatings
- Nano-sized copper-based coatings
- Electro-conductive coatings

In the last decade, environmental concerns about the long-term effect of leachable antifouling biocides have led to increased interest in the development of environmentally friendly alternatives. Several products have reached the commercial market and claimed their effectiveness in the prevention of marine biofouling in an environmentally friendly manner. Lots of research activities are focused on biodegradable toxic compounds and non-toxic adhesion inhibitors. However, based on the information from the "IMO Anti-Fouling Convention: TBT Alternatives", many companies are active in the production of biocide-free antifouling products, but still the most antifouling products contain biocides as ingredients.

8.2 Fouling-Release Coatings

These are coatings with a very low surface energy and lower surface roughness than traditional biocidal coatings. Consequently, the adhesion strength of settling marine biota is less:

- Biocide-free SPC coatings
- Non-stick coatings
- Stenoprohiluric coatings (which prevent fouling by creating and sustaining a biofilm that utilizes *metallic* copper in a unique resin system to create an environment that inhibits settling of undesirable organisms)
- Non-toxic fibre coatings.

9 Concluding Remarks: CW Design Considerations

Important criteria for the design of CWS to ensure minimisation of biofouling and other related problems are summarized below:

- Maintain sufficient water velocity to prevent settlement and growth of macrofouling organisms (threshold values are mentioned below).
- Avoid a regime with long periods of low velocities favourable to the development of biofouling, followed by periods with unfavourable higher velocities, as the larvae can settle and begin growth which will then be temporarily halted. When pumps operate alternately on several circuits, frequent rotation is desirable so as not to leave one circuit at a low velocity for more than 1–2 consecutive days.
- Avoid temporarily suspending all circulation in a circuit invaded by macrofouling for a period of more than 3 days. During the summer thermal peak, organisms die in about 5 days. Upon start-up of the pumps, they are massively detached and filters at the inlet to heat exchangers become clogged and often damaged by the many shells that block the filter.

  Consider the following preventive measures in the design phase of the CWS:

- Avoid low water velocity zones (e.g. excess piping, T-joints, man-holes)
- Apply smoothed hydrodynamic outlines of surfaces, avoid sharp bends

- Avoid over-sizing of intake structures, since these are subject to heavy fouling
- Design intake, such that intake of debris is minimized
- Avoid low water velocities in cooling water conduits (<2.5 m/s)
- Avoid low water velocities in heat exchanger tubes (<2 m/s)
- Apply non-toxic, foul-release coatings on fouling sensitive spots
- Apply corrosion-resistant materials for heat exchangers (e.g. titanium)
- Use reinforced plastics for conduits, heat exchanger inlet and outlet boxes

In the design phase of the CWS, the following provisions should be considered:

- Cooling water intake should be designed according to BAT-guidance with respect to intake velocities, trash rack and filter screens, including fish return system
- Dosing racks that ensure good mixing of the biocide with the cooling water
- The application of targeted dosing, or section dosing
- Small tubing connections for monitoring devices at crucial points (e.g. heat exchanger)
- Application of coatings

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Chapter 5
Barnacles and Their Significance in Biofouling

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1 Introduction

Barnacles are among the "most-unwanted" by ship owners and those involved in the marine industry, especially people entrusted with maintaining marine structures as smooth as possible. Barnacles are arthropods, in the same major group as insects and spiders. They are closely related to crabs, prawns, and lobsters. The name barnacle has a curious origin. Its sudden appearance was similar to that of maggots which appear from nowhere on rotting meat. It was thought that barnacles would be in the ocean for a length of time and led people to believe that this organism also originated from the woods like the "Geese" (Arctic bird and a species of water fowl) presently known as barnacle goose, which breeds in the Arctic, a fact which was not known for long time. As no one ever witnessed the bird breeding, it was thought to spontaneously generate from trees along the shores or from rotting woods.

In fact, as different as the two creatures might appear to us, they share a similar trait: barnacles have long feathery cirri that are reminiscent of a bird's plumage. Barnacles attracted man's attention as early as 1678, when Sir Robert Moray, a founder of the *Philosophical Transactions of the Royal Society*, proposed that they were the eggs of barnacle goose. Thus, these two creatures were closely linked in popular perception. Over time, the crustacean became the central referent of the word, and the bird was called the *barnacle goose* for clarity, making *barnacle goose* an early example of what we now call a retronym.

In 1846, Charles Darwin began working on barnacles. Darwin's interest in barnacles began during his *Beagle* voyage, when he discovered a tiny burrowing barnacle, in a conch shell. Subsequently, Darwin spent 8 long years (from 1846 to 1854) and dissected several barnacles and published four volumes, two on the

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known living species and two on fossil species, summarily titled *Monographs of the sub-class Cirripedia* (Darwin 1851a, b, 1854a, b). He became the world's foremost barnacle expert. Barnacles have relatively recent evolutionary radiation. They are reasonably well represented in Mesozoic and especially Tertiary rocks. About 800 species have been named from recent times. However, the fossil record of the history of barnacle evolution is undoubtedly incomplete (Foster and Buckeridge 1987).

The name barnacle is applied to crustaceans belonging to subclasses Ascothoracica, Rhizocephala, and Cirripedia. Subclass Cirripedia is divided in to super order *Acrothoracica* and *Thoracica*. *Thoracica* includes the acorn and pedunculate barnacles. The classification of thoracican cirrepedes was established by Darwin (1851a, b, 1854a, b). Thoracica is an extremely diverse order and includes the ordinary barnacles found along the seashore. Representatives are found in almost all marine and estuarine environments. Knowledge of barnacles from Darwin to present was reviewed by Newman (1987). Besides the shelled barnacles, there are naked barnacles belonging to *Acrothoracica*, which live inside holes they drill in shells and corals. In some cases barnacles live on, and in some cases parasitize other invertebrates (*Rhizocephala*) (Newman 1987). Barnacles with a calcareous shell include the gooseneck barnacles, which are attached to the substratum by means of a stalk or peduncle and the acorn or rock barnacles, which are attached directly to the substratum.

2 Ascothoracica

Free-living ancestors of cirripedes were similar to Ascothoracicans (Newman 1974). This group constitutes a small, cosmopolitan group of some 20 genera and 77 species, all of which are parasites of coelenterates and echinoderms. They range from relatively motile forms capable of moving about on their host and from host to host, to fixed external parasites. Sexes are generally separate. Males are capable of depositing flagellated sperm in seminal receptacles located at the bases of most of the thoracic limbs of the female. Females shed eggs into the space beneath the carapace from genital apertures at the base of the first thoracic limbs as in the barnacles. The free-living adults swim by beating of the thoracopods in conjunction with strokes of the abdomen and furcal rami, and they grasp their hosts by means of their first antennae, which are not provided with cement glands as in barnacles. Feeding is by piercing mouth parts, the only obvious adaptation to parasitism in motile forms (Newman 1987).

3 Rhizocephala (Parasitic Barnacle)

These barnacles parasitize crustaceans, particularly decapods. They invade tissues of crabs and other crustaceans and become visible only when an egg-sac forms under the abdomen of the host (Barnes 1989). An up-to-date account of rhizocephalans has been given by Hoeg and Lutzen (1985). Until the discovery of their larval forms it was not known that they were crustaceans. The nonfeeding nauplii (as many as four stages), are equipped with frontolateral horns, and the cyprid stage is provided with first antennae having cement glands, an aspect typical of cirripedes (Newman 1987). In some cases, the hatching embryo is a nauplius and sometimes a cypris. They were initially thought to be hermaphrodites, perhaps with complemental males, but were later on found to have separate sexes (Newman 1987).

4 Cirripedia

Cirripedia includes the *Acrothoracica* (burrowing barnacles) and *Thoracica*. *Thoracica*, the principal order of Cirripedia, was divided into three families by Darwin (1851a, b, 1854a, b): *Lepadidae*, the stalked or pedunculate barnacels, *Verrucidae*, the asymmetrical sessile barnacles and *Balanidae*, the symmetrical sessile barnacles.

5 Acrothoracica (Burrowing Barnacle)

The burrowing barnacles (*Acrothoracica*) are nonparasitic, have soft mantle without calcareous plates and burrow into calcareous substrata (e.g., limestone, corals, and mollusc shells). Burrowing barnacles are usually a few mm in length and the females are about ten times longer than the males (Barnes 1989). The tiny males are generally found near the aperture of the females in a pocket of the mantle tissue near the area of the ovary (Barnes 1989). They are predominantly found in warm temperate regions and generally in shallow (30 m) water (Ross and Newman 1969; Zullo 1979). However, a few are also from deep waters.

6 Thoracica

6.1 Lepadomorphs (Gooseneck Barnacles)

Lepadidae or goose barnacles are similar to acorn barnacles; they are often protected by calcareous shell. They have a long flexible tubular muscular stalk which is unprotected. They are pelagic, as they live in the open seas adhering to floating objects. With their long stalks they hang down from the floating object. The stalk of gooseneck barnacles is simply an elongation of the attached end of the animal's body. They are filter feeders using their legs to filter plankton, which is then passed to their mouth.

The capitulum is ventral, often protected by calcarious plates and is held away from the substratum by the peduncle (Fig.5.1a). It is roughly oblong with five smooth white plates, separated by red/brown or black tissue. The capitulum consists

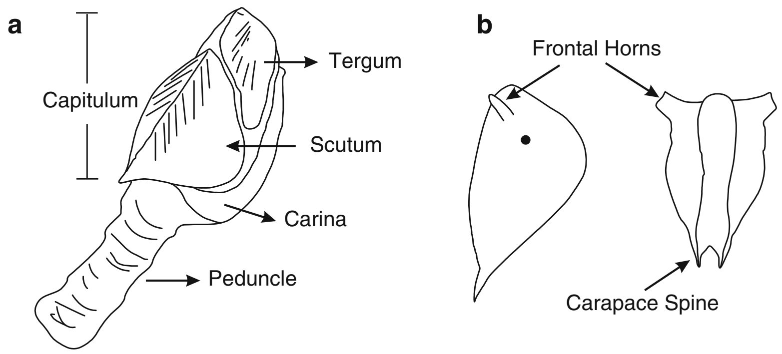

Fig. 5.1 (**a**) Adult gooseneck barnacle: *Lepas* sp. (**b**) Larval stage and cyprid with protruded frontal horns and carapace spines

of most of the animal, including the appendages, the gut, mantle (carapace), and mantle cavity. It is covered by a series of large calcareous plates and numerous smaller ones. The larval stages in *Lepas* include *nauplii* and cypris. *Lepadomorph nauplii* are characterized by elongated body spines and large growth increments between molts (Moyse 1987). Cyprid larvae of some species of *Lepas* retain vestiges of the naupliar frontal horns and carapace spines (Fig 5.1b) which are not found in the cyprid larvae of common balanids (Moyse 1987).

6.2 Verrucomorphs

The asymmetrical sessile barnacles of the genus *Verruca* include some 60 species (Zullo 1982). The shell wall consists of a box of four plates attached to the substratum and covered by a two plated, hinged lid. Darwin (1854a) deduced from the shapes and articulation of the various plates that the four plates of the wall were the rostrum and carina meeting on one side and an articulated scutum and tergum interposed (fixed) between them on the opposite side. The lid, hinged to the rostrocarinal side of the orifice of the wall, consists of the other articulated (movable) scutum and tergum. Having the tergum and scutum of one side immovably incorporated into the wall gives Verruca its asymmetry and is a most important feature (Newman 1987).

6.3 Balanomorphs (Acorn/Rock Barnacles)

Balanomorpha consists of barnacles belonging to the genera *Pollicipes*, *Tetraclita*, *Chthamalus*, and *Balanus*. In general terms, they are referred as acorn or rock barnacles. Balanomorph barnacles are the most common barnacles as they are mostly found in the macrofouling community on man-made structures or industrial systems and also in the marine intertidal regions.

A brief overview of different types of barnacles is presented in the above sections. However, as the objective of this chapter is to address the issues relevant to biofouling, the emphasis is laid on acorn barnacles belonging to *Balanidae*.

7 Chthamalids

Chthamalids are mostly seen in supralittoral and littoral habitats. The zone of *Chthamalus* appears distinctly in the upper part of the intertidal community and the population density is more near the high water level (Kato et al. 1960). The highest level to which barnacles extend is usually occupied by various species of *Chthamalus* as they are probably equipped better to survive dessication and/or higher temperature. They have six wall plates (Fig. 5.2), but the alae and radii overlap in a different way when compared to those of *Balanus* sp. (Harris 1990).

There is no calcareous basis and interlocking pegs, and the shell is firmly anchored to the chitinous basis by numerous attachment fibers. The shells of *Chthamalus* consist of a single layer, which is a single series of growth bands which run parallel to the inner surface. They appear to have a sheath, especially thickened in the region of the insertion of the opercular membrane and above. Reproduction mainly occurs through the exchange of sperm between adjacent individuals, leading to cross-fertilization.

8 Balanids

Members of the family *Balanidae* are sessile with bilaterally symmetrical shells. Shell is made up of four to six (sometimes more) calcareous wall plates or parietes, which are attached to the substratum without a peduncle or stalk. The shell remains open at the top, but can be closed by an operculum of four plates (a pair of tergum

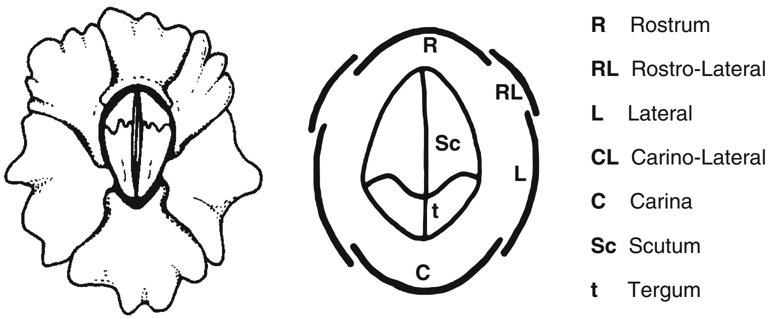

Fig. 5.2 Arrangement of wall plates in *Chthamalidae*

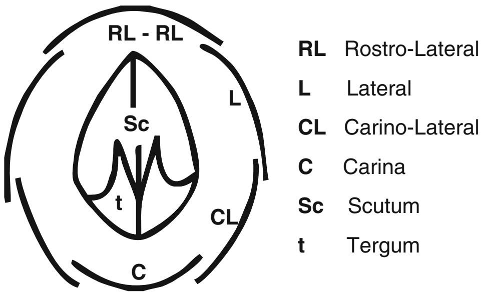

Fig. 5.3 Arrangement of wall plates in *Balanidae*

and scutum each) (Fig. 5.3). A slit-like aperture between the four plates can be opened to allow the limbs to be thrust out for feeding.

Among the balanids, *Balanus amphitrite* is the most commonly employed organism in experimental work related to intertidal ecology and antifouling studies, because of its rapid larval development, ease of raising synchronous mass cultures and predictable settlement in static conditions.

Taxonomy of *B. amphitrite* is complex and several investigators have addressed this issue (Harding 1962; Henry and McLaughlin 1975; Utinomi 1967; Wagh and Bal 1971; Fernando 1990; Yamaguchi 1977). Fernando (1990) worked on the systematic aspects of some fouling barnacles from Indian waters. Originally Darwin classified *B. amphitrite* complex into nine varieties namely *communis, venustus, pallidus, niveus, modestus, stutsburi, obscurus, variegatus*, and *cirratus*. Harding (1962) attempted to reexamine the original specimens of different varieties of *B. amphitrite* which Darwin studied and dissected and designated lectotypes and proposed a revised nomenclature. He divided the nine varieties described by Darwin into four separate species, namely *B. amphitrite*, *B. pallidus*, *B. venustus* and *B. variegatus*. *B. amphitrite* var. *communis* was placed into the species *B. amphitrite* var. *amphitrite*. The varieties *pallidus* and *stutsburi* were placed in the species *B. pallidus*. Darwin's varieties *venustus*, *niveus*, *modestus*, and *obscurus* were placed in the species *B. venustus*. The varieties *variegates* and *cirratus* were accommodated as varieties under the species *B. variegatus*. The taxonomical studies of *B. amphitrite* (Utinomi 1967) revealed that Darwin had put two species under the same taxa; *B. amphitrite* and *Balanus reticulatus* which were subsequently verified by Southward (1975). Utinomi (1967) stated that Darwin's inadequate description and inadvertent muddling of separate varieties, samples, and opercular valves from different sources lead to confusion among varieties of *B. amphitrite.*

Advancement in understanding the taxonomy of *B. amphitrite* group came through an extensive study of morphology by Henry and McLaughlin (1975). In their taxonomic revision of the *B. amphitrite* complex based on previous work and examination of numerous specimens from various localities, they defined amphitrite complex and concluded that only *B. amphitrite amphitrite* was most closely allied only with the recognized subspecies *B. amphitrite saltonensis* (Rogers 1949). Later on, in 1985, based on genetic analysis, Flowerdew (1985) suggested the synonimization of the *amphitrite* variety *saltonensis* with the variety *amphitrite*. Pitombo (2004) illustrated the major phylogenetic revision of the *Balanidae* (Leach 1817) and carried out analysis utilizing a new suite of morphological characters, which resulted in the phylogenetic revision and in a new family *Amphibalanidae*. As a consequence, the major fouling species *B. amphitrite* was renamed as *Amphibalanus amphitrite*. Clare and Hoeg (2008), responding to change in nomenclature, urged taxonomists to exercise caution before introducing new formal nomenclature which should be based on several independent lines of evidence. However, Carlton and Newman (2009) suggest that the changes are in accordance with the International Code of Zoological Nomenclature and help workers understand which fouling barnacles are closely related to each other and help in synthesizing knowledge of the biology and ecology of fouling species. Obviously, knowing the organism is an important facet of any fouling related study. In addition, it is important to understand the larval ecology, settlement, and attachment of larvae for evolving suitable control measures.

On rocky shores, barnacle zones may be very precisely defined with regard to tidal height, and are frequently visibly obvious (Foster 1987). Differential barnacle zonation on shores implies varying adaptations to the gradients of factors between tides. The upper limits are largely determined by physical factors associated with tidal immersion and, lower limits are set by complex biotic relationships. The shell is clearly a protection against predators. Its relative impermeability is also handy preadaptation for sessile existence intertidally. But if breeding is to occur, it needs to be combined with adequate behavior and tolerances of physical stresses, such as reduced feeding time, wider temperature ranges, and the problems of too much fresh water or water loss (Foster 1987). Barnacles have a fugitive biology; they can find themselves in far-ranging environments, right from supralittoral to subtidal zones. Some forms are eurythermal and euryhaline, e.g., *B. amphitrite* (Anil et al. 1995). Barnacles have also been reported from Nile river delta (Shatoury 1958). It is important to understand how they are capable of surviving extreme environments and the answer lies in their biology.

9 Anatomy

The carapace forms a complete covering or mantle over the rest of the body and is usually strengthened by calcareous plates. The body within the mantle consists of a mouth region and thorax (Fig. 5.4). The abdomen is usually vestigial. Typically, the mouth appendages are paired mandibles with palps, maxillulae, and maxillae. The thorax bears six pairs of biramous appendages (cirri) composed of numerous segments, each with a considerable armament of setae. The body is oriented in an upside down posture with the anterior or head end attached to the anterior pair of valves. This is a functional necessity to allow the cirri to project up into the surrounding water as a feeding net. The light-perceptive organs present in the various life stages are: (a) nauplian—a median eye, (b) metanauplian—a median eye and two compound eyes, (c) cyprid—a median eye and two compound eyes, (d) adult—two simple eyes (Fales 1928). When the cypris metamorphoses into an adult, the

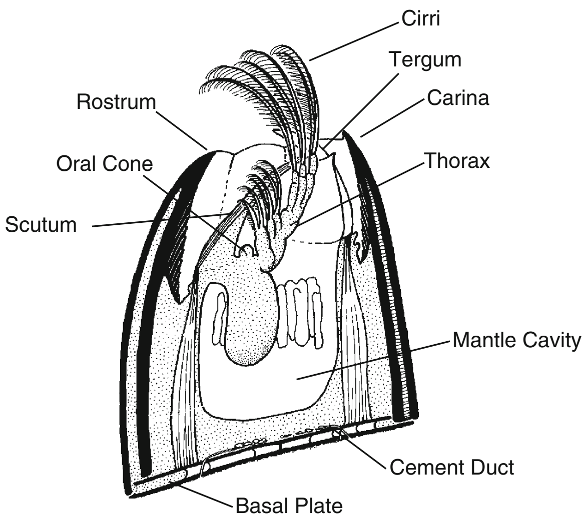

Fig. 5.4 Anatomy of acorn barnacle

median eyes divides into two parts which form the simple paired eyes of the adult, that function as the sole light-perceptive organs of the adult (Fales 1928).

Barnacles do not release their gametes into the sea, but are able to cross-fertilize. Typically, balanomorph barnacles are hermaphrodites. However, in some species young barnacles in their first season are functional males without ovaries (Walker 1980) and later become hermaphrodites. When ready to reproduce, an adult barnacle uncoils its long tubular penis and extends it out through the operculum to search for a nearby receptive neighbor. When the sperm is transferred, the fertilized eggs are brooded within the shell, until they develop into nauplius larvae.

The numerous nauplii are then released into the water as plankton. The nauplius has antennae, an eye spot, jointed appendages, and a shield-shaped body. As the nauplius grows and develops, it undergoes several molts until it develops into cypris larval stage, which does not feed (Fig. 5.5). The cyprid's body is contained within a hinged carapace (Fig. 5.6). The cyprid larvae have chemical and touch sensors that can recognize adults of their own species and hard substrata suitable for settlement. The cypris larva uses special cement glands in its antennae to attach itself to the substratum. The larva then molts and undergoes metamorphosis, rotating its body so that the appendages now face upward.

Barnacles occupy different tidal regimes and they need to adapt to feeding only when submerged. In this context, different species display different capabilities. For example, *Chthamalus* have a lower metabolic rate than the organism which occupies a lower level in the intertidal habitat. Barnacles have also evolved themselves to survive desiccation and respire by taking air into the mantle cavity. As there is marked reduction in metabolic activity during emersion, aerobic respiration has been found to satisfy nearly all their metabolic needs (Newell 1979).

Salinity and temperature are two important physical parameters that determine the distribution of organisms in the marine environment. Some barnacles when

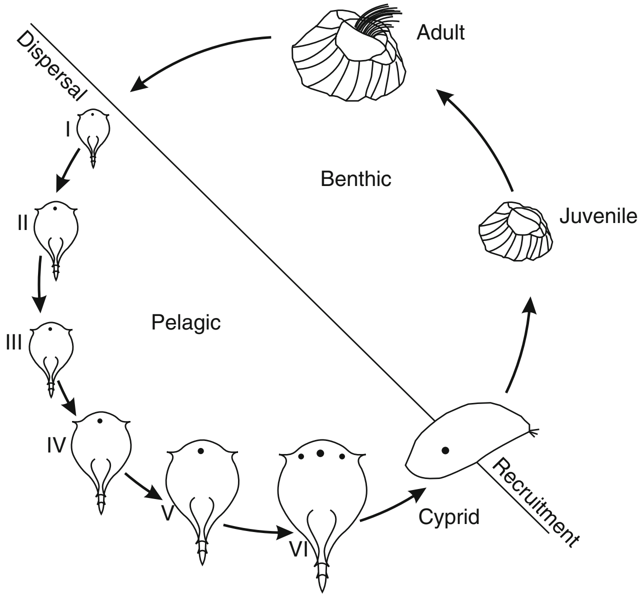

Fig. 5.5 Life cycle of acorn/rock barnacle

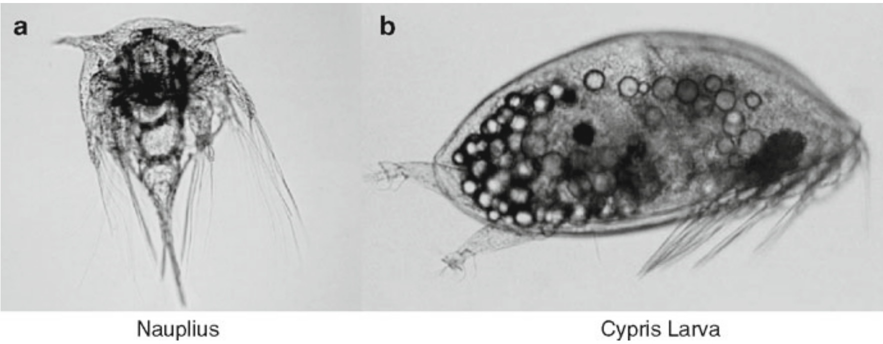

Fig. 5.6 Larval stages of *Balanus* sp. (**a**) Nauplius, (**b**) Cypris larva

immersed in diluted sea water switch to anaerobiosis, e.g. as seen in the case of *Semibalanus balanoides* (Davenport 1976). In the case of *B. amphitrite,* the capability to tolerate wide ranging salinity gives them an advantage to distribute to fringes of habitats and to have a cosmopolitan distribution. Barnacles inhabiting the intertidal regions can tolerate elevated temperatures by increasing the levels of heat-shock proteins, as an induced heat-shock response (Berger and Emlet 2007; Somero 2002).

10 Larval Ecology

Barnacles have small microscopic pelagic larval life stages, which are planktotrophic (feeding on other plankton). Survival of larvae depends on different key factors such as predation, starvation or limited food resources, and different oceanographic conditions that may transport larvae to environments which are unfavorable (Crisp 1976; Olson and Olson 1989; Anil et al. 1995; Anil and Desai 1997; Pineda et al. 2007). It is reported that barnacle spawning is synchronized with phytoplankton blooms (Barnes 1957; Crisp 1962; Starr et al. 1990, 1991). Spatial and temporal variations in the concentration of available phytoplankton can lead to considerable difference in the opportunities of feeding for planktotrophic marine invertebrate larvae (Litaker et al. 1993). Starvation or food limitation is as an important cause of reproductive loss in marine invertebrate larvae (Lang 1979; Desai and Anil 2000, 2004; Anil et al. 1995). Anil et al. (1995) and Desai and Anil (2004) underlined the importance of starvation in recruitment ecology. Starvation could arrest larval development at second instar nauplii in most barnacles (Lang 1979). An investigation carried out to determine the starvation tolerance in *B. amphitrite* larvae indicated that temperature is an important factor determining starvation threshold levels. The threshold level varied with the age of the larvae. The larval development duration also increased after starvation (Desai and Anil 2000, 2004).

Timing of release of larvae by an adult is another important factor that determines barnacle recruitment success (Anil et al 1995). Apart from that, the quality of larvae released is also important in determining their ultimate recruitment success. In rearing experiments, larvae obtained from adults during late autumn and early winter showed poor development capability when compared to those obtained during summer (Anil et al. 1995). Studies detailing the influence of energy metabolism of eggs on larval development may be able to answer questions related to changes in quality of larva during different seasons and further our understanding of macrofouling ecology of cirripedes (Lucas and Crisp 1987). Studies carried out to understand the influence of temperature, food concentrationm, and salinity (Anil et al. 1995; Anil and Kurian 1996) indicated that the total naupliar duration increased with increase in the salinity and food concentration at different experimental temperatures. However, the duration to complete naupliar development was longer at lower temperature (Anil and Kurian 1996). In the case of another barnacle species, *Megabalanus rosa* the total development duration to reach the cypris stage at higher salinity (30%) with a difference of 5°C (25–30°C) temperature, resulted in a difference of 3 days, at 20°C the total development duration increased by 5 days. At 15°C, nauplii could not develop. At 10 and 20% salinity, the larvae could not complete development (Fig. 5.7a, b). In the case of *Balanus albicostatus* (at 20 and 30% salinity) (Fig. 5.7c), larvae could complete development at all the temperatures (15–30°C). Only at 10‰ salinity, they could not complete development. *Balanus eburneus* and *B. amphitrtie* showed successful development at all the salinities and temperature. Duration of larval development was maximum at the lowest salinity (10%) and temperature (15°C) (Anil 1991). Such variation in the larval

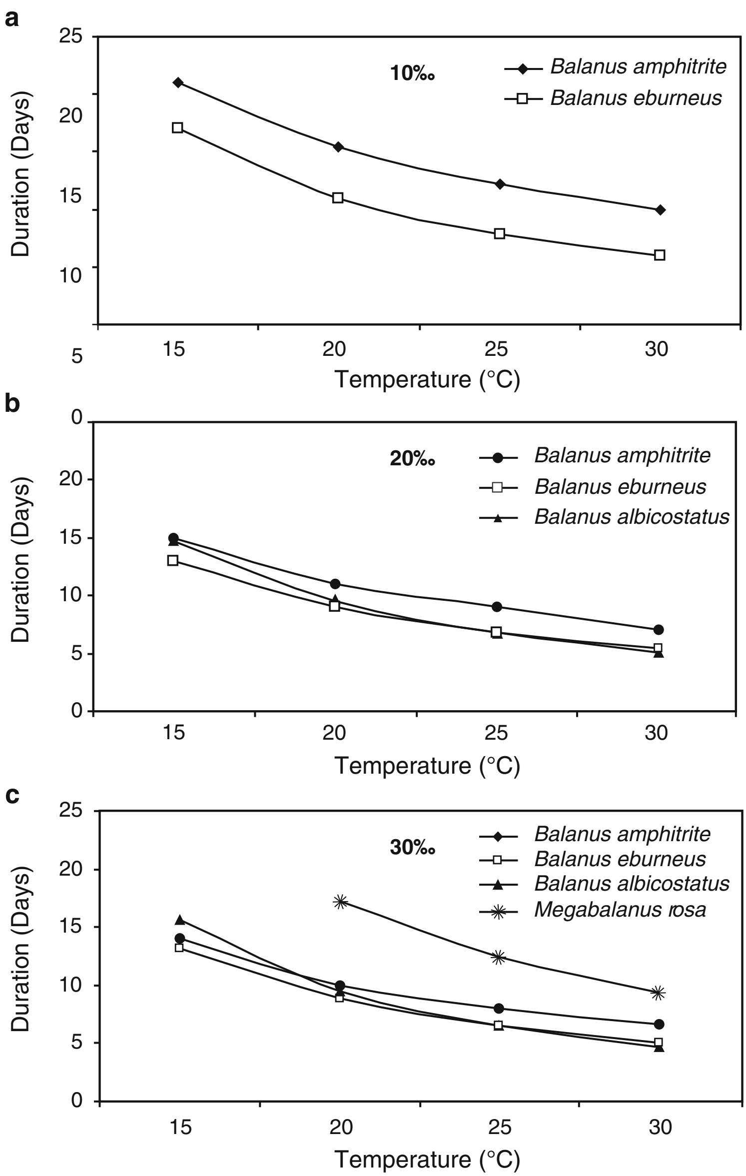

Fig. 5.7 Influence of salinity (**a**) 10% (**b**) 20% (**c**) 30% at different temperatures on the total development duration of different barnacle species

development duration with temperature and salinity has strong impact on the settlement and recruitment processes.

The larval food clearance rate is proportional to the length of the ciliated band (Strathmann et al. 1972), which commonly increases with increase in body length of the larvae (McEdward 1984). The inter-setular distance in case of cirripede larvae is likely to increase with successive molts (Stone 1988). *B. amphitrite* nauplar feeding was reported to vary with the larval age and type of food. Early larvae fed better on diatom *Chaetoceros calcitrans* (4–6 μm), whereas advanced instars fed more successfully on *Skeletonema costatum* (2–16 μm, pervalvar axis; 2–12 μm, diameter). The reason for such a difference was attributed to differential grazing rates owing to variations in the size of the diatoms (Desai and Anil 2004). The stage II nauplii of this species have most (~45%) of the setules spaced 3–5 μm apart and some (~16%) of the setules spaced 7–9 μm apart on the antennal endopodite and exopodite. In VI instar nauplii, a few (~15%) setules are spaced 3–5 μm and most (~42%) are spaced 9–14 μm (Desai and Anil 2004). The early instar larvae, compared to the advanced instars, would more efficiently feed on *C. calcitrans*, which is smaller in size. Though there is a fringe of closely spaced setae along the preaxial edge of the exopodite in the stage VI nauplius, such fringes are unimportant in the feeding process (Stone 1986). A study was carried out on the comparison of food organisms *Chaetoceros gracilis* (6–10 μm) and *Chaetoceros wighami* (7–18 μm) for the larvae of *B. amphitrite*, which indicated that *C. gracilis* was a good food for larval rearing (Thiyagarajan et al. 1996). Considering the inter-setular distance of *B. amphitrite*, *C. gracilis* can be considered as a better food as both early and advanced instars can effectively filter this food organism.

Food concentration and the temperature at which larvae are raised have been found to variably influence the starvation capability. In the tropics, the settlement of the barnacle *B. amphitrite* is recognized to be largely nonseasonal, except in regions influenced by monsoons (Desai and Anil 2005). A study carried out in a semi-enclosed bay in Japan indicated temperature to have a significant influence on barnacle settlement (Anil et al. 1995). Thus the changes in the levels of temperature, salinity, and food concentration would significantly influence the population biology of the organisms and their biofouling potential. Increased exposure to starvation temperature eliminated the effect of doubling of food concentration on starvation threshold levels (Desai and Anil 2004). Even the longer developmental duration at low temperature did not compensate for build up in nutrition (Anil et al. 2001). This shows that the conditions in which the larvae are raised have a clear impact on larval energetics and food compensation. Prolonged larval development at lower temperature may not correspond equally with larvae raised at higher temperature (Anil et al. 2001).

Assessment of the food value of various flagellates and diatoms for cirripede larvae was carried out by Moyse (1963) and Moyse and Knight-Jones (1967), who stated that the larvae of the Arctic-boreal *Balanus balanoides* require diatoms for food, where as those of the Lusitanian and tropical species *Chthamalus stellatus, Lepas anatifera*, and *L. pectinata* need flagellates. Some experimental results also show that barnacle nauplii are omnivorous grazers, incorporating significant fractions of heterotrophs in their diets. In accordance with their feeding mechanisms and body size, barnacle nauplii were able to feed on autotrophic picoplankton (<5 μm) but did not consume the largest phytoplankton cells (Vargas et al. 2006). Experiments to evaluate the fecal pellets produced by barnacle larvae indicated

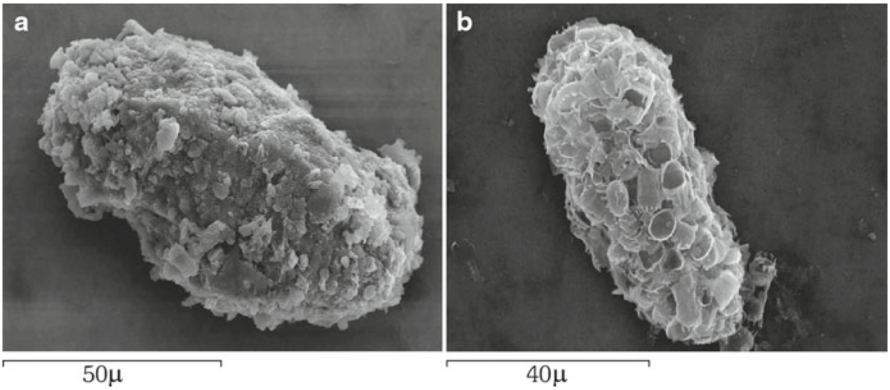

Fig. 5.8 SEM pictures (**a**) fecal pellet produced by nauplii collected from the field, and (**b**) fecal pellet produced by the laboratory reared nauplii fed on mono-species culture of *Skeletonema costatum*

their capability to feed on food particles other than diatoms (Figs. 5.8a, b). In fact, quantitative analysis of fecal pellet production and its content would provide insights about the preference of larval food in the wild. This is a difficult task to be accomplished and requires molecular techniques to identify signatures of food organisms. Nevertheless an attempt by Gaonkar and Anil (2010) indicated a seasonal shift in food availability and its influence on development and metamorphosis.

11 Dispersion

Studies of marine invertebrates have led to the emergence of new paradigms in population dynamics, which differ sharply from classical models of population growth that apply, for example, to terrestrial taxa. Indeed, recruitment, rather than reproductive output, is the key concept for demography of marine species, and has been recognized as one of the main determinants of spatial and temporal variations in population size. Most marine taxa have complex life cycles with planktonic larvae that settle and metamorphose into sessile benthic adults. In this case, populations must be considered as open systems, in that settling larvae may come from remote places. For this reason, recruitment is a critical factor, and is not necessarily correlated with local reproductive output (Roughgarden et al. 1988; Bence and Nisbet 1989).

Barnacle larvae, depending upon the bioregion, have differential developmental duration and the cues provided for metamorphosis could vary. In addition to this, variability in physical processes can yield different dispersion scenarios. As the larval life span of barnacles is considerably long, the capability to disperse to distant localities cannot be negated and it has been recognized as one of the pathways of reproductive loss. This pattern of larval dispersion is critical in determining the intensity of fouling in virgin localities. For example, biofouling in offshore environments, where it is expected to be limited, gets aggravated with the constant contact with transport vessels/ships.

Marine populations are typically connected over greater spatial scales than their terrestrial counterparts due to many species having highly dispersive, planktonic larval phase. However, high levels of larval mortality in the plankton may reduce connectivity between populations (Jessopp et al. 2007). Larval mortality diminishes the number of surviving larvae with time and distance from their source (Cowen et al. 2006). Suboptimal temperatures, absence of adequate settlement substrata, offshore transport of larvae, starvation, and predation have long been regarded as important contributors to the high mortality of larvae (Thorson 1950). Larval transport is a key component of the settlement rate, the rate at which planktonic larvae establish permanent contact with the substratum (Connell 1985), and a key component of recruitment rate, the rate at which juveniles join the population. Phenomena influencing settlement include processes influencing the larval pool, physical transport, micro-hydrodynamics, substrate availability, and behavior (Pineda 1994, 2000).

12 Cypris Attachment

In the life cycle of barnacles, the cypris stage is the transitory stage between the pelagic and sessile life. Larval settlement is an active behavioral process influenced by environmental factors and depends on the properties of the hard surface. There are a number of reviews in which the significance of biotic and abiotic environmental factors in larval settlement is considered (Scheltema 1974; Crisp 1984; Rittschof and Bonaventura 1986; Morse 1990; Pawlik 1992; Abelson and Denny 1997; Rittschof et al. 1998; Clare and Matsumura 2000, Khandeparker and Anil 2007).

Barnacle larvae have evolved complex photoreceptors and elaborate phototactic behaviors, which help them to identify suitable habitats for feeding and settlement. It was demonstrated that environmentally realistic levels of UV-B radiation can induce ocular damage, thereby impairing phototactic behavior and reducing the settlement success of the cyprids. On the other hand, effect of the UV radiation on microbial films may indirectly affect larval settlement. Results indicated that increased UV radiation, which might occur due to ozone depletion, may not significantly affect the barnacle recruitment by affecting the inductive larval attachment cues of microbial films (Hung et al. 2005).

The ability of cyprid to discriminate between surfaces determines its successful transition. In all Cirripedia, the cypris is assigned the task of locating a suitable substratum for settlement. Experiments on cypris larvae of *Elminius modestus* and *B. balanoides* showed that moderate velocity gradients can sweep the cypris past the surface before they can attach. For large objects exposed to turbulent flow, the critical velocity gradient corresponds approximately to a flow of 1–2 knots. However, an attached cypris cannot be pulled off the surface even by gradients greatly in excess of those which prevent attachment.

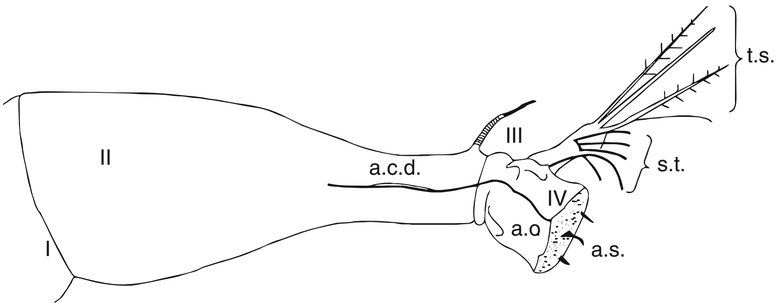

Fig. 5.9 Cypris antennule showing segments I–IV with *a.o.* attachment organ on third segment, *a.c.d.* axial cement duct, *a.s.s.* axial sensory seta, *s.t.s.* subterminal setae, *t.s.* terminal setae

Barnacles use cement for permanent attachment. The cement is an underwater adhesive insoluble protein complex. Barnacle cement has been recognized as long-lasting and toughest connection in the living aquatic world (Abbott 1990). Once the cypris encounters a surface, a search is initiated by employing the antennular disc which acts as an adhesive organ, for temporary attachment to the substratum (Nott and Foster 1969). Cypris has a pair of antennules. The antennules consist of four segments, out of which the two most distal ones carry the major part of the sensory setae (Lagersson et al. 2003).

Temporary attachment by the antennules retains the larva on the substratum and enables it to explore the surface (Walker et al. 1987). However, if a substratum proves inappropriate, the cypris can detach and swim off to find other suitable surfaces. The various factors influencing settlement site selection are outlined by Crisp (1974), among which the chemical factors are sensed by antennular disc apical sense organ and terminal setae of fourth antennular segment (Fig. 5.9).

The cypris larva does not feed; it derives its energy from stored lipids accumulated during the earlier planktotrophic phase. It prolongs its larval duration in the absence of appropriate stimuli. However, once delayed, larvae settle in a less discriminatory manner (Rittschof et al. 1984), probably because energy reserves are depleted in the searching process (Lucas et al. 1979), which jeopardizes post-metamorphic growth and/or survival (Pechenik and Cerulli 1991; Pechenik et al. 1993). This signifies the importance of energy reserves and/or nutritional conditions of the larvae in the process of settlement and attachment. In the laboratory, the cypris that are used to assess the influence of different cues are raised using traditional rearing protocols and preconditioned at 5°C for a day or two prior to settlement assays. While studying the age-related settlement success by *B. amphitrite* cyprids, Satuito et al. (1996) concluded that after molting to the cyprid stage, larvae may still require a settlement-competence attainment period involving the utilization of cyprid major protein. Settlement ability may thereafter be lost with depletion of cyprid major protein reserves which is temperature dependent. Thiyagarajan et al. (2007) documented that acute exposure of cypris larvae of *B. amphitrite* to low salinity stress negatively affects juvenile growth rates as severely as delayed metamorphosis, which may ultimately influence juvenile and adult population dynamics in the field.

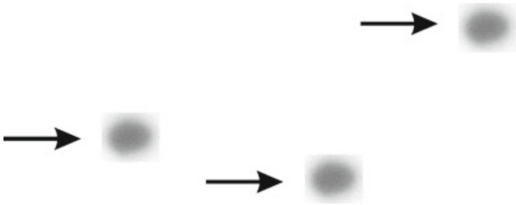

Fig. 5.10 Footprints deposited by the cypris of *Balanus amphitrite* on the surface of the polystyrene multiwells (the foot-prints measured ~30–37 μm across)

The physiological condition of the cyprid larvae is largely determined by their energy reserve (i.e., larval feeding history) and physiological age (Miron et al. 2000; Harder et al. 2001). Thiyagarajan et al. (2003) showed that cyprid age has stronger impact on juvenile growth and survival than cyprid energy reserve. The magnitude of the effect of cyprid energy reserve on growth varied among different sites and was directly linked to the surplus and high-quality food (Thiyagarajan et al. 2005). Holm (1990) indicated that temporal variation in cypris behavior may be a result of changes in larval culture conditions and/or the conditions under which the adults grow.

Laboratory and field studies have demonstrated that barnacle cyprids show gregarious behavior, a tendency to settle on or near conspecifics. This behavior has been attributed to a glycoprotein (arthropodin) present in the adults (Crisp and Meadows 1963). Native barnacle pheromones are thought to be a heterogeneous group of 3,000–5,000 Da peptides (Rittschof 1985). Recently, a settlement-inducing protein complex (SIPC) from the adult extract of barnacle, *B. amphitrite* has been isolated, which is composed of three major subunits with molecular weights of 76, 88, and 98 kDa (Matsumura et al. 1998). Rittschof et al. (1986) suggested that settlement might be effected by a signal transduction pathway that involves the stimulation of adenylate cyclase. Evidence for the involvement of cyclic AMP (cAMP) in the settlement of this species is provided by Clare et al. (1995). Cyclic AMP acts as an intracellular signaling molecule in all prokaryotic and animal cells. Yamamoto et al. (1995) demonstrated that a protein kinase C (PKC) signal transduction system also plays an important role in larval metamorphosis of *B. amphitrite*. Subsequently, the expression and involvement of six barnacle cypris larva-specific genes (bcs) was reported during the process of cypris attachment and metamorphosis (Okazaki and Shizuri 2000). Recently, SIPC responsible for gregarious settlement of barnacle, *B. amphitrite* has been identified as a cuticular glycoprotein with sequence similarity to the α_2—macroglobulin protein family (Dreanno et al. 2006a, b).

An interesting feature of barnacle cypris is that they leave behind “footprints” of temporary adhesive, which are secreted by the glands of the antennular disc while exploring surfaces (Fig. 5.10). An attractive substratum acquires relatively more number of footprints. The presence of footprints further increases the attractiveness of a substratum and can act as an inductive cue for gregarious settlement, even in the absence of conspecific adults (Walker and Yule 1984; Yule and Walker 1985; Khandeparker et al. 2002b). Khandeparker et al. (2002b) reported that in the absence of adult extract (AE), sugar-treated cyprids did not deposit footprints.

Concurrently, the cyprids treated with sugars deposited footprints when exposed to adult extract coated multiwells. As earlier hypothesized by Yule and Walker (1987) that sugars in solution adsorb electrostatically through -OH groups to polar groups associated with the cypris temporary adhesive (CTA), the detection of AE and deposition of footprints (exploration) were attributed to availability of alternate sites for pheromone reception.

Microbial biofilms are generally observed to stimulate the settlement of macrofouling organisms (Crisp 1974). Monospecies bacterial films show varying effects on cypris attachment. The same bacterium may also elicit different responses in different fouling organisms. For example, the bacterium, *Deleya marina*, stimulated the settlement of spirorbid polychaete larvae but inhibited the settlement of both bryozoan (Maki et al. 1989) and barnacle larvae (Maki et al. 1992). Maki et al. (1990) showed that the same bacterium when adsorbed on different substrata induced different attachment responses in barnacle larvae. Biofilms generally inhibited settlement of *B. amphitrite* cypris (Olivier et al. 2000), although some biofilms were inducive or had neutral effect (Wieczorek et al. 1995). The inhibitory effect by biofilms has been mainly credited to the bacterial components (Maki et al. 1988; Anil and Khandeparker 1998; Khandeparker et al. 2002a, 2003). However, larvae are likely to respond to more than one sensory stimulus when searching for a settlement location, and some factors such as naturally produced bacterial metabolites may override the importance of others (Maki et al. 1989). The biochemical composition of bacterial inducers change with the availability of different nutrients and this triggers the larvae to settle or swim away (Khandeparker et al. 2006). Competing cues in such assemblages pilot the larvae to their settlement destination (Khandeparker et al. 2003).

Bacteria also produce surface-bound and soluble compounds that either stimulate or inhibit larval settlement (Kirchman et al. 1982; Maki et al. 1990, 1992; Szewzyk et al. 1991). Surface-associated cues mediate settlement and metamorphosis, whereas waterborne ones are suggested to be more significant in locating the conducive substratum, for example, the detection of biofilm by the exploring larvae (Khandeparker et al. 2006). The role of lectins in larval settlement and piloting has also been investigated in several studies (Kirchman and Mitchell 1984; Kirchman et al. 1982; Mitchell 1984; Mitchell and Kirchman 1984; Mitchell and Maki 1988; Khandeparker et al. 2003). Lectins are proteins or glycoproteins that exist in almost all living organisms and can recognize and bind carbohydrates specifically and non-covalently. Studies have revealed the role of lectins in altering signals of bacteria and it was hypothesized that production of such lectins by adults can pilot larvae to their destination (Khandeparker et al. 2003).

Neal and Yule (1994b) demonstrated that the age of the biofilm, rather than surface wettability of substratum was the main factor determining larval adhesion. After adsorbing to the surface, the attached bacteria can alter the substratum characteristics either by changing the surface wettabilty or by exposing different types of exopolymeric substances (Anil et al. 1997; Khandeparker et al. 2002a). These exopolymers and other microbial secretions are involved in settlement of macrofoulers and metamorphosis induction (Holmström and Kjelleberg 1994). The structure of bacterial exopolymers is important in determining the larval choice to attach or detach (Yule and Walker 1984). Diatom exopolymers have also been shown to influence the settlement of *B. amphitrite* cypris which shows varying responses against different diatom species (Patil and Anil 2005).

Similarly, natural microbial communities found on estuarine and marine substrata, containing a diversity of bacterial species, can stimulate, inhibit, or have no effect on permanent attachment of barnacle cypris (Maki et al. 1990). The age of the natural microbial film seems to influence the settlement response of cypris. Changes in the bacterial community profile in a biofilm determine the settlement success of cypris of *B. amphitrite* (Qian et al. 2003; Hung et al. 2008). The relative proportion of inhibitory or stimulatory bacterial strains in biofilms differs with environmental conditions (Dobretsov et al. 2006). In case of cypris of *B. albicostatus*, 1- and 2-day-old natural biofilms showed higher metamorphosis when compared to 5-day-old biofilms (Khandeparker et al. 2005). While studying the vertical distribution of subtidal barnacle *Balanus trigonus*, it was shown that neither the abundance of bacteria and diatoms in the microbial film nor the biomass correlated with the attachment preference of cyprids (Thiyagarajan et al. 2006).

13 Cement Secretion

Barnacle cement is secreted by a pair of ovoid or kidney-shaped glands (Fig. 5.3), which are located behind the compound eyes of cypris. Each antennule has 20 glands (Nott 1969; Nott and Foster 1969; Walker and Yule 1984). Walker (1971) examined these glandular structures before and after the cementing of the cypris to a substratum in order to establish the origin and composition of the cement. He observed the presence of two types of secretory cells in these glands, one of which produced protein phenolic compounds and phenolase enzyme, whereas the other produced only protein. He further pointed out through the work of Brown (1950) and Pryor (1962) that,

$$\text{Protein} + \text{Diphenol} \xrightarrow{\text{Polyphenol oxidase}} \text{Protein} + \text{Quinone} = \text{tanned protein.}$$

Some barnacles (balanids) possess a basal plate whereas others (chthamalids) do not. The mode of discharge of secretion from the cells differs among the membrane- and calcareous-based barnacles. In the former, there is a series of collecting canals within the cytoplasm of the cement cells (intracellular canals), which join with larger extracellular cement ducts. Secretion passes into the intracellular canals and is moved along to the larger cement ducts, which have an inner chitin lining. In the latter (calcareous base), there are no intracellular collecting canals. Secretions are thought to pass from the cement cells into the cement duct directly. The cement ducts in the calcareous-based forms are not chitin lined. The cement, which is initially a fluid of low viscosity, solidifies within a short time after secretion (Lindner 1984).

Properly detached barnacles can be reattached to other surfaces thus indicating that the duct systems connected to these areas are still functional and the passages are still open (Lindner 1984). In the course of normal development, the new cement does not go beyond the outermost and newest vesicle, because the rest of the main channel and duct network is filled with the flushing fluid, leaving no room for the cement material. However if the basis separates from the substratum, the cement seal of some duct ends breaks and the flushing fluid drains out of the corresponding ducts and vesicles. A comparison of barnacles grown on non-sticky surfaces to those grown on easy-to-attach surfaces revealed difference in the calcified part of the barnacle base as well as in the adhesive's ultrastructure (Wiegemann and Waterman 2003). In contrast to barnacles grown on easy-to-attach substrata, barnacles on nonstick surfaces typically possessed a bell-shaped base plate and a thick multilayered adhesive plaque. This peculiar feature was thought to be a result of downward growth of the parietal plates and subsequent detachment of the weakly adhered base area (Wiegemann and Waterman 2003). The adhesion strength of barnacles was measured during the course of desiccation and it was found that the shear force required to remove barnacles belonging to different genera was different; this was attributed to specific base morphologies (Wiegemann and Watermann 2004). The adhesion strength is also known to vary with environments. An investigation was designed to measure the differences in biofouling and biofouling adhesion strength on three known silicone formulations and an epoxy control at seven static immersion sites located in California, Florida, Hawaii, Hong Kong, India, Italy, and Singapore. The study found that while the relative performance of the coatings was similar at each site, there were statistically significant differences in the type and intensity of fouling that developed on the coatings and in barnacle adhesion strength among sites. The results emphasize the importance of evaluating potential coatings at more than one static immersion site (Swain et al. 2000) as barnacle adhesion strength varied with environments. The measurement on liquid barnacle adhesive indicated that solids (coatings) with surface-free energies lower than 12 dynes cm^{-1} are needed to prevent attachment (Lindner 1992). Hence, a low surface-free energy approach has been suggested for the control of marine biofouling.

14 Menace of Barnacle Fouling in Industrial Systems

Estimates of economic losses due to biofouling indicate that US Navy spends about $150 million to overcome the drag created by ship hull fouling (Haderlie 1984). Similarly, a 15 cm thick fouling load on an offshore platform was estimated to cause 46% wave loading on the structure, requiring an additional amount of 50 mm steel (DePalma 1984). A review on barnacle fouling and its prevention (Christie and Dalley 1987) inferred that the total cost of barnacle fouling to human activity would be £2×10^8 per annum and would be many folds higher today in light of the increase in oil price. The estimate was based on the consideration that physical hull roughness of 10 μm can raise power penalty by 1%. Realistic estimates of penalties to global economy due to biofouling have also to include cost associated with underwater cleaning and increase in the cost of production of plants which use seawater as coolant (Lackenby 1962). Biofouling in the condenser cooling conduits and service water systems of coastal power plants is another universal problem. Activity of biofouling organisms growing inside the seawater intake tunnel brings about alterations in cooling water characteristics such as increase in turbidity, total suspended matter, particulate organic matter, and ammonia and a decrease in the dissolved oxygen (Venugopalan and Nair 1990). A study carried out to evaluate biofouling and its control in a tropical power plant showed that the green mussel, an important fouling organism in the plant, had distinct breeding season—which spanning over a protracted period of time, ensures larval supply for longer durations. This necessitates continuous maintenance of the cooling water circuits adding extra burden on the cost of operation (Rajagopal et al. 1991). The continuous treatment with either chlorine or any other chemical may alter the habitat in the vicinity of discharge water, thereby altering the community pattern.

The most extensively used preventive measure for the control of biofouling is antifouling coatings. A review of paint development by Christie and Dalley (1987) shows the progression in paint technology from metallic soap containing copper sulfate as the toxic agent, to the self-polishing copolymer paint (SPC) loaded with tributyltin (TBT) as the biocide. In fact, with the advent of TBT-SPC, suddenly fouling became a problem of the past. The SPC paints, introduced in 1974, were so called to indicate the polishing effect as the polymer dissolves away during normal vessel operation, releasing TBT. TBT kills settling fouling organisms and at the same time, the surface becomes smoother. Being very lipid soluble, TBT is rapidly taken up by cells, where it inhibits energy transfer processes in respiration and photosynthesis. The SPC system was extremely successful but TBT was shown to affect nontarget organisms, including a number of shellfish, at very low concentrations, leading to imposex (imposition of male sexual characters on female) (Vishwakiran and Anil 1999). With enforcement of a ban on TBT, copper-based paints were supplemented with "booster biocides," including herbicides that replaced the organotins in antifouling paints (Liu et al. 1997; Turley et al. 2005). The impact of TBT on the aquatic environment has also led to an increase in the regulations affecting the use of all other antifouling biocides and only a few are now employed. Most commonly used are Sea-Nine 211 (an isothiazolone), zinc pyrithione (an antidandruff fungicide), and Irgarol 1051 (a triazine herbicide). While about 18 compounds are currently used worldwide as antifouling biocides, Irgarol 1051 was the first to gain prominence (Kostantinou and Albanis 2004). The settlement of cypris of *B. albicostatus* Pilsbry could be prevented by exposing them to biofilms treated with Irgarol 1051. Inhibition of metamorphosis of competent larvae of polychate *Pomatoleios kraussii*, Baird was also observed when natural bioflilms were treated with Irgarol 1051 (Khandeparker et al. 2005). All of these compounds are used mainly as co-biocides with copper, especially to increase efficacy against algae. A new self-polishing system based on copper acrylate is reported to provide control of fouling comparable to the TBT-containing SPC paints (Callow and Callow 2002).

Taking cues from the undesirable effects, the international community responded to the serious marine environmental issues by adopting antifouling systems (AFS) convention (IMO 2001). One of the most important provisions of the AFS Convention is contained in Article 6, which allows for the ban of future antifouling systems that pose a threat of serious or irreversible damage to the marine environment and human health. With the ratification of this convention, there would be total exclusion of harmful compounds as biocide in the antifouling paints. However, this opens up a requirement for identifying suitable effective environment-friendly antifouling coatings.

Silicon-fouling release coatings have been developed as an alternative to biocide-containing paints. They function by minimizing the adhesion strength of attached organisms, which are removed as the vessel moves through water. Data on the strength by which barnacles adhere to silicones can be used to predict the ship-operating conditions required for self cleaning. Macroalgae and some hard foulers such as barnacles detach relatively easily from such surfaces, but diatom slimes, oysters, and tubeworms are attached tenaciously and are not easily removed, even at high speed. Silicon elastomers are also expensive and prone to tearing, so are only employed at the present time for specific applications, such as on high-speed vessels and in locations where toxic paints are prohibited (Callow and Callow 2002).

In case of biofouling control in power plant cooling systems, chlorination (in both intermittent and continuous mode) has been widely used all over the world. Heat treatment has also been found to be very effective in combating biofouling. The latter has the added advantage of being environmentally more acceptable than chemical control measures (Satpathy 1990). Other chemicals such as ozone, chlorine dioxide, bromine chloride, acrolein, and organic biocides and methods like UV irradiation, ultrasound, radiation, and electric fields have also been examined by various workers (Satpathy 1990). Rittschof et al. (2003) argued that the pharmaceuticals that are compatible with existing coatings technology should be considered as antifouling agents. Fusetani (2004) in his review on biofouling and antifouling, focused on important antifoulants derived from marine organisms, together with their ecological roles and industrial application. Pérez et al. (2006) showed that copper tannate, which was not lethal at low concentrations, had excellent potential as antifouling agent. Aldred et al. (2008) studied the effect of serine protease alkalse and found that alkalse reduces the effectiveness of the cyprid of *B. amphitrite* adhesives and indicated that proteolytic enzymes have considerable antifouling potential. Milne (1990), calculated the economic advantages of the foul-release coatings to the world fleet per annum and indicated (1) direct fuel savings of 4% due to improved smoothness and less fouling, (2) extended dry-docking intervals, (3) improved plant utilization, and (4) savings on reduced transport of fuel to the bunkering ports. If foul-release can achieve parity with TBT-SPC in terms of smoothness and fouling control, then it also has the supremacy of nontoxicity.

15 Conclusions

While efforts are underway to look for novel antifouling strategies by either modifying the surface characteristics or application of injectible biocides, it would be important to understand how the fouling larvae react to such situations. In this context it is not only important to evaluate the substratum–larva interaction, but also to know how these larvae reach the substratum and the way they sense the suitability of the surface. Physical processes facilitate larval dispersion, taking them to vicinity of the substratum. In spite of the fair amount of understanding how the larvae sense the substratum by olfaction and contact chemoreception, the capability of the larvae to visualize the substratum has not received the attention duly required. The response of cypris to environmental cues is coordinated by nervous system and appropriate behavioral response. However, very little attention has been paid to this neural processing facet of settlement and understanding of this would be beneficial in the development of novel antifouling strategies.

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Chapter 6
Microbial Fouling and Corrosion: Fundamentals and Mechanisms

Toleti S. Rao

1 Introduction

Formation of nontransient adherent communities of microorganisms on submerged surfaces (biofilm) is a ubiquitous phenomenon. Over 90% of the all aquatic bacteria are found associated with interfaces such as the sediment–water interface and surface micro-layer of aquatic systems (Lappin-scott and Costerton 1989; Cowan et al. 1991). "Biofilms constitute a consortium of biotic elements like bacteria, cyanobacteria and algae attached to a substratum by microbially produced extracellular polysaccharide matrix which entraps soluble and particulate matter, immobilizes extracellular enzymes and acts as a sink for nutrients and inorganic elements." The biofilm composition may vary both spatially and temporally with respect to different waters, and greatest differences are usually associated with shifts in the relative importance of autotrophic and heterotrophic microorganisms (Robb 1984; Abu et al. 1991; Rao et al. 1997a).

Mutual interactions in biofilms among various microbial species result in community formation, which are habitat specific. The presence of various species of bacteria and algae in successive layers of the biofilm provides clues about the energy and substrate transfer within the biofilm. Water quality parameters affect the biofilm formation because of their role on the regulation of bacterial metabolism (Rao et al. 1997a). A limited number of investigations have been carried out to understand the mechanisms of biofilm development and the physiological activities of the microorganisms associated with biofilms (Liu et al. 1993). Differences or changes in the structural or physicochemical properties of biofilms are determined by the organic and inorganic constituents of the surrounding environment (Keiding and Nielsen 1997). Some important reports on biofilm characterization in marine and fresh water

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systems include Characklis and Cooksey (1983), Srivastava et al. (1990), Venugopalan et al. (1994), Rao et al. (1997a), Rao (2003), and Saravanan et al. (2006). Various physical, chemical, and biological factors govern the formation of biofilms. Among them, nutrient concentrations attain much significance (Rao et al. 1997a).

The adhesion of microorganisms to solid surfaces has practical implications in industrial systems (Sjollema and Busscher 1990; Allison and Gilbert 1992). Following adhesion to a surface, a bacterial cell undergoes a phenotypic change and starts cell division, which would lead to the development of microcolonies. The microcolony is the basic unit of biofilm and each biofilm bacterium lives in a customized microniche and enjoys a measure of homeostasis, circulatory system, and metabolic cooperativity, in a complex microbial community (Costerton et al. 1995). Although 90% of the microbial population in nature occurs in biofilms (Characklis and Marshall 1990), most of the laboratory studies on microorganisms have been based on suspensions. With the development of biofilm reactor (Pedersen 1982) and flow cells (Lawrence et al. 1987; Sjollema and Busscher 1990; Mueller et al. 1992), studies on microcolony/biofilm formation under laboratory conditions got augmented (Saravanan et al. 2006). The outcome of the research efforts provided valuable information on the behavior of mono- and mixed culture bacterial biofilms under various flow conditions mimicking industrial cooling circuits (Characklis and Marshall 1990), on ordering characteristics (Rao et al. 1997b) and behavior of bacteria in the hydrodynamic boundary layer (Lawrence et al. 1987). Stewart et al. (1993) used light microscopy to observe the depth variability in *Pseudomonas aeruginosa* biofilms; the data provided refined fluid frictional coefficients and models for molecular diffusion. Currently, with modern tools like confocal scanning laser microscopy (CSLM) one can make direct observation of structure and function of living biofilms. Thus, examination of *Pseudomonas fluorescens* biofilms by CSLM has thrown light on spatial variability that exists within pure cultures (Stewart et al. 1997). Costerton et al. (1995) have reported that adhesion of microbes to surfaces triggers the expression of a σ factor that derepresses a large number of genes, so that biofilm cells are phenotypically distinct from their planktonic complement.

Microbial biofilms cause fouling of water distribution systems, industrial equipments such as heat exchangers, cooling towers, submerged sight glass and sensors, and ship hulls (Bott 1993). Biofilms can significantly decrease conductive heat transfer (Bott 1995). It has thermal conductivity similar to that of water (about 0.6 W/m/K). Rheological measurements indicate that biofilms are viscoelastic in nature (Characklis and Marshall 1990). Therefore, biofilms can cause significant energy losses as they contribute to increased fluid frictional resistance. It is well accepted that the major problem concerning biofilm formation on heat transfer systems is the resultant costly reduction in heat exchanger performance. Biofilms can readily form the largest resistance to heat transfer in systems cooled by water within the temperature ranges conducive to microbial growth (Characklis and Marshall 1990; Bott 1995). Biofilm control in industrial systems, pipelines, and ship hulls is a costly process, usually based on mechanical treatment or use of antimicrobial agents. Although chlorine and other chemical formulations are in use for biofouling control, their use probably will be restricted or prohibited in future due to their toxic effects on the ecosystem (Clare 1998). Controlling adhesion alone in order to control the total biofilm accumulation is presently quite unrealistic (Christensen 1989). However, Davies et al. (1998) reported the involvement of an intercellular signal molecule in the development of *P. aeruginosa* biofilms. They further concluded that control of biofilm differentiation through interfering with quorum sensing has important implications in biofilm control.

2 Description of Various Stages of Biofilm Growth

Generally, biofilms constitute a growth phase of microorganisms that are distinctly different from the planktonic microflora. The typical structure of biofilm formation on surfaces is outlined in the following phases (Fig. 6.1).

2.1 *Phase 1: Reversible Adhesion*

This important step in biofilm formation involves the approach of microorganisms to the conditioned surface. This process may be active or passive, depending on whether the bacteria are motile or transported by the surrounding aqueous phase. During the initial attachment phase, the physicochemical properties of the bacterial

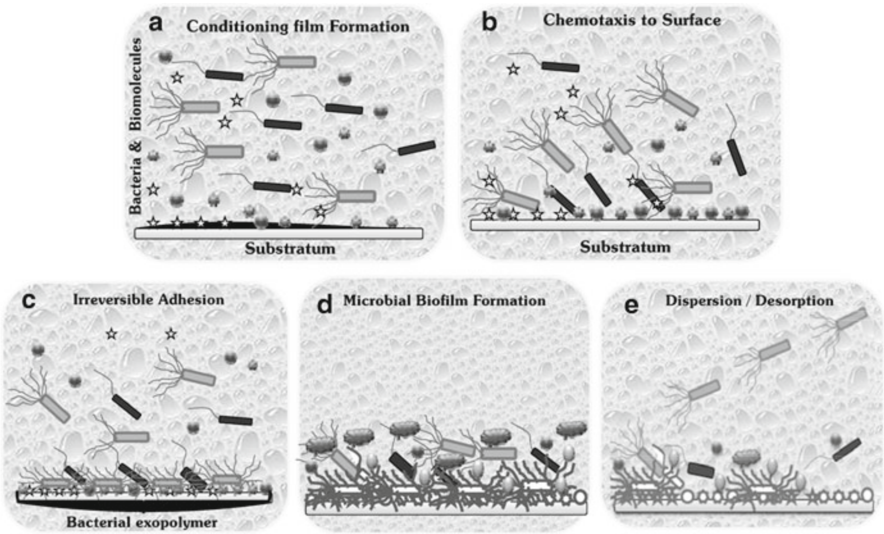


Fig. 6.1 Images depicting development of biofilm on material surfaces. (**a**) Conditioning film formation, (**b**) chemotaxis of motile bacteria, (**c**) irreversible phase, (**d**) micro-colony formation and (**e**) biofilm dispersal

cell surface are important in determining whether the cell will attach or not. The chief forces causing cell adhesion as well as polymer adsorption on to low energy surfaces in water are polar (hydrogen bonding) forces, which are the main driving forces for hydrophobic interactions and to a smaller degree apolar or Lifshitz-van der Waals forces (Busscher and Weerkamp 1987; Rao et al. 1997b). Bacteria are of colloidal dimensions and possess a net negative charge at pH levels normally encountered in natural habitats. This creates an apparent problem in the adsorption process, since substratum surfaces in nature either are negatively charged or rapidly acquire a negatively charged conditioning film (Marshall et al. 1971; Loeb and Neihof 1977; Marshall 1980). It is reported (Lawrence and Caldwell 1987) that the main body of the bacterium does not make direct contact with the substratum surface. The degree of their alignment at solid–liquid interface may be variable and can be explained in terms of colloidal chemistry. However, when considering such theories it is important to remember that the majority of bacteria are not smooth, round particles. Although their surfaces are charged with the same sign as that of substratum, still the bacterium may approach a surface, attracted by van der Waals forces (Busscher et al. 1990; Allison and Gilbert 1992). Desorption may occur during this stage as a result of the release of reversibly adsorbed cells due to fluid shear forces (Characklis and Marshall 1990; Allison and Gilbert 1992).

2.2 Phase 2: Irreversible Adsorption

This is a critical step in biofilm development wherein irreversible attachment of the microorganisms occurs. Although forces of repulsion prevent the body of the bacterium from making direct contact with the surface, they can still adhere to the surface by producing surface appendages. Since electrostatic repulsion depends on radius of curvature, bacterial surface appendages such as flagella, fimbriae, and exopolysaccharide fibrils can readily penetrate the energy barrier and enter the primary minimum (Allison and Sutherland 1987). Cells can hover at this point and participate in a variety of short-range interactions including dipole-dipole, ion-dipole, and hydrophobic interactions. Polymeric fibrils form a bridge between the bacterium and the surface, thereby irreversibly reinforcing the association. During this period, the attached cells begin to secrete additional polymers (exopolymeric substances, EPS) which further cement the cells to the surface and stabilize the colony against fluctuations in the surrounding macro-environment. The exopolymers produced by bacteria provide stability and structural framework to the biofilms (Allison and Sutherland 1987; Christensen 1989; Fletcher et al. 1991).

2.3 Phase 3: Microbial Biofilm Formation

Bacterial colonization of the surface may result in utilization of the macromolecules almost as rapidly as they adsorb at the surface and it depends on the nutritional characteristics of the bacteria found at the surface. Biofilm demonstrates significant functional homogeneity, the individual cells and their activities are dependent on the structural integrity of the biofilm in toto. Costerton et al. (1995) suggested that biofilm could be considered as a "quasi tissue" with measurable rates of respiration and nutrient uptake. Biofilms resemble tissue in their physiological cooperativity and protect themselves from variations in the bulk phase conditions by a primitive homeostasis (Costerton et al. 1995). The spatial organization of microbial cells in the biofilm is also subject to variations. The growth characteristics and metabolic activities of biofilm bring in structural heterogeneity. The physiological congruity observed in biofilms is a typical feature of mixed microbial communities (Costerton et al. 1995). With time, the biofilm reaches a plateau phase with certain thickness and metabolic capacity. The biofilm can now provide the basis for successional development, whereby colonization by higher organisms is supported (Characklis and Marshall 1990). This leads to the process of macrofouling, a common problem described especially in marine systems (Flemming 2002).

2.4 Phase 4: Biofilm Detachment and Dispersal

In order to achieve propagation, the biofilm bacteria detach, disperse, and colonize new niches. This requirement is analogous to that of higher organisms such as the mycelial fungi that grow attached to surfaces. At different points in their life cycle, these organisms differentiate and produce spores which are spread to new locations. Bacterial growth in biofilms also brings with it the need to disperse (Costerton et al. 1995). Biofilm accumulation increases surface roughness and also provides shelter from shear forces and increases both the surface area and convective mass transport near the surface. The sessile accretions of microbial cells would produce surface roughness that increases turbulence and mass transport at the colonized surface (Characklis and Marshall 1990; Allison and Gilbert 1992; Bott 1995).

3 Distribution of Bacteria in Fresh Water and Seawater Cooling Systems

The distribution of microorganisms in fresh water and seawater environments differs with seasons during a year. This is more particularly seen in marine environment because of the dynamic nature of the sea. Figure 6.2 describes the distribution bacteria in freshwater and seawater, specifically tropical power plant cooling systems. Figure 6.2 details the distribution of culturable bacteria in a freshwater cooling system. The bacteria present in circulating water as well as in the biofilm formed on the cooling circuit material vary by 3–4 orders of magnitudes. This denotes that bacteria present in the circulating water hardly influence the microbial population at the metal–biofilm interface. This also provides a message to the power plant operators that the commercially available kits which assay the bacterial population in the circulating cooling water do not provide the correct representation of the bacterial

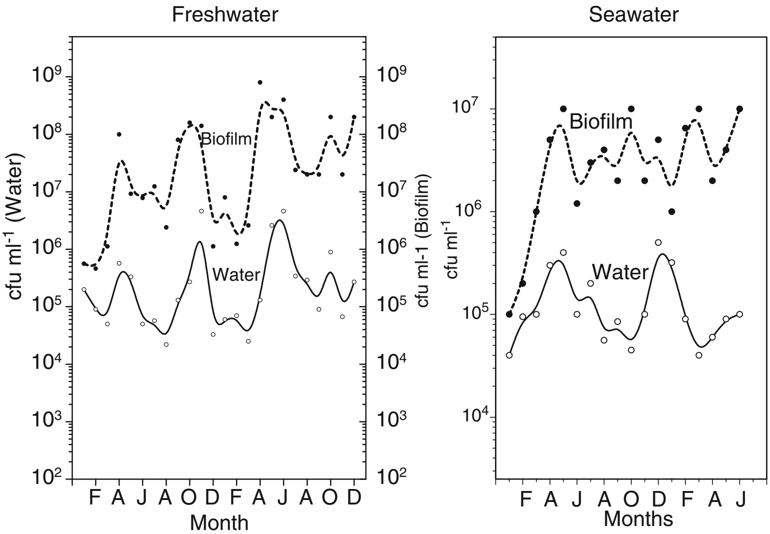


Fig. 6.2 Distribution of bacteria in cooling water and biofilm in a fresh water cooling system and a seawater cooling system

population which is going to initiate fouling and corrosion. On the contrary, the bacterial population in case of the seawater cooled power plant showed a different picture wherein the population was two orders of magnitude less when compared to the fresh water system. This also typifies that bacterial populations in cooling waters are contrasting and differ from place to place and also between seawater and freshwater.

4 Microbes Associated with Corrosion

Microorganisms which promote corrosion generally include not only bacteria but algae and fungi also. Five categories of corrosion causing bacteria are commonly recognized; they are the iron oxidizing, sulfate reducing, sulfur oxidizing, nitrate reducing, and the exopolymer-producing bacteria. Sulfate-reducing bacteria (SRB) like *Desulfovibrio* are involved in the reduction of sulfate to sulfide. Iron-oxidizing bacteria and SRB are typical examples of the aerobic and anaerobic synergistic interaction which is most frequent in microbial corrosion of iron and steel alloys. Microbiologically influenced corrosion (MIH) is responsible for the deterioration of a wide range of materials. Bacteria on surfaces can exist in different metabolic states. Those that are actively respiring, consuming nutrients, and proliferating are said to be in a logarithmic phase of growth. Some microbes exist in a dormant phase because of unfavorable conditions and are said to be in a "resting" or lag phase, while some bacteria modify themselves according to the surrounding environment and form spores that can survive extremes of temperature, long dehydrating conditions, and starvation. However, when favorable conditions are available, the dormant bacterial cells quickly respond and adapt to the surrounding milieu and start multiplying. Therefore, when an environmental or a field sample is processed for isolation of the bacteria or for microscopic observation, it should be understood that most or all of the cell or morphological forms observed can be alive or capable of regrowth. Bacteria of public health concern have been isolated from distribution systems pipelines, cooling systems, and air conditioning cooling ducts. They include; *Legionella* sp., *Klebsiella pneumoniae*, *Yersinia enterocolitica*, *Staphylococcus aureus*, *P. aeruginosa*, *Aeromonas hydrophila*, *Enterobacter* sp., *Citrobacter* sp., and others. Additionally, some fungi and actinomyces have the potential to act as opportunistic pathogens or allergens for certain risk groups in the population. The following are some important group of corrosion bacteria of industrial relevance with images of some of the important microbes (Rao et al. 2000; Videla 2001).

4.1 Iron-Oxidizing Bacteria

The common iron-oxidizing bacteria viz. *Gallionella*, *Sphaerotilus*, *Crenothrix*, and *Leptothrix* oxidize ferrous ions to ferric state to obtain their energy. They deposit ferric oxide on carbon steel pipeline surfaces and thereby promote tubercle formation. The most common iron-oxidizing bacteria are found in long sheaths and belong to the class Chlamydobacteriales. These long filaments are readily seen under the microscope and have a characteristics pattern. Filamentous iron bacteria are "omnipresent" in carbon steel and iron distribution system pipelines. These bacteria are commonly reported in deposits associated with tuberculation (Dendro 1975).

Oxidation of ferrous ions is thought to be one of the most typical characteristics of *Sphaerotilus—Leptothrix* group of bacteria. It was reported that *Leptothrix* sp. would grow autotrophically utilizing the energy liberated upon the oxidation of ferrous ions (Ghiorse 1984). *Leptothrix* sp. are gram negative bacteria and the most common iron storing ensheathed bacterium apparently occurring in slow running ferrous iron-containing waters. *Leptothrix* sp. are also interesting for ecological and biogeochemical reasons. Like algae they also develop in natural habitats as colonies of huge masses (Mulder 1989). The sheath formation characteristics of these organisms indicate their relationship with cyanobacteria, which under favorable conditions often form a gelatinous or fibrous sheath. Originally, thin sheaths are secreted which later become heavier, by excretion of more organic matter and by depositing or impregnation of iron oxide, which makes the sheath heavy and highly resistant to decomposition (Fig. 6.3). The presence of sheath has an ecological and nutritional consequence for the organism. The sheath enables the bacteria to attach on solid surfaces (pipelines); this ability favors the growth in running water and pipelines (Mulder and Deinema 1986). Attachment of sheathed bacteria to solid surfaces may be achieved by holdfasts. Such appendages are formed by *Sphaerotilus natans* and *Leptothrix lopholea* (Mulder 1989) but not by other members of the iron bacteria

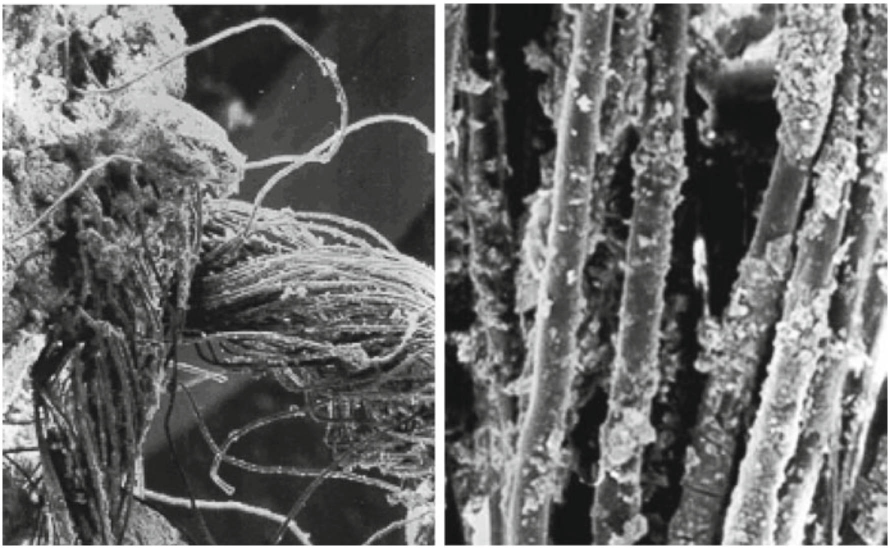


Fig. 6.3 SEM image of filamentous iron-oxidizing bacteria (*Leptothrix* sp.)

family. Holdfast originates from swarmer cells that when contacting a surface become attached to the end opposite to the flagellum, presumably by a sticky substance which soon hardens. The sheaths of *Leptothrix* sp. assist in the formation of a membrane that is relatively impervious to oxygen, and in the process decrease the quantity of oxygen in the tubercle vicinity, thus establishing a micro-electrochemical cell. With increasing thickness, the inside of the tubercle becomes more anaerobic, the difference in the potential between inside and outside the tubercle increases, and corrosion gets accelerated (Mulder and Deinema 1986; Emerson and Moyer 1997).

4.2 Iron Reducing/Exopolymer (Slime) Bacteria

Slime formers are a diverse group of aerobic bacteria that produce extracellular polymers. The principal slime-forming bacterial genera include *Pseudomonas*, *Bacillus*, *Flavobacterium*, and *Aerobacter*. Most of the slime formers that colonize metal surfaces produce polymers and form a gel matrix on the metal. The exopolymers influence interfacial processes by immobilizing water at the biofilm–metal interface, trapping various inorganic and organic moieties and thereby decreasing diffusion. These exopolymers are acidic and contain functional groups that bind metal ions from the aqueous phase. Aerobic slime formers are important mainly because "slime" complexes metal ions and promote corrosion. Slime formers are "scrubbers" of oxygen; they create an ideal site for growth of anaerobic bacteria. The exopolymers are actually a sophisticated network of sticky strands that bind the cells to the surface. Apart from aiding in adhesion, the exopolymers also protect the bacteria from grazing by protozoans or bacteriovores. The exopolymer matrix is capable of intercepting the penetration of biocides and antibiotics and protects the microbes; it also gives structural stability to the biofilm. Slime formers initiate corrosion by concentrating metal ions, which result in galvanic cell formation commonly seen in copper alloys (Geesey 1982; Sutherland 1997).

4.3 Nitrate-Reducing Bacteria

Nitrate-reducing bacteria are environmentally significant bacteria constituting up to 50% of microbial population present in aquatic systems. Nitrate reduction takes place in waters enriched with organic matter and nitrate. *Achromobacter*, *Bacillus*, *Corynebacterium*, *Micrococcus denitrificans*, *Pseudomonas*, *Serratia*, and *Vibrio* species are examples of extremely active nitrate reducers (Rao 2003). Since nitrate serves as an electron acceptor, the growth rate of denitrifiers depends on nitrate concentration. Denitrifying bacteria require an electron donor to carry out denitrification process, which is served by organic matter. A possible mechanism of ammonia formation by denitrification process has been proposed by Tiedje (1988), which involves four stages viz.; reduction of nitrate to ammonia via nitrite, hyponitrite, and hydroxyl amine. Nitrate reduction is driven by nitrate and nitrite reductase ((6.1)–(6.4))

$$NO_3^- + 2H^+ + 2e \rightarrow NO_2^- + H_2O \tag{6.1}$$

$$2NO_2^- + 4H^+ + e \rightarrow N_2O_2^- + 2H_2O \tag{6.2}$$

$$N_2O_2^- + 6H^+ + 5e \rightarrow 2NH_2OH \tag{6.3}$$

$$NH_2OH + 2H^+ + 2e \rightarrow NH_3 + H_2O \tag{6.4}$$

Ammonia produced due to nitrate reduction is bad for copper alloys. Ammonia levels >1 ppm induce stress corrosion cracking (SCC) in copper bearing alloys (Rao and Nair 1998).

4.4 Sulfate-Reducing Bacteria

SRB are environmentally important group of microorganisms particularly active in the sediments and sediment water interface of aquatic systems. Their predominance can be divided into ecological processes and economic effects (Gibson 1990). Development of SRB in surface microbial films can be expected whenever environmental conditions such as redox potential or oxygen tension and nutrients are suitable for their growth. The most significant aspect of SRB metabolism is the production of hydrogen sulfide (H_2S) which, being a very strong reducing agent is able to inhibit the growth of most aerobic bacteria. The microbiological reduction of sulfate is a respiratory activity in which sulfate substitutes for oxygen as the terminal electron acceptor (Lee et al. 1995). Several sulfur anions are involved as intermediates, which are metastable and susceptible to microbiological oxidation. The initial step in the biological sulfate reduction pathway is the transport of exogenous sulfate across the bacterial membrane into the cell. Once inside the cell, sulfate reduction forms the highly active molecule adenosine phosphor-sulfate (APS). This molecule is then rapidly converted to sulfite by the cytoplasmic enzyme APS reductase. Sulfite is further reduced to form the sulfide ion, this production of H_2S make SRB extremely important bacteria in the oil industry where their growth can cause corrosion and degrade oil which is a great economic problem (Peck and LeGall 1982; Pankhania 1988). SRB induce pitting in the form of large radial growth patterns on iron surface which are shallow in nature. SRB also corrode copper alloys and titanium (Rao et al. 2000, 2005).

4.5 Sulfur-Oxidizing Bacteria

The common sulfur-oxidizing bacterium *Thiobacillus thiooxidans* is a chemolithotroph utilizing thiosulfate and sulfide as sources of energy to produce sulfuric acid. This broad family of aerobic sulfur bacteria derives energy from the oxidation of sulfide or elemental sulfur to sulfate. This group of bacteria can oxidize the sulfur compounds to sulfuric acid, resulting in pH values as low as 1.0. The *Thiobacillus* strains are most commonly found in mineral deposits, and are largely responsible for mineralization processes in acid mine drainage. They proliferate inside sewer lines and can cause rapid deterioration of concrete mains and the reinforcing steel therein. They are also found on surfaces of stone buildings and statues and probably account for much of their damage. *Thiobacillus* bacteria associated with corrosion are always accompanied by SRB. Thus, both types of organisms are able to draw energy from a synergistic sulfur cycle (Schippers et al. 1996).

4.6 Methanogenic Bacteria

Methanogens are archaea bacteria that produce methane as a metabolic byproduct. Examples of methane producing genera are *Methanobacterium*, *Methanosarcina*, *Methanococcus*, and *Methanospirillum*. Methanogenic bacteria are widespread in nature, and are found in mud, sewage, and sludge and in the rumen of animals. Methanogens typically thrive in environments in which all other electron acceptors (such as oxygen, nitrate, sulfate, and trivalent iron) have been depleted. Some bacteria of the group are called hydrogenotrophic, which use carbon dioxide as a source of

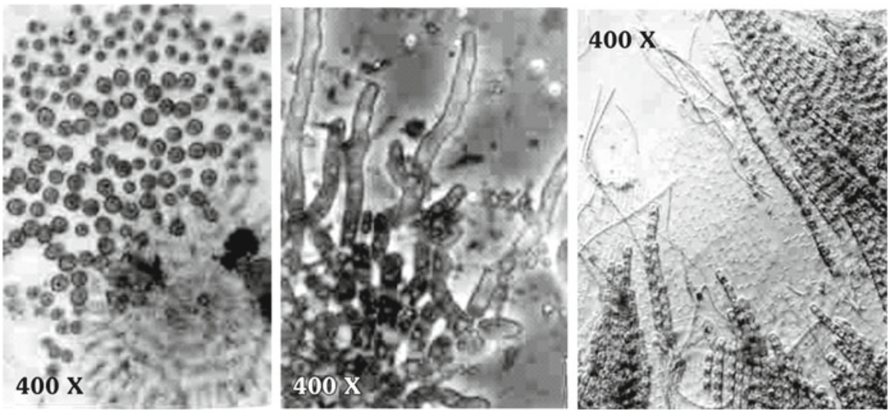


Fig. 6.4 Algal biofilm consisting of *Micrococcus* sp., cyanobacteria and unidentified filamentous algae

carbon and hydrogen as a source of energy (hydrogen functions as a reducing agent). Some of the carbon dioxide is reacted with the hydrogen to produce methane. In natural environments, methanogens and SRB frequently coexist in a symbiotic relationship: SRB produce hydrogen, carbon dioxide, and acetate by fermentation, and methanogens consume these compounds. Methane-producing bacteria are also believed to be responsible for corrosion. Like SRB, methanogens consume hydrogen and thus are capable of cathodic depolarization and can aid in corrosion process (Girguis et al. 2005).

4.7 Algae

Algae and eukaryotic organisms are ubiquitous in nature (Fig. 6.4). They are present in various sizes, shapes, and range from unicellular to multicellular forms. Algae are autotrophic and derive their energy from carbon dioxide, water, and sunlight. Algal growth results in drastic changes in dissolved oxygen and pH in a water body. The general classification of the algae is based partly upon the nature of the chlorophylls and accessory pigments, Chlorophyta (green algae), Rhodophyta (red algae), and Phaeophyta (brown and other pigmented algae).

In industrial units algae generally flourish on wetted, well-lit surfaces such as cooling towers, storage tanks, and distribution systems. Due to their capability to generate oxygen, organic acids, and nutrients for other organisms, algae play an indirect role in microbial proliferation and deterioration of materials. The corroding action of the algae is very slow and results in very thin layer of corrosion products. Algae also promote corrosion of materials by carbonic acid formed from carbon dioxide liberated during their respiration (Hoagland et al. 1986).

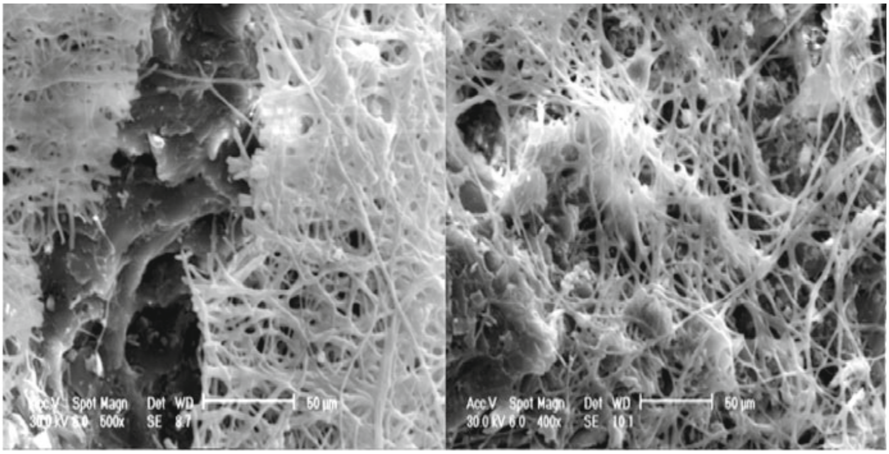


Fig. 6.5 SEM image of fungal biofilm growing on ebonite surface (*Cladosporium* sp.)

4.8 Fungi

Fungi are among the most common microorganisms found in the air, soil, foodstuffs, paint, textiles, bird feathers, and on live and dead plants. Most fungi are capable of producing organic acids and are implicated in the corrosion of steel and aluminum, especially in failure of aircraft fuel tank. In addition, fungal growth produces anaerobic sites for SRB and metabolic byproducts that are useful for growth of various bacteria. Among the fungi, the important ones are the molds and yeasts. Fungi deteriorate cooling tower wood and some like *Cladosporium resinae* are involved in the corrosion of aluminum alloys. *Cladosporium* is the most common member of the so-called black molds (Fig. 6.5). It produces a black pigment that protects it from ultraviolet light. This fungus breaks down aromatic ring compounds to simpler hydrocarbons and utilizes them for its metabolism. It produces organic acids by metabolizing fuel components in aircraft fuel tanks, leading to fuel breakdown and corrosion of fuel tank. It is also reported that the *C. resinae* produces a bio-surfactant that degrades aircraft fuel by allowing water to partially mix with it, creating an emulsion; this affects the combustive qualities of the fuel, ultimately resulting in fuel failure and machine damage (Little and Wagner 1996; Rao et al. 2007).

5 Microbial Corrosion of Various Metals in Cooling Water Systems

Microbial corrosion is a multifaceted phenomenon, the dimension of which has slowly been realized during the present century. Iron age brought in the problem of iron corrosion. Interestingly, the iron produced in antiquity, of which the Ashoka

Pillar in Delhi is the most famous example, remains even today freer from corrosion than that manufactured in later years. The laws of electrochemistry laid down by Faraday gave the relationship between chemical action and the generation of electric current, upon which the theory of electrolytic corrosion was based.

The possibility that microorganisms exert an influence on the corrosion of metals was first mentioned by Garrett (1891). He reported that the increase in corrosion of lead might be due to the ammonia, nitrites, and nitrates produced by bacterial action. Gaines (1910) suggested that the corrosion of iron in aqueous and soil environments might be caused by SRB, sulfur bacteria, and iron bacteria. The iron bacteria *Gallionella ferruginous* was isolated from the corrosion products and high concentration of sulfur and organic matter were noted. Von Wolzogen Khur and van der Vlugt showed that iron could also be attacked in the absence of oxygen (anaerobically) as a result of the activities of SRB. They provided convincing evidence that, cast iron water pipes in anaerobic soils was corroded due to graphitization (Seed 1990). Later investigations into bacterial corrosion process were pursued by many workers and resulted in reviews and many articles (Costello 1969; Pope et al. 1984; Seed 1990; Little et al. 1991; Videla 2001; Rao et al. 2005).

The basic cause of corrosion is the thermodynamic instability of metals in their refined forms (Seed 1990; Little et al. 1991; Videla 2001; Rao et al. 2005). "Principally, the theory of corrosion is simple but in process it is extremely complex. The corrosion cells formed due to surface chemistry heterogeneities are influenced by environmental factors (chemical or biological) which sustain or augment the corrosion process." Accordingly, if the outside factors are microorganisms; the process is generally referred to as MIC. The primary effect by microbe would be the formation of differential concentration cells on the metal surfaces. The respiring colony of microorganisms causes a difference in oxygen concentration between its microenvironment and the surrounding area. This will give rise to potential differences, with subsequent corrosion currents variations between the microbial colony sites and the surrounding metal surface. Direct removal of corrosion products, e.g., a respiring microbial colony removing the oxidized metal (at anodic sites) or processes which utilize hydrogen (at cathodic sites) will cause electrochemical corrosion reactions to be biased toward metal dissolution.

5.1 Iron (Carbon Steel)

Corrosion is a leading cause of pipeline failures and is a main component of the operating and maintenance costs of power, process, and gas industries. Quantifying the cost of corrosion generally, and more specifically the cost associated with microbial corrosion, is not easy exercise; moreover, the data reported are controversial. It was estimated in 2001 that the annual cost of all forms of corrosion to the major industries was $13.4 billion, of which microbially influenced corrosion accounted for about $2 billion (Zhu et al. 2003). It has been estimated that 40% of all internal pipeline failures can be attributed to microbial corrosion (Zhu et al. 2003).

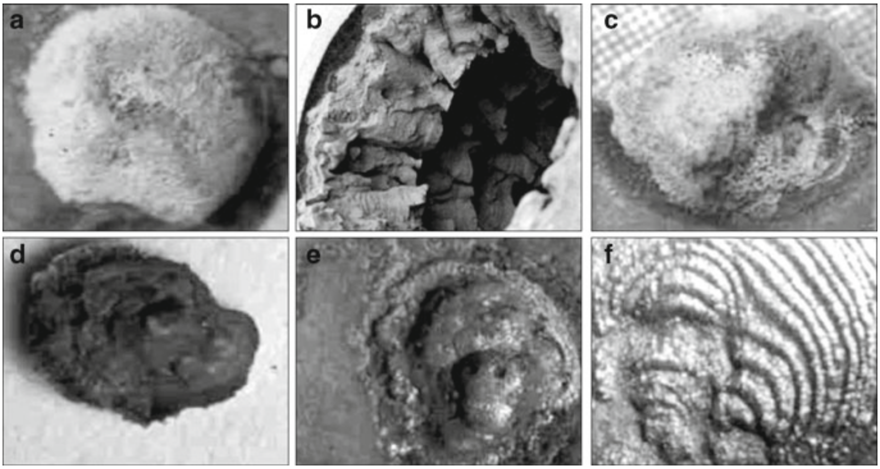


Fig. 6.6 Images of carbon steel corrosion in freshwater: (**a**) typical tubercle on carbon steel specimen, (**b**) iron pipeline showing extensive tuberculation blocking water flow (with permission of Bennett P. Boffardi), (**c**) section of a tubercle showing iron corrosion products, (**d**) bottom of the tubercle showing *black* corrosion deposit of iron sulfide and magnetite, (**e**) image of pitting corrosion of carbon steel with corrosion products and (**f**) typical concentric ring pattern of carbon steel corrosion induced by SRB

A rust layer, so called protective rust layer, on a weathering low-alloy steel has strong protective ability for atmospheric corrosion of the steel. However, iron-oxidizing or -reducing bacteria can break down the protective layer and accelerate the corrosion process. In this section, details of the conditions which lead to the failure of iron pipelines in a nuclear test reactor cooling water system will be discussed. The service water system of the test reactor which is mostly made of carbon steel (CS) is designed to provide cooling water to critical plant components such as fuel pits, coolers, pump oil, gear box, and seal condenser. After commissioning the test reactor, the cooling water system had problems such as flow blockage, pipe punctures, and relatively high corrosion rates of carbon steel (Rao et al. 1993). In order to understand the causative factors for the failures and to formulate appropriate control strategy, detailed water quality and microbiological analyses were carried out.

During the initial period of operation of the cooling circuit, corrosion rates of CS ranged from 3 to 13.5 mpy. However, over the years stringent cooling water monitoring and fine-tuning of the biocide dosage resulted in low corrosion rates of <2.0 mpy and also curtailment of the bacterial population. Clean carbon steel pipes are subjected to rapid corrosion during the initial stages of tubercle formation (Fig. 6.6). The bacteria thrive at the edge of the tubercle, where oxygen and iron are readily available, since iron bacteria require oxygen for their growth. Water velocity is a major parameter in predicting the selective growth of iron bacteria. Stagnant or low velocity water appears to deprive the iron bacteria of required oxygen, which reduces their growth (very low corrosion rate of 1.75 mpy was observed in sterile

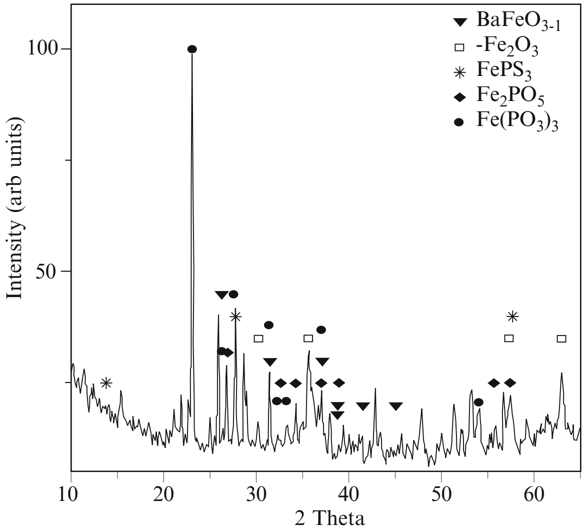


Fig. 6.7 XRD spectrum of the carbon steel corrosion deposits

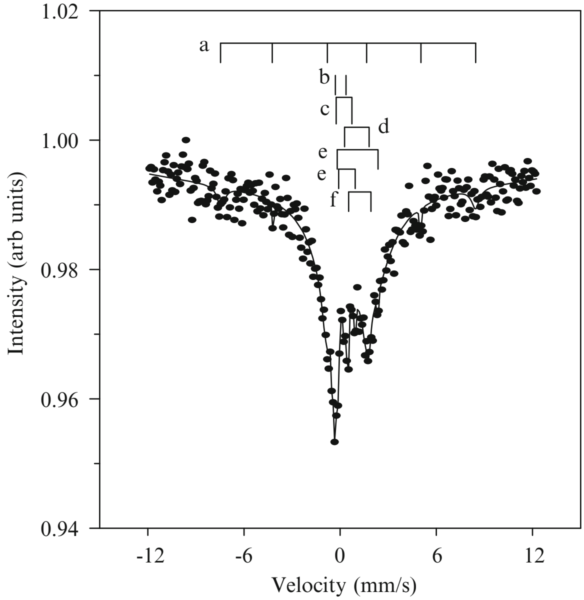


Fig. 6.8 Mössbauer spectrum of iron corrosion products (**a**) γ-Fe_2O_3 (**b**) Fe_2PO_5 (**c**) $FePS_3$ (**d**) $Fe(PO_3)_3$ (**e**) $BaFeO_{(3-x)}$ and (**f**) amorphous phase

conditions). The X-ray diffraction pattern (Fig. 6.7) of the carbon steel corrosion product gave qualitative information about the possible iron phases present. The phase identification, done using a search-and-match fit of the XRD data to the patterns in the ICDD database, revealed that Fe $(PO_3)_3$ was the predominant phase. The other phases identified were γ-Fe_2O_3, Fe_2PO_5, and $BaFeO_{3-x}$. Apart from peaks corresponding to various crystalline phases, features corresponding to poorly crystallized phase were also observed. Figure 6.8 illustrates the Mössbauer spectrum of the corrosion product. Analysis of the Mössbauer data revealed sub-spectra corresponding to $Fe(PO_3)_3$, γ-Fe_2O_3, Fe_2PO_5, $BaFeO_{3-x}$, and $FePS_3$, which are shown as stick diagrams.

Metal-depositing bacteria create environments that are conducive to sustaining their growth and subsequently promote corrosion. The iron bacteria species which infested the test reactor cooling circuit was identified as *Leptothrix* sp. This is the most common iron storing ensheathed bacterium apparently occurring in slow running, ferrous iron-containing waters, which are poor in decomposable organic material. The sheaths of *Leptothrix* sp. assist in the formation of a membrane that is relatively impervious to oxygen, and in the process decrease the quantity of oxygen in the tubercle vicinity, thus establishing a micro-electrochemical cell. With increasing thickness, the inside of the tubercle becomes more anaerobic and favors SRB growth. The difference in the potential between the iron surface underneath and outside the tubercle increases, and thus corrosion gets accelerated. Differential aeration cells formed due to microbial colonization leads to corrosion by dissolution of ionized material or oxides at the grain boundaries (Seed 1990; Little et al. 1991; Rao et al. 2000; Videla 2001). Under these conditions there will be pronounced growth and activity of the iron bacteria, giving rise to the accumulation and sedimentation of large quantity of ferric hydroxide. The iron bacteria in water have not shown much variation during the course of this study (10^4–10^5 cfu/mL). There were variations in SRB numbers on the carbon steel coupons and cooling water. The SRB counts varied from 7×10^2 to 9×10^3 cfu/cm^2 during the year. SRB population in the cooling water ranged from 10 to 35 cfu/mL. The culturable aerobic heterotrophic bacteria (CAHB) of the source water and the test reactor cooling water ranged from 10^5 to 10^8 cfu/mL.

Under anaerobic conditions normal electrochemical corrosion does not occur because the cathode becomes polarized by the buildup of a layer of atomic hydrogen. This cathodic polarization stifles the dissolution of iron at any anodic site (Iverson 1987). The activity of SRB is thought to stimulate the normal electrochemical corrosion mechanism by the removal of cathodic hydrogen or by formation of iron sulfide which itself is cathodic to steels (Seed 1990). It is well established in the case of SRB that the major corrosion effect is due to the biogenic production of sulfide. Rapid corrosion occurs when sulfide is added or when SRB growth is stimulated by addition of nutrients. The initial corrosion product formed, as far as SRB are concerned, is mackinawite, rich in iron sulfide, which forms a poorly protective layer on the metal surface (Seed 1990). It has been reported that more the iron sulfide formation, the higher is the corrosion rate of carbon steel. Videla (2001) has reported that presence of sulfide could explain the pit morphology. SRB induces pitting in the form of large radial growth patterns (Fig. 6.6) on carbon steel surface. However, in this investigation, the distinctive corrosion pattern on carbon steel is the presence of pits as disk-shaped concentric rings, which are similar to those obtained in the presence of sulfides due to fast radial pit growth. Iverson (1987) suggested that in addition to iron sulfide, SRB also produce a highly corrosive metabolite (iron phosphide), a soluble compound containing phosphorous, which enhances the dissolution of iron under anaerobic conditions at neutral pH. However, during the course of this study, many phosphate compounds were observed (Figs. 6.7 and 6.8). Earlier studies showed the ability of SRB to produce hydrogen sulfide in a medium containing barium sulfate as the only sulfate source. The SRB culture not only utilized insoluble barium sulfate but in the process also produced significant amount of soluble barium ion (120 mg/L). The presence of $BaFeO_{3-x}$ compound could be the result of the interaction of iron oxide with barium (Rao et al. 2000). Similarly, the presence of $FePS_3$ compound could be due to two possible reasons: (1) Iverson (1987) reported that SRB produced colloidal iron phosphate and Seed (1990) further confirmed that phosphate increased the rate of corrosion of carbon steel in the presence of SRB. Because reduced phosphorus is highly reactive, it could contribute to corrosion of iron. Furthermore, in a sulfide environment, the iron phosphorus complex formed could have reacted with sulfide to form the $FePS_3$ compound. (2) It is well known that ferrous sulfide layer is formed on metal surface by Fe^{2+} reacting with hydrogen sulfide produced by SRB. The crystalline nature of iron sulfide has profound influence on iron corrosion. The phosphate based water treatment program in operation at the test reactor could have resulted in the phosphorus ions reacting with the iron sulfide, thereby leading to the formation of the $FePS_3$ compound (Figs. 6.7 and 6.8).

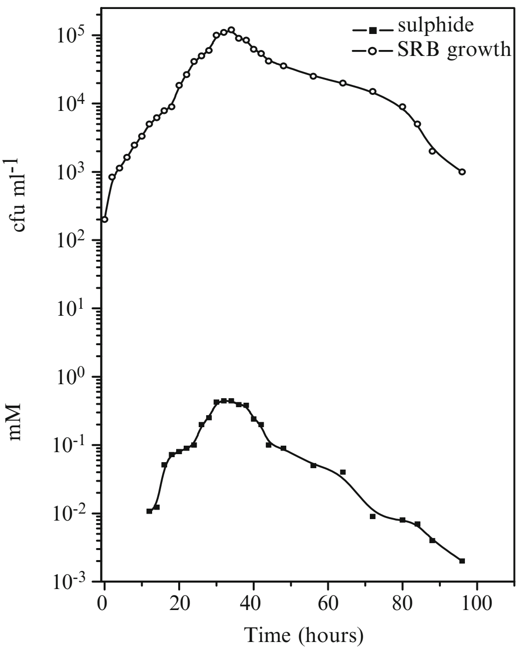
5.2 Stainless Steel

SRB are among the principal corrosion causing bacteria implicated in many instances of microbial corrosion of stainless steel (Seed 1990). Since SRB grow beneath the biofilm, the presence of high levels of dissolved oxygen in the bulk water may not affect their growth. SRB presence is often considered as a marker for biocorrosion, just as *Escherichia coli* is used as an indicator for potable water contamination (Rao et al. 2005). Till date, qualitative demonstrations regarding the presence of SRB have yielded little useful information. However, the quantitative association of SRB with industrial corrosion problems has not been addressed in detail and such information is warranted. Though many cooling circuit failures of stainless steel are being implicated due to SRB activity, the finer details of SRB growth and hydrogen sulfide in initiating corrosion of stainless steels are lacking. In the following section, the effect of a marine SRB isolated from seawater cooling system on the pitting corrosion of Stainless steel-304 is detailed.

The SRB isolate used for this study was categorized as *Desulfovibrio* sp. after confirming with various biochemical tests including the desulfoviridin test. The growth curve and sulfide production by *Desulfovibrio vulgaris* are presented in Fig. 6.9. In the experimental study, the SRB culture was maintained in the log phase and the sulfide concentrations ranged from 0.02 to 0.05 mmol/L. Electron micrographs showed SRB cells embedded in the corrosion deposit. The pits had significant SRB population and were in hemispherical shape.

A mechanism of microbial pitting in stainless steel has been published confirming the effect of sulfur compounds other than sulfides on the corrosion behavior

Fig. 6.9 SRB growth curve and sulfide production



of iron (Hamilton 1985). The author found that oxidation of mixed sulfate/sulfide solutions readily produce an environment that is able to pit SS-304, even in the absence of chloride ions. Thiosulfate is reported to be a more effective pitting agent than sulfides at low concentrations (Gibson 1990). The SRB isolate could have been responsible for both the low redox potential and the acceleration of pitting (since no chloride ion or salt was used in the medium preparation). Generally, decay of the passive layer due to the formation of sulfide by SRB activity could give a rough indication of the initiation of a localized corrosion process such as pitting (Rao et al. 2005). Morales et al. (1993) reported that the presence of bacteria can cause the apparent thinning of external $Fe_2O_3 \cdot xH_2O$ layer in steels. Hence, in such cases a decrease in the electro-reduction charge can be observed, which can be related to the outer passive layer. SRB influence the metal in a similar manner to non-biogenic sulfide, which shifts the pitting potential to a more active value. The pitting potential is defined as the potential where current increases dramatically. The pitting potential becomes more noble as the biofilm becomes thicker both at low and high substrate loading rates. This indicates that the pitting tendency of steel becomes more difficult with time provided that the SRB biofilm is thick enough to ennoble the metal surface (George et al. 2000). Pankhania (1988) and George et al. (2000) reported that biofilms possibly increase the activation energy for hydrogen reduction and also recombination of the same with sulfide on metal surface. The hydrogen sulfide released by SRB decreases the corrosion resistance since it promotes active dissolution, delay re-passivation and render the passive film non-protective (Rao et al. 2005). Studies reported elsewhere indicated that the decrease in pitting potential was associated with the total concentration of sulfide generated by SRB. Thus, bacterial growth could promote a decrease in the passive film resistance, probably by producing acidic metabolites and complexing substances. Thus, the SRB growth and sulfide activity of SRB would contribute to the rapid decay of passive film layer. This would favor the initiation of localized corrosion process such as pitting.

5.3 Copper Alloy

Industrially, copper and its alloys are most commonly used in the fabrication of heat exchangers in cooling water systems (Bott 1993, 1995). The alloys depend on their natural oxide layer for corrosion resistance (Syrett and Coit 1983). This oxide film (Cu_2O) is a defective film with vacancies in the cuprous oxide lattice into which cuprous ions can migrate. As copper metal (Cu^o) oxidizes to cuprous ion (Cu^{+1}), the cuprous ions move into the vacancies of the oxide lattice. As the ions migrate through these vacancies, they get oxidized to the cupric ion (Cu^{2+}). Copper corrosion occurs with the outward movement of the cuprous ion rather than the inward movement of oxygen. Cu_2O protective film can be disrupted by a variety of cooling water parameters which include pH, water velocity, chlorides, ammonia, and biofouling. Addition of such elements as aluminum, zinc, tin, iron, and nickel to copper have been successfully used to modify the cuprous oxide film to make it more corrosion resistant. However, copper is susceptible to rapid attack in oxidizing acids, oxidizing heavy-metal salts, sulfur, ammonia (NH_3), and some sulfur and NH_3 compounds (Rao and Nair 1998).

The problem of condenser tube (admiralty brass) failure at an atomic power station was investigated by Rao and Nair (1998). The failure of the condenser tubes led to the leakage of cooling water into the boiler, thereby violating the boiler water technical specifications. Earlier metallurgical analyses of the failed tubes have revealed that the tubes were damaged due to SCC (Khatak et al. 1985). However, no systematic study of interaction between microbial biofilms and metal has been attempted. A detailed study was carried out to look into the environmental conditions or causative agent, which could have led to the failure of condenser tubes. Comprehensive water quality analysis of the lake water, which was being used as source of cooling water for the power plant, was carried out. In addition, biofilms developed on perspex and different metal coupons were characterized for various physical, chemical, biochemical, and biological parameters in a time-series study, to understand the biofilm parameters which could have contributed to the copper alloy corrosion and failure (Rao and Nair 1998).

Comparison of the water quality data between the intake and outfall showed increase in dissolved oxygen (DO), chlorine demand, ammonia, and nitrite and decrease in nitrate values in the outfall waters of the power plant condenser. The observed increase in pH from intake to outfall could possibly be due to the formation of ammonia in the cooling system. Similarly, the reduction in TDS from intake to outfall indicated that a large number of bacteria were thriving inside the cooling system, and dissolved salts were being consumed by the bacteria, thereby reducing the TDS content in the outfall water. Relatively high values of nitrate-reducing bacteria were found in the lake water (10^4 cfu/mL). This was an added evidence in support of the view that nitrate was being reduced to nitrite in the condenser circuit. The presence of SRB in the intake water and their increasing number in the outfall water was again a notable feature as it is also known that SRB can reduce nitrate to ammonia. The high total viable count (10^8 cfu/mL), extensive growth of algae, fungi (7×10^4 cfu/mL) and SRB indicated the vulnerability of the cooling circuit material to microbial attack. Scrapping from the metal (admiralty brass) coupons exposed online showed the presence of high organic matter (27%). According to Licina (1989), if the organic content of the corrosion deposits is greater than 20% the corrosion process is likely to be biologically mediated.

Two metallurgical studies of the failed condenser tubes of the power plant showed that the tubes corroded due to SCC (Khatak et al. 1985). SCC is a fracture or cracking phenomenon caused by the combined action of tensile stress, a susceptible alloy, and a corrosive environment. The metal normally shows no evidence of general corrosion attack, although slight localized attack in the form of pitting may be visible. Usually, only specific combinations of metallurgical and environmental conditions cause SCC. This is important because it is often possible to eliminate or reduce SCC sensitivity by modifying either the metallurgical characteristics of the metal or the makeup of the environment. In the present case, SCC was initiated due to the formation of active corrosion agent, Cu $(NH_3)_4(OH)_2$ (tetra amino copper (II) hydroxide). There was a possibility of existence of relatively high concentration cells of ammonia at the metal–biofilm interface on account of the biofilm matrix, which can locally shield ammonia levels, thereby preventing diffusion into the flowing water. When the oxide layer depleted metal surface comes in contact with ammoniac environment, the anodic reaction is triggered, because the copper ions produced are known to complex with ammonia to form the highly soluble $Cu(NH_3)_2^+$ ions (Rao and Nair 1998).

The overall cathodic reaction is oxygen reduction, which could be achieved by an intermediate reaction, the oxidation of Cu $(NH_3)_2^+$ ions to Cu $(NH_3)_4^+$ ions. This reaction is rapid and can occur throughout the biofilm, wherever ammonia concentration cells are formed. The Cu $(NH_3)_4^+$ ions are then reduced in the cathodic reaction at the metal surface to reform the Cu $(NH_3)_2^+$ ions (Rao and Nair 1998). Second, Syrett and Coit (1983) report that carbon dioxide released by the respiring microbes in ammonical environments can significantly increase corrosion rates of copper alloys. XRD analysis of the admiralty brass corrosion products revealed the presence of copper ammonium complex as major peak (Fig. 6.10) along with copper ammonium sulfate, copper, zinc, copper nitrate, and copper (II) oxide as the other peaks. The presence of copper ammonium complex indicated that the active corrosion agent was formed on the admiralty brass surface. Presence of copper peak indicated that copper was getting leached by anodic reaction triggered by biofilm formation and zinc (by dezincification process as reported by Khatak et al. 1985) was also getting leached from the admiralty brass surface. Glycolipids, oligopeptides and polysaccharides concentrations were reported in biofilms developing on copper alloys and these compounds have been implicated in corrosion processes

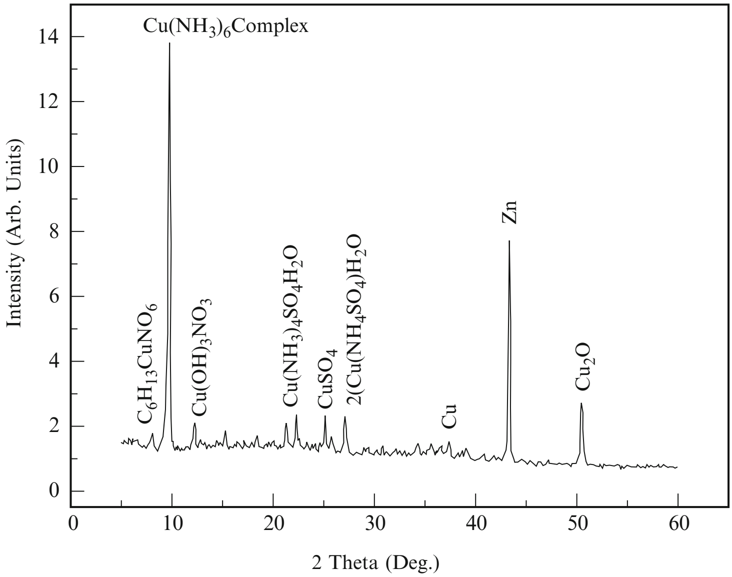


Fig. 6.10 XRD spectrum of admiralty brass corrosion products

(Little and Wagner 1996). Therefore, it is essential to achieve a deeper understanding of microbial biofilms and their role in corrosion processes and then implicate them in the corrosion mechanism. Such studies will result in devising better control measures for combating microbial corrosion (Videla 2001).

5.4 Titanium

Titanium condensers, shell and tube heat exchangers, and plate and frame heat exchangers are used extensively in power plants, refineries, air conditioning systems, chemical plants, offshore platforms, surface ships, and submarines. The life span and dependability of titanium are demonstrated by the fact that, of the millions of feet of welded titanium tubing in power plant condenser service, there have been no reported failures due to corrosion on the cooling water side (Schutz 1991). The excellent corrosion resistance of titanium alloys results from the formation of very stable, continuous, highly adherent, and protective oxide films on the metal surface. Because titanium metal is highly reactive and has an extremely high affinity for oxygen, these beneficial surface oxide films form spontaneously and instantly when fresh metal surface is exposed to air and/or moisture. In fact, a damaged oxide film can generally reheal itself instantaneously if at least traces of oxygen or water are present in the environment. However, anhydrous conditions in the absence of a source of oxygen may result in titanium corrosion, because the protective film may not be regenerated if damaged. Although this naturally formed film is typically less than 10 nm thick and is invisible to the eye, it is highly chemically resistant and is attacked by very few substances, including hot, concentrated HCl, H_2SO_4, NaOH, and (most notably) HF. This thin surface oxide is also a highly effective barrier to hydrogen (Casillas et al. 1994).

General corrosion of titanium is characterized by a relatively uniform attack over the exposed surface of the metal. Titanium alloys may be subject to localized attack in tight crevices exposed to hot (>70°C) chloride, bromide, iodide, fluoride, or sulfate-containing solutions. Till date there are no published reports on the stability of the titanium dioxide (TiO_2) layer in an obligate anaerobic milieu of SRB. With increasing use of titanium in industrial cooling systems and its vulnerability to biofouling, the potential significance of SRB induced corrosion of titanium should be of concern to process engineers, chemists, and material scientists.

Biocorrosion experiments were carried out using ASTM grade 2 titanium obtained in plate form (2 mm thick). Specimens (2.0 × 1.5 cm) were polished on progressively finer silicon carbide papers to a final grit size of 1,000. After polishing they were rinsed in distilled water and then in acetone for degreasing. Later, the specimens were immersed in 70% ethanol for 4 h. The glassware used for the study was autoclaved at 121°C for 15 min and later dried in a hot air oven. SRB were cultured using standard medium containing no chloride ion. Filter-sterilized dithiothreitol was added to reduce the redox potential of the medium below −200 mV to aid the growth of obligate anaerobe SRB (Postgate 1984). The medium was not purged with any inert gas. The SRB strain used for the study was isolated from a fresh water-cooled service water system of a nuclear test reactor (Rao et al. 1993, 2000).

Prior to incubation (at room temperature) the flasks were inoculated with 10 mL of log phase SRB culture (3×10^5 cfu/mL). A semi-continuous mode of SRB growth was used for this study i.e., 75% of the culture broth is drained and replaced with equal amount of fresh medium every 4 days to maintain SRB growth rate in log phase throughout the study period. A control set of titanium coupons exposed to sterilized SRB medium was also observed for a similar period of time. In order to prevent any possible contamination of the medium in the control set, formalin was added to a final concentration of 0.1% (v/v). Titanium body implants are generally preserved in 10% formalin and there are no reports of formalin reacting with the oxide layer of titanium. The study was repeated thrice in triplicate sets employing four coupons in each experiment.

The SRB isolate used in the study was categorized as *D. vulgaris* after carrying out various biochemical tests, including the desulfoviridin test. The growth curve and sulfide production by *D. vulgaris* are presented in Fig. 6.9. The SRB count on titanium coupons ranged from 10^4 to 10^5 cfu/cm. The sulfide production in the log phase was rapid and continued through the stationary phase. The semi-continuous culture kept the SRB growth in the log phase throughout the experimental period and the sulfide concentration was 0.2–0.4 mM.

Figure 6.11 shows SEM picture of titanium surface colonized by typical rod shaped SRB cells. In the pitted region, signals for peaks with respect to Ti, Fe, O, C, and P were observed. CSLM was used to observe the pitting corrosion of the titanium specimen. Pits of 50 μm diameter and 25 μm deep were observed, along with numerous micro pits which were ~5 μm in diameter.

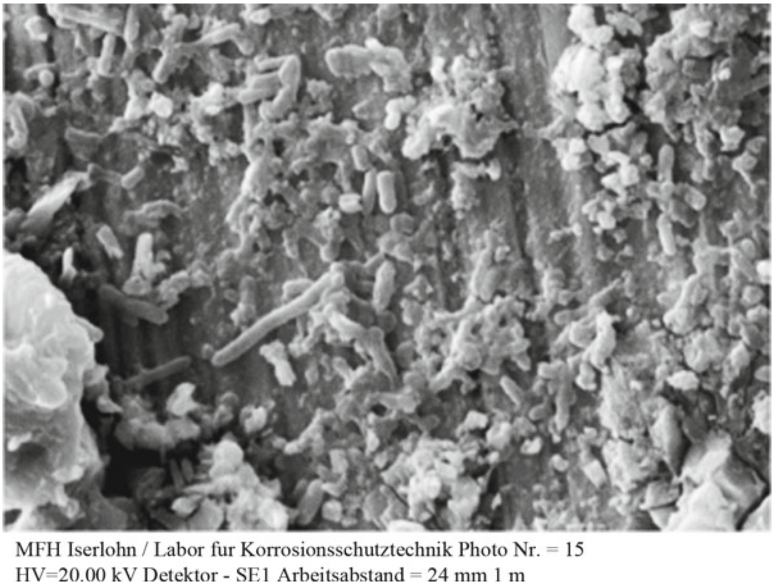


Fig. 6.11 SEM picture showing long rod-shaped bacteria, typical of SRB on corroded titanium surface

The most significant aspect of SRB metabolism is the production of hydrogen sulfide (H_2S). Hydrogen sulfide is a very strong reducing agent and also inhibits the growth of most aerobic bacteria. SRB produce sulfide at concentrations that range from 0.1 to 10 mM. In this study the SRB strain *D. vulgaris* produced sulfide in the range of 0.2–0.4 mM. In general, about one third of the total sulfide produced by SRB remains as undissociated acid and about two thirds as the HS^- ion. The undissociated H_2S in solution will be in dynamic equilibrium at the air–water interface with H_2S gas (Gibson 1990; Seed 1990). SRB are associated with two corrosive mechanisms: (1) they create a biofilm having a crevice like geometry on the metal surface, and (2) produce H_2S as well as Phosphine (PH_3). H_2S enhances the corrosion reactions—anodic dissolution and cathodic hydrogen evolution (Seed 1990). XPS analysis of the exposed titanium specimen (after removal of the SRB film) showed the presence of Ti^{4+} and trace levels of sulfur and phosphorous (Fig. 6.12). XPS analysis of the SRB film showed peaks for sulfur (S^0, S^{2-} and S^{6+}) and phosphorous (P^{5+}).

Titanium passivates in most environments and is virtually inert unless conditions are very reducing. Schutz (1991) reported that under highly reduced conditions the oxide film may break and corrosion can occur. Casillas et al. (1994) explained pitting corrosion of titanium in halide solutions. Their studies revealed that the electrical conductivity of the TiO_2 film is abundantly nonuniform, and that this spatial heterogeneity was associated with the mechanism of oxide film breakdown, resulting in rapid corrosion of titanium (Fig. 6.13). The point defects of TiO_2, specifically oxygen vacancies, provide sites for chemisorption with constituents of aqueous

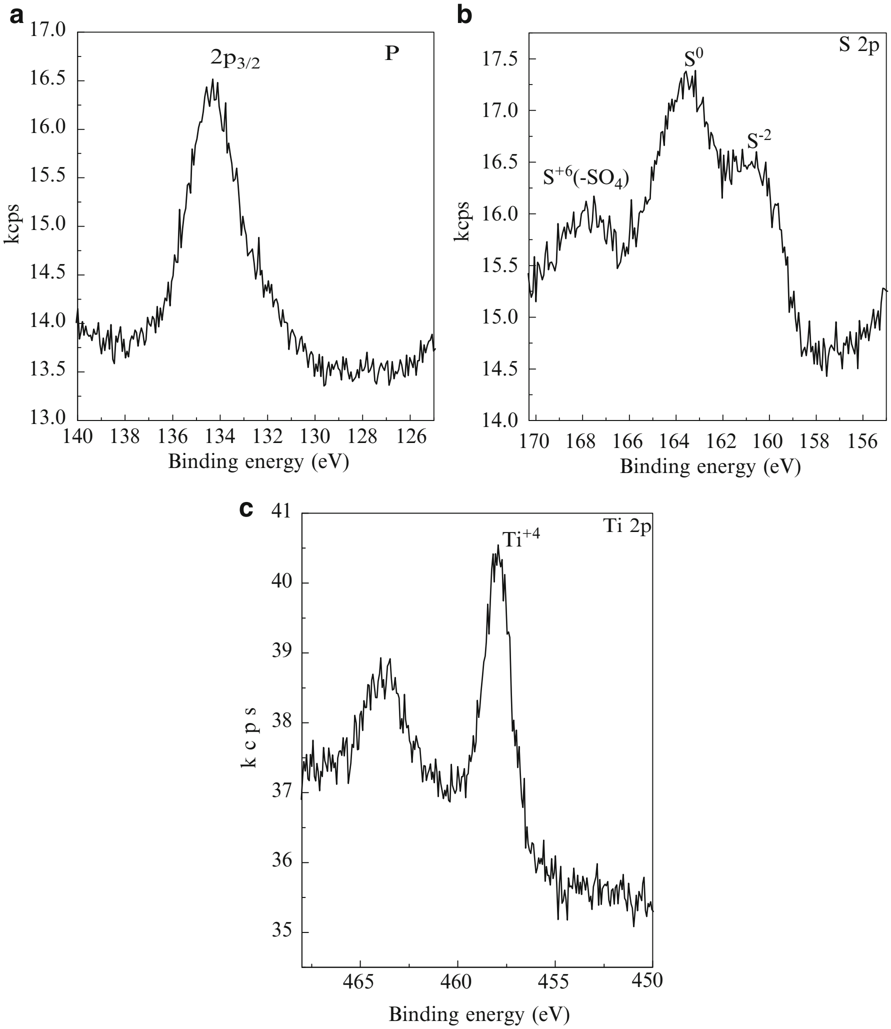


Fig. 6.12 XPS spectra (Phosphorus, Sulphur and Titanium) of SRB induced corrosion products on titanium. Binding energy spectra (**a**) Phosphorus, (**b**) Sulphur and (**c**) Titanium

environment. The oxygen vacancies in TiO_2 contribute to the sulfide adsorption activity (Rao et al. 2005). A reducing gas such as hydrogen increases active surface accessible to H_2S. The reaction of hydrogen with the oxide sorbent increases the pore size of the oxide layer, thereby enhancing the mobility of the H_2S into the metal matrix. Pitting corrosion is a complex but important problem, which is the root cause of many corrosion failures (Casillas et al. 1994; Rao et al. 2005). Pitting is defined as localized corrosion attack occurring on openly exposed metal surfaces in the absence of any apparent crevices. When the anodic breakdown potential of the metal is equal to or less than the corrosion potential under a given set of conditions,

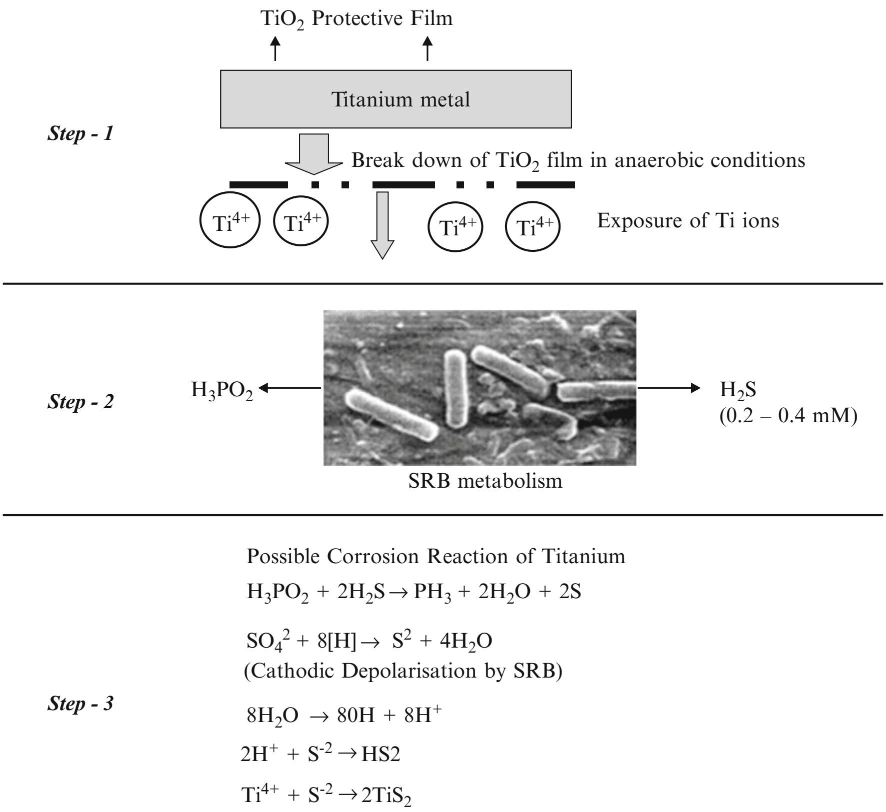


Fig. 6.13 Proposed mechanism of pitting corrosion of titanium

spontaneous pitting can be expected. Majority of microbial corrosion is seen as pitting type corrosion, the microbes at the metal/biofilm interface create conditions in which, incipient pitting leads to localized corrosion (Videla 2001). A general fact that is often not taken into account in formulating corrosion mechanisms is that metal surfaces are rarely free from deposits of various types (oxides, hydroxides or even biofilms). Under these circumstances, any mechanism proposed to explain corrosion process must refer to breakdown of the passive film by the aggressive metabolic products released into the immediate milieu by the bacterial growth. Generally, microbial colonization promotes a decrease in the passive film resistance by producing acidic metabolites and complexing substances (Seed 1990; Little et al. 1991). Hence, rapid decay of the passive film favors the initiation of localized corrosion process such as pitting. The anodic and cathodic reactions that comprise corrosion, separate spatially during pitting. The anodic sites are not inhibited, thereby triggering the metal to corrode. Generally, sulfide is cathodic to the metal and sulfide ions could react with titanium ions (Ti^{2+}/Ti^{4+}) released at the anode to form titanium sulfide (Rao et al. 2005).

This study provides a clear evidence for pitting corrosion of titanium on exposure to a semi-continuous culture of SRB. To arrive at the exact mechanism of pitting attack, further detailed investigations including electrochemical studies are required. Such studies are being undertaken to arrive at a better picture about the SRB induced pitting attack on titanium. Complete identification of the defect and especially how it could be eliminated, will be of fundamental and technological importance in view of the vulnerability of titanium to biofouling and its extensive use in process, power, and offshore industries.

6 Nature and Extent of the Corrosion Problem

Corrosion may be defined as the destruction or deterioration of metals and its alloys by chemical reaction with both biotic and abiotic environment. Some of the fluids which cause corrosion serious enough to warrant actual investigation are the following: fresh, distilled, salt, and mine waters; rural, urban, and industrial atmospheres; steam and other gases such as chlorine, ammonia, oxygen, sulfur dioxide, and fuel gases; mineral acids such as nitric, sulfuric, and hydrochloric; organic acids such as acetic, formic, and citric; alkalis such as caustic and ammonium hydroxide; soils; solvents such as alcohols and dry cleaning materials; vegetable and petroleum oils and a variety of food products. Two of the most common and most plentiful materials known—namely, air and water—also cause corrosion, and considerable effort and money have been spent to minimize their destructive effects. It is also well known that failure of industrial components or failure of equipment to function properly because of corrosion is increasing day by day (Tiller 1982; Bott 1995; Flemming 2002).

7 Cooling Water Treatment

A successful water treatment program depends on the properties of the available water supply. In a cooling water system, notwithstanding the careful design, the quality of the source water can deteriorate plant material and equipment. Water quality properties vary depending on location and source. Well water which originates from ground, where considerable amount of minerals and salts are available will be relatively hard. Surface waters from river or streams usually are of better quality because their source is rainfall.

Cooling water technology in industrial water treatment has made major advances in the past 2 decades. However, the objectives of successful cooling water treatment program have remained the same over the decades:

1. To maintain efficient heat transfer in the condenser unit
2. To extend cooling water system equipment life

The said objectives aim to accomplish low corrosion rates of system metals as well as to reduce deposition on metal surfaces. The cooling water treatment programs in the early nineteenth century have addressed the concerns related to corrosion, scale inhibition and deposit control. Major changes or breakthroughs have taken place in last 3 decades in terms of developing specialty chemicals for cooling water treatment (Flemming 2002; Yebra et al. 2004; Videla and Herrera 2005).

Recent trends in cooling water systems program are mainly in following areas.

- Alkaline cooling water treatment
- Automatic dosing of biocides, corrosion inhibitors, dispersants, and monitoring
- Green technology by using environmentally safe chemicals

7.1 Alkaline Cooling Water Treatment

Most industrial cooling water systems are operated at pH >7 in order to take advantage of the alkalinity of the water for corrosion control. Several different combination programs are available, offering corrosion and scale control in various combinations, depending on the type of cooling system requirement. The deposit control option of the program utilizes a polymer technology that allows the pH to be controlled at levels previously thought to be too high. Besides, the entire cooling water program should include biofouling control as an integral part of the operation. Plant operators should never run the cooling water system without treatment. Alkaline cooling water systems are generally well into the scaling range and will precipitate calcium carbonate quickly if scale inhibitors are not present. At times recovery from such disasters may be difficult and is expensive.

Conventional chromate/zinc and chromate/zinc/orthophosphate programs have traditionally been controlled at pH limit below 7 (and often much lower) to avoid excessive precipitation of salts. In modern water treatment; chromate has been discontinued due to its toxicity and environmental considerations. Currently, almost all the major power and process companies use alkaline cooling water technology and take advantage of lower corrosivity of high pH water saturated with respect to calcium carbonate. Alkaline waters are generally less aggressive at near neutral pH water, because of their higher buffering capacity.

7.2 Automatic Dosing of Biocides, Online Monitoring and Corrosion Inhibitors

It is a well known practice to subject a water body to exhaustive chemical and biological analyses, prior to its use as a cooling medium. Based on the data thus accumulated, a comprehensive treatment program is drawn up which is to be rigorously adhered to during the operation of the plant. In addition, water quality parameters should be regularly monitored throughout the operational phase to check for any possible changes occurring over a period of time.

Online monitoring of vital cooling water parameters provides key inputs for sustained performance of cooling circuits. Tracking microbes and biofilm activity online also provides useful feedback for evaluating effectiveness of biocide dosing regimes. Polarographic membrane probes have been shown to provide details for better management of fouling without need for electrode cleaning systems. Polarographic membrane cells are a closed cell amperometric device with pH correction. This novel technology allows for continuous chlorine measurement at high stable pH without use of chemical buffers. Chlorine monitoring is one of the most important analyses that need to be conducted during the water treatment process. New technologies coming onto the market have improved the performance of monitoring systems and reduced or eliminated the need for reagents and offline analyses. An electromechanical device can record losses due to reduction in performance of heat exchanger due to microbial fouling. In this device, cooling water flow and discharge temperature signals are sent to a microprocessor continuously to calculate and display the individual condenser tube heat transfer coefficient. To exploit future growth opportunities in automation and online monitoring, there is a need to invest in further research and develop sensors/monitors which can detect the parameter of interest with less corrections or reagents (Clare 1998; Flemming 2002).

7.3 Green Technology for Cooling Water Treatment

Cooling towers result in environmental problems when water escapes from the system in the form of droplets. Such water droplets carry with them various chemicals that are used in the system. Some of these chemicals are environmentally harmful. Besides, the cooling tower is a harbinger of various microorganisms which could be health concern. In comparison to the highly toxic chromate inhibitors used earlier, the recent substitute chemicals are relatively innocuous and do not present the same environmental problems that chromates do. Nevertheless, the impact of substitute chemicals on the environment must be carefully analyzed before actually using them (Karlsson and Eklund 2004).

Scrutinizing the recent work on cooling water treatment reveals that the published literature has been mainly dedicated to the search for environmentally safe corrosion and scale inhibitors. The recent research deals with types, structure, efficiency, biodegradability and advantages of new compounds “mixtures.” A promising approach is represented by the combination of biodegradable polymers and environmentally safe amounts of phosphorous and chromium. Furthermore, guidelines for the future work on industrial water treatment chemicals are being redefined (Videla and Herrera 2005).

Basic research to increase our understanding of the microbial species involved in corrosion and their interactions with metal surfaces and with other microorganisms will be the basis for the development of new approaches for the detection, monitoring, and control of microbial corrosion. A thorough knowledge of the causes of microbially influenced corrosion and an efficient and effective means of detecting and preventing corrosion are lacking. It is well recognized that microorganisms are a major cause of corrosion of metal pipes, but despite decades of study it is still not known with certainty how many species of microorganisms contribute to corrosion, how to reliably detect their presence prior to corrosion events, or how to rapidly assess the efficacy of biocides and mitigation procedures (Angell 1999).

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Chapter 7
Invasive Species: Implications for Industrial Cooling Water Systems

Sanjeevi Rajagopal and Gerard van der Velde

1 Introduction

Non-indigenous organisms can get introduced to new areas by human activities, lifting the barriers for dispersal from other biogeographic areas. When these species arrive, they may die if the conditions are not good for survival. However, if the conditions match with their requirements, for example, with respect to habitat and climate, they can survive, establish, and reproduce. Subsequently, when their populations flourish and disperse fast, we speak of species invasion. Such species interact with native species and flourish at the expense of the local native populations. They can affect the new habitat environmentally, ecologically, and economically (Van der Velde et al. 2006).

Invasive species are often characterized by features such as rapid reproduction, fast growth rate, and tolerance to wide range of environmental conditions, reaching high population densities. Invasive species are not a random selection of species (Karatayev et al. 2009). Many invasive species are sessile and have planktonic propagules (larvae, spores, etc.), which enhance their chance to travel long distances, attached to substrata or suspended in water, carried over the ocean or from lake to lake by shipping, fishing, angling, and other human activities. These species are profiting from anthropogenic eutrophication. For example, plants take up the nutrients directly when there is light, while filter-feeding animals take up detritus

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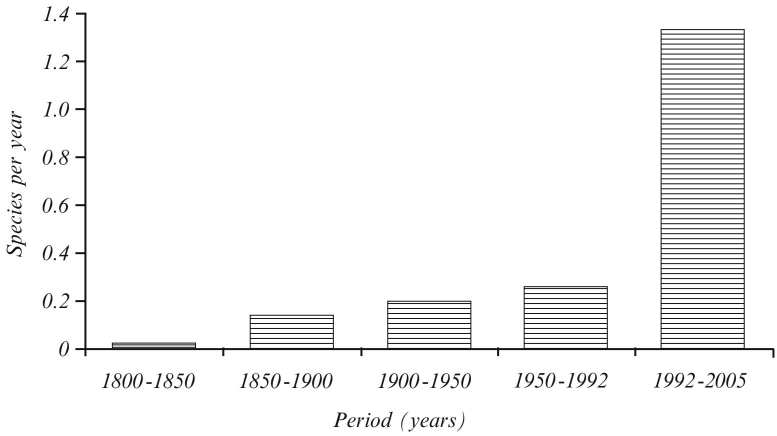

Fig. 7.1 Annual average number of non-indigenous species colonizing the freshwater sections of the river Rhine (modified after Leuven et al. 2009)

and plankton even in the dark. Furthermore, hard substrata are provided by water works, dam construction, riparian protection, etc. so that these species can build up high density populations in human-influenced areas. In industrialized areas also, cooling water is discharged, which makes the survival of subtropical exotic species in temperate areas possible. The consequence of all these developments is that the global biofouling scenario has become more complex with the introduction and establishment of new species (Fig. 7.1), resulting in higher costs for control than before. In this chapter, we shall discuss the key features of some of those prominent non-indigenous species, whose success as invasive species merits close examination. Many of these species are transported by ships, either via ballast water or via ship hulls, as part of the fouling assemblage. Another main cause of their introduction is the shellfish culture industry. Also, canals connecting seas or rivers for shipping purposes contribute to the wide dissemination of these species. In addition to threatening the biodiversity of the locality, some of the introduced species continue to place enormous burden on the economy of the countries affected (Van der Velde et al. 2006, 2010). Biofouling of industrial cooling water systems is but one aspect of their wide-ranging economic impact (Rajagopal et al. 2010a). Many of the recent invasive species are sessile benthic in their habitat and hence are potential biofouling organisms (Fig. 7.2).

Of all biofouling organisms, bivalves (mussels, oysters, and clams) and barnacles in particular are known to have successfully invaded new geographical locations and caused serious fouling problems to industrial cooling water systems. However, there is a wide range of other sessile species which can potentially cause macrofouling problems such as hydroids, tube worms, tube-building amphipods, bryozoans, and ascidians. We treat some important marine, brackish water, and freshwater-invasive sessile bivalves and some other important invasive fouling species, giving emphasis to control aspects. Measures to control the invasive bivalve species will also control the other indigenous biofouling species, depending on their tolerance.

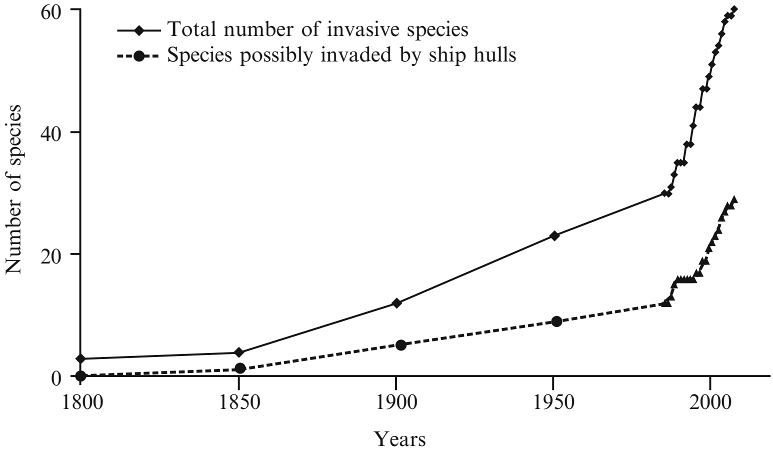

Fig. 7.2 Total number of invasive species and species possibly invaded by ship hulls in river Rhine from 1800 to 2007

2 Bivalvia

Bivalves are molluscs possessing two calcareous valves which protect the soft living body. The two valves can be opened to allow the siphons to pump water in and out, in order to obtain oxygen and food. Food consists of organic suspended matter (detritus, phyto-, and zooplankton) that is sorted into an edible fraction which is transported to the mouth and digested and an inedible fraction which is ejected as pseudofaeces (particles stuck together by mucus) by valve movements. Undigested food (faeces) and pseudofaeces sink to the bottom and contribute to sedimentation and form food for other macroinvertebrates. All bivalves are filter feeders. They have also a foot which can extend out of the valves and by which they can move as long as they are not totally fixed to one place. The byssus gland in the foot produces byssus threads, by which the animals can fix themselves to hard substrata. All fouling bivalve species produce, as juvenile and adult, many byssus threads (e.g. mussels, dreissenids) or only one as juvenile (e.g. Asian clams). The life cycle of bivalves is, in general, with a planktonic phase (fertilized eggs, larvae, trochophora, veliger, pediveliger), a settlement phase (settling pediveliger, plantigrade, spat), a juvenile and an adult phase. In the adult phase the gonads are developed. The bivalves are usually dioecious; there are males and females which spawn by releasing eggs and sperm into the water. But hermaphroditism, self-fertilization, brood care, and protandry can also occur. Larvae can settle in the cooling water circuits and grow fast, as there are hardly any predators, and there is plenty of oxygen and food coming along. During settlement, they show gregarious behaviour, resulting in carpets of bivalves covering the entire available surfaces.

3 Oysters: Ostreidae

Oysters generally constitute a serious biofouling pest in coastal power stations using seawater for condenser cooling purposes. They attach to surfaces by cementing one of the two calcareous valves to the substratum. Therefore, oyster fouling creates more problems than mussel fouling, because unlike in the latter, the shell remains attached to the substratum even after the death of the animal. Moreover, because of their normal distribution in the supra and midlittoral zones, oysters possess a great capacity to tolerate variations in temperature, salinity, and desiccation.

3.1 Pacific Oyster Crassostrea gigas (Thunberg 1793)

Crassostrea gigas is a common Pacific marine oyster enjoying wide distribution in the coastal and estuarine environments. It has a rough shell that is highly fluted and laminated. Shells are usually whitish with purple streaks and spots. It is a commercially important species with appreciable quantities being fished and cultured. Since *C. gigas* was introduced for shellfish culture from Japan, it is also known as the Japanese oyster. The Pacific Oyster was introduced from Asia across the globe. It is nowadays distributed throughout Great Britain and Ireland, and widely along the Atlantic coast of continental Europe (Spain, Portugal, France, Belgium, The Netherlands, Germany, Denmark, Sweden, and Norway) (Wrange et al. 2010). In North America, the Pacific oyster is found from Southeast Alaska to Baja California. It is cultivated primarily on oyster farms in protected coastal estuaries; however, wild beds exist in Washington and British Columbia. The oyster prefers firm surfaces and usually attaches to rocks, debris, or other oyster shells. However, they can also be found on mud or mud-sand bottoms. The shell can reach 23 cm in length in ideal conditions. *C. gigas* is a valuable shellfish resource and is the most widely cultured oyster in the world, having been introduced in countries like United States, France, England, New Zealand, and Australia. It is known to settle into dense aggregations and imperil native intertidal species. *C. gigas* feeds primarily on phytoplankton and protists (CIESM 2000; NIMPIS 2002). It is known to spread through placement of hatchery-produced seed. Its introduction from France to Britain is thought to have been through ships' hulls (Fletcher and Manfredi 1995; Eno et al. 1997).

C. gigas is known for its tendency to colonize areas of coastline many kilometres away from its parent organisms. Spat have been documented spreading up to 1,300 km on ocean currents. Once established, they have the potential to smother other marine life, such as scallops, destroying habitat, and causing eutrophication that affects water quality. This could result in limitations of food and space availability for other intertidal species (NIMPIS 2002). *C. gigas* ingests bacteria, protozoa, a wide variety of diatoms, larval forms of other invertebrate animals, and detritus (PWSRCAC 2004).

They develop first as males, and after a year, start to function as females. Spawning is temperature-dependent and occurs in the summer months. Temperature plays a role in the maturation of the gonads, which sustain during the winter months at temperatures of 8–11°C (Fabioux et al. 2005). *C. gigas* females can produce between 30 and 40 million eggs per spawning. Fertilization takes place externally. The planktonic larvae develop for 3–4 weeks before attachment. Pacific oysters have high growth rates (75 mm in the first 18 months) and high rates of reproduction. *C. gigas* can live for up to 10 years and reach an average size of 150–200 mm (CIESM 2000). High temperatures combined with a poor food quality during low tide as those reached on clear summer days are an important stressor for oyster spat and it was found that, at a temperature of 32°C, spat of *C. gigas* showed poor growth (Flores-Vergara et al. 2004). Bourles et al. (2009) reported *C. gigas* living in an Atlantic pond at water temperatures ranging from 3 to 30°C.

Carrasco and Barón (2010) analyzed the potential geographic range of *C. gigas* based on surface sea water temperature satellite data (SST) and atmospheric (AT) temperature climate charts with the coast of South America as a study case. They found that in its native range, self-sustaining populations maintain in thermal SST regimes ranging from 14.0 to 28.9°C for the warmest month and −1.9°C for the coldest month of the year. For settlement, these figures are for AT 15–31°C (warmest month) and −23 to 14°C (coldest month).

3.2 European Flat Oyster *Ostrea edulis* (Linnaeus 1758)

Ostrea edulis is native to Europe and the Mediterranean and is usually found in coastland, estuarine habitats, marine habitats, and riparian zones. It is found at the Atlantic coast of Norway, Sweden, Ireland, the U.K., Denmark, the Netherlands, Germany, France, Morocco, the Mediterranean Sea, the Black Sea, France, Italy, Greece, Croatia, Ukraine, Portugal, and Spain (Diaz-Almela et al. 2004; Ruesink et al. 2005; Jonsson et al. 1999; Kennedy and Roberts 1999; Jackson 2003).

The oyster prefers the firm bottoms of mud, rocks, muddy sand, muddy gravel with shells, and hard silt (Jackson 2003). *O. edulis* can be found in muddy areas attached to hard surfaces at depths of 9 m. It has been introduced to the northwestern Atlantic Ocean for aquaculture, before which it had long (for 6,000 years) been harvested for food (Diaz-Almela et al. 2004). As an introduced species, its geographic range includes Japan, Tonga, Fiji, US, Canada, Namibia, Israel, Mauritius, New Zealand, and South Africa (Carlton 1992; Ruesink et al. 2005; Ray 2005). *O. edulis* can grow up to 20 cm or more and live up to 20 years. It has a rough scaly shell, the two halves of which are different in shape; the left shell is concave and attached to the substratum and the right is flat and acts as a lid. The inner surface of *O. edulis* is smooth and white or bluish-grey and shiny with some dark blue spots. The narrow ends of the shell have stretch ligaments which hold the shells together.

As in the case of other oysters, *O. edulis* feeds mostly on phytoplankton. Autotrophic flagellates and diatoms are also important food for *O. edulis* (Jonsson et al. 1999). It is a protandric hermaphrodite that changes sexes twice during one season. They are males early in the spawning season and become females later and vice versa. Jonsson et al. (1999) have reported that completion of larval development depends upon the proper intake of omega-3 polyunsaturated fatty acids. *O. edulis* start their lives as males and mature sexually as males between 8 and 10 months. After this period, they change sex regularly. Temperature can affect the sex of *O. edulis*; if the temperature reaches 16°C, *O. edulis* becomes a female every 3–4 years. Cooler water temperatures force the oysters to revert back to males. During reproduction, female gametes are released into the pallial cavity where they are fertilized by externally released sperm. Females produce between 500,000 and 1,000,000 fertilized eggs per spawning period. The eggs are incubated for about 8–10 days (depending on temperature) and released into the water. In their native range, *O. edulis* spawns between late June and mid-September. Young oyster spat can be seen from late summer in Strangford Lough, Northern Ireland (Kennedy and Roberts 1999). In the Adriatic Sea, the larvae are present from May till September, with a peak in July (Bratos et al. 2002). Gonadal maturation occurs during season of high suspended matter, followed by single spawning period (Ruiz et al. 1992).

Depending on temperature tolerance, *O. edulis* exists as a number of physiological races. In Spain, one low temperature race occurs which requires 12–13°C for spawning. A temperature of 25°C is required in the Norwegian fjords for spawning, and in France, *O. edulis* spawns between 14 and 16°C. In Canada, spawning was recorded at 18°C (Burke et al. 2008). After hatching, the larvae spend 8–10 days in a pelagic state before settlement. In this pelagic state, *O. edulis* goes through two metamorphoses. After the first metamorphosis, the trochophore transforms into a veliger with two ciliated wing-like protrusions. A second metamorphosis changes the veliger into a bivalve small oyster that uses its byssus threads to cling to suitable substrata. Prior to attachment, *O. edulis* explores the substrate with its foot protruded in the front, which functions as a tactile sense organ. Metamorphosis can be delayed if a suitable attachment site is not available (Cole 1938).

Healthy larval growth and survival rates occur at salinities as low as 20% and some can even survive at 15% salinity. Burke et al. (2008) recorded salinities between 18 and 30% for spat and recorded more than 225,000 larvae per m^3 water and 22,000 individuals per spat collector. Feeding rate (measured as faecal matter production) decreased at 18% and ceased at 16%. Spat exposed to such a low salinity did not regain their vitality again (Rodstrom and Jonsson 2000). Very low salinities combined with high temperatures caused the highest mortality (Rodstrom and Jonsson 2000) as also was demonstrated by Hutchinson and Hawkins (1992) at the combination 19% and 25°C. Further information about salinity–temperature responses can be found in Fisher et al. (1987) and Robert et al. (1988).

3.3 Pearl Oysters-Pteriidae

These oysters are known for their ability to produce pearls. This family consists of the genera *Pteria* and *Pinctada*. In these species, both the valves are similar and winged.

3.3.1 Pearl Oyster *Pinctada radiata* (Leach 1814)

Pinctada radiata, originating from the Indo-Pacific, is one of the important invasive marine bivalve species, successfully adapted to subtropical environment. The invasion of *P. radiata* has been reported from different areas of the Mediterranean and other subtropical and tropical parts of the world. The invasion of *P. radiata* has probably occurred both via the Suez Canal and intentional introduction for pearl oyster fishery. As a fouling species, it attaches by byssus to hard substrata and is found from very shallow to the mid-water depths. It can reach a shell length of 100 mm (Tlig-Zouari et al. 2009).

It occurs in a wide temperature range of 13–30°C, from the littoral zone on hard bottoms down till a depth of 150 m. It is a protandric hermaphrodite species with a sex inversion at a shell size of 32–57 cm. Males can be found as small as 23-mm shell length (Derbali et al. 2009).

Gonad maturity is controlled by water temperature and is nearly year-round in the Mediterranean with spawning mainly in summer and early autumn. Pelagic larvae are dispersed by water currents (Galil 2006). In Bahrain waters, spat settlement took over a long period (July to November). The most intense spat settlement was recorded throughout August, indicating that spawning started at the end of July. Most settlement can be found on dead oyster shells, at a depth of 0.5–1.5 m. Growth after settlement (July–August) was 0.204–0.248 mm day^{-1} till December-January, in which period growth was slowed down by a drop in water temperature from 27–33 to 17–18°C (Al-Sayed et al. 1997a). In Bahrain, the shells can grow to 80 mm and they become especially large at salinities of 40–42%. They become smaller at higher salinities of 50–60% (Al-Sayed et al. 1997b).

Qatari waters are rich in pearl oyster beds. Three pearl oyster species, viz. *P. radiata*, *Pinctada margaritifera*, and *Pteria marmorata*, were reported from Qatari waters. However, *P. radiata* is the most dominant species, representing about 95% of the total oyster catch (Mohammed and Yassien 2003). Though the biology and physiology of the pearl oyster *P. margaritifera* are well documented in the literature, there is lack of information on *P. radiata* (Mohammed and Yassien 2003).

Based on their recruitment pattern, Mohammed and Yassien (2003) suggested that *P. radiata* was a semi-continuous breeder in Qatari waters. However, different breeding seasons of this species are reported from nearby areas. Al-Sayed et al. (1993) have recorded continuous spawning from Bahrain waters, with peaks in hot summer. The spawning season of *P. radiata* in Kuwait was restricted between May and September (Al-Matar et al. 1993).

4 Mussels: Mytilidae

Mussels are mostly marine bivalves with valves equal in size and shaped in an elongated oval-triangular form. The shell is not thick, but has a thick periostracum. The shell lacks a prism layer. The anterior muscle is small. All mussels are biofoulers and important fouling genera are *Mytilus*, *Modiolus*, *Brachidontes*, *Septifer*, *Perna*, and *Limnoperna*.

4.1 *Mediterranean Mussel Mytilus galloprovincialis (Lamarck 1819)*

Mytilus galloprovincialis is a marine species which has succeeded in establishing itself at widely distributed locations around the globe, with nearly all introductions occurring in temperate regions and at localities where there are large shipping ports (Branch and Steffani 2004). Ship hull fouling and transport via ballast water have been implicated in its spread and its impact on native communities and native mussels has been highlighted in a number of studies (Carlton 1992; Robinson and Griffiths 2002; Geller 1999).

The mussel is dark blue or brown to almost black. The two shells are equal and nearly quadrangular. The outside is black-violet coloured; on one side the rim of the shell ends with a pointed and slightly bent umbo, while the other side is rounded, although shell shape varies by region. It also tends to grow larger than its relatives, up to 15 cm, although typically only 5–8 cm. In its native range, *M. galloprovincialis* can be found on exposed rocky outer coasts and sandy bottoms (Ceccherelli and Rossi 1984). As an invader, it typically requires rocky coastlines with a high rate of water flow. In fact, unlike the other 26 Asian and Atlantic molluscs introduced into Pacific regions, only *M. galloprovincialis* occurs in open coast such as high energy environments of the Pacific coast; all remaining species are restricted to bays and estuaries (Carlton 1992). It is known that *M. galloprovincialis* is capable of outcompeting and displacing native mussels to become the dominant mussel species in many localities.

The native range of this mussel includes Mediterranean Sea, Black Sea, and adjacent part of the European Atlantic coast. Due to taxonomical problems, it is unclear whether it is occurring in the outer coasts of France, Britain, and Ireland as *Mytilus edulis* can have broad-shelled individuals too which means that identification is only possible based on a combination of characters and molecular data (Groenenberg et al. 2011). The introduced range includes Southern Africa, east and west North America, Hawaii, and north-eastern Asia (Branch and Steffani 2004). Shipping is believed to be the most probable original mode of introduction of *M. galloprovincialis* to South Africa (Grant et al. 1984, in Branch and Steffani 2004) and to Mexico (Carlton 1992). Late twentieth century distribution of *M. galloprovincialis* was probably enhanced by ballast water transport as well as ship fouling (Carlton 1992). Schneider (2007, 2008) demonstrated that *M. galloprovincialis* was more warmwater-adapted than its relative *Mytilus trossulus* and suggested that *M. galloprovincialis* would be more common due to global warming. Mussels at air exposure kept at 20°C lost their intra-valve water within approximately 60 h and became dead within 4 days, while mussels kept at 5°C survived (Angelidis 2007). In South Africa, where *M. galloprovincialis* invaded, *Perna perna* is an indigenous species. Attachment strength of *P. perna* is higher than that of *M. galloprovincialis*. *M. galloprovincialis* showed higher gamete production than *P. perna* and can more effectively colonize free space (Zardi et al. 2007).

As a filter-feeder, it feeds on a wide range of planktotrophic organisms. Filtration rates at 20 and 26°C are not different. Filtration at high phytoplankton concentration remained low for a standard individual of 1 g dry weight (0.2–0.4 $L\,h^{-1}$), but with lower phytoplankton concentrations 0.5–2.5 $L\,h^{-1}$ was measured (Denis et al. 1999). This species prefers fast moving water that is free of sediment and thrives in regions where upwelling brings in nutrient-rich water.

Reproduction involves simultaneous spawning of males and females. *M. galloprovincialis* has high fecundity and spawns at the time of the year when the water temperature is the highest (Bayne 1976). The larvae develop into juveniles, which settle and attach using byssus threads in 2–4 weeks (Matson 2000). Spawning is temperature-related and occurs in spring and summer, leading to post-larvae in late summer and early autumn in the plankton of intertidal zone of exposed rocky shores or near mussel culture rafts. Low numbers or absence of post-larvae in plankton samples near the surface away from the shore indicate that planktonic dispersion at larger distances is considered unlikely (Caceras-Martinez and Figueras 1998a). Gametogenesis in NW Spain takes place in spring and early winter. Several spawns may occur until early summer (Caceras-Martinez and Figueras 1998b). Settlement in the Dardanelles was high at 0.5 and 4 m, and low at greater depths until 12 m. Pediveligers can be found in the Dardanelles throughout the year (Yildiz and Berber 2010). Karayucel et al. (2002) found no difference in spat settlement between 3- and 7-m depth in the Southern Black Sea.

4.2 Golden Mussel Limnoperna fortunei (Dunker 1857)

Limnoperna fortunei is an epifaunal freshwater mytilid, native to Chinese and south-eastern Asian rivers, creeks, and estuaries. It occurs in temperate and subtropical areas. It became established in Hong Kong in 1965, and in Korea, Japan, and Taiwan in the 1990s. In 1991, it invaded the Plata Basin in South America, from where it invaded large areas over the continent. The introduction into South America was unintentional through the ballast water of ocean-going vessels. Attachment to vessels is the most important dispersion mechanism within South America (Boltovskoy et al. 2006).

L. fortunei is known to cause great economic damage to water intakes and cooling systems of facilities. In South America, it has similar impact as the zebra mussel during invasions (Karatayev et al. 2007). The filtration rate is one the highest ever measured for bivalves including *Dreissena polymorpha*, *Dreissena rostriformis bugensis*, and *Corbicula fluminea*. Sylvester et al. (2005) recorded 125–350 mL $ind^{-1}\,h^{-1}$. Pestana et al. (2009) recorded a filtration rate of 724 mL $ind^{-1}\,h^{-1}$ for *L. fortunei*. Just as in the zebra mussel, very high densities (hundreds of thousands per square metre) can be reached (Sylvester et al. 2005). Portella et al. (2009) recorded settlement up to 149,000 individuals per square metre at a Brazilian Power Plant reservoir at a depth of 0.5–1 m. The species was mixed up with the invasive hydroid *Cordylophora caspia*. *L. fortunei* can reach a shell length of 36 mm (Belz et al. 2010).

In South American water bodies, the reproductive output is reduced in winter time, while in summer a dip is found related to cyanobacterial blooms. There is a long period of larval occurrence, varying from 6 to 10 months per year (Boltovskoy et al. 2009a). The fastest development of larvae occurs at a water temperature of 28°C (Caltaldo et al. 2005). In South America, they occur mostly settled on the water hyacinth (*Eichhornia crassipes*). They feed selectively on phytoplankton and zooplankton, in particular cladocerans, rotifers, and euglenophytes (Molina et al. 2010).

L. fortunei can tolerate (90% survival) salinity shock up to 2% for a period of at least 10 days. High-salinity fluctuations are not tolerated for very long (Angonesi et al. 2008). *L. fortunei* has a broader environmental tolerance than *D. polymorpha* and can occur in regions dominated by acidic, soft (low calcium), high temperature, and contaminated water with low oxygen (Cataldo et al. 2003; Boltovskoy et al. 2006; Karatayev et al. 2007). Desiccation for 6 days is tolerated and cannot be a very effective control method (Montalto and de Drago 2003; Darrigran et al. 2004). The mussel has the potential to invade continents other than South America with stronger impacts than the zebra mussel (Boltovskoy et al. 2009b).

4.3 Brown Mussel Perna perna (Linnaeus 1758)

P. perna is native to the tropics and the subtropics and is widely distributed in Africa, Europe, and South America (Segnini de Bravo et al. 1998; Rajagopal 1997). It is a smooth-shelled, elongate low-shelled bivalve occurring in estuarine and marine habitats. The mussel is recognized by its brown colour (hence the name brown mussel). Its best identifying characteristic is an internal divided posterior retractor mussel scar. The shell of *P. perna* is thin around the edges and thickens posteriorly. The mussel reaches a maximum size of 90 mm in intertidal zones and a maximum size of 120 mm is reached in sublittoral zones. Maximum shell size is influenced by vertical distribution (Gulf States Marine Fisheries Commission 2003).

P. perna has invaded North America, around the Gulf of Mexico (Rajagopal et al. 2006a). It is thought to have been introduced by ballast-water releases from ships of Venezuela (Hicks and Tunnell 1995). In the Gulf of Mexico, the mussel was probably dispersed southward by long range and inshore currents (Gulf States Marine Fisheries Commission 2003). It is quickly becoming a nuisance in cooling water systems of power stations and other industries that use seawater. In the Gulf of Mexico, *P. perna* has been found colonizing jetties, navigation buoys, oil platforms, wrecks, and other artificial hard substrata, as well as natural rocky shores (Hicks and Tunnell 1995). According to Hicks and McMahon (2002), the long-term, incipient lower and upper thermal limits of this species are 7.5 and 30°C, respectively, similar to the seasonal ambient water temperature range of 10–30°C reported for other populations worldwide. Its narrow incipient thermal limits, limited capacity for temperature acclimation, and poor freeze resistance may account for its restriction to subtidal and lower eulittoral zones of cooler subtropical rocky shores. Salomão et al. (1980) reported that the salinity tolerance range of adult is 19–44‰.

Hicks et al. (2000) recorded even a wider salinity tolerance range of 15–50%. *P. perna* shows physiological compensation to salinity increases but not to salinity decreases, in contrast to *Perna viridis*, which can compensate for both changes in salinity (De Bravo 2003). In its native range, *P. perna* is an integral component of rocky shore ecosystems, where dense populations provide a complex three-dimensional matrix, which is home to a wide range of organisms such as limpets, polychaetes, barnacles, snails, and algae (Brereton-Stiles 2005).

In *P. perna* the sexes are separate and can be distinguished during breeding season by the mantle colour (Lasiak 1986). Gonad production in Venezuela correlated with chlorophyll a increase and temperature decrease. Somatic tissue increase correlated with increasing amounts of organic material, seston, and chlorophyll-a (Acosta and Prieto 2008). The mussels spawn through external fertilization by releasing eggs and sperm into the water. Spawning is thought to be triggered by a 3–4°C drop in temperature, brought about by coastal upwellings during the winter months (Carvajal 1969). Veliger larvae are formed after fertilization. The critical period for development is during and after metamorphosis. Metamorphosis of the brown mussel larvae is marked by the secretion of byssal threads 10–12 days post-fertilization. The survival of the larvae depends mainly upon settling on a stable, hard substratum, usually a rock, at the initial phase of metamorphosis in optimal temperatures between 10 and 30°C and salinity of 30.9–32.1%. Optimum temperature and salinities delay the completion of this initial stage allowing a greater amount of time for the larvae to settle on a substratum. The larvae settle in dense aggregations on rocky shores (Gulf States Marine Fisheries Commission 2003). In Venezuela, *P. perna* grew faster than *P. viridis* and showed higher survival due to coastal upwelling. Lower temperatures and higher plankton levels caused better gonad development. Moreover, under these conditions, its reproductive activity started earlier than that of *P. viridis* (Acosta et al. 2009).

4.4 Green Mussel Perna viridis (Linnaeus 1758)

P. viridis is a marine bivalve mussel native to the Asia-Pacific region, where it is widely distributed. The east–west distribution ranges from the Persian Gulf to the Indonesian coast west of New Guinea and some of the Pacific islands, where *P. viridis* has been experimentally introduced (Vakily 1989). It is a fairly large mussel, 80–100 mm in length, occasionally reaching 165 mm (Rajagopal et al. 2006a). The shell has a smooth exterior surface characterized by concentric growth lines and slightly concave ventral margin. The shell is covered with greenish (variable in older mussels) periostracum; periostracum is generally intact in young ones and with patches peeled off in older ones. The colour of the periostracum is bright green in juveniles, fading to brown with green edges as it matures. The inner shell surface is smooth and iridescent with a bluish green hue. The ridge which supports the ligament connecting the two shell valves is finely pitted. The beak has interlocking teeth: one in the right valve and two in the left. Wavy posterior end of the pallial line and the large kidney-shaped retractor muscle scar are characteristic features. Anterior adductor muscle is absent in this species (Rajagopal et al. 2006a).

P. viridis generally inhabits the intertidal and subtidal zones and is primarily found in estuarine habitats where the salinities range from 18 to 38% and temperature from 11 to 32°C (Rajagopal et al. 1998a, b). It has a broader salinity and temperature tolerance than *P. perna* (Segnini De Bravo et al. 1998). Gonad maturation was reported to start in spring, when water temperatures increase to 8–10°C and spawning occurs at temperatures higher than 18°C. Gonad maturation coincides with particulate organic matter peaks (Duterte et al. 2009). At temperatures of 33 and 35°C, total mortality of larvae occurs after 24 h. At 24°C, larvae take longer to settle than at temperatures of 27, 29, and 31°C. Optimum larval development, growth, and survival occur at 31°C and for settlement at 29°C (Nair and Appukuttan 2003). The mussel attaches to hard substrata using byssus threads and is capable of relocating. Dense colonies (up to 35,000 mussels per m^2) can develop in optimal temperature and salinity conditions, sometimes with thousands of individuals per square metre. The mussel is an efficient filter/suspension feeder, feeding on small zooplankton, phytoplankton, and other suspended fine organic material.

P. viridis has been introduced around the world through ship ballast, hull fouling, and experimental introduction for farming. The introduction of the mussel from the Indo-Pacific into the Gulf of Mexico has been attributed to fouling on boat hulls or ballast-water traffic (Chapman et al. 2003). It can quickly form dense colonies in a range of environmental conditions. Impacts include causing blockage in intake pipes of industrial plants, clogging crab traps and clam culture bags, and impeding commercial harvest. *P. viridis* can also out-compete many other fouling species, causing changes in community structure and trophic relationships. *P. viridis* is also capable of accumulating high levels of toxins and heavy metals and is linked to shellfish poisoning in humans. It is one of the most troublesome fouling species in many coastal power stations located in the tropics (Rajagopal et al. 2006a). Temperature permitting, the mussel can be expected to expand in Atlantic habitats because of its dispersed spawning nature, lack of local predators, fast growth, and high tolerance of environmental conditions.

Sexes in this species are separate and fertilization is external. Sexual maturity typically occurs at 15–30 mm shell length (corresponding to 2–3 months age). Spawning generally occurs twice a year between early spring and late autumn; however, in the Philippines and Thailand spawning occurs throughout the year (NIMPIS 2002). Year-round spawning with seasonal peaks has been observed in India also (Rajagopal 1991, 1997). Fertilized eggs develop into veliger larvae. Larvae remain in the water column for 2–3 weeks, after which they settle and attach onto hard substrate using byssus (Yap et al. 2003). During the planktonic period of *P. viridis*, larvae will be widely dispersed by physical processes, but may aggregate periodically at certain depths through a variety of biological processes, most notably diel vertical migration (Folt and Burns 1999; Hayes et al. 2005). The mussel settles in large congregations and adult populations may reach densities of 35,000 individuals per square metre (Ingrao et al. 2001). The life span of *P. viridis* is typically 2–3 years. Growth rates are influenced by environmental factors such as temperature, food availability, and water movement (Rajagopal et al. 1998a). First year growth rates vary between locations and range from 49.7 mm year^{-1} in Hong Kong to 120 mm year^{-1} in India (Rajagopal et al. 1991).

Large populations of *P. viridis* can clog cooling water pipes and accumulate on pilings, buoys, and other man-made structures. In the same manner, the mussels may clog crab traps, clam culture bags, and other mariculture equipment, altering maintenance routines, harvest times, and may restrict water flow thus affecting product quality. Ecological damage stems from the fact that they out-compete many other species, causing changes in community structure and trophic relationships.

5 Zebra Mussel Family: Dreissenidae

This family consists of relatively small bivalves which, in spite of their name, are not closely related to the true mussels (Mytilidae) or oysters, but to heterodonts such as *Corbicula*. Their impact is similar and they can be considered the fresh or brackish water equivalents of the marine mussels. They form, just as the true mussels, dense covers with layers of up to 20 cm thick and maximum densities of hundred thousands per square metre. They have high filtering capacity. The life cycle stages are given by Conn et al. (1993). The important genera with respect to biofouling are *Dreissena* (species originating from European Ponto-Caspian area) and *Mytilopsis* (originating from America).

Adult dreissenids attach to natural hard substrata and to man-made structures made of concrete, metal, steel, nylon, fibreglass, or wood. Attachment is by a holdfast of proteinaceous byssal threads produced from a gland just posterior to the foot. Individual mussels attach using byssus to the shells of other mussels, forming encrusting mats many shells thick (10–30 cm). When such thick encrustations of mussels form on man-made structures or within raw water systems, they can affect the operation considerably. Dreissenid species can have major detrimental impacts on recreational boating and commercial shipping as well as on raw water-using industries, potable water treatment plants, and electric power stations (Ussery and McMahon 1995).

Being filter feeders, they compete with planktivorous zooplankton for food and can potentially affect natural food webs. Apart from that, they can also cause sedimentation of suspended organic matter in the form of faeces and pseudofaeces, shifting energy and nutrient balances from the pelagic to the benthic zone. The ensuing enhancement of water clarity favours increased photosynthesis by rooted aquatic macrophytes and benthic algae and negatively affects pelagic fish species that prefer slightly turbid conditions and become devoid of food by the filtering activity of the zebra mussels. Zebra mussels settle in high numbers with many byssus threads on native clams (Unionidacea), causing suffocation, starvation, and energetic stress, leading to death. Loss of native mussel populations has increased dramatically where zebra mussels are present, particularly in the Great Lakes and Hudson and Mississippi rivers. Dense colonization of hard substrata is beneficial to benthic invertebrates, as habitat complexity increases, so does availability of organic matter.

Dreissenid mussels are strong filter feeders. Each adult mussel is capable of filtering one or more litres of water each day, where they remove phytoplankton, zooplankton, algae, and even their own veligers (Snyder et al. 1997). Any undesirable particulate matter is bound with mucus and ejected as pseudofaeces (Richerson 2002). They cause changes in the structural characteristics of zooplankton like total abundance, biomass, and species composition. The general trend is a decrease in these characteristics in areas that support massive populations of *Dreissena*. There is an inverse relationship between zooplankton abundance and biomass and density of *Dreissena* mussels, which results from the predation pressure on zooplankton exerted by the mussel (Grigorovich and Shevtsova 1995). Dreissenid mussels (*D. polymorpha* and *D. rostriformis bugensis*) have caused impacts on unionid populations, when introduced in the Great Lakes and Rivers that flow from them. *Dreissena* infestations have caused upwards of 95% reduction in unionid numbers and extirpated eight species of unionids in some areas (Schloesser et al. 1998; Schloesser and Masteller 1999).

5.1 Zebra Mussel Dreissena polymorpha (Pallas 1771)

Zebra mussels have been nominated as among 100 of the "World's Worst" invaders. They are native to the rivers and lakes in the Caspian and Black Sea areas, but are now established in the USA, Canada, Eastern, Western, and Southern Europe including UK, Ireland, Spain, and Italy. These mussels, with a maximum size of about 3 cm, attach to surfaces using many byssus threads. Growth of mussels starts at 3–6°C. The upper temperature limit appears to be 32–34°C, while salinity range is 0.007% (minimum) to 12% (maximum) in the Aral Sea. Normally they can tolerate salinity up to 6% and temperatures up to 29°C; however, they do not settle when currents are faster than 2 $m\,s^{-1}$. They have been known to interfere with the ecological functions of native molluscs and are responsible for considerable economic losses (Van der Velde et al. 2010 and literature therein).

Zebra mussels filter organic and inorganic particles between 7 and 400 μm, but they preferentially select algae and zooplankton between 15 and 40 μm. Larval stages feed on bacteria. The larvae may be transported during fish stocking. Juveniles and adults attach to anchors, outboard engine propellers, and boat hulls and are transported from one place to another. It has been reported that range expansion of this species within North America and Europe was very rapid due to downstream transport of planktonic larvae in rivers.

Zebra mussels are dioecious and fertilize externally. They spawn in relatively shallow water at a minimum temperature of 12°C; in deeper water they have no clear spawning period. The larvae are planktonic for several weeks before settling and attaching to substrata. It is estimated that a female produces up to 1.5 million eggs per year, though survival to adult stage may be less than 1%. Fertilized eggs hatch into trochophore larvae (40–60 μm). After spending several days (8–180 days or more, depending on water temperature) as free-swimming developing larvae, they settle as plantigrade mussels and attach to substrata as juveniles. Under optimal conditions, they mature within the first year of life, though maturity in the second year is more common. Zebra mussels have a life span of 3–5 years.

5.2 *Quagga Mussel Dreissena rostriformis bugensis (Andrusov 1897)*

The Quagga mussel is native to two rivers in the Ukraine. Its release into Great Lakes waters is linked to discharge of ship ballast water (Mills et al. 1999). It extended its area also in Eastern Europe. Recently, it invaded Western Europe through the Netherlands, from where it spreaded very fast over large areas (Van der Velde et al. 2010 and literature therein). *D. rostriformis bugensis* is morphologically very similar to *D. polymorpha*, but they can be distinguished based on their shell morphology. Since its introduction, it has begun to replace *D. polymorpha* as the most dominant invasive *Dreissena* and is able to colonize at much deeper depths. *D. rostriformis bugensis* has begun impacting zooplankton abundance, biomass, and species composition, causing decreases in native diversity. They affect recreational boating and commercial shipping as well as raw water-using industries, potable water treatment plants, and electric power stations.

D. rostriformis bugensis typically occurs in fresh water but can thrive in salinities up to 1% and can reproduce in salinities below 2–3%. Salinities exceeding 6% will cause mortality (Ussery and McMahon 1995; Wright et al. 1996). A study conducted by Ricciardi et al. (1995) revealed that, given temperate summer conditions, adult *D. rostriformis bugensis* may survive overland transport (e.g. on small trailered boats) to any location within 3–5 days drive of infested water bodies.

In both North America and in Europe, *D. rostriformis bugensis* is slowly dominating *D. polymorpha* populations. Some industries even built their intake structures and piping at depths too low for *D. polymorpha* colonization; however, when *D. rostriformis bugensis* were discovered at lesser water depths, these new structures became vulnerable to colonization (Mills et al. 1999; Richerson and Maynard 2004).

D. rostriformis bugensis is a prolific breeder. This species is dioecious and exhibits external fertilization. A fully mature female mussel is capable of producing up to one million eggs per season. Spawning starts at a minimum temperature of 8°C. After fertilization, pelagic larvae, or veligers, develop within a few days and these veligers soon acquire minute bivalve shells. Free-swimming veligers drift with the currents for 3–4 weeks, feeding by their hair-like cilia while trying to locate suitable substrata to settle. Mortality in this transitional stage from planktonic veliger to settled juveniles may exceed 99% (Richerson 2002).

5.3 *Dark False Mussel Mytilopsis leucophaeata (Conrad 1831)*

Mytilopsis leucophaeata is a highly euryhaline species which means that it is capable of living in a wide range of salinities and occurs in brackish waters (Rajagopal et al. 2002a). It is native to the Gulf of Mexico and a part of Atlantic coast of the US and was introduced to Europe and North America (Therriault et al. 2004). Local dispersal could involve fouling on boats or transport in live wells or bilge systems. *M. leucophaeata* can attach to man-made and natural structures and is a major fouling species in industrial cooling water systems. The three dreissenid species that are spreading most rapidly and belonging to the family Dreissenidae, false dark mussel *M. leucophaeata*, the zebra mussel *D. polymorpha*, and the quagga mussel *D. rostriformis* (*bugensis*), are difficult to distinguish. As of now, there is no simple, reliable method for morphologically separating veligers or immature states of these mussels. Rajagopal et al. (2002a) and Verween et al. (2010) describe *M. leucophaeata* as a biofouling and nuisance organism, causing problems in industrial cooling water systems. Cooling water conduits of a power station provide an ideal habitat for *M. leucophaeata*. Given these conditions, settlement occurs readily and growth can be rapid until it begins to interfere with the operational systems. Bergstrom (2004) reports that *M. leucophaeata* also causes severe fouling on cages, boats, ropes, etc. and that the species competes with barnacles and other filter feeders.

The salinity range at which *M. leucophaeata* is recorded is 0.2–26.4%. *M. leucophaeata* does not tolerate salinities higher than 31%. The temperature range at which *M. leucophaeata* has been recorded is 7–30°C (Van der Velde et al. 2010, and literature therein).

M. leucophaeata are dioecious with external fertilization. Verween et al. (2010) have monitored that in European waters, *M. leucophaeata* has yearly spawning period of 4 months with spawning peaks within that period. Spawning starts at a minimum temperature of 12°C, but in other areas higher minimum temperatures are recorded (Van der Velde et al. 2010 and literature therein). Larval stages show wide temperature (between 10 and 30°C) as well as salinity (between 0 and 25%) tolerances with mortality. Maximal survival of 4-h-old embryos was found at 22°C at salinity 15% (Verween et al. 2007). *M. leucophaeata* has a life span of 5 years and can grow up to a shell length of 27 mm (Van der Velde et al. 2010 and literature therein).

5.4 Black-Striped Mussel, *Mytilopsis sallei* (Recluz 1849)

Mytilopsis sallei is found in intertidal and shallow waters, for example, coastal lagoons, usually not any deeper than a few metres. *M. sallei* occurs naturally in the West Indies, along the Caribbean coast of Central and South America from Yucatan to Venezuela, and in southern peninsular Florida, USA (Bax et al. 2002).

M. sallei is a small, fingernail-sized mussel, with shell lengths ranging 8–25 mm, with a maximum width of 9.68 mm and a maximum height of 12.58 mm. It shows variation in shell coloration, from black through to a light colour, with some small individuals having a light and dark zig-zag pattern. The right valve overlaps the left valve and is slightly larger. *M. sallei* has wide temperature (up to 35°C), salinity (fresh water up to 35‰), and oxygen tolerances. *M. sallei* has high fecundity, rapid growth, and fast maturity rate. Raju et al. (1975) recorded 50% as upper salinity for

M. sallei. During their lifespan, individuals change sex, with a proportion of mussels in any population present as hermaphrodites. Eggs and sperm are released into the water column, where external fertilization takes place. Tens of thousands of eggs are released. Spawning appears to be triggered by changes in salinity. In its native range, *M. sallei* has two periods of intense spawning activity, apparently stimulated by rapid drops in salinity resulting from seasonal freshwater outflow (Puyana 1995; in Bax et al. 2002). A pelagic larva develops within a day of fertilization and then settles (NIMPIS 2002; CSIRO 2001). Juveniles grow rapidly and are considered mature after 1 month. Maximum size is reached within 6 months, and mussels live for about 12–13 (maximum 20) months. *M. sallei* settles in clusters and is rarely seen as a single individual (NIMPIS 2002). It attaches to all types of substrata but prefers vertical surfaces and objects. It is capable of shedding its byssus and reattaching to new surfaces. Younger mussels develop byssus apparatus at shorter intervals, and hence move more often, but adults are relatively passive (Udhayakumar and Karande 1989; Morton 1981; NIMPIS 2002; CSIRO 2001; Bax et al. 2002; Rajagopal et al. 2006b).

M. sallei has been reported from Australia (Darwin harbour; Bax et al. 2002), Hong Kong, Taiwan, Japan, Fiji (CSIRO 2001), India (Mumbai and Vishakhapatnam harbours; Anil et al. 2002) and Singapore (Sin et al. 1991). Hull fouling is often an important factor in incursions, such as the introduction of *M. sallei* to Darwin Harbour, Australia in the 1990s (Hutchings et al. 2002). However, spread via ballast water appears less likely because of the short duration of the larval stage (CSIRO 2001). It can be introduced to new areas via fouling on aquaculture equipment (CSIRO 2001).

M. sallei is a major fouling species, forming dense monocultures. It is a suspension feeder, feeding on zooplankton, phytoplankton, and other suspended particulate organic matter (NIMPIS 2002). It has been responsible for massive fouling on wharves and marinas, seawater systems (pumping stations, vessel ballast, and cooling systems), and marine farms. In preferred habitats, it forms dense monospecific groups that exclude most other species, leading to a substantial reduction in biodiversity (NIMPIS 2002; CSIRO 2001). *M. sallei* dominates the intertidal pier community within the Government Dockyard in Victoria Harbour, Hong Kong and thereby altered the whole ecosystem (Morton 1989). In India, *M. sallei* displaces much of the native fauna in Mumbai waters (Subba Rao 2005).

6 Asian Clams: Corbiculidae

6.1 Asiatic Clam, Corbicula fluminea (Müller 1774)

The Asiatic Clam is native to freshwater systems in south-eastern China, Korea, south-eastern Russia, and the Ussuri Basin (Aguirre and Poss 1999). In the United States, *C. fluminea* has been introduced and spread to 38 states of the USA and the District of Columbia (Foster et al. 2000). It also invaded South America (Callil and

Mansur 2002) while Europe was invaded after the 1980s, subsequently showing a very fast dispersal over nearly the whole of Europe (Vincent and Brancotte 2002).

It has caused millions of dollars worth of damage to intake pipes used by power, water, and other industries. *C. fluminea* occurs in estuarine habitats and freshwater lakes and water courses; it requires well-oxygenated waters and prefers fine, clean sand, clay, and coarse sand substrata in which they bury (Aguirre and Poss 1999). They can tolerate salinities of up to 13% for short periods (Aguirre and Poss 1999) and temperatures between 2 and 30°C (Balcom 1994). It is generally intolerant of pollution and is usually found in moving water because it requires high levels of dissolved oxygen. *C. fluminea* spreads when it is attached to boats as juveniles or is carried in ballast water, used as bait, sold through the aquarium trade, and carried with water currents. Many native clams are declining as *C. fluminea* out-competes them for food and space reaching very high densities in sediments (PNNL 2003).

The introduction of *C. fluminea* into the United States has resulted in the clogging of water intake pipes, affecting power, water, and other industries. Nuclear service water systems (for fire protection) are very vulnerable, jeopardizing fire protection. In 1980, the costs of correcting this problem were estimated at one billion dollars annually. *C. fluminea* causes these problems because juveniles are weak-swimmers, and consequently they are pushed to the bottom of the water column where intake pipes are usually placed. They are pulled inside the intakes, where they attach as juveniles, breed, and die. The intake pipe became clogged with live clams, empty shells, and dead body tissues. Buoyant, dead clams can also clog intake screens.

C. fluminea is a hermaphrodite (both sexes are found on one organism) and is capable of self-fertilization (Rajagopal et al. 2000). The larvae are released through the exhalent siphon and sent out into the water column. Spawning can continue year around in water temperatures higher than 16°C. The water temperature must be above 16°C for the clams to release their larvae. In North America, spawning occurs from spring to fall (Aguirre and Poss 1999). Maximum densities of *C. fluminea* can range from 10,000 to 20,000 m^{-2}, and a single clam can release an average of 400 of juveniles a day (PNNL 2003) and up to 70,000 per year. Reproductive rates are highest in fall (Aguirre and Poss 1999). Larvae spawned late in spring and early summer can reach sexual maturity by the next fall (Aguirre and Poss 1999). *C. fluminea* has a lifespan of about 2–4 years (PNNL 2003); the maximum lifespan can be as much as 7 years (Aguirre and Poss 1999).

7 Other Important Invasive Fouling Species

Apart from the bivalves, which form the major component of the invasive fouling species, organisms such as barnacles, tube worms, and hydroids also are important from the viewpoint of biofouling in industrial cooling water systems. Practical experience confirms that barnacles are inherently better equipped to colonize different man-made structures due to their possession of the unique cypris larvae (Crisp 1984). A good introduction to the barnacles is provided by Southward (2008).

7.1 *Amphibalanus improvisus* (Darwin 1854)

The brackish water barnacle *Amphibalanus improvisus* (synonym *Balanus improvisus*) is an estuarine species and has a wide geographic distribution around the world (Newman and Ross 1976; Furman 1990). *A. improvisus* might be originated from the east coast of the US and be transported to Europe early in the nineteenth century from where it has spread extensively during the twentieth century (Gislén 1950; Sneli 1972; Southward and Newman 1977; Furman et al. 1989; Leppäkoski 1999).

The species feeds itself by filtering detritus. The barnacles reach the adult stage at a basal diameter of 6–8 mm. Some individuals can reach an age of 4 years (Subklew 1969). *A. improvisus* is hermaphroditic. They can reproduce by cross- as well as self-fertilization (Furman and Yule 1990). An individual can produce several broods per year. Two broods have been reported in the Baltic Sea. Under favourable conditions, it produces broods with intervals of 6 weeks or even with intervals of 4–5 days. Reproduction by release of nauplii starts in spring when the temperature rises above 10°C and ends when the temperature falls below that level in autumn (Luther 1987). Free-swimming nauplius larvae hatch out into the water, where they live as part of the zooplankton for 2–5 weeks, feeding on phytoplankters. This duration may be as short as 1–2 weeks at optimum conditions when temperature is around 14°C. The nauplii pass six stages to reach the last one called cypris stage (0.5 mm long). The cypris, a non-feeding stage, searches for a suitable substratum and finally settle using cement secreted by specialized cement glands (Furman et al. 1989). Settlement occurs at temperatures above 20°C. The cypris larva cements itself to a substratum and metamorphoses into the typical barnacle.

The species is eurythermal, but is sensitive to temperatures below zero. It is sensitive to desiccation and therefore does not occur at places that fall dry frequently. It is sensitive to strong water turbulence. The species tolerates pollution very well. The species is extremely euryhaline during all stages and can withstand a very wide range of salinities from sea water to fresh water and, therefore, it is able to penetrate landward in estuaries, canals, and harbours (Rainbow 1984). Its occurrence is most frequent at salinities of 5–15‰. Normally, it does not occur at salinities higher than 25% (O'Connor and Richardson 1994). The adults can easily be transported attached to ship hulls after which planktonic larvae can be released. The duration of the larval stage is relatively short, which restricts the dispersal possibilities of the larvae (Furman et al. 1989). Settlement as high as 37,200 numbers m^{-2} has been observed near the intake gates of Velsen power station in the Netherlands (Van der Gaag et al. 1999). The maximum settlement was observed at 2 m depth.

7.2 *Ficopomatus enigmaticus* (Fauvel 1923)

The brackish water serpulid tube worm, *Ficopomatus enigmaticus* (formerly named *Mercierella enigmatica*), is a major fouling organism on surfaces such as power station intakes, canal walls, and ship hulls (Straughan 1972). *F. enigmaticus* is capable of settling in water velocities up to 55 cm s^{-1} and able to build massive (8.5 cm thick) layers of calcareous tubes within a year (Ten Hove 1979). *F. enigmaticus* was originally a subtropical species and dispersal occurred probably through navigation (Dixon 1981). The species is widely spread in the brackish water of harbours, estuaries, and lagoons. This species is believed to have originated from Australia (Allen 1953) or from the subtropical austral region (Dixon 1981). Their distribution is reported from northern and southern hemisphere, Denmark to North Africa, Mediterranean, Black Sea, Caspian Sea, South Africa, Japan, Southern Australia, Hawaii, California, New Jersey, Gulf of Mexico (Texas), Uruguay, North Argentina, Thames estuary (England), and canal de Caen (France) (Rioja 1924; Monroe 1938; Allen 1953; Kirkegaard 1959; Ten Hove and Weerdenburg 1978; Dixon 1981; Rajagopal et al. 1995). In The Netherlands, this species was reported in the harbour of Vlissingen (Flushing, SW Netherlands) and Noordzeekanaal (near Amsterdam and Velsen) (Wolff 1969; Van der Velde et al. 1993). In the tropics, the closely related *Ficopomatus ushakovi* (Pillai 1960) occurs, which is also an euryhaline species (Ten Hove and Weerdenburg 1978; Zibrowius 1983), often confused with *F. enigmaticus*, e.g. by Hill (1967), Lacourt (1975), and Straughan (1968, 1970, 1972).

F. enigmaticus can osmoconform at salinities of 1–55%; at salinity below 1%, osmoregulation takes place (Skaer 1974). The species can be found in pure sea water as well as in fresh water, but the species flourishes only in brackish water. In the Netherlands, the species occurs at salinities of 3.2–10% (Wolff 1968; Van der Velde et al. 1993). The development of the larvae is rapid at salinities of 10–30%. Salinity lower than 3% is unfavourable for the development towards the trochophore larval stage (Hartmann-Schröder 1967). At low salinities, tube building is hampered by lower calcium concentrations than in salt water. *F. enigmaticus* can tolerate short periods of extremely high salinities from 55% till fresh water (Van der Velde et al. 1993).

The northern boundary of the distribution of *F. enigmaticus* is the July isotherm of 15.5°C (Vaas 1975). Frost periods damage this species, while tube formation stops below 7°C (Van der Velde et al. 1993). The species flourishes often at power station outfalls under these conditions. The maximum settlement of *F. enigmaticus* (10×10^6 m^{-2}) was reported from Millpond at Emsworth, UK (Thorp 1987). Ten Hove (1979) suggested that competition with other animals, mainly for space, may decide the settlement success of *F. enigmaticus*. Evidence from panel studies suggests that space was a limiting factor for the successful settlement of *F. enigmaticus* in regions like the Noordzeekanaal, since their settlement was associated with competitively superior species like the bivalve *M. leucophaeata* and the hydroid *C. caspia* (Rajagopal et al. 2002b). The tube growth of *F. enigmaticus* was found to be very fast in the first few weeks (up to 10 mm $week^{-1}$ in the first 4–6 weeks). Later, growth decreases and the tubes attain a length of 60–70 mm within 1 year. They can grow to 10 cm with a diameter of 1.5 mm.

The animals are male or female. Reproduction takes place depending on the temperature regime. The minimum temperature for reproduction seems to differ between populations. Dixon (1981) and Hartmann-Schröder (1967) report that the water temperature in, for example, the Thames (Great Britain) must be 17–18°C, while Thorp (1994) at Emsworth (West Sussex, Great Britain) observed reproduction at water temperatures from 10°C. In areas where the temperature is higher than these levels, reproduction can occur the whole year round. In temperate areas, gametogenesis takes place during January-July, but the release of the sperm and eggs takes place in August-September, when the water temperature is the highest. The duration of the planktonic larval stage can vary from 1 to 3.5 months. They feed on unicellular green algae. Larval settlement takes mainly place in October-November (Dixon 1981). Settlement of *F. enigmaticus* may occur almost on any solid substrate. When other individuals of this species were already present on the substrate, larvae were attracted to settle there (Straughan 1972). Animals of 10 mm length (not tube length) can reproduce already (Fischer-Piette 1937); in temperate areas, it takes 4 months, and this generation will reproduce in the next season. The animals can reach the age of 4–8 years (Ten Hove 1979). The fully grown attached worms are suspension feeders and take all suspended matter (detritus, diatoms, flagellates, and ciliates) in the size range 2–16 μm (Dixon 1977). The species occurs at permanent water levels, but can tolerate a dry falling period of 4–5 days (Kühl 1977). Water with low oxygen level is tolerated for some days (Kühl 1977).

The effect of chlorine on *F. enigmaticus* is unknown. Some serpulids such as *Pomatoceros triqueter* and *Hydroides elegans* (under the name *H. norvegica*) showed better growth when chlorine was added to the sea water of the cooling water systems of an oil refinery (Zibrowius and Bellan 1969).

7.3 *Cordylophora caspia (Pallas 1771)*

C. caspia (synonym *C. lacustris* Allman) is a colonial hydrozoan originating from the Ponto-Caspian area that occurs in brackish waters and in fresh waters with altered ionic composition (Arndt 1965; Kinne 1956). *C. caspia* is generally found on submerged objects such as stones, wooden piles, and macrophytes. *C. caspia* has nowadays a worldwide distribution from the cold boreal and antiboreal to the subtropical regions (Roch 1924; Arndt 1984). The species is common in estuaries, lagoons, and coastal lakes, where colonies can grow large in brackish water (Arndt 1989). Well-developed colonies of *C. caspia* are usually found at salinities between 2 and 12% with relatively constant conditions and considerable tidal influence (Arndt 1989). Vervoort (1946) recorded a salinity range of 0.3–10% with optimal development at a salinity of 1–5%, but also occurrence of poorly developed colonies at lower (0.08%) and higher salinities (up to 35%). *C. caspia* has also been reported from fresh water (Fulton 1962) under favourable conditions such as fast flow, high oxygen availability, positive ion anomalies (calcium, magnesium, and sodium), and permanent twilight (Kinne 1956; Arndt 1989). *C. caspia* shows many growth forms described by Schulze (1921). According to Arndt (1973), different colonies can have different optima for temperature and salinity. Temperatures below 10°C are generally suboptimal for *C. caspia*. The species is very plastic to variation in temperature (10–31°C), pH (6–9), oxygen tension, and light (see also Hutchinson 1993). Microsatellite studies showed that in *C. caspia*, cryptic diversity is present (Schable et al. 2008) and another genetic study showed that perhaps various species are hiding under the name *C. caspia* (Folino-Rorem et al. 2009).

C. caspia shows a temperature and drought-resistant stage, called the menont. This stage makes dispersal over larger distances by ships, floating wood or waterfowl possible. The distribution of *C. caspia* over the globe is very discontinuous (Roch 1924; Arndt 1984). Menonts can grow out to polyps even in concentrated sea water (ca. 40‰) (Vervoort 1946).

Hydroids are often the first macrofouling colonizers on experimental panels and provide rough substratum for the subsequent settling of other fouling species. In *C. caspia*, the colonies are formed by asexual budding, which leads to increase in the number of countable units rather than increase in size of a single unit (Fulton 1963). The hydroid colonies are found to feed mainly on copepods and dipteran larvae, which are paralyzed by nematocysts in the tentacles (Mace and Mackie 1970). Several parameters including light, ionic concentrations, nutrition, oxygen tension, the presence of symbiotic organisms, substratum, and temperature have been reported to influence the growth in *C. caspia* (Kinne 1956; Fulton 1962). The sexual generation (hydromeduse) originates also by budding from the polyp. When the medusa stays in reduced form on the polyp, it develops into a gonophore. Male and female gonophores develop on the same colonies at short distance below the hydranths and are covered by a thin periderm. The development to planula larva takes place within the female gonophores (Vervoort 1946). Many gonophores of *C. caspia* release the planula larvae covered with cilia into the water, where they live planktonically. The planula settles on a suitable substratum and forms an adhesive disc, from where the upright polyp develops. The disc and polyp are covered with the periderm consisting of a chitin-like substance. Jormalainen et al. (1994) studied growth and reproduction of *C. caspia* in the northern Baltic Sea. Mean size of the uprights varied cyclically. During early summer, growth and sexual reproduction showed a clear peak towards mid-summer, and thereafter sexual reproduction ceased but growth continued.

In Noordzeekanaal, Netherlands, Rajagopal et al. (1995) observed the settlement of *C. caspia* between May and October, when the temperature and salinities were relatively high. The maximum biomass of 5.2 kg m^{-2} (dry wt, after 118 days) was recorded near the Velsen power station. High settlement of hydroids in the condenser tubes (i.e. Velsen power station) affects the heat transfer efficiency and therefore necessitates frequent manual cleaning, even after using intermittent chlorination as a control measure (Rajagopal et al. 2002b). Chlorination leads only to curtailing of the growth of the hydroids, as it cannot kill the whole polyps. Hence, they can grow out again (Rajagopal et al. 2002b; Folino-Rorem and Indelicato 2005). Thermal control is another option. Folino-Rorem and Indelicato (2005) found that *C. caspia* polyps died within 8 h of exposure to temperatures of 37.7 and 40.5°C, but survived within that period below 36.1°C.

8 Control Methods

Domination of aquatic systems by invasive species brings into focus the need for effective control measures, which may have to be tailored to suit the characteristics of the species in question. Quite often, colonization by these organisms becomes so intense that normal control measures may be found inadequate to deal with the fouling situation, unless special attention is paid to the tolerance of the species to the method used (see Fig. 7.3). Recent publications have highlighted different aspects of the issue related to invasive species and their control (Rajagopal et al. 2010a, b).

Two of the most commonly used fouling control measures in coastal power stations are chlorination and heat treatment (Rajagopal et al. 1996). A variety of other control methods has also been proposed for controlling exotic species: oxygen deprivation, thermal treatment, dessication, radiation, high-pressure jetting, mechanical filtration, removable substrata, molluscicides, ozone, antifouling coatings, electric currents, and sonic vibration. However, the utility of many of these methods is yet to be commercially demonstrated. Mechanical measures, such as using screens and traps, can effectively eliminate mussels and their shells from the system. Desiccation is an effective, readily applied, and environmentally neutral technique that can be used against invasive mussels. It would be most effective in raw water systems such as navigation locks and water intake structures, which are designed for periodical dewatering for maintenance.

8.1 Comparative Tolerance of Various Bivalve Species

Many of the predominant invasive species are extremely tolerant to many conventional control measures (Rajagopal et al. 2006b). Biofouling in industrial cooling water systems is generally dominated by a few species which are adapted to the conditions within the cooling water systems (Rajagopal et al. 2010a). It is possible that invasive species are the most prolific among them. In such situations, it would be necessary to know the relative tolerance of the dominant species to the control strategy being adopted. For example, *M. leucophaeata* is a common fouling organism in CWS of power stations in Netherlands, where it can coexist at relatively high salinities with *M. edulis* and at low salinities with *D. polymorpha* (Rajagopal et al. 1995, 2002a, 2003). *M. leucophaeata* and *D. polymorpha* are invasive species in Netherlands. A comparison of the chlorine tolerance of these three species showed that *D. polymorpha* was the least tolerant among the three. The chlorine residual levels required to control a mussel fouling community consisting of *M. leucophaeata*, *M. edulis*, and *D. polymorpha* are to be chosen based on the tolerance of *M. leucophaeata*, which is the most tolerant among the three (refer to Rajagopal 2012 for details). Previous studies have shown that various factors can also significantly influence chlorine tolerance such as mussel size, spawning season, acclimation temperature, and status of byssal attachment (refer to Rajagopal et al. 2010a for details). Therefore, chlorine bioassays using mussels (or similar organisms) need to be carried out after taking the above factors into consideration (Rajagopal et al. 2002c).

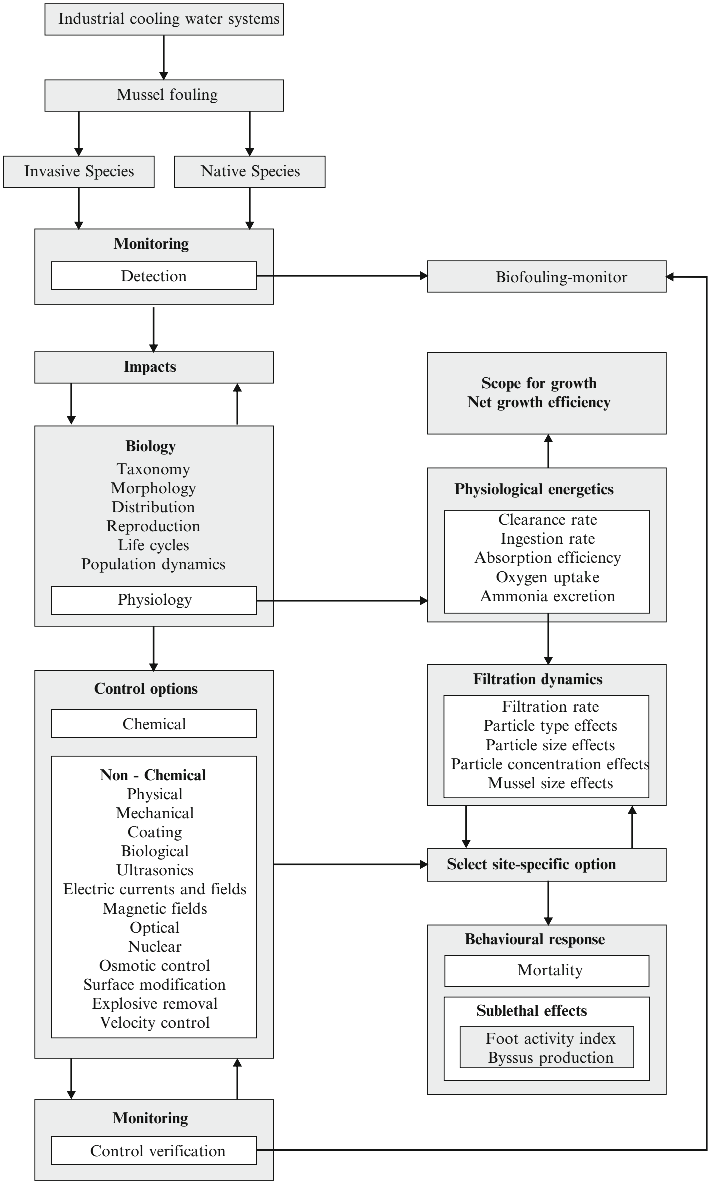

Fig. 7.3 Schematic representation of the options available for invasive species control in industrial cooling water systems

In a fouling control programme involving heat treatment, the heated effluents, instead of being discharged, are re-circulated through the pre-condenser sections (Jenner 1982; Jenner et al. 1998). This recirculation is continued until the water flowing through the conduits has attained sufficient temperature to kill all the fouling organisms existing inside. Generally, the temperature difference between intake and outfall (ΔT) is maintained below a stipulated limit to prevent any potential damage to the environment, resulting from the discharge of heated effluents. Nevertheless, there are problems with this method, particularly the production penalty due to excess heat on the turbines (Rajagopal et al. 2010b). It requires major design modifications of the cooling systems in stations already operating. Furthermore, it is often expensive or technically difficult. In spite of this, many power stations have successfully adopted heat treatment for fouling control.

Time-temperature-mortality curves of marine bivalves (as well as many other organisms) are typically characterized by a steep increase in mortality within narrow ranges of temperature, the range being typical of the organisms being tested. Interestingly, near extinction of invasive mussel *P. perna* from Texas Gulf of Mexico waters was observed in the summer of 1997, when the mean surface-water temperatures approached its incipient upper limit of 30°C (Hicks and McMahon 2002). Jenner (1982) and Rajagopal et al. (2005b) have observed that in most of their experiments on the response of mussels to temperature, either all animals were killed or all survived. Hence, the point of death was fairly sharp defined with little variation from one individual to the other. Similarly, Wright et al. (1983) and Rajagopal (1997) recorded only small differences between temperatures causing little or no mortality and those producing a complete kill in *Crassostrea virginica*, *Mulinia lateralis*, *Argopecten irradians*, *Mercenaria mercenaria*, *Spisula solidissima*, *P. viridis*, and *P. perna*. The simplicity and effectiveness of thermal treatment of mussel control make it a viable alternative to chlorination and, therefore, can be recommended to affected industries.

Data available in literature showed that 100% mortality of all bivalve species could be achieved by raising the temperature to 42°C and maintaining that temperature level for about 120 min (Rajagopal et al. 2010b). Published data on *M. edulis* (Rajagopal et al. 2005a), *M. leucophaeata* (Rajagopal et al. 2005b), and *C. gigas* (Rajagopal et al. 2005c) from the Netherlands obtained under comparable experimental conditions are presented in Fig. 7.4. As described earlier, *M. leucophaeata* and *C. gigas* are invasive species in The Netherlands and elsewhere in Europe. The exposure time required for 100% mortality of *C. gigas* at different temperatures was much longer than that required for *M. edulis* and *M. leucophaeata*. In most of the cases, it is also reported that the treatments that are effective against bivalves are also successful against most other fouling organisms. Therefore, antifouling treatments must be based on the most tolerant species present. Heat treatment as an alternative to chlorination must be explored by the utilities and, if found economical, must be practised more widely.

9 Concluding Remarks

Industries all over the world will have to cope with an increasing number of invasive species that find their way into their cooling water intakes. This has been amply demonstrated in the case of species such as Asiatic clams, Zebra, and Quagga

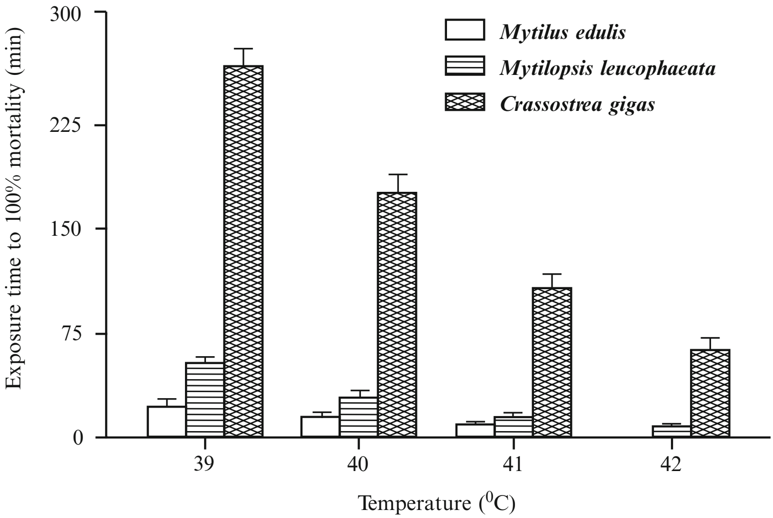

Fig. 7.4 Comparison of exposure times to reach 100% mortality of *Mytilus edulis* (Rajagopal et al. 2005a), *Mytilus leucophaeata* (Rajagopal et al. 2005b), and *Crassostrea gigas* (Rajagopal et al. 2005b) at different temperatures (all from The Netherlands). Test methods and mortality determinations were similar in all temperature tolerance studies of the different species (modified after Rajagopal et al. 2005c)

mussels in the Great Lakes and in the river Rhine (Figs. 7.1 and 7.2). Operators and engineers have to be aware of new invasive species in their cooling water circuits. It is advisable to monitor the systems continuously for the presence of new species. Often it may happen that the invaders are much better equipped to tolerate adverse environmental conditions than the native species they replace. Hence, the control measures adopted should be such that they address the invasive species rather than the native ones (Fig. 7.3). Tolerances with respect to control measures differ between species (Fig. 7.4). Control measures used for the most tolerant species are also expected to control other less tolerant species. Unfortunately, adequate toxicity data are not available for several of the potential biofouling invasive species. This lacuna needs to be addressed and it is expected that researchers would pay attention to generation of such data, so that environmentally acceptable control measures can be evolved for the ever-increasing number of exotic biofoulers.

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Chapter 8
Chlorination and Biofouling Control in Industrial Cooling Water Systems

Sanjeevi Rajagopal

1 Introduction

Chlorine, a powerful oxidizing biocide, was first used in Europe and North America in the early 1900s for the disinfection of drinking water and resulted in a dramatic decline in typhoid and cholera cases. At the present time, it is largely used as for water treatment, such as taste and odour control, disinfection of drinking water and wastewater, in the food industry and for biofouling control. Of all the disinfectants, it is certainly the most extensively studied with regard to chemistry, toxicity and ecotoxicity. Due to its well-tried technology, its long-term worldwide industrial uses and its reasonable cost, chlorine remains the most common antifouling treatment in industrial cooling water systems. An ideal biocide is toxic to one particular organism or group of organisms, but has no harmful effects on "non-target" organisms. It is not consumed by reactions with substances in the water (i.e. there is no "demand"), and soon after it enters the environment, it breaks down into non-toxic forms. Chlorine is a long way from being an ideal biocide: it is non-specific and reacts with virtually all constituents of natural waters—including man-made pollutants—to yield products having varying degree of persistence and toxicity. Nevertheless, it continues to be used for biofouling control in power plant cooling water systems (Jensen 1977; Opresko 1980; Rajagopal et al. 2010).

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2 Water Chlorination

Chlorine is a powerful oxidant, capable of destroying biological molecules (Costlow and Tipper 1984; White 1999). However, the very oxidizing nature of chlorine makes it highly active and it gets involved in a number of side reactions with organic and inorganic substances present in water. Consequently, chemistry of chlorination in water is very complex and involves many reaction products. A significant fraction of chlorine added to water, therefore, gets lost and will not be available for biocidal action. The fraction of chlorine that is used up in such side reactions is called chlorine demand (Fig. 8.1). Chlorine residual is the term given to the amount of chlorine (as well as its reaction products, which still retain some oxidative power) that remains after such side reactions. It consist of (1) free chlorine (hypochlorous acid, HOCl and hypochlorite ion, OCl^-), produced as a result of hydrolysis of chlorine and (2) chloramines, which are produced as a result of chlorine's reaction with ammonia, as shown below.

$$Cl_2 + H_2O \rightarrow HOCl + HCl \tag{8.1}$$

$$HOC \leftrightarrows lH^+ + OCl^- \tag{8.2}$$

$$HOCl + NH_3 \rightarrow NH_2Cl + H_2O \tag{8.3}$$

$$NH_2Cl + HOCl \rightarrow NHCl_2 + H_2O \tag{8.4}$$

Free chlorine in the form of undissociated hypochlorous acid is the most desirable form from the viewpoint of biofouling control because being uncharged, it can freely

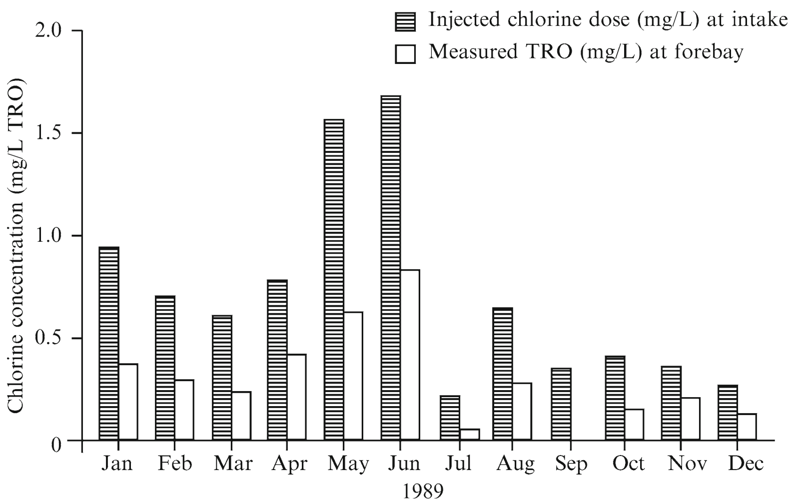

Fig. 8.1 Injected chlorine dose (data obtained from MAPS log book) and measured total residual oxidants in the Forebay during 1989 in Madras Atomic Power Station (MAPS), Kalpakkam, India

diffuse into cells. Ambient pH, which plays an important role in the speciation of free chlorine, therefore, has a significant modulating effect on the biocidal efficacy of chlorine. Higher pH (>8) values favour formation of hypochlorite ion. Cooling water systems, which generally operate at alkaline pH (favourable from corrosion point of view), are, therefore, at a disadvantage in this regard. Chlorine chemistry gets further complicated in seawater, which contains significant amount of bromide. Bromide is readily oxidized by free chlorine to hypobromous acid (HOBr), which further indulges in reactions with ammonia, just as HOCl does. All the above-mentioned oxidants can also react with organic matter present in water to produce halogenated organics. Therefore, chemistry of chlorination is complex, involving many molecular and ionic species, with often confusing terminology (refer to Khalanski and Jenner 2012 for a full discussion on the chemistry of chlorine).

3 Measurement of Chlorine Residuals

Several techniques, such as amperometric titration, potentiometric titration or colorimetric titration, are available for the measurement of chlorine residuals in water (Standard Methods 2005). Simple colorimetry (using *N*,*N*-Diethyl-*P*-Phenylenediamine—DPD method) is generally used, especially under field sampling conditions. This has the ability to differentiate between free and combined forms of chlorine. It also allows rapid analysis following sample collection, reducing the chances of chorine loss through decay reactions. It has a practicable threshold detection level of about 0.02 mg/L (Jenner et al. 1998; Khalanski and Jenner 2012).

4 Environmental Discharge Criteria

Chlorine discharged along with effluents can cause adverse effects on aquatic systems (Brook and Baker 1972; Eppley et al. 1976; Whitehouse et al. 1985; Choi et al. 2002; Rajagopal et al. 2010). Therefore, environmental release of chlorine residuals is controlled in many countries through legislation, though the permitted levels vary from country to country (Fischer et al. 1984; Jenner et al. 1998; Turnpenny et al. 2012). For example, in The Netherlands, the permitted limit of chlorine residuals (0.2 mg/L for 2 h/day) is much less than that in India (0.5 mg/L).

5 Chemical Treatment Strategies

Claudi and Mackie (1994) and Jenner et al. (1998) have defined five basic chemical treatments strategies to eliminate mussels fouling, which can be more generally applied to all the macrofouling. The various chemical treatments commonly adopted in industrial cooling water system against different fouling organisms are described here.

5.1 End-of-Season Treatment

This treatment is used against the adults and juveniles established in the system at the end of the settlement period of the fouling species. It is only convenient when the operation is not threatened by the excessive development of fouling during the breeding and settling season. Depending on the chemical and the dosage, the required time can be shorter than a day or can cover some weeks.

5.2 Periodic Treatments

This can be applied if the critical density of fouling is reached in the system before the “end-of-season”. This treatment is a variant of the end-of-season treatment.

5.3 Intermittent Treatments

This treatment involves frequent dosing (every day or every 3 days, for example) for short period of time (a few minutes to a few hours). This procedure generally kills or removes the settled fouling organisms, but it must be applied over all the settling season of the target organisms.

5.4 Continuous Dosing

In this mode, low levels of chemical biocide are continuously dosed in order to inhibit the settlement of larvae in the cooling conduits. It is observed that this treatment stops or reduces drastically the growth of fouling and kills or removes the biofouling in the long-term more effectively than it is achieved with intermittent dosage.

5.5 Semi-Continuous Dosing

Here a low dose of the chemical is applied for a short period (15–60 min) and then stopped for an equally brief period. This long-term, high-frequency treatment (for instance 30 min on/45 min off) can have the same effect as continuous dosing at the same low level (Claudi and Mackie 1994, 2009). Regarding efficacy, four selection criteria of chemicals have to be considered:

(a) The biology of the target biofouling, in particular the location and duration of the settlement period
(b) The growth rate of the target species depending mainly on the trophic resource level

(c) The mode of action and the toxicity of the chemical (acute or chronic biocidal strategy)
(d) The maximum fouling density acceptable in the cooling system to be protected (operational tolerance)

For various ecological and economic reasons, continuous or semi-continuous dosing at sub-acute (chronic) toxicity levels is often found to be the most pragmatic option.

6 Porous Surfaces for Biocide Delivery

Injectable biocides are mainly used to control biofouling in industrial cooling systems. Unlike paints, they are injected into the bulk water, from where they diffuse to the water-material interface (which is the actual site of biofilm/biofouling formation), building up a concentration sufficiently strong enough to deter biological attachment or kill already attached forms. One major deficiency of this method (as compared to an antifouling paint) is that a large portion of the added biocide is wasted to “treat” the bulk water, where the presence of biocide is not really required. As biofouling essentially is an interfacial problem, the required biocide concentrations must be available at the water substratum interface, rather than the bulk water. Therefore, this method entails a larger biocide inventory than what is required, had the treatment been truly “interfacial” and results in unnecessary damage to organisms in the bulk water and the discharge zone. A more logical method is to deliver the right concentration of biocide at the very interface, so that effective concentration is maintained at the actual site of fouling, leaving the bulk water concentrations largely negligible (Fig. 8.2).

Rajagopal et al. (2009) have attempted to test the use of porous surfaces as a biocide delivery vehicle using dynamic experimental system. Porous ceramic surfaces were used to deliver chlorine and the response of mussels (*Perna viridis*) to different chlorine concentrations was studied in a laboratory flow-through system. The mussels were tested at three different chlorine concentrations (1, 2 and 3 mg/L TRO). In addition, Pulse-chlorination® experiments also were carried out, consisting of a cycle of 30-min chlorination, followed by a 30-min break in chlorination (Fig. 8.3). Pulse-chlorination® technology makes use of the time lag between stoppage of chlorination and full resumption of mussel feeding. Chlorination is resumed a little before the mussels start feeding after a bout of chlorination, with the result that they experience the total period as continuous chlorination, even though it is, in fact, intermittent chlorination. But if this break in chlorination is continued well beyond the recovery period, the mussels can make use of the period for feeding. More importantly, the length of recovery period is different for different mussels, the duration ranging from 7 min for *Mytilopsis leucophaeata* to 15 min for *Dreissena polymorpha* (Rajagopal et al. 2003a). Therefore, this procedure has to be employed

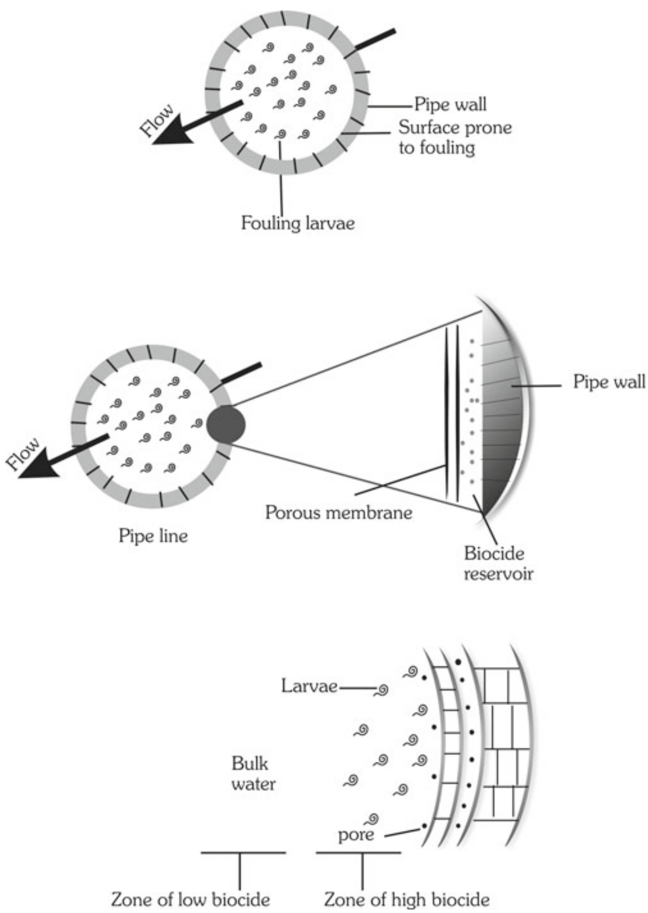

Fig. 8.2 A simplified schematic diagram of porous membrane and mode of action in an imaginary industrial cooling water system

judiciously, depending on the species one is dealing with. When appropriately applied, Pulse-chlorination® can result in considerable economic (due to reduced chlorine inventory) and ecological (due to reduced discharge levels) gain for the utility (Jenner et al. 1998).

From the results of the study, they concluded that chlorine reduction to the extent of about 60–75% can be easily achieved by using porous ceramic surfaces in place of conventional bulk water continuous chlorination for controlling mussel fouling. Flow velocity of seawater was an important factor in fouling control with porous ceramic surfaces. Flow velocity between 1.5 and 3 m/s would keep injected biocide near the surface (Fig. 8.2). The specific advantages arising out of use of porous membrane are reduced biocide inventory, reduced environmental discharge and improved fouling control.

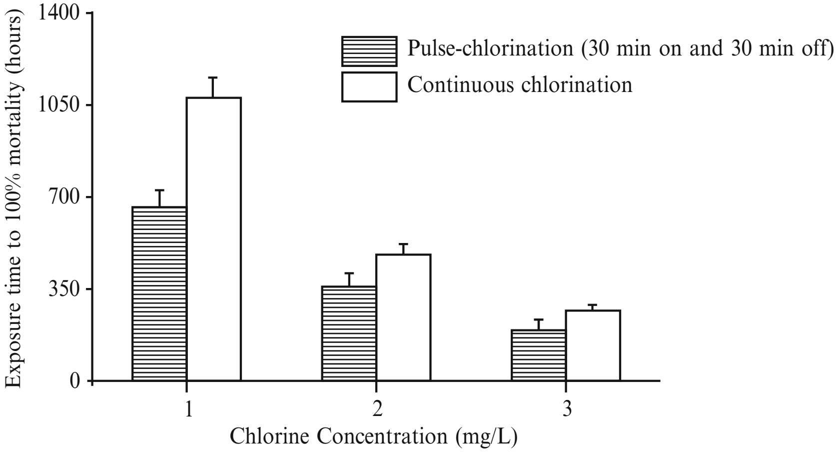

Fig. 8.3 Comparison of exposure time to reach 100% mortality of *Perna viridis* (96 mm size group mussels) under Pulse-Chlorination (30 min on and 30 min off) and continuous chlorination regimes. Data are expressed as mean ± SD ($n = 24$–48)

7 Chlorine Storage and On-Site Production

Chlorination of natural waters is done in one of three ways.

7.1 Dissolution of Chlorine Gas

Chlorine gas (Cl_2) can be kept under pressure in tanks, which presents the advantage of storing large amounts of chlorine in a small volume and of allowing for treatment of water at high flow rates. Chlorine gas is the least expensive of chlorine products. A few accidents during transport or storage have led industry to prefer sodium hypochlorite. Great progress has recently been made, however, in ensuring safe storage of chlorine gas.

7.2 Mixture with a Sodium Hypochlorite Solution

Like chlorine gas, sodium hypochlorite (NaOCI) in concentrated solutions is stored on-site in tanks with no metal walls to prevent decomposition. In the dark, decay is temperature-dependent. The recommended maximum storage time is 1 month. Commercially available sodium hypochlorite has an active chlorine concentration of 10–15%. To improve mixing with cooling water, the concentrated solution can be diluted prior to dosing to about 0.5–2.0 mg/L.

7.3 Production of a Sodium Hypochlorite Solution In Situ by Electrolysis of Seawater

At marine sites, when large amounts of chlorine are required to treat cooling water, electro-chlorination enables on-site production of the sodium hypochlorite required by the demand, by means of the following chemical reaction:

$$NaCl + H_2O \rightarrow NaOCl + H_2 \quad (8.5)$$

This process is somewhat more costly than purchasing sodium hypochlorite due to the investment cost of the electrolysis cells, energy consumption and maintenance costs (Jenner et al. 1998). Electro-chlorination is largely used to treat the cooling water of large marine power stations in the UK, France, Italy and Spain. Recently, problems with malfunction have led some power station operators to change over to sodium hypochlorite or chlorine dioxide.

8 Chlorination and Fouling Control

8.1 Factors Influencing the Chlorine Toxicity

The response of an organism to chlorine would vary depending on a number of factors. Among the various factors, the type of organism is an important criterion (Rajagopal et al. 2002a; Rajagopal and Van der Velde 2012). Shelled organisms (such as mussels) can withstand relatively long-term exposure to chlorinated water (Rajagopal et al. 2002b, c, 2006a), when compared to soft-bodied organisms, such as hydroids or ascidians (Rajagopal et al. 2002d). A review of literature clearly indicates most other fouling organisms succumb faster than mussels (Rajagopal et al. 2010). Therefore, chlorine regime targeted against the toughest mussels would also eliminate most other fouling organisms (Rajagopal et al. 2006a, b).

8.1.1 Mussel Species

Efficacy of chlorine as an antifoulant depends on various parameters, most importantly residual levels of chlorine and contact time (Mattice and Zittel 1976; Rajagopal et al. 2005a–d). A survey of existing literature shows that at residual levels as high as 1 mg/L, mortality takes several days (Fig. 8.4). For example, at 1 mg/L TRO, continuous chlorination, *Mytilus edulis* (blue mussel) takes about 480 h for 100% mortality (Lewis 1985). On the other hand, among tropical marine mussels, *P. viridis* (green mussel) takes about 816 h for 100% mortality when 1 mg/L residual chlorine is applied continuously (Rajagopal et al. 2003b). In *D. polymorpha*

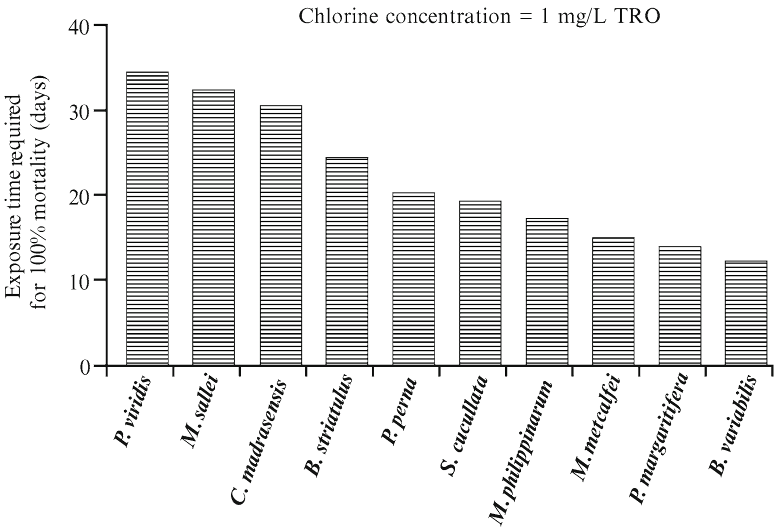

Fig. 8.4 Comparison of exposure times to reach 100% mortality in different tropical bivalve species: *P. viridis* (Rajagopal et al. 1995), *Mytilopsis sallei* (Rajagopal, unpublished data), *Crassostrea madrasensis* (Rajagopal et al. 2003c), *Brachidontes striatulus* (Rajagopal et al. 1997a), *Perna perna* (Rajagopal et al. 2003d), *Saccostrea cucullata* (Rajagopal, unpublished data), *Modiolus philippinarum* (Rajagopal et al. 2006c), *Modiolus metcalfei* (Rajagopal et al. 2006c), *Pinctada margaritifera* (Rajagopal, unpublished data) and *Brachidontes variabilis* (Rajagopal et al. 2005b) at 1 mg/L chlorine concentration. Test methods and mortality determinations were similar in all toxicity studies of species

(zebra mussel), 95% mortality is observed after about 552 h exposure to 1 mg/L residual chlorine (Van Benschoten et al. 1995). In comparison, *M. leucophaeata* (dark false mussel) takes about 1,104 h to achieve 100% mortality at 1 mg/L residual chlorine (Fig. 8.5). The exposure time required for 100% mortality of *M. leucophaeata* at different chlorine concentrations is much higher than that required for *D. polymorpha* (588 h) and *M. edulis* (966 h) (Fig. 8.5). Chlorine sensitivity can be significantly different even among closely related species, as is shown in Fig. 8.6.

8.1.2 Mussel Size

In the case of common fouling organisms such as mussels and barnacles, it is often seen that the size (or age) of the organism is an important factor that influences its sensitivity to chlorine (Rajagopal 1991). It has been shown that for several organisms, there is a size-dependent variation in the response, with larger organisms showing increased tolerance (Rajagopal 1997). However, such size-dependent nature of toxicity is not universal and there are organisms which exhibit uniform sensitivity to chlorine, irrespective of size. An example for mussel size influencing tolerance to chlorine is the mussel *M. leucophaeata* (Rajagopal et al. 2002a). Here, the tolerance is maximum in medium size mussels (about 10 mm), while smaller

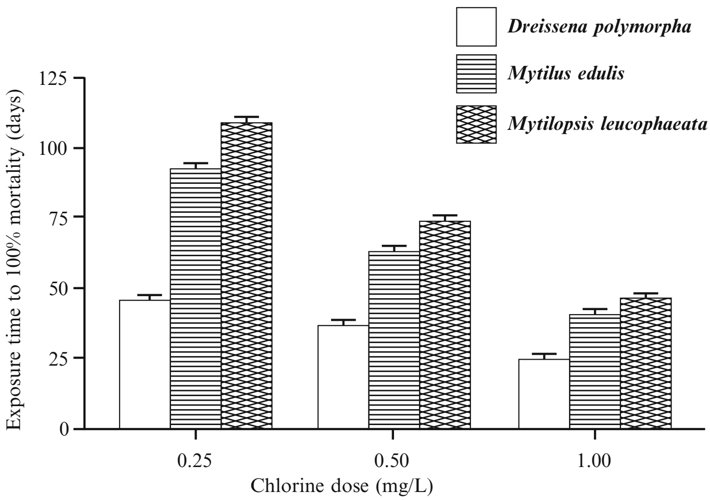

Fig. 8.5 Comparison of exposure times to reach 100% mortality of *Mytilopsis leucophaeata* (shell length in mm ± mm; 10.3 ± 0.7), *Dreissena polymorpha* (20.1 ± 0.7) and *Mytilus edulis* (21.2 ± 1.6) at different chlorine concentrations. Mortality data are expressed as mean ± SD ($n = 80$) of four replicate experiments ($n = 20$ in each experiment). Test methods and mortality determinations were similar in all toxicity studies (modified after Rajagopal et al. 2003a)

(2 mm) and larger (20 mm) mussels show greater sensitivity. This pattern is in contrast with the results reported for *M. edulis*, where the tolerance linearly increases with shell size (Rajagopal et al. 2005a). In the case of *D. polymorpha*, mussel size has no effect on the sensitivity of the organism to chlorine (Kilgour and Baker 1994; Rajagopal et al. 2002b). Therefore, the relationship between mussel size and chlorine toxicity is not comparable across different mussel species and generalizations regarding the size effect should be made after careful observation.

8.1.3 Byssus Attachment

Mussels use byssus threads to attach themselves to hard substrata. The status of attachment is an important criterion that determines the response of mussels to chlorine (Rajagopal et al. 2002b, 2005a). It has been experimentally shown that mussels, which normally are attached with the help of their byssus threads, become more sensitive to chlorine when they are exposed in unattached condition (Fig. 8.7). Once detached from a substratum, the mussel tries to reattach itself by producing new byssus threads. For this, it has to open its bivalve shell and extend its "foot" outside. This kind of enhanced byssogenic activity inadvertently increases the exposure of the soft tissues of the mussel to chlorine, thereby increasing the toxic effect. On the other hand, mussels which are already attached are byssogenically less active; in a chlorinated environment, their shells remain mostly closed, thereby protecting their soft body from chlorine (Lewis 1985; Rajagopal 1991).

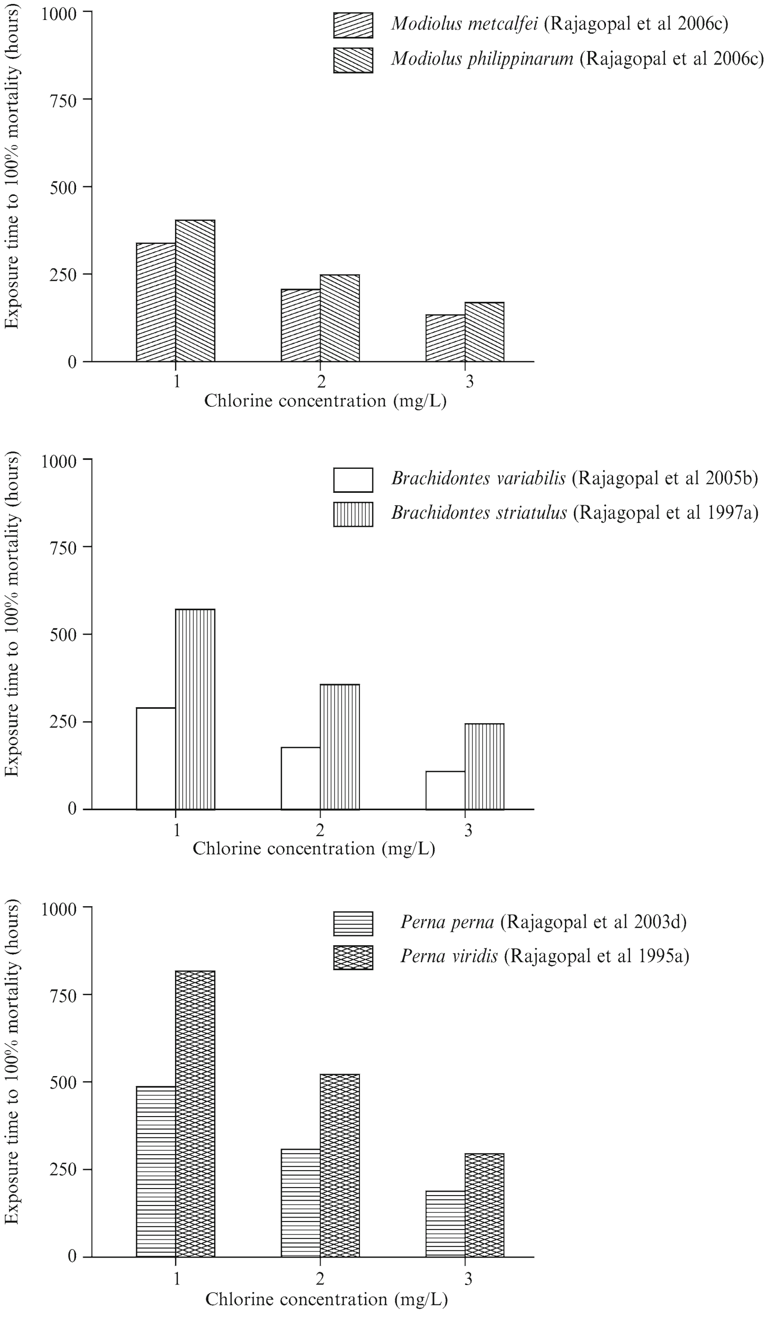

Fig. 8.6 Comparison of exposure times to reach 100% mortality of different tropical mussel species, *P. viridis* (Rajagopal et al. 1995), *P. perna* (Rajagopal et al. 2003d), *B. striatulus* (Rajagopal et al. 1997a), *B. variabilis* (Rajagopal et al. 2005b), *M. philippinarum* (Rajagopal et al. 2006c) and *M. metcalfei* (Rajagopal et al. 2006c) at different chlorine concentrations. Test methods and mortality determinations were similar in all toxicity studies

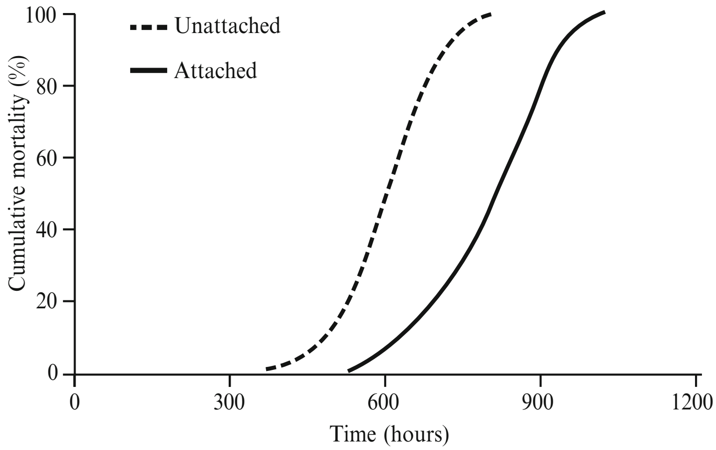

Fig. 8.7 Cumulative mortality (%) of attached and unattached *M. leucophaeata* at 1 mg/L chlorine concentration (modified after Rajagopal et al. 2005a)

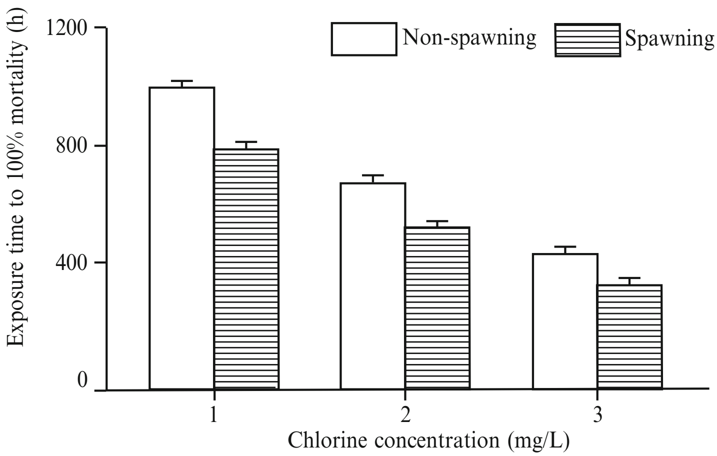

Fig. 8.8 Time required for 100% mortality of spawning and non-spawning *M. leucophaeata* at different chlorine concentrations (modified after Rajagopal et al. 2002a).

8.1.4 Spawning Season

Physiological status of the organisms is also an important factor that influences chlorine toxicity. Research using a number of organisms has shown that chlorine toxicity is significantly higher during breeding seasons than during non-breeding seasons. Mussels collected during the spawning season and those collected during non-spawning season behave quite differently with respect to their sensitivity to chlorine (Fig. 8.8). Mussel species collected during their spawning season were less tolerant to chlorine, while those collected during the non-spawning season were more tolerant. The difference in tolerance between the two groups was nearly 29% (Rajagopal et al. 2002a). Kilgour and Baker (1994) and Jenner et al. (1998), who reported similar results for *D. polymorpha*, attribute the greater tolerance of mussels during the non-spawning season to low metabolic rates and reduced filtration rates, which would result in reduced exposure to the toxicant. Lower energetic demands during non-breeding seasons may be the reason for reduced toxicant uptake. On the other hand, mussels tend to be weaker after spawning when they have little energy reserves in the body (Bayne et al. 1976), with the result that they are less tolerant to biocide. The data point to the importance of judicious selection of test animals while carrying out toxicity experiments using seasonal breeders.

8.1.5 Fed vs. Non-Fed Mussels

Status of feeding may have an effect on the toxicity of chlorine to organisms. Kilgour and Baker (1994) showed that mussels *D. polymorpha*, when maintained on a diet of *Chlorella*, were consistently more sensitive to hypochlorite than starved mussels. The effect was attributed to active water filtration, which increases the exposure of their body parts to chlorine. Mussels, which are fed with microalgae, are likely to filter more water than those which are unfed. On the other hand, Rajagopal et al. (2003b) showed that in the case of the mussel, *P. viridis*, fed and starved individuals showed similar mortality rates when exposed to chlorine. It must be borne in mind that chlorine may act as a strong suppressant of filtration activity in bivalve mussels. This has been shown by Rajagopal et al. (1997b) using Mussel-Monitor®, an automated instrument with which one can remotely monitor the opening and closing of mussel shells (Jenner et al. 1998; Rajagopal et al. 1997b, 2003a). Shell valve movement of *M. leucophaeata* tested with unfiltered brackish water from the Noordzeekanaal in The Netherlands showed little or no filtration in the presence of 1 mg/L residual chlorine. Obviously, presence of microalgae would have no significant effect on *M. leucophaeata* at a residual chlorine concentration of 1 mg/L. Rajagopal et al. (2002e) have also shown that filtration activity in *D. polymorpha* stops almost completely at residual chlorine level of 0.5 mg/L and higher.

8.1.6 Acclimation Temperature

Temperature is yet another important factor that influences the sensitivity of organisms to chlorine. Mussels acclimated to different temperatures show significantly different tolerances to chlorine. Decrease in acclimation temperature from 30 to 5°C increases chlorine tolerance (at 0.5 mg/L residual chlorine) of *M. leucophaeata* by 52 days. Such increase in chlorine tolerance at lower acclimation temperatures has also been reported for other mussel species such as *D. polymorpha* (Van Benschoten et al. 1995; Rajagopal et al. 2002c) and *M. edulis* (Lewis 1985; Jenner et al. 1998). However, at acclimation temperatures above 35°C, temperature has overriding effects, when compared to chlorine. Harrington et al. (1997) showed that at 36°C, combined use of temperature and chlorine resulted in mortality of *D. polymorpha* at rates similar to that obtained with heat alone.

8.2 Mode of Chlorination

Various types of chlorination (continuous, semi-continuous and discontinuous) are used in industrial cooling water systems, largely due to cost factors and the need to reduce discharge levels (Claudi and Mackie 1994; Jenner et al. 1998). A review of literature indicated that majority of industries which follow intermittent chlorination use from 1 to 4 h chlorination, followed by up to 8 h break cycle, depending on the water temperature and breeding season of mussels (Claudi and Mackie 1994; Rajagopal et al. 1996, 2010; Jenner et al. 1998). At Maasvlakte power station (Rotterdam, The Netherlands), an intermittent chlorine regime of 4 h on and 4 h off (0.2–0.3 mg/L TRC) is used to control mussel fouling (Jenner et al. 1998). Rajagopal et al. (2003a) have selected 4 h chlorination followed by 4 h break cycle in order to assess the effects of intermittent chlorination on *M. leucophaeata*. While adult mussels of *M. leucophaeata* can be killed in 588 h under continuous chlorination (*M. leucophaeata*), similar doses applied intermittently failed to achieve any significant mortality (Fig. 8.9). Although chlorine concentrations as high as 3 mg/L were used in the experiment, *M. leucophaeata* was able to protect themselves against chlorine by closing their shell valves, surviving for long periods. Data of Rajagopal et al. (2003a), therefore, indicate the inherent limitation of intermittent chlorination (4 h on and 4 h off cycle) in situations where mussels are involved. It may be possible that organisms other than mussels, which do not have the capacity to seal off their body parts against toxic environment, will succumb to intermittent chlorination much earlier than mussels (Fisher et al. 1999; Rajagopal et al. 2002d, 2010).

Literature data on the efficacy of intermittent chlorine treatment programme to control mussel fouling are conflicting. At the Martigues-Ponteau plant on the French Mediterranean coast, hypochlorite injection for 1 h every 8 h at 2.5–3.0 mg/L was successful against mussels, *Mytilus galloprovincialis* (Jenner et al. 1998). Turner et al. (1948) and Anderson and Richards (1966) observed that intermittent chlorination was not effective in preventing settlement and growth of *M. edulis* in power station cooling circuits. Similar data were also presented by James (1967) for the Carmarthen Bay power station, England (*M. edulis*), by Khalanski and Bordet (1980) for the Dunkerque power station, France (*M. edulis*), by Jenner (1985) for the Maasvlakte power station, The Netherlands (*M. edulis*), by Rajagopal et al. (2003a) for the Velsen and Hemweg power stations, The Netherlands (*M. leucophaeata*) and by Rajagopal (1997) and Rajagopal et al. (1997a, 2003b, 2006b) for the Madras Atomic Power Station, India (*P. viridis*, *Perna perna*, *Brachidontes striatulus*, *Brachidontes variabilis* and *Modiolus philippinarum*). It is reported that in food-rich environment, intermittent chlorination lasting for a few hours per day or a few days per month even at higher concentrations (3–5 mg/L) does not kill mussels

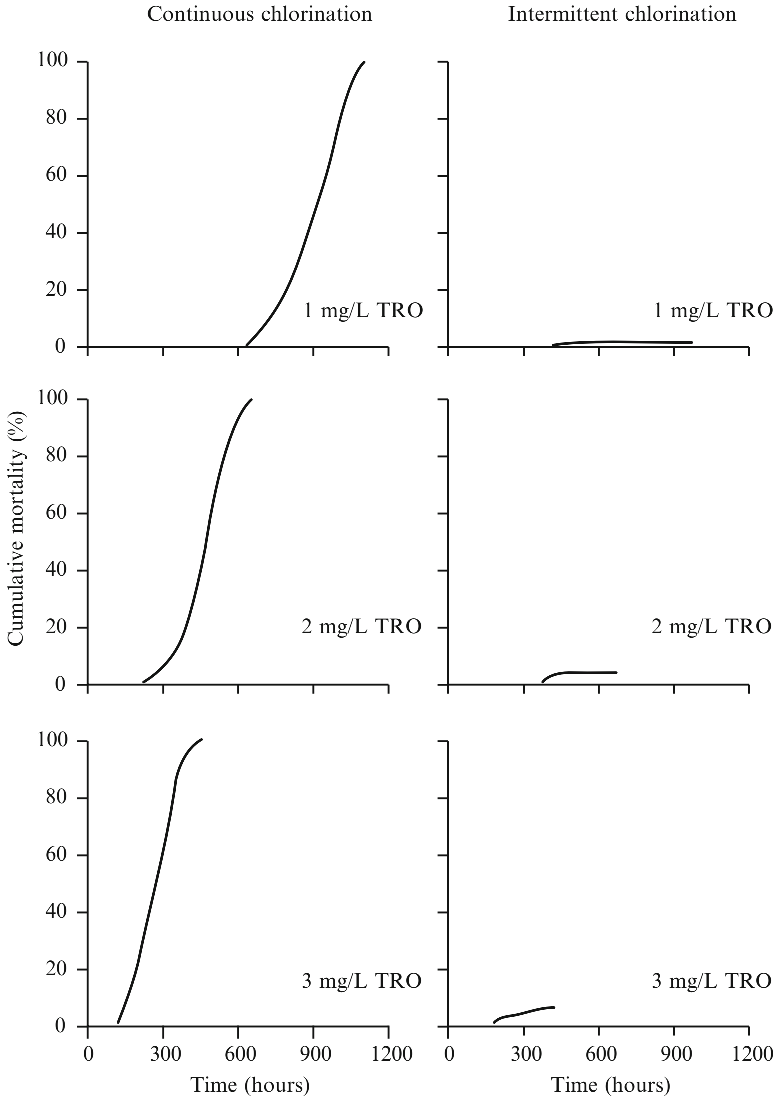

Fig. 8.9 Cumulative mortality (%) of *M. leucophaeata* subjected to continuous and intermittent chlorination at different concentrations (modified after Rajagopal et al. 2003a)

because the mussels close their shell valves during chlorine treatment and start feeding a few minutes after chlorination is stopped (Lewis 1985; Rajagopal 1997; Rajagopal et al. 2010). On the contrary, similar treatment in food-poor waters (e.g. Martigues-Ponteau plant) may effectively control mussel growth by trophic limitation (Jenner et al. 1998). Therefore, knowledge about the trophic status of the site would be helpful in predicting whether intermittent chlorination would be effective against bivalve mussels. Due to the somewhat conflicting literature on mussel control,

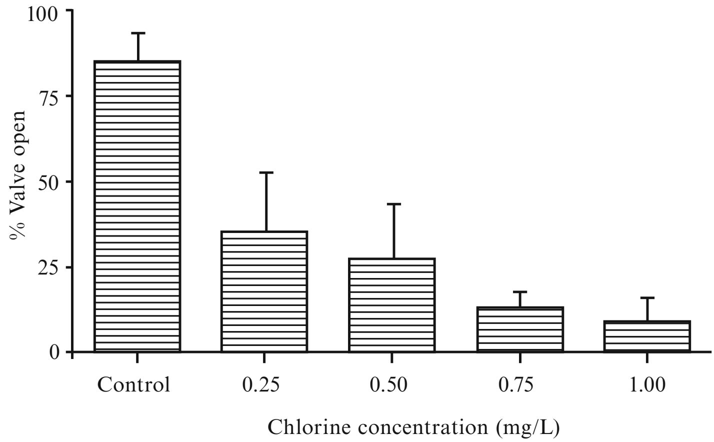

Fig. 8.10 Mean percentage shell valve opening of *M. leucophaeata* at different chlorine concentrations and control experiments (modified after Rajagopal et al. 2002a)

it would be worthwhile to investigate whether intermittent chlorination will be able, and under what conditions, to control mussel fouling under actual operating conditions. It must be borne in mind that while shell valve opening under chlorination permits the mussel to feed, it also entails a risk that the soft tissues are exposed to the toxic environment (Rajagopal et al. 2002b). Since shell valve opening during chlorination would be the major factor deciding the survival of mussel specimens, Rajagopal et al. (2003a) used a Mussel-monitor® to supplement mortality data of *D. polymorpha*, *M. leucophaeata* and *M. edulis* along with filtration rate, foot activity index and byssus thread production. These are excellent indicators of the propensity of the mussel to open its valves during chlorination (Fig. 8.10). Mussel-monitor® data showed that, as compared to control, the valve activity of *M. leucophaeata* decreased more than 85% (Fig. 8.10), when exposed to 1 mg/L chlorine concentration (Rajagopal et al. 2003a).

The response of mussels to intermittent chlorination is quite different from that to continuous chlorination. It is well known that chlorination adversely affects the pumping rate, feeding, shell opening and byssus production in mussels, and therefore, growth rate is reduced (Rajagopal 1991; Bidwell et al. 1999). However, in intermittent chlorinated waters, recuperation of mussels is possible, because during the breaks in chlorination they can actively feed and produce byssus threads (Klerks and Fraleigh 1991; Rajagopal et al. 1996; Jenner et al. 1998). Lewis (1985) reported that in *M. edulis*, 20 days of starvation during chlorination could be compensated by 1 day of feeding under good conditions. To make matters worse, high flow conditions that exist in power plant cooling circuits invariably ensure increased food availability and removal of metabolic wastes (Perkins 1974; Neitzel et al. 1984). Therefore, mussels can easily compensate any resource drain caused by short-term chlorination (Rajagopal et al. 1991a; Jenner et al. 1998). However, in continuously chlorinated waters (Fig. 8.9), mussels are forced to shut their valves and exist on stored food reserves and anaerobic respiration, until energy resources are depleted or metabolic wastes reach a toxic level (Lewis 1985; Rajagopal et al. 1991b). Obviously, regular breaks in chlorination would allow mussels to recuperate their energy losses. Intermittent chlorination regimes practiced in some power stations need to be reexamined in the light of experimental results presented by Rajagopal et al. (2003a, 2010).

9 Concluding Remarks

Chlorine, despite its many shortcomings, continues to enjoy prime position as an antifouling biocide in cooling water systems. Chlorine administration is done based on the anticipated type and intensity of fouling at a given location. Accordingly, different types of dosing regimens are employed such as intermittent, continuous, semi-continuous, pulsed, etc. Recent data indicate that newer method of chlorine administration may help reduce the chlorine inventory and thereby reduce the environmental burden caused by discharge from power plant cooling systems. Data available in the literature show that various factors can influence the sensitivity of organisms to chlorine. Among the parameters, fouling species, animal size, spawning season, acclimation temperature, trophic status and status of attachment seem to have significant influence on chlorine tolerance.

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Chapter 9
Chlorination Chemistry and Ecotoxicology of the Marine Cooling Water Systems

Michel Khalanski and Henk A. Jenner

1 Introduction

Since 1893, when chlorine was applied for the first time at a plant in Hamburg (Germany), chlorination has been used for disinfection of drinking water. It is still largely used as a powerful oxidising agent for bleaching and water treatments such as taste and odour control, disinfection of tap water and waste water in the food industry and for biofouling control. Of all the disinfectants, it is certainly the most extensively studied with regard to chemistry, toxicity and ecotoxicity (White 1999; Jolley 1976; Jolley and Carpenter 1983; Jolley et al. 1978, 1980, 1985, 1990). Due to its well-tried technology, its long term worldwide industrial use and its acceptable cost, chlorine remains the most common antifouling treatment to date.

The major environmental concern regarding chlorination is the production of numerous compounds formed by complex reactions between chlorine and mineral or organic constituents present in natural waters. Some of them are persistent and have been proved or suspected to be toxic, mutagenic or carcinogenic for animals or humans on a long-term exposure basis. As a consequence, guidelines have been established by the World Health Organisation for the chlorination by-products in drinking waters (WHO 1993), and limit concentrations for these substances have been implemented in national regulations. On the other hand, the use of chlorine to control the development of the biofouling in cooling water systems (CWS) is submitted to restrictions by national or local regulations which impose limit concentrations in the chlorinated effluents, or even it is totally banned. If the environmental aspects of the chlorination of fresh water were relatively known, it appeared in the

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middle of 1970s that we missed knowledge on the chemistry of the chlorination of seawater and on the effects of the discharges of chlorinated seawater on the marine biota (Block et al. 1977). Many research programmes were undertaken between 1980 and 1990.

The operators of once-through marine power stations, equipped with large CWS requiring as much as hundreds of m^3/s of seawater, developed impact assessment studies focused on the low-level chlorination process used to protect the CWS against the excessive development of biofouling.

In this chapter, an overview is presented of the basic knowledge on the chemistry and ecotoxicology of oxidants and halogenated organic compounds formed by the chlorination of seawater and its applications to anti-fouling treatments of CWS.

In particular, some experimental and field data collected at European marine power stations are summarised in order to characterise the oxidants and the main halogenated organic compounds formed in the cooling water, to quantify their production and to assess their toxicity to the marine biota. Majority of the data we used come from a collaborative study conducted at ten marine power stations in the United Kingdom, France and the Netherlands (Jenner et al. 1997), a general synthesis on cooling water treatments in European power stations (Jenner et al. 1998) and recent studies carried out at EDF R&D (Allonier 2000; Khalanski 2003).

2 Chlorination Procedures for Marine CWS

Chlorination of seawater is still considered to be one of the most effective available technologies for the control of micro- and macrofouling organisms. The chlorination of marine CWS has two main objectives:

(a) To control the settlement and growth of marine biota in CWS and to avoid the blockage of heat exchangers (condensers and auxiliary heat exchangers) by detachment of shells or hard parts of the "biofouling".
(b) To control the development of bacterial slime on condenser tubes and auxiliary heat exchangers, and to maintain maximum heat transfer capacity for optimal plant efficiency.

Chlorination is an effective disinfection method to eliminate thermophilic bacteria, potentially pathogenic, such as halophilic vibrios, which can be produced in the biofilms located in some parts of the CWS.

Claudi and Evans (1993) defined four chemical treatment strategies to eliminate macrofouling in freshwater CWS:

(a) End-of-season to kill the macrofouling at the end of the settlement period; it is only convenient when plant operation is not threatened by the excessive development of fouling; *which is only the case for freshwater cooled power stations and certainly not for the majority of marine power stations*.
(b) Periodic treatments can be applied if a critical density of fouling is reached in the system before the "end-of-season"; *which is in general only applicable in freshwater cooling systems*.

(c) Intermittent treatments, every day or every 3 days e.g. for some minutes to 1 h; *this method must be applied over all the settling season of the target species and must be monitored carefully to avoid unexpected clogging problems*.

(d) Continuous dosing of chemical biocide at low-level is effective to stop the settlement of larvae, to drastically reduce the growth of settled individuals and finally to kill them in the long-term; *this approach can be dangerous because low-level means that the hypochlorite* (*dosing*) *concentration during the breeding seasons of particular fouling species should be high enough for a continuous toxic effect. Only adequate monitoring of the biofouling settlement and growth can give reliable insight in to the overall antifouling effect*.

Discontinuous chlorination procedures can be efficient in waters containing low amounts of organic matter. In a lot of European marine coastal areas enriched in nutrients from terrestrial inputs, the plankton and benthos productivity reaches high levels, favouring the growth of macrofouling species. The settlement period of the different species (mussels, oysters, barnacles, hydroids, tube worms, etc.) extends over several months a year. The settled individuals grow very fast in the eutrophic habitats and only continuous chlorination treatments or Pulse-Chlorination® can be effective.

A review of the European experience in anti-fouling treatments applied to marine power stations has shown that low-level continuous or semi-continuous chlorination procedure is effective against macrofouling and can generally control slime development (Jenner et al. 1998). Low-level continuous chlorination consists in chlorinating the CWS while the macrofouling species can settle and grow; in most of European countries for 6–9 months of a year, from the spring to the fall. Chlorine is added to the cooling water at a dosage of 0.5–1.0 mg/L to a level ≥0.25 mg/L on all the sections of the CWS to be protected, until the outlet of the condenser.

Experiments made on the marine mussel *Mytilus edulis* (Khalanski and Bordet 1981), and on the freshwater zebra mussel *Dreissena polymorpha* (Wiancko and Claudi 1994) have shown that brief, frequently repeated chlorine shocks reduce dramatically their filtration rate. The mussels cannot recover their filtration capacity when the treatment is suspended for less than 1 h. In the Netherlands, the development by KEMA, RIVM and TNO of the valve movement monitor, confirmed the inhibition of the valve movement and measured the recovery of the normal activity to optimise a Pulse-Chlorination® procedure. Compared with continuous chlorination, this procedure can achieve at least 50% reduction of hypochlorite consumption, and it has been implemented at number of power stations world wide.

Both low-level chlorination procedures are generally effective for controlling the slime inside heat exchangers except at sites where the development of the bacterial biofilm is very high. In that case, condensers are equipped with automatic mechanical cleaning systems based on passage of rubber (abrasive) sponge balls to remove the slime.

To minimise the residual oxidant concentration at the outfall of CWS, and to comply with EPA regulation, a specific method called Targeted Chlorination was developed in the US to control the slime development in the condensers of power stations.

Targeted Chlorination consists in to chlorinate alternatively each section of a condenser for a few minutes each day at a high chlorine dosage (>10 mg/L as Cl_2/L). The mixing of the chlorinated water with the much larger amount of non-chlorinated water reduces the residual oxidant concentrations below the detection limit at the end of the discharge pipe. This procedure, requiring special equipments (Mussali et al. 1985), was found effective to control the bacterial slime (Moss et al. 1985).

Two main sources of chlorine are commonly used on CWS: dissolution of chlorine gas or addition of a Na-hypochlorite solution which may be stored on site or produced by electrolysis of seawater. At marine power stations, where large amounts of chlorine (up to tens of tons a day) are required to treat cooling water, electro-chlorination enables on site production of Na-hypochlorite following the global reaction:

$$NaCl + H_2O \rightarrow NaOCl + H_2 \tag{9.1}$$

Generally, the transit time of chlorinated seawater in CWS at power stations does not exceed 10–20 min from the water intake to the outfall. In some specific cases, when long intake or discharge pipes or canals exist, this time can be extended to some tens of minutes.

3 Chemistry of Oxidising Species

3.1 Terminology and Measurement Methods

In actual practice, regarding the oxidising chemical species formed by chlorination of saline waters, containing bromide ions at relatively high concentrations, three major categories are classified: free oxidants, combined oxidants and total oxidants.

1. Free oxidant means hypochlorous acid (HOCl) and hypobromous acid (HOBr) and their dissociated forms hypochlorite ion (OCl^-) and hypobromite ion (OBr^-). The ions are less effective as disinfectants that non-dissociated acids.
2. Combined oxidants include the chlorinated and brominated amines. These halo-amines are all oxidising substances.
3. Total oxidant is the sum of 1 and 2.

Residual oxidant is the pool of oxidising compounds persisting after the "chlorine demand" has been met. In natural waters with low concentrations of bromide, residual oxidants include free residual chlorine, combined residual chlorine and total residual chlorine (TRC). In saline waters, it is more appropriate to designate the residual compounds as residual oxidants which bring together the forms chlorinated and brominated. TRO means Total Residual Oxidants.

Chlorine demand is defined as the difference between the amount of chlorine added (dosage) and the residual chlorine remaining at the end of a specified contact time.

When using oxidant terminology, it is important to remember that the instrument or method used for measurement was almost certainly developed and calibrated for chlorine and that (strictly) the result should be expressed as “mg/L TRO as Cl_2”. Generally, the calibration curve is drawn for free chlorine in HOCl-dominant solutions, which means that chloramines, bromamines and brominated oxidants are measured as free chlorine equivalents.

To summarise, it is more precise and thus preferable in most situations to use the term residual oxidant prefaced by free, combined or total as appropriate, with “as Cl_2” implicitly understood.

3.2 Free Oxidant Chemistry

Chlorine added to water hydrolyses very rapidly to produce a mixture of hypochlorous acid (HOCl) and hypochlorite ions (OCl^-):

$$Cl_2 + H_2O \rightarrow HCl + HOCl \tag{9.2}$$

$$HOCl \rightarrow H^+ + OCl^- \tag{9.3}$$

If the source of chlorine is sodium hypochlorite or calcium hypochlorite, hypochlorite ions are directly formed in solution:

$$NaOCl \rightarrow Na^+ + OCl^- \tag{9.4}$$

$$Ca(OCl)_2 \rightarrow Ca^{++} + 2OCl^- \tag{9.5}$$

In brackish- and seawater, the added chlorine will oxidise bromide ions present at relatively high concentrations (ca. 65 mg/L in seawater) to form hypobromous acid and hypobromous ions as follows:

$$HOCl + Br^- \rightarrow HOBr + Cl^- \tag{9.6}$$

$$HOBr \rightarrow H^+ + OBr^- \tag{9.7}$$

In seawater the overall reaction with 99% conversion within 10 s at full salinity and within 15 s at half salinity is complete in approximately 10 s (Hergott et al. 1978).

Hypochlorous acid and hypobromous acid are both weak acids, but they have very different dissociation constants Ka = [H^+] [OX^-]/[HOX]:

$$\text{HOCl: Ka} = 3.210^{-8}\,\text{M.l}^{-1}\text{at } 25^{\circ}\text{C} \quad \text{(Morris 1966)}$$

$$\text{HOBr: Ka} = 2.0610^{-9}\,\text{M.l}^{-1}\text{at } 25^{\circ}\text{C} \quad \text{(Farkas et al. 1949)}$$

For a given pH value, HOBr ionises tenfolds less than HOCl (Fig. 9.1). Since non-ionised oxidants are more effective in disinfection or biofouling control (probably due to easier membrane transport of the uncharged molecule), the free bromine present in seawater at pH 7.9–8.3 is more effective than the free chlorine at the same pH range.

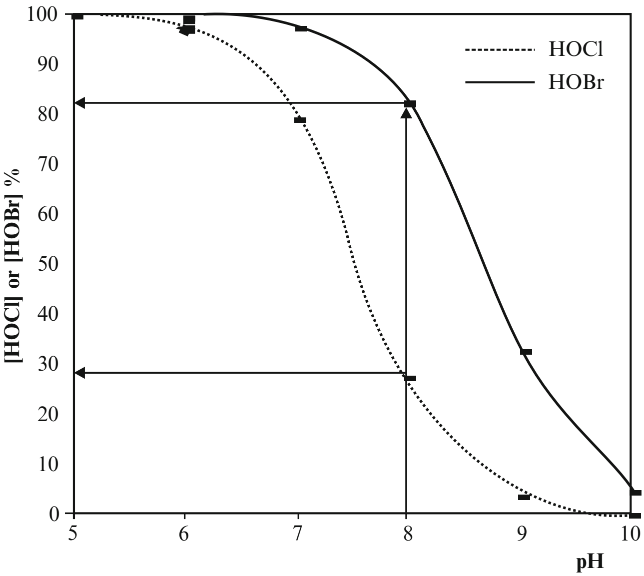

Fig. 9.1 Comparison of the dissociation of hypochlorous acid and hypobromous acid with changing pH at 20°C

3.3 Formation of Combined Oxidants by Reactions with Ammonia and Amines

Hypochlorous acid and hypobromous acid react with ammonia and nitrogen-containing organic compounds to form halamines: chloramines and bromamines. The reaction with ammonia and amines proceeds by sequential substitution of each of the hydrogen atoms as follows:

– With hypochlorous acid

$$NH_3 + HOCl \rightarrow NH_2Cl + H_2O\,(\text{monochloramine}) \tag{9.8}$$

$$NH_2Cl + HOCl \rightarrow NHCl_2 + H_2O\,(\text{dichloramine}) \tag{9.9}$$

$$NHCl_2 + HOCl \rightarrow NCl_3 + H_2O\,(\text{trichloramine / nitrogen trichloride}) \tag{9.10}$$

– With hypobromous acid

$$NH_3 + HOBr \rightarrow NH_2Br + H_2O\,(\text{monobromamine}) \tag{9.11}$$

$$NH_2Br + HOBr \rightarrow NHBr_2 + H_2O\,(\text{dibromamine}) \tag{9.12}$$

$$NHBr_2 + HOBr \rightarrow NBr_3 + H_2O\,(\text{tribromamine / nitrogen tribromide}) \tag{9.13}$$

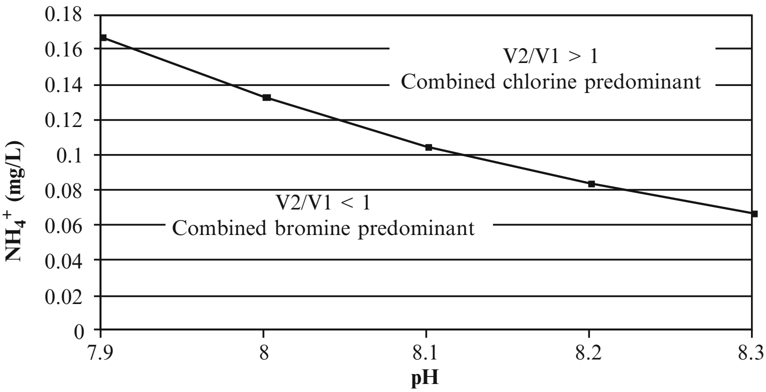

Fig. 9.2 Formation of monochloramine and combined bromine species depending on seawater pH and initial ammonia concentration at 20°C

Organic chloramines and bromamines are formed by similar reactions of HOCl or HOBr on nitrogen-containing organic compounds such as amino acids.

In seawater with relative high ammonia concentrations (low Cl_2/N ratio), or in estuarine waters of lower bromide and high ammonia concentrations, the rate of formation of chlorinated and brominated oxidants can be nearly equal and a mixture of halamines would be expected, as indicated by the following reactions (Jolley and Carpenter 1983):

$$NH_2Cl + HOBr \rightarrow NHBrCl + H_2O \tag{9.14}$$

$$NHBrCl + HOBr \rightarrow NHBr_2Cl + H_2O \tag{9.15}$$

The terms "combined (residual) chlorine", "combined (residual) bromine" or "combined (residual) oxidant" refer to such halogenated nitrogen compounds.

Although the oxidation of bromide ions by the hypochlorous acid is very rapid, this reaction is in competition with the reaction of hypochlorous acid with ammonia nitrogen. The formation of monochloramine depends on the kinetics of these reactions (Doré 1989):

$$HOCl + Br^- \rightarrow HOBr + Cl^- \quad V_1(M.s^{-1}) = K_1.[HClO].[Br^-], K_{1-20^\circ C} = 3.110^3.M^{-1}\ s^{-1}$$

$$NH_3 + HOCl \rightarrow NH_2Cl + H_2O \quad V_2(M.s^{-1}) = K_2[HClO].[NH_3], K_{2-20^\circ C} = 5.810^6.M^{-1}\ s^{-1}$$

At a given temperature, V_2/V_1 depends on pH and ammonium content as shown in Fig. 9.2. The formation of monochloramine occurs at high pH and high ammonium concentrations, when $V_2/V_1 > 1$.

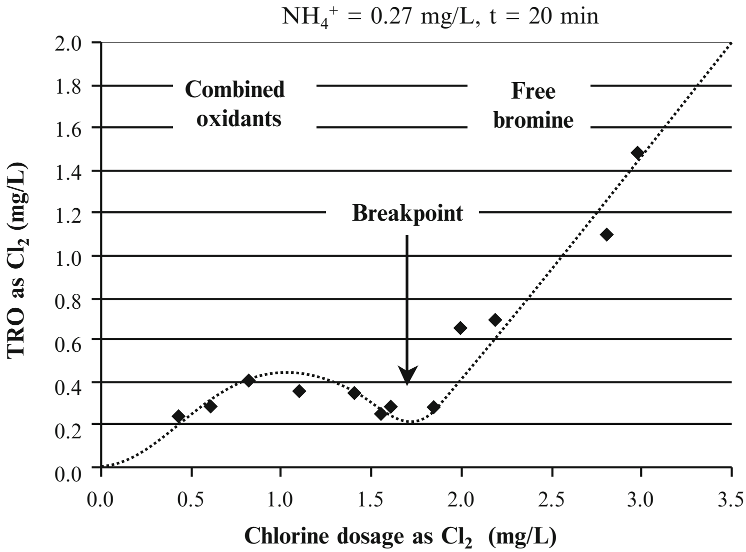

Fig. 9.3 Breakpoint curve in seawater collected at Gravelines (French North Sea coast) Salinity = 34.1‰, pH = 8.1. TRO measured by colorimetric DPD. The theoretical breakpoint value is pointed by an arrow at a Cl_2/N-N molar ratio of 1.5 corresponding to a chlorine dosage of 1.6 mg/L

At a given temperature, V_2/V_1 depends on pH and ammonia content as shown in Fig. 9.2. The formation of monochloramine is predominant at high pH and high ammonia concentrations, when $V_2/V_1 > 1$.

In seawater, at relatively stable pH and bromide concentration (pH 8.1–8.3, salinity 31–35 g/L) the chlorine-to-ammonia molar ratio is the main factor which directs the formation of halamines. Thus, the three halamines (i.e. $NHCl_2$, NH_2Br and $NHBr_2$) dominate at Cl_2/N ratios <1.5. At pH 8.1, monochloramine cannot be formed at NH_4^+ concentration <0.1 mg/L.

Ammonia present in the chlorinated waters is supposed to be completely oxidised by the chlorine or bromine according to the overall reactions:

$$3Cl_2 + 2NH_3 \rightarrow N_2 + 6Cl^- + 6H^+ \tag{9.16}$$

$$3Br_2 + 2NH_3 \rightarrow N_2 + 6Br^- + 6H^+ \tag{9.17}$$

Halamines disappear and the TRO decreases to a so-called minimum "breakpoint" value theoretically located at the chlorine-to-ammonia molar ratio of 1.5. At molar ratio >1.5, only free oxidants would exist: HOCl or HOBr. In fact, a mixture of residual oxidants persist at the breakpoint at least for reaction times of tens of minutes or so, and NBr_3 could be found at ratios ≥1.5 and associated with HOBr and OBr^- (Courtot and Peron 1979). However, chlorination of seawaters produces breakpoint curves very similar to those observed on freshwaters as shown in Fig. 9.3, and the minimum of the curve is located close to the theoretical break point.

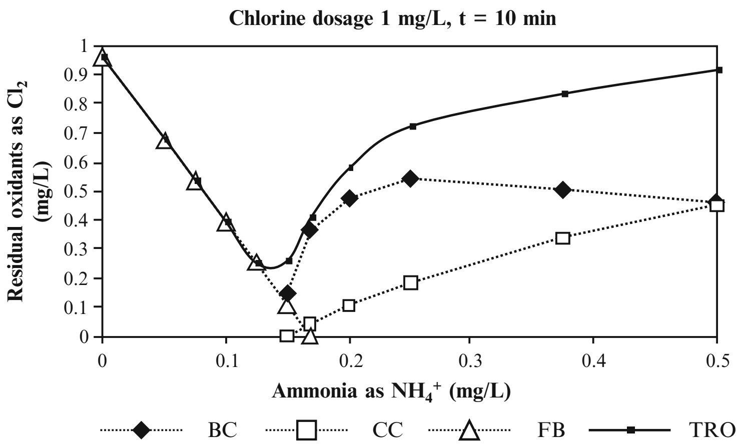

Fig. 9.4 Evolution of free bromine (FB), combined bromine (CB), combined chlorine (CC) and total residual oxidants (TRO) in seawater with increasing ammonia concentrations. Data from Fiquet (1984, 1985)

An experimental study on seawater collected on the English Channel coast (pH 8.0, salinity 31.6 g/L) was conducted by Fiquet (1984, 1985). The water was treated to have a very low chlorine demand and was enriched in ammonia, in order to provide data on the formation and decomposition of halamines after chlorination at 1 mg/L. Combined bromine—brominated amines and combined chlorine—chlorinated amines formation is observed at $NH_4^+ > 0.17$ mg/L (chlorine-to-ammonia molar ratio $R < 1.5$). However, combined bromine predominates on combined chlorine up to $NH_4^+ = 0.50$ mg/L (Fig. 9.4). In reality, the ammonia content in natural waters never reaches such a high level and combined chlorine will stay below the combined bromine concentration. This experiment supplies another important result concerning the temporal formation of halamines, which is very fast (Fig. 9.5).

Unlike monochloramine added to the seawater that is relatively stable, bromamines and chloramines formed by chlorination disappear quickly. The kinetics of disappearance of combined bromine and combined chlorine depends on the ratio Cl_2/N, it is maximum near the breaking point. In their study on the kinetics of decomposition of monochloramine in presence of bromide, Trofe et al. (1980) have found that the decomposition of monochloramine in ammonia is a relatively slow process, whereas monobromamine reacts rapidly with monochloramine to produce a mixed halamine (bromochloramine):

$$2H_2O + NHCl_2 + 2Br^- \rightarrow NH_3 + 2HOBr + 2Cl^- \text{(slow reaction)} \quad (9.18)$$

$$NHBr_2 + NHCl_2 + H_2O \rightarrow NHBrCl + NH_2Br + Cl^- + OH^- \text{(fast reaction)} \quad (9.19)$$

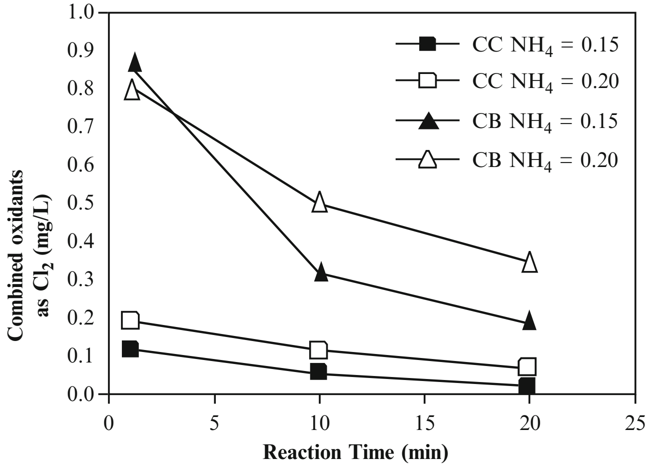

Fig. 9.5 Decomposition of CC and combined bromine (CB) in 20 min after chlorination at $Cl_2 = 1$ mg/L and for two ammonia concentrations: $NH_4^+ = 0.15$ mg/L and $NH_4^+ = 0.20$ mg/L. Experimental data of Fiquet (1984, 1985)

Fiquet (1984) suggested that the monochloramine can be destroyed by the overall reaction with dibromamine:

$$NHBr_2 + NH_2Cl \rightarrow N_2 + 2HBr + HCl \tag{9.20}$$

However, the chloramines are much more persistent in freshwaters. Despite a lower acute toxicity, they are quite useful in open recirculating cooling tower systems (see Dotson and Helz 1984).

4 Chemistry of Chlorination By-Products

4.1 Terminology and Measurement Methods

Chemical species generated by reactions of oxidation, addition and substitution with organic matters are called chlorine by-products (CBPs). When applied to chlorination of saline waters, this term refers to a huge number of chlorinated and brominated compounds. Among them several categories have been identified and quantitatively measured in low-level chlorinated cooling water of coastal power stations (Jenner et al. 1997; Allonier et al. 1999b; Allonier 2000; Taylor 2006).

4.1.1 Organohalogens (OX)

They can be measured globally by an electro-chemical method: micro-coulometry of halogens. Three categories have been defined depending on their physical and chemical properties:

(a) *Purgeable organohalogens* (*POX*) are all volatile compounds which can be purged from the water to be analysed by a gas flow; the trihalomethanes (THMs) represent generally the major proportion of POX.
(b) *Absorbable organohalogens* (*AOX*) designates all the heavy non-volatile organohalogens as well as some volatile compounds, absorbable on activated carbon. If the AOX measurement is performed after elimination of the volatile compounds, AOX represents only the non-volatile compounds and total organohalogens. TOX is the sum of AOX and POX.
(c) *Extractable organohalogens* (*EOX*) designates organohalogens extracted in an organic solvent. As for the AOX, some of the volatile compounds may persist in the extract, so that EOX represents the sum of non-volatile compounds and some volatile compounds.

In fact POX and AOX are difficult to measure in natural waters due to the matrix with relative high concentrations of chloride ions (>1 g/L). EOX was specially developed for measurements in solutions and is used for chlorinated seawater.

4.1.2 Trihalomethanes (THMs)

Chlorine and bromine react with a lot of organic substrates (phenolic compounds, aromatic acids, ketons) to produce chlorinated and brominated methane (Doré 1989): chloroform: $CHCl_3$, bromodichloromethane (BDCM): $CHBrCl_2$, chlorodibromomethane (CDBM): $CHBr_2Cl$ and bromoform: $CHBr_3$. All of them are more or less volatile and they are currently measured by gas chromatography using a purge-and-trap extraction.

4.1.3 Haloacetic Acids

Haloacetic acids are, with the THMs, among the most frequently found CBPs in chlorinated waters (Miltner et al. 1990). They are formed not only by reactions with organic compounds but also by hydrolysis of haloacetonitriles. In chlorinated seawaters, two brominated acetic acids have been frequently identified: monobromoacetic acid (MBAA): $BrCH_2COOH$, dibromoacetic acid (DBAA): $Br_2CHCOOH$. Haloacetic acids are polar compounds not sufficiently volatile to be extracted by the purge-and-trap method; they need to be extracted in solvents such as pentane, hexane, methyl-tertiary-butyl-ether (MTBE) or ethyl acetate (Allonier 2000). They are separated and measured by GC/MS.

4.1.4 Haloacetonitriles

Haloacetonitriles are notably formed by reactions with amino acids (Doré 1989). In chlorinated seawater, dibromoacetonitrile (DBAN): Br_2CHCN has been found (Jenner et al. 1997). Haloacetonitriles are extracted in ethyl acetate after acidification and measured by GC/MS (Allonier et al. 1999a).

4.1.5 Halophenols

They are measured by GC/MS after derivation with acetic anhydride, extraction and concentration (Allonier et al. 1999a).

4.1.6 Bromate

In freshwater, column liquid ion-chromatography techniques usually achieve detection limits ranging between 5 and 10 μg/L, but in seawater in presence of chloride ions (Cl^- = 20 g/L) the classical methods suffer from poor sensitivity, with a quantification limit of 5 mg/L as BrO_3^-. It means that bromate ions cannot be measured by this way in coastal waters where the chlorinated effluents are highly diluted and measurements are only possible in the hypochlorite solution prior to mixing into the cooling water (IARC 1986). However, a new technique using anion-exchange chromatography and coupled plasma mass-spectrometry (IC-ICP-MS) has been developed to avoid the interference of chloride, which has detection limit of 2–3 μg/L in seawater samples (Chen et al. 2007). With this method, it is possible to detect traces of bromate in marine waters.

4.2 Bromoform

Using an experimentally determined Henry's law constant, Lyman et al. (1982) calculated a volatilisation half-life of 7 h for a model river (1 m deep, flow: 1 m/s, wind velocity: 3 m/s). Mattice et al. (1981) reported an experimental half-life of bromoform in seawater of 7 h. Stewart et al. (1979) found a bromoform half-life of 17 h in a natural, well-mixed seawater body of 1 m depth. Both authors consider the loss of bromoform to be caused by volatilisation.

Helz and Hsu (1978) proposed a simple model to estimate the volatilisation of THMs from sea water, depending on a constant rate coefficient and the water depth. In a well-mixed water mass, the THM concentration can be calculated using the following equation:

$$C_t = C_0 \exp(-k_1 t / L), \tag{9.21}$$

Where, C_t = concentration at time t, C_0 = initial concentration at time 0, L = mean water depth in cm, k_1 = transfer coefficient in cm/h, t = time in hour. Half-life ($t_{1/2}$) in hours = ln(0.5)*L/−k_1

Table 9.1 Half-lives (days) of THMs in seawater for increasing water depths according the kinetics model of Helz and Hsu (1978)

		Mean water depth (m)			
THM	K_1 (cm/h)	5	10	20	50
$CHBr_3$ (bromoform)	4.1	3.52	7.04	14.09	35.22
$CHBr_2Cl$ (DBCM)	6.8	2.12	4.25	8.49	21.24
$CHBrCl_2$ (BDCM)	8.9	1.62	3.25	6.49	16.23
$CHCl_3$ (chloroform)	11.4	1.27	2.53	5.07	12.67

The volatilisation process kinetics is very sensitive to depth as shown in Table 9.1. The half-life of the three brominated THMs (Bromoform, DBCM, BDCM) in shallow littoral waters (5–10 m depth) does not exceed 1 week, whereas it reaches 3–4 weeks in deep areas (50 m depth).

Adsorption to sedimentary material is probably limited, because of the low log K_{ow}. Using the estimated log K_{ow}, a relatively low log BCF of about 1.6 is estimated for bromoform in whole fish (Lyman et al. 1982). Hydrolysis and photo-degradation were not expected to be important processes. A hydrolysis half-life of 686 years was calculated using QSARs by Mabey and Mill (1978) which is in sharp contrast with the results of Bouwer and McCarthy (1984) from anaerobic tests with a methanogenic biofilm column. They observed that more than 99% was removed after a 2-day retention time and no biodegradation was found. However, aerobic biodegradation is slow: Tabak et al. (1981) incubated 5 and 10 mg/L bromoform with domestic waste water at 25°C for 7 days, followed by 3 weekly subcultures (aerobic static flask procedure). After 7 days they found 11 and 4% degradation, respectively and after 28 days, 48 and 35%.

AKZO NOBEL (1994a) performed a biodegradability study in an aerobic aquatic medium by means of a (prolonged) closed-bottle test according to OECD guidelines and ISO standard. It was concluded that bromoform should not be classified as readily biodegradable. AKZO NOBEL (1994b) also carried out biodegradability tests, by inoculating with activated sludge and seawater. Bromoform was not biodegraded (28 days and prolonged). Since bromoform caused a reduction in the endogenous respiration, it was considered inhibitory to the inoculum: the inability of micro-organisms to grow on bromoform may be caused by this toxicity. It was noted that the absence of biodegradation in the closed-bottle tests does not mean that bromoform is not biodegradable in the natural environment, because of the stringency of the test procedures (AKZO NOBEL 1994a, b). A simplified overview of the fate of THMs in the atmosphere is given in Fig. 9.6. In the atmosphere, the loss of bromoform occurs mainly by photolysis and reaction with OH. Bromoform lifetime in the atmosphere calculated by Sinnhuber and Folkins (2005) is between 10 days at 2,000 m and 25 days at 15,000 m.

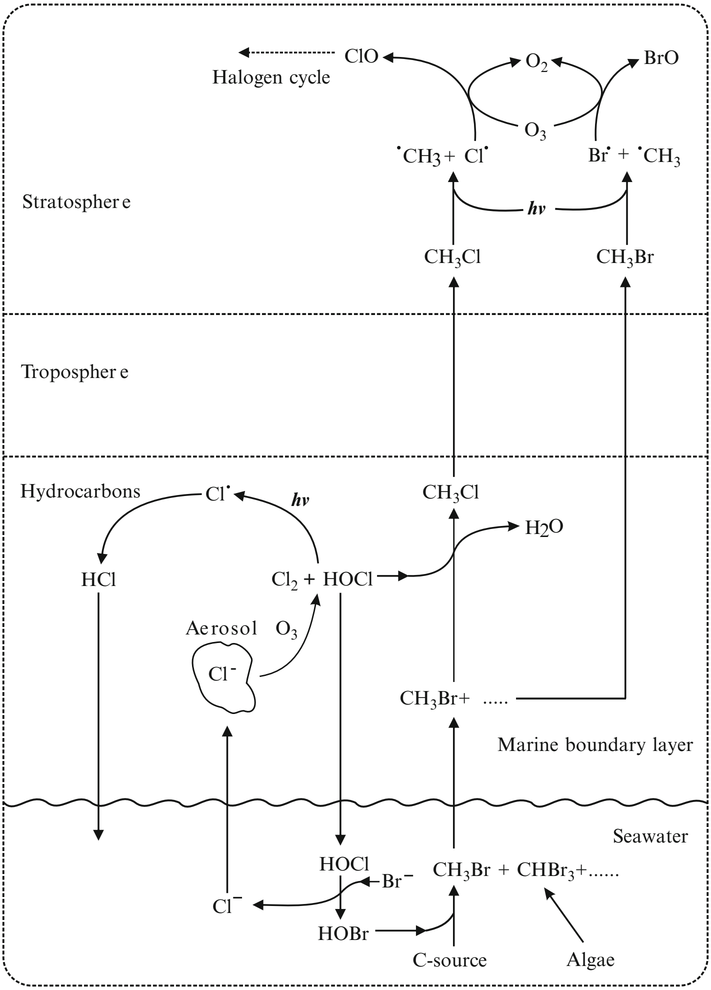

Fig. 9.6 Halogen cycle in the marine environment (from Hoekstra and De Leer 1995)

4.3 Bromodichloromethane and Chlorodibromomethane

The Henry's law constant of both BDCM and CDBM suggests significant volatilisation from water. Based on experimentally determined gas transfer rates, the volatilisation half-life of BDCM from rivers and streams has been estimated to range from 33 min to 12 days (average of 35 h) (Kaczmar et al. 1984). For CDBM, these figures amount to 43 min to 16.6 days with an average of 46 h (Kaczmar et al. 1984). Significant volatilisation was observed from laboratory tanks, with a half-life of about 1 h for both BDCM and CDBM. Adsorption is not considered to be of great importance as an environmental route for BDCM and CDBM. Using the water solubility and log K_{ow}, the estimated log BCF (Bioconcentration factor) of BDCM and CDBM

Table 9.2 Half-lives of dihaloacetonitriles at 25°C (Bieber and Trehy 1983)

	Half-life (h)			
	pH 7.4	pH 8.3	pH 9.0	pH 9.8
Dichloroacetonitrile (DCAN)	–	30	19	0.75
Bromochloroacetonitrile (BCAN)	500	55	–	–
Dibromoacetonitrile (DBAN)	–	85	–	–

amounts to 0.7–1.4, and 0.7–1.5 respectively (Lyman et al. 1982). The aqueous hydrolysis half-life, calculated using QSARs, at 25°C and pH 7 amounts to 137 years for BDCM, and 274 years for CDBM (Mabey and Mill 1978).

Direct photolysis or aquatic oxidation is not significant fate processes (Mabey et al. 1982). Aerobic biodegradation is reported to be slow. Tabak et al. (1981) report 51–59% loss of BDCM, and 25–39% loss of CDBM after 28 days of incubation with domestic waste water (static flask). When volatilisation is excluded, anaerobic biodegradation may be the major removal process. Anaerobic tests with mixed methanogenic bacterial cultures from sewage effluent showed total degradation of both BDCM and CDBM within 2 weeks (43–50% was lost in sterile controls after 6 weeks). No degradation was noted in aerobic tests (Bouwer et al. 1981); under anoxic conditions denitrifying bacteria caused more than 50% degradation after 8 weeks; no degradation was observed in sterile controls (Bouwer and McCarthy 1983).

4.4 Dihaloacetonitriles

Dihaloacetonitriles gradually hydrolyse into non-volatile products (Bieber and Trehy 1983). Hydrolytic attack occurs on the nitrile function, and produces dihaloacetic acid, via dihaloacetamide. In the case of dibromoacetonitrile (DBAN) into dibromoacetic acid (DBAA) reaction equation is: $CHBr_2CN + H_2O \rightarrow CHBr_2CONH_2$ (dibromoacetamide), followed by the faster reaction: $CHBr_2CONH_2 + H_2O \rightarrow CHBr_2CO_2H + NH_3$ (Exner et al. 1973). Electron withdrawing substituent on the alpha carbon of a nitrile facilitates nucleophilic attack on the nitrile function. Since Cl is more electron-withdrawing than Br, the hydrolysis half-life increases in the order $CHCl_2CN$ (DCAN) > CHBrClCN > $CHBr_2CN$ (DBAN).

The rate of hydrolysis depends upon pH, temperature, and the presence of oxidants or reducing (de-chlorinating) agents. In samples buffered at pH 7.2 and held for a week at room temperature, Peters et al. (1990b) found that 20% of the dihaloacetonitriles were lost. Little or no loss occurred when the samples were maintained at 5°C. Oliver (1983) measured DBAN and DCAN concentrations in water over a period of 10 days at different pH values. DCAN by decreased by 10% at pH 6, and by 60% at pH 8. DBAN decreased by 5% at pH 6, and by 20% at pH 8; Peters et al. (1990a) report a DCAN half-life of 35 min at pH 10, and no noticeable changes in concentration at pH 7 and pH 4. In the presence of chlorine, the hydrolysis of DCAN was faster: the half-life amounted to 10 min at pH 10, 25 min at pH 7, and 60 min at pH 4 (see Table 9.2).

De-chlorinating agents (e.g. sulphite, thiosulphate and ferrocyanide) also have an accelerating effect on the disappearance of dihaloacetonitriles (Bieber and Trehy 1983).

These agents can be added to water samples for analysis in order to stop additional halogenation. The order of reactivity toward the dihaloacetonitriles is: $SO_3^{2-} > Fe(CN)_6^{2-} > S_2O_3^{2-}$. The effect is greatest on DBAN and smallest on DCAN. Table 9.2 gives the half-lives of dihaloacetonitriles at several pH values in chlorinated natural waters (Bieber and Trehy 1983). The authors do not specify the relative importance of hydrolysis (*e.g*. compared to biodegradation). Using Henry's law constants estimated from QSARs, Lyman et al. (1982) calculated a volatilisation half-life for DCAN of 10 days, and for DBAN of 127 days in a model river (1 m deep, flowing at 1 m/s, wind speed of 3 m/s). The log K_{ow} and log K_{oc} for DCAN and DBAN—estimated from their molecular structure—amount to be respectively 0.29 and 1.11 for DCAN and 0.47 and 1.11 for DBAN (Meylan and Howard 1992). Adsorption to sediment is therefore not expected (SRC 1996). Lyman et al. (1982) calculated a log BCF of −0.01 and 0.13 for DCAN and DBAN (no bio-concentration).

4.5 Haloacetic Acids

Monochloroacetic acid (MCAA) has a pK_a of 2.86–2.88 (Sergant and Dempsey 1979) and will be completely ionised at environmental pH values. Evaporation from water will therefore not be a significant route (SRC 1996). MCAA has a very low log K_{ow} of 0.22 (Hansch and Leo 1981), and is therefore not expected to adsorb appreciably to soil, nor to bioconcentrate in fish (SRC 1996). MCAA does not absorb UV radiation above 290 nm appreciably (Draper and Crosby 1983), and would therefore not directly show photolysis in the natural environment (SRC 1996).

In water, MCAA is expected to biodegrade. Mineralisation in river water has been observed with 73% of MCAA being converted to CO_2 in 8–10 days at 29°C (Boethling and Alexander 1979). Trichloroacetic acid (TCAA) is non-volatile (White-Stevens 1976). Soil studies indicate that TCAA is subject to microbial decomposition (Kearney and Kaufman 1975). Exner et al. (1973) give degradation half-lives for dibromoacetic acid (DBAA), at different temperatures and pH values.

The degradation reaction of DBAA is:

$$CHBr_2CO_2H + H_2O \rightarrow CHOCO_2H + 2Br^- + H_2 \tag{9.22}$$

The half-life of this reaction at pH 7.4 is about 300 days, and is followed by the faster reaction:

$$2CHOCO_2H + 2H_2O \rightarrow HO_2CCO_2H + 2CO_2 + 3H_2 \tag{9.23}$$

4.6 Halophenols

Nearly all information in literature regarding the environmental fate of halophenols deals with chlorophenols. With a pK_a between 6.3 and 7.9, the halophenols are partially ionised at most environmental pHs. The fate and transport—*e.g*. volatilisation—will therefore be affected by the pH of the water. Halogenated aromatics and phenols are known to be resistant to hydrolysis (Lyman et al. 1982). Using a Henry's law constant estimated from QSARs (SRC 1996), Lyman et al. (1982) calculated a volatilisation half-life for 2,4-dichlorophenol (2,4-DCP) of about 13 days in a model river (1 m deep, flowing at 1 m/s, wind speed of 3 m/s).

The ionised form of 2,4-DCP adsorbs poorly to sediment and soil (Johnson et al. 1985). For the non-ionised form, sediment log K_{oc} values of 2.4–3.6 are reported (Isaacson and Frink 1984; Schellenberg et al. 1984), which suggest that adsorption is important. In a field study, the concentration of 2,4-DCP was found to be much greater in the aquatic sediments than in the associated water column (Wegman and Van den Broek 1983). Bio-concentration of 2,4-DCP is expected to be low. Freitag et al. (1985) report a log BCF of 2.4 for algae (*Chlorella fusca*) over a 1-day exposure, and a log BCF of 2 in golden ide fish (*Leuciscus idus melanotus*) after a 3-day exposure. Kabayashi et al. (1979) measured a log BCF of 1.6 in goldfish. Both authors do not mention the experimental pH.

Photo-degradation in surface water can take place by direct photolysis, or by reaction with sunlight-formed oxidants (single oxygen and peroxygen radicals). Hwang et al. (1986) determined the rates of photolysis of (chlorinated) phenols in estuarine water by means of exposure to midday-sunlight for 4 h in sealed flasks. In distilled water, the photo-degradation half-life of 2,4-DCP amounted to 0.8 h (summer) and 3.0 h (winter). In estuarine water (pH 7.7) the half-life amounted to 0.7 h (summer) and 2.0 h (winter). The photo products of polychlorinated phenols were rapidly degraded by microbes. It should be noted that the rate of photo-degradation strongly depends on water depth. In natural waters during midday sunlight, half-lives of 62 and 69 h were estimated for the reaction with single oxygen and peroxygen radicals (Scully and Hoigne 1987; Mabey and Mill 1978; SRC 1996).

Aly and Faust (1964) reported decomposition of 2,4-DCP by UV light. The rate of photolysis in distilled water decreased, as pH decreased. UV light degraded 50% of 2,4-DCP in 2 min at pH 9.0, in 5 min at pH 7.0 and in 34 min at pH 4.0. Aquatic hydrolysis is not expected to be an important fate process (SRC 1996). Various biodegradation studies have demonstrated that 2,4-DCP is biodegradable under both aerobic and anaerobic conditions. Microbial degradation of 2,4-DCP yields succinic acid (USEPA 1980). In an aerobic static flask study with domestic waste water, Tabak et al. (1981) found 99–100% biodegradation after 7 days (initial concentrations amounted to 5 and 10 mg/L). Main results from a biodegradation study of 2,4-DCP by Kuiper and Hansveit (1984): DCP is probably removed by a combination of biodegradation, photo-degradation, and chemical degradation; laboratory tests indicate the formation of relatively stable intermediates; inhibitory effects after disappearance of 2,4-DCP indicate the formation of a more toxic intermediate during the degradation. For 2,4,6-trichlorophenol (2,4,6-TCP) the evaporation half-life from water at 20.7°C in an indoor experimental pond 10.2 cm deep with a wind velocity of 1.7 m/s and an initial concentration of 177 ppb was 48 h (Sugiara et al. 1984).

Although extensive bioaccumulation of 2,4,6-TCP is not expected, it is important in some species of fish and invertebrates. Reported log BCFs are: 2.4–2.5 for golden orfe (fish) (Freitag et al. 1982; Korte and Klein 1982); 1.5–1.8 for the mussel *Mytilus edulis* (Geyer et al. 1982); 1.7 for the alga *Chlorella fusca* (Freitag et al. 1982). Using a log K_{ow} value of 3.7 the estimated log BCF of 2,4,6-TCP amounts to 2.4 (Lyman et al. 1982). Based on these BCF data, the bio-concentration potential can be classified as being low to moderate. Substantial bioaccumulation of 2,4,6-TCP has also been observed in *Lymnaea* (snails) and *Poecilia* (fish) (Virtanen and Hattula 1982). 2,4,6-TCP is a weak acid in aqueous solution and it will exist appreciably in the ionised state where it exhibits a UV maximum at 311 nm, making it susceptible to photo-degradation (Drahanovosky and Vacek 1971). A half-life of 2.1 h is reported for an aqueous solution irradiated at >290 nm (Kotzias et al. 1982). Blades-Filmore et al. (1982) report biodegradation half-lives in river water with suspended sediment ranging from 3 days at 10 g suspended solids per litre, to 70 days at 1 g suspended solids per litre. Tabak et al. (1981) found 100% biodegradation after 7 days incubation with domestic waste water (static flask initial concentrations amounted to 5 and 10 mg/L).

Summarised, the following can be stated from the literature study and the KEMA study: for THMs—like bromoform—the main route of disappearance from the water phase is volatilisation. For a water body with a depth of 1 m, the volatilisation half-lives amount to 1 or 2 days. In open reaction vessels, the concentrations of THMs in chlorinated seawater decreased to very low levels over 7 days (from 15 to <0.25 μg/L). The following volatilisation half-lives were determined: bromoform 28 h; chlorodibromo-methane 22 h; bromodichloromethane 9 h. The literature reported half-live in water of dibromoacetonitrile varies from several days to several weeks, depending on pH. The main process seems to be gradual hydrolysis into dibromoacetic acid. In the experimental study, in both open and closed reaction vessels more than 90% of the initial dibromoacetonitrile concentration in chlorinated seawater was lost within 40 h. A half-life of 14 h was determined. Very little information is available in literature on abiotic degradation, and biodegradation of dibromoacetic acid. It has a reported degradation half-life of 300 days (pH 7.4). Halophenols are partially ionised at environmental pH values. The volatilisation half-lives of the non-ionised forms of 2,4-dichloro- and 2,4,6-trichlorophenol amount to 2 weeks (river, 1 m deep). Halophenols are susceptible to photo-degradation which is probably a major fate process (half-life of several days in natural water). Biodegradation half-lives amount to about 7 days. Adsorption to solid matter (and bio-concentration) can be classified as moderate.

4.7 Bromate

Bromate is a disinfection by-product that is formed when ozone reacts with naturally occurring bromide in drinking water.

An often forgotten by-product in chlorination chemistry is the formation of bromate BrO_3^-. All surface waters containing bromide (Br^-) will produce low concentrations of bromate. In drinking water installation it is a serious phenomenon because bromate is implicated in kidney tumour induction and is carcinogenic (both initiation and promotion = CMR compound). The WHO level for tap water is set at 0.5 μg/L at a risk of 10^{-5}. Problem is that the detection limit is about 5 μg/L. Removal of bromate is highly problematic. Research done at Electricité de France shows that bromate can be formed in the hypochlorite storage tanks of seawater cooled power stations, but the formation kinetics is very slow. The authors suggest to uses the smallest retention time of sodium hypochlorite in storage tanks used for the chlorination process.

Two potential ways of formation are possible:

(a) Immediate electrolytic formation

$$Br^- + 6OH^- \rightarrow BrO_3^- + 3H_2O + 6e^- \tag{9.24}$$

(b) Oxidation of bromides by active chlorine (slow kinetics)

$$Br^- + HClO \rightarrow HBrO + Cl^-$$

$$HOBr + 2\ HClO + 3\ H_2O \rightarrow BrO_3^- + 2\ Cl^- + 3\ H_3O^+ \tag{9.25}$$

Global reaction:

$$Br^- + 3\ HClO + 3\ H_2O \rightarrow BrO_3^- + 3\ Cl^- + 3\ H_3O^+ \tag{9.26}$$

Of course, the greater chlorine concentration the more bromate formation, up to the total transformation of bromide ions. In liquid sodium hypochlorite, bromate is a component always present in low concentrations (up to some dozens of micrograms per litre).

5 Ecotoxicity of Oxidants and Chlorination By-Products in Chlorinated Cooling Waters

Among the numerous substances produced by the complex chemistry of chlorine in seawater, two categories of chemical species are usually distinguished: oxidants and non-oxidants. This distinction is particularly pertinent to characterise their ecotoxicological properties. Oxidant compounds disappear very rapidly in seawater, they are not bio-accumulated, but they exhibit short-term toxicity for the marine flora and fauna. CBPs are much more persistent, some are accumulated in animal fats, they are not toxic in the short-term, but some produce genotoxic effects. In this chapter we shall present data from studies carried out at different European power stations to assess the environmental impact of chlorination of cooling water.

Maasvlakte is a power station located near the Rotterdam harbour on the North sea coast. Flamanville, Paluel, Penly and Gravelines are large nuclear power stations (NPS) located in France on the Channel and the North Sea coast. The Sizewell, Hartlepool, Bradwell and Dungeness and Fawley power stations are located on the

North Sea coast of the United Kingdom. Dungeness is located in the Southeast of England, Wylfa NPS is located in the upper North-West corner of Wales and Heysham NPS is located at the west coast at the Morecambe bay.

5.1 Oxidants: Concentration Levels and Toxicity Thresholds

5.1.1 TRO Decay in CWS and Discharge Plumes

As pointed out earlier, the oxidants generated by addition of chlorine in seawater are dominated by brominated substances: hypobromous acid (HOBr) and hypobromite ion (OBr^-). Free bromine reacts with ammonia and amines to produce combined bromine—bromamines. Residual oxidants present in seawater are thus mainly constituted by free and combined bromine; they are globally measured as total residual oxidants (TRO).

Some specific difficulties are met in field studies to characterise the distribution of residual oxidants in marine coastal waters and to evaluate their toxicity to marine biota. Most methods for determining total or free residual oxidants are subjected to various problems such as relatively low sensitivity. The quantification limit of the current chemical method (colorimetric DPD) mainly depends on the water colour and turbidity, it can also be affected by chemical interferences. In practice, the quantitative measurement limit for colorimetric DPD in natural waters is much higher than the theoretical threshold of 0.01 mg/L Cl_2 equivalent. It can frequently reach 0.05 mg/L in turbid coastal waters. On the other hand, the response of electrochemical methods depends on the water temperature and conductivity. Field measurements require specific apparatus adapted to take in to account the rapid decay of residual oxidants during the dilution process of the chlorinated effluents. Water sampling in discharge plumes must be designed to minimise the time needed to carry the sample to the analytical equipment. Measurements are often made on board a ship and sometimes it is necessary to use a helicopter to sample a large area in the short time of a tide.

Various components explain the oxidant demand in natural waters—chemical reaction with dissolved organic compounds and ammonia, consumption by the organic biofilm covering the walls of the cooling system and solar light.

In the cooling system of a large power station, the water flows from the intake point to the discharge point generally in about 10 min and it can be driven to a canal or to an offshore outlet by a submarine pipe in 10–20 min. At the Penly Nuclear Power Station, for a chlorine dosage of 0.8 mg/L, during this short period of time the TRO decreases to 0.3 mg/L at the condenser and to less than 0.1 mg/L at the end of outlet pipe, 800 m offshore (Fig. 9.7). Additionally, the major loss of oxidants occurs during the initial mixing of the hypochlorite solution in the chamber of the drum screen. In this huge basin, the water renewal time is 5 min and shows variations depending on the tide phase.

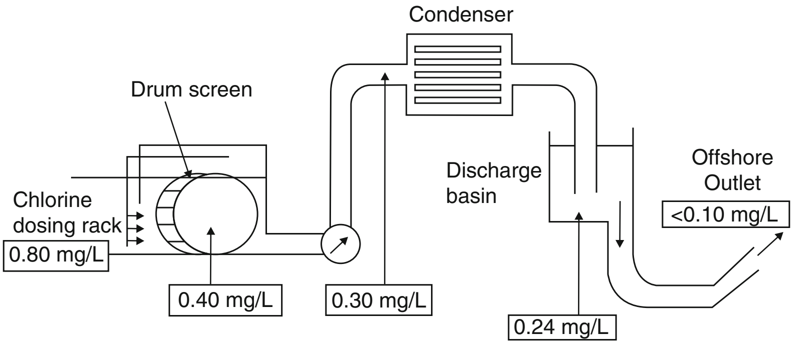

Fig. 9.7 Decay of TRO in a CWS at the Penly nuclear station (Jenner et al. 1998)

In the decade 1980–1990, measurement campaigns were carried out on site at coastal NPS in the UK (Coughlan and Davis 1985) and in France (Khalanski and Lutz 1987) to study the dissipation of residual oxidants in the cooling water discharge. Plumes and maps of the TRO concentration contours were drawn. From the field data, it appeared that the dissipation of the residual oxidants did not follow the dilution of the cooling water. The loss of TRO was more rapid than the temperature decay. A simple semi-empirical model was developed and validated using field data (Davis and Coughlan 1983).

In this model, the chemical oxidant demand explaining the decrease of the TRO is represented by an instantaneous demand and the exponential decay of the remaining oxidants indicating an approximation of first-order kinetics:

$$C_t = (C_{\mathrm{in}} - C_{\mathrm{id}})\exp^{(-\mathrm{k}t)}, \tag{9.27}$$

Where, C_{in}—initial oxidant concentration, C_{id}—instantaneous demand, t—time, k—constant.

In the discharge plume area, the decay is represented by two terms: dilution rate D and an additional demand by the non-chlorinated water fD. The demand fD plays an important role in the decrease of the TRO as shown in Fig. 9.8, where the effect of dilution only (mixing curve) is compared to the measurements.

In the near field of the plume, the water temperature can be treated as a conservative pollutant and D can be approximated by the temperature decay rate. Thus, the concentration of TRO in the plume at time t minutes from discharge is given by (refer to legends of formula (9.27)):

$$C_t = \frac{(C_{\mathrm{in}} - C_{\mathrm{id}})\exp(-\mathrm{k}t)}{(\mathrm{D} + \mathrm{fD})}. \tag{9.28}$$

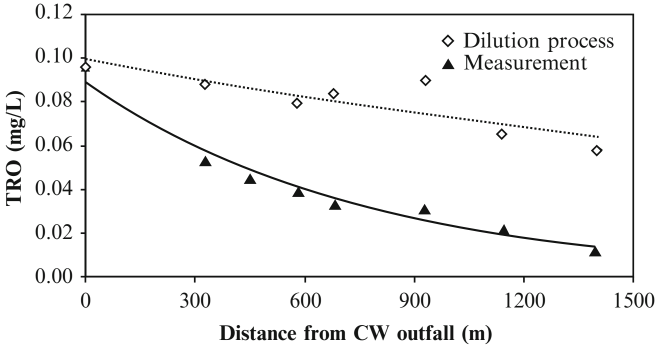

Fig. 9.8 Comparison of TRO decay in the discharge plume at the Sizewell nuclear power station (UK) computed according to the dilution process only and measured by colorimetric DPD (modified after Coughlan and Davis 1985)

5.1.2 Experimental Data on Residual Oxidants Toxicity

To a certain extent, laboratory bioassays using the current chemical method are subjected to the same analytical limits as in the field studies. Moreover, it is quite impossible to maintain a stable oxidant concentration in the water for long-term experiments, especially in very low concentration range. We can assert that, with the current analytical methods, there are no reliable measurements of TRO in seawater at concentrations lower than 0.01 mg/L and that only experimental data with special designed protocols can produce accurate data at levels in the range of 0.01–0.05 mg/L.

The acute and chronic bioassays on fish carried out as a contribution to the Ocean Thermal Energy Conversion project (OTEC) is an example of the almost impossibility of maintaining a stable level of TRO in toxicity bioassays lasting several days. The authors (Venkataramiah et al. 1983) mentioned the extreme difficulty to maintain a precise TRO concentration "despite the extensive precautions taken". In spite of the big variations of TRO measured during the experiments, the findings (Table 9.3) give invaluable information on the effect of the age of the individuals on their sensitivity to residual oxidants and on the order of magnitude of the lethal TRO concentrations for the youngest stages of these fishes: 0.15 mg/L. These results are on the other hand in agreement with the observations made in the discharge canal of the Gravelines power station. In spring, shoals of adult mullets enter the discharge canal at the Gravelines power station and swim against the current in the warm chlorinated water (TRO = 0.1 mg/L) to feed on the organic foam floating at the surface of the water.

Among the great number of short-term and long-term experiments on residual oxidants and marine organisms found in the scientific literature, majority of the data concern toxic effects observed in the range 0.05–5 mg/L. Mattice and Zittel (1976), in their review of the literature data proposed to set toxicity thresholds "by enclosing all the data points, most of which were 50% effect levels, and then adjusting the line to zero mortality levels". They derived by this method a TRO chronic toxicity threshold for zero-mortality levels of 0.02 mg/L. For times lower than 2 h, the acute toxicity threshold

Table 9.3 Acute (96 h) and chronic (21 day) toxicity of residual oxidants on a marine fish, the mullet *Mugil cephalus*

		TRO concentration (mg/L)				
Weight/ duration	Mortality	Mean (mg/L)	Standard deviation	Range (mg/L)	Food consumption	Growth
0.3 g	0%	0.15	0.02	0.13–0.20		
96 h	60%	0.21	0.02	0.18–0.27		
	100%	0.29	0.04	0.25–0.34		
	LC1	0.16				
	LC10	0.18				
	LC50	0.21				
	LC99	0.28				
10.0 g	0%	0.40	0.21			
96 h	LC1	0.53				
	LC10	0.57				
	LC50	0.61				
	LC99	0.69				
1.1 g	0%	0.13	0.03	0.07–0.18	Same as control	Same as control
21 days	0%	0.20	0.04	0.14–0.31		
	23%	0.27	0.07	0.18–0.34	1–2% of control	Reduction
	93%	0.27	0.09	0.14–0.36		

Lethal concentrations (LC) are computed data. From tables and figures in Venkataramiah et al. (1983)

depends on the exposure time; it reaches 0.06 mg/L at 10 min and 0.04 mg/L at 30 min. In some studies published more recently, lethal or sublethal effects such as growth reduction are observed even for short-term exposures with TRO concentrations of 1–10 µg/L. If the measurement methods of residual oxidants are correct in these studies, it means that there is no practical chronic toxicity threshold for marine biota.

5.1.3 Field Studies

Such field studies have been carried out in particular in the United Kingdom and in France (Bamber and Spencer 1984; Turnpenny and Coughlan 1992; Khalanski and Lutz 1987; Langford 1990). Our purpose here is to summarise the main conclusions arising from the European experience.

According to the field data, at power stations using continuous low dose (≤1.0 mg/L) chlorination, the impact of residual oxidants can be classified in three categories:

(a) Transit impact on entrained organisms.
(b) Impact on the marine biota located in the discharge canals and in the vicinity of the cooling water outlet, which are exposed to low concentrations of TRO (about 0.05–0.1 mg/L) during all the period of chlorination (about 6 months a year).
(c) Impact on the marine biota located in areas where the TRO is detected with some uncertainty (TRO in the range of 0.01–0.05 mg/L).

A lot of experiments and in situ studies were made to determine the effects of the transit impact on marine plankton. The plankton are entrained into the CWS and subjected to the maximum concentration of TRO (generally in the range of 0.1–0.5 mg/L) for a short time (generally in the range of 10–30 min). Field studies confirmed the experimental data showing the high sensitivity of bacteria and plankton algae to residual chlorine. Brominated oxidants are very efficient disinfection agents. Routine measurements made at Gravelines NPS since 1980 by Institute Pasteur de Lille have shown almost total disappearance of living bacteria in the chlorinated water at $TRO \geq 0.2$ mg/L. The water chlorination in operation during the summer months eliminates potentially pathogenic vibrios. However, the very low level of TRO near the walls of the discharge canal, 1.5 km long, and in the thermal plume (<0.05 mg/L) is not sufficient to stop the development of thermophilic vibrios. At the outlet of the cooling system a loss of phytoplankton biomass (chlorophyll a) and production to the extent of 50–90% was found at five sites of power stations in the United Kingdom (Coughlin and Davis 1983) and two sites in France (Khalanski 1976; Khalanski and Lutz 1987). At Gravelines, progressive recovery of bacterial and phytoplankton metabolism was observed in the plume area, where the TRO decays from 0.05 to 0.01 mg/L.

Zooplankton, a complex mixture of biological groups and developmental stages, cannot be considered as a whole. Micro-crustaceans (copepods) are relatively resistant to the residual oxidants. Coughlin and Davis (1983) found no significant mortalities at $TRO < 0.2$ mg/L, while mortalities increased linearly to reach 20% at $TRO = 1.0$ mg/L; French experiments and on-site measurements confirm this point. However, embryonic stages of oysters *Crassostrea gigas* are much more sensitive to chlorination according to the assays made with an Entrainment Mimic Unit, reproducing the same pressure, temperature and chemical variations as in a typical power station cooling system (Bamber et al. 1994). Deleterious effects on the development are observed on 50% of the embryos at $TRO = 0.05$ mg/L and the development was stopped at $TRO \geq 0.15$ mg/L.

A great variety of species settled on the rocky substrata (benthos) are found on the walls of the cooling water basins, pipes and heat exchangers. They constitute what the plant operators call “biofouling”. According to the experience of plant operators in European countries, the continuous chlorination treatment aimed at elimination of the biofouling in marine CWS requires to maintain a minimum TRO concentration of 0.2 mg/L (Jenner et al. 1998). Lower residual concentrations (0.05–0.1 mg/L) are generally not effective to control the biofouling.

Summarised, there are no observed biological effects on the plankton and on the benthos beyond the mixing zone of the chlorinated effluents which is limited by the concentration in TRO of 0.01–0.03 mg/L. In tidal seas, the exposure of the benthos lasts half of the time because of the movement of the discharge plume.

In a near future, specific programs of surveillance will be set up in all the member states of the European Union to check the application of the water framework directive, the objective of which is to reach the “good ecological status” for all water bodies and to protect specific areas.

5.2 Production and Field Measurements of Persistent CBPs

5.2.1 The CBPs Spectrum in Chlorinated Cooling Waters

As shown in Table 9.4, four groups of organohalogens have been identified in cooling chlorinated waters: THMs, haloacetonitriles, haloacetic acids and halophenols. In addition, it is important to mention that a lot of organic substrates are susceptible to be halogenated. Despite their inorganic structure, bromate ions must be considered as, a by-product of hypobromous acid.

Table 9.4 Non-exhaustive list of CBPs identified in chlorinated seawater or freshwaters at high bromide concentration (Allonier 2000)

Organohalogenated compounds	Chemical formula	References
Trihalomethanes		
Chloroform	$CHCl_3$	Heller-Grossman et al. (1993)
Bromodichloromethane (BDCM)	$CHCl_2Br$	Heller-Grossman et al. (1993)
Dibromochloromethane (DBCM)	$CHBr_2Cl$	Fayad and Iqbal (1987); Heller-Grossman et al. (1993)
Bromoform	$CHBr_3$	Carpenter et al. (1981); Fayad and Iqbal (1987); Heller-Grossman et al. (1993)
Haloacetonitriles		
Dibromoacetonitrile (DBAN)	Br_2CHCN	Jenner et al. (1997)
Haloacetic acid		
Monochloroacetic acid (MCAA)	$ClCH_2COOH$	Peters et al. (1991)
Dichloroacetic acid (DCAA)	$Cl_2CHCOOH$	Peters et al. (1991); Heller-Grossman et al. (1993)
Trichloroacetic acid (TCAA)	Cl_3CCOOH	Peters et al. (1991); Heller-Grossman et al. (1993); Kristiansen et al. (1996)
Monobromoacetic acid (MBAA)	$BrCH_2COOH$	Peters et al. (1991)
Dibromoacetic acid (DBAA)	$Br_2CHCOOH$	Peters et al. (1991); Heller-Grossman et al. (1993); Kristiansen et al. (1996)
Bromochloroacetic acid (BCAA)	$BrClCHCOOH$	Peters et al. (1991); Heller-Grossman et al. (1993)
Halophenols		
2,4,6-tribromophenol (TBP)	2,4,6-$Br_3C_6H_2OH$	Bean et al. (1978); Bean et al. (1983); Jenner et al. (1997)
2,4-dibromophenol (DBP)	2,4-$Br_2C_6H_3OH$	Bean et al. (1978, 1983); Jenner et al. (1997)
Bromophenol	BrC_6H_4OH	Bean et al. (1983)
Others		
2-bromocyclohexanol	$BrC_6H_{10}OH$	Fayad and Iqbal (1987)
1,2-dibromocyclohexanol	$Br_2C_6H_9OH$	Fayad and Iqbal (1987)
bromate ion	BrO_3^-	Macalady et al. (1977)

Table 9.5 Bromoform and DBAN at the power station outfalls

Power station	Period/data	No. Samples	NaOCl dosage (mg/L as Cl_2)	Bromoform (µg/L)	DBAN (µg/L)
Heysham (UK)	11/08/92–15/12/92	9	0.5–1.0	29.20 ± 24.25 5 samples	3.15 ± 3.59 4 samples
	12/01/93–07/09/93	9	0.5–1.0	23.00 ± 8.24 9 samples	2.12 ± 1.08 9 samples
Dungeness (UK)	03/08/93	1	0.75–1.0	5.75	0.20
Wylfa (UK)	21/09/93	1	0.3–0.4	27.50	0.87
		1		27.00	0.79
Bradwell (UK)	19/10/93	1	0.6–1.0	25.00	0.87
Hartlepool (UK)	17/08/93	1	0.5–1.0	3.50	<0.1
Sizewell (UK)	23/08/93	1	0.6–1.0	14.50	<0.1
Paluel (FR)	14/10/92	1	0.37	3.10	0.10
		1	0.82	9.65	1.05
Penly (FR)	27/05/93–18/08/93	11	0.62 ± 0.10	13.37 ± 4.17	NA
	21/06/94–27/07/94	18	0.50 ± 0.08	15.01 ± 3.22	NA
Gravelines (FR)	13/04/93–18/04/93	3	0.64	6.37 ± 4.62	NA
	03/05/93–25/10/93	26	0.80	18.63 ± 3.70	NA
Maasvlakte (NL)	02/07/92–22/10/92	16	0.8–1.5	11.54 ± 5.40 10 samples	0.83 ± 0.56 6 samples
	16/05/93–10/08/93	10	0.8–1.5	8.35 ± 12.35 7 samples	0.94 ± 1.22 3 samples
Average				16.32 ± 2.10	1.48 ± 0.56

All data are averages of duplicate samples
NA not available

5.3 *Measurements of Chlorination By-Products in Chlorinated Cooling Waters*

Based on earlier research by KEMA in co-operation with Akzo Nobel, Dow Benelux, British Energy, Electricité de France (EDF) and the Dutch power generation companies, the production of CBPs in coastal power stations and their essential properties of CBPs are listed below. With the data collected in this survey, it is possible to show that the most dominant organohalogen produced was bromoform (Table 9.5). The results show that at the point of discharge, bromoform concentrations varied from 29.20 µg/L (maximum 53.45 µg/L) to 3.1 µg/L and dibromoacetonitrile concentrations from 11.39 to 0.1 µg/L. Other compounds at discharge detected in the surveys were bromodichloromethane (BDMC) and dibromochloromethane (DBMC), with concentrations of 0.8 and 0.7 µg/L, 2,4,6-tribromophenol at 0.25% µg/L and 0.29 µg/L and 2,4-dibromophenol at 0.055 µg/L.

On the basis of the data collected in this survey, the first conclusion is that bromoform represents 93–97% of the total THM. The second conclusion is that there is high temporal variability in the concentrations measured at each site and a high

Table 9.6 Yield of formation of bromoform in seawater from Golfe de Fos (Mediterranean Sea), Gravelines (North Sea), Penly and Paluel (English Channel), and ratio of DBCM and CDBM to bromoform

	Fos	Gravelines	Penly	Paluel
	Gasification plant	Power station	Power station	Power station
$CHBr_3/CD$	0.026	0.037	0.025	0.040
$CHBr_2Cl/CHBr_3$	0.035	0.034	0.016	0.046
$CHBrCl_2/CHBr_3$	0.002	0.005	0.003	0.003

CD chlorine dosage

inter-site variability. The ratio ((DBCM + BDCM)/Bromoform) calculated on mean concentrations is about 3% at Heysham and Gravelines and 7% at Maasvlakte. Chloroform was below the detection limit (0.1 μg/L) at all marine power stations. The only exception was Hartlepool located on an estuary with a concentration of 1.5 μg/L. The ratio (DBAN/bromoform) calculated on the mean values remain in the range 3–11%; the ratio calculated on the mean values of all the samples was 8.6%.

From 1993 to 1998, EDF R&D carried out a long-term survey of the CBPs level at three NPS on the Channel and the North Sea coast: Paluel, Penly and Gravelines (Allonier 2000; Khalanski 2003). The first analytical method developed at EDF R&D was ECGS- Purge and Trap, suitable for measurement of THMs. Further methodological developments lead to measure haloacetonitriles, haloacetic acids and halophenols on samples of cooling waters collected at the power stations (Allonier et al. 1999a; Allonier 2000). This set of data was used to characterise and to quantify CBPs. Data show some variability due to water quality changes and, more importantly, to the uncertainty on the chlorine dosage in the circuits. We know precisely the chlorine concentration in the hypochlorite solution but the flow of this solution actually injected into the distribution pipes can vary in large proportions and the mixing process with the cooling water varies during a tide. On the other hand, measurements of residual oxidants on samples collected on the top layer in large discharge basins are quite unrepresentative. However, the large number of data collected over several years partly compensates the effect of these sources if variability and this data set are suitable to estimate the formation yields depending on the chlorination regime.

Bromoform represents 95–98% of the total THMs. The formation yield of bromoform, expressed as the ratio between the bromoform concentration and the chlorine added in the cooling water, is estimated by the slope of linear regressions on measurements made using water samples collected at three power stations and a gasification plant (Table 9.6). The bromoform formation yield ($CHBr_3/CD$) at the power stations is in the range of 2.5–4.0% and this yield on chlorinated Mediterranean water is in this range as well. The ratio ((DBCM + BDCM)/Bromoform) is minimum at Paluel (1.9%); the values at the other sites are in the range 3.7–4.9%.

Chloroform was sometimes measured above the detection limit, but there is no correlation with the chlorine dosage or the bromoform concentration. The mean

Table 9.7 Mean CBPs concentration measured in the cooling water at the three power stations and their ratios to bromoform (Allonier et al. 1999b; Allonier 2000)

	CBPs (μg/L)			Ratio to bromoform		
Power station	DBAA	DBAN	2,4,6-TBP	DBAA/ $CHBr_3$	DBAN/ $CHBr_3$	TBP/ $CHBr_3$
Gravelines ($n=20$)	9.5 ± 1.96	3.61 ± 1.11	0.37 ± 0.05	0.355	0.135	0.014
Paluel ($n=16$)	10.19 ± 3.95	2.83 ± 0.74	0.14 ± 0.05	0.380	0.106	0.005
Penly ($n=16$)	7.25 ± 2.29	0.94 ± 0.84	0.10 ± 0.04	0.984	0.128	0.014

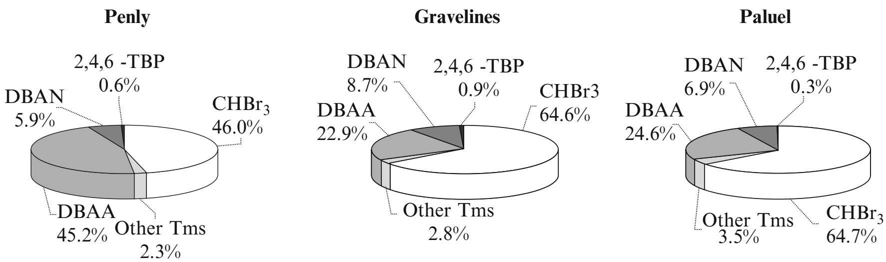

Fig. 9.9 Relative distribution of the major CBPs in the chlorinated cooling water at three nuclear power stations: Penly, Gravelines and Paluel. *$CHBr_3$* bromoform; *DBAA* dibromoacetic acid; *DBAN* dibromoacetonitrile; *TBP* tribromophenol

concentration of chloroform was 0.25 and 0.26 μg/L in the samples from Paluel and Gravelines. The origin of chloroform is probably the hypochlorite solution rather than the formation in the cooling water. At Gravelines, Paluel and Penly, hypochlorite used to chlorinate the cooling water is produced on site by electrolytic cells at a chlorine concentration of 0.5–1.0 g/L; chlorinated THM have been detected in this solution.

In 1997–1998, determinations of THM, halophenols, haloacetonitriles and haloacetic acids were carried out at the three power stations and dibromoacetic acid was found to represent 35 and 38% of bromoform at Gravelines and Paluel, reaching 98% at Penly (Table 9.7). In fact, the hydrolysis of DBAN leads to the formation of DBAA. Thus, in the chlorinated effluents the four major CBPs are in the following order (Fig. 9.9): Bromoform > DBAA > DBAN > (DBCM + BDCM) > TBP. Some traces of other chlorinated compounds were detected (dichlorobromoacetic acid, trichloroacetonitrile, dichloroacetic acid).

Some experiments were made on the formation kinetics of CBPs. The experimental data show that bromoform is relatively rapidly formed in water (93% in 3 h) but 2,4,6-TBP and DBAA are slowly formed: in 6 h only 30% for 2,4,6-TBP and 52% for DBAA. The data for DBAN indicate a slower process than for DBAA probably due to the hydrolysis of DBAN.

Table 9.8 Production of bromoform by seaweeds incubated in filtered seawater at 20°C for 24 h under light at 200 μE/m²/s (Allonier 2000)

Seaweed species	Production of bromoform (μg/g dry matter/day)
Laminaria saccharina	5.45 ≥ 0.12
Ascophyllum nodosum	1.01 ≥ 0.10
Laminaria digitata	0.99 ≥ 0.09
Ulva lactuca	0.92 ≥ 0.10
Fucus vesiculosus	0.79 ≥ 0.08
Fucus serratus	0.17 ≥ 0.05
Gigartina stellata	0.06 ≥ 0.01

5.4 Natural Production of Halogenated Organic Compounds in Seawater

Marine and terrestrial organisms contain haloperoxidases that halogenate organic compounds in the presence of chloride, bromide or iodide ions, and about 2,000 natural organohalogens have been identified (Gribble 1994). In sea water, bromoform, other THMs and non-volatile compounds as bromophenols are produced by benthic and planktonic algae. The bromoform concentration reached up to 50 ng/L (0.05 μg/L) in February 1989 in the southern part of the North Sea (Nightingale 1991). Such relatively high levels of bromoform from natural origin were measured in the English Channel: 82.4 ng/L in a "non-polluted" site (Connan et al. 1996). Maximum concentrations in the coastal zone are found very close to macroalgae beds.

On the Great Cumbrae Island coast, Nightingale et al. (1995) measured bromoform in the range between 170 and 460 μg/L. According to literature data, bromoform is the most important brominated compound produced by marine algae. The quantities produced are:

(a) 5.8–72.0 μg/g of carbon per day by planktonic algae.
(b) 0.5–1.0 μg/g dry weight per day by benthic algae.

Experimental measurements were made by EDF R&D on samples of nine species of seaweeds collected from the Normandy coast. The bromoform production varied between 0.06 and 5.50 μg/g dry weight per day (see Table 9.8).

The natural production of bromoform on the Brittany coast in France was estimated from the biomass of benthic brown algae and found to be about 371 tons per year (Khalanski and Allonier 1998). On this basis, the natural production of bromoform in the English Channel is probably between a few hundred and several thousand tons per year. This can be compared with the production of bromoform of the world oceans, estimated at one or two million tons (Harper 1995) and with the bromoform produced by the French power stations: approximately 210 tons in 2000.

5.5 THM Decay in the Discharge Plume

The volatilisation process is not fast enough to have a significant effect on the rate of decay of the THM in the discharge plumes. Measurements made on the plume at Heysham and at Sizewell have shown that the bromoform concentration is strongly correlated with the temperature rise and follows almost strictly the dilution of the cooling water (Fig. 9.9). Volatilisation is efficient to eliminate the THM in the longer term (weeks to months), depending on the water depth.

5.6 Toxicity of Persistent CBPs

Literature data show a much lower toxicity on aquatic biota for THMs than for oxidising compounds (Table 9.9). However, results of Stewart et al. (1979) show relatively high sensitivity of oyster larvae to bromoform.

5.6.1 Toxicity Assays Using CBPs and Cooling Water at EDF Marine Nuclear Power Stations

In the EDF R&D programme on CBPs, six bioassays were used: the common Microtox© toxicity test on a marine bacteria, an inhibition bioassay on a marine plankton algae, and three methods among the most sensitive to determine the toxicity of the major CBPs:

(a) Cytotoxicity test on culture of bivalve cells from the gill of the marine clam *Ruditapes decussatus*; the bivalve cell viability was assessed by using the MTT reduction method (Allonier 2000).
(b) Embryo-larval bioassay on sea urchin *Paracentrotus lividus* (His et al. 1999).
(c) Embryo-larval bioassay on oyster larvae *Crassostrea gigas* (His et al. 1999). In embryo-larval assays, the number of abnormal larvae was determined on the test samples and in the control samples.
(d) Growth inhibition bioassay on a marine Diatom: *Phaeodactylum tricornutum* (NF EN ISO 10253 (2003)).

Wherever possible, two toxicity thresholds were derived from the data: the lower effective concentration (LOEC) and the “no observed effect concentration” (NOEC) (see Table 9.10). The embryo-toxicity assay with DBAN gave the minimum NOEC of 50 μg/L. The other NOEC were in the range of 500 μg/L to 80 g/L.

Some embryo toxicity bioassay with sea urchins, oysters (His et al. 1999) and growth inhibition assays with marine phytoplankton (NF EN ISO 10253) were conducted using filtered cooling water collected in May, June and July 1998 at Gravelines, Paluel and Penly. No significant toxicity was detected in any of the bioassays (Table 9.11).

Table 9.9 Literature data on the THMs toxicity to aquatic biota (Allonier 2000)

Species, biological stage	Compound	Toxicity data in mg/L	Reference
Vibrio fisheri	Chloroform	5 min EC50 = 2,464	Kaiser and Devillers (1994)
Marine bacteria			
Skeletonema costatum	Bromoform	96-h EC50 = 11.5–12.3	USEPA (1980)
Marine Diatom			
Selenastrum capricornutum	Bromoform	96-h EC50 = 112–116	USEPA (1980)
Freshwater alga			
Daphnia magna	Chloroform	48-h LC50 = 29	Le Blanc (1980)
	Bromoform	48-h LC50 = 46	Le Blanc (1980)
Freshwater Crustacean	Bromoform	48-h LC50 = 46.5	USEPA (1980)
Daphnia pulex	Bromoform	96-h LC50 = 44	Trabalka et al. (1980)
Freshwater Crustacean			
Mysidopsis bahia	Bromoform	96-h LC50 = 24.4	USEPA (1980)
Marine Mysid shrimp			
Micropterus salmoides	Chloroform	96-h LC50 = 45–56	Anderson and Lusty (1980)
Salmo gairdneri		96-h LC50 = 15–22	
Ictalurus punctatus		96-h LC50 = 75	
Lepomis macrochirus		96-h LC50 = 13–22	
Freshwater fish			
Lepomis macrochirus	Bromoform	96-h LC50 = 29	Buccafusco et al. (1981)
Freshwater fish			
Cyprinus carpio	Chloroform	96-h LC50 = 161	Trabalka et al. (1980)
	BDCM	96-h LC50 = 119	
	DBCM	96-h LC50 = 53	
	Bromoform	96-h LC50 = 76	
Carp embryos	Chloroform	96-h LC50 = 97	Mattice et al. (1981)
	BDCM	96-h LC50 = 67	
	DBCM	96-h LC50 = 34	
	Bromoform	96-h LC50 = 52	
Cyprinodon variegatus	Bromoform	96-h LC50 = 17.9	USEPA (1980)
Seawater fish		Embryo-larval: chronic value = 6.4	
Crassostrea virginica	Bromoform	24-h LC50 = 1	Stewart et al. (1979)
Oyster larvae		LOEC = 0.05	

5.7 Bioaccumulation of Persistent CBPs

Bioaccumulation of pollutants in aquatic organisms and biomagnification in food chains greatly depend on the ability of an organic substance to accumulate in fats. As a consequence, the water solubility and the octanol/water partition coefficient are two basic chemical characteristics to evaluate the bioaccumulation potential.

According to the data presented in Table 9.12, haloacetic compounds (DBAA and DBAN) are water soluble, with low octanol/water partition coefficients. THMs are relatively water soluble and their Log K_{ow} values remain low. For these compounds, the bioconcentration factor should be in the range of 2–50. Tribromophenol

Table 9.10 LOEC and NOEC (mg/L) data for CBP toxicity on marine organisms

Compound	Clam gill[a]	Urchin[b]	Oyster[c]	Algae[d]	Bacteria[e]
Bromoform	LOEC: 1.00 NOEC: 0.50	LOEC: 2.50 NOEC: 1.00	LOEC: 1.80 NOEC: 1.00		LOEC: 5.12 NOEC: 3.41
DBCM		LOEC: 5.00 NOEC: 2.50			LOEC: 47.41 NOEC: 31.60
CDBM		LOEC: 5.00 NOEC: 2.50			LOEC:>250 NOEC:>250
Monobromo-acetic acid					LOEC: 10.28 NOEC: 6.85
DBAA	LOEC: 1.00 NOEC: 0.50	LOEC: 5.00 NOEC: 2.50	LOEC: 24.0 NOEC: 18.0	LOEC: 26.2 NOEC: 18.1	
DBAN	LOEC: 1.00 NOEC: 0.50	LOEC: 0.10 NOEC: 0.05			LOEC: 2.39 NOEC:1.00
2,4,6-tribromo-phenol (TBP)		LOEC: 2.50 NOEC: 1.00			LOEC: 2.25 NOEC:<2.25
Sodium bromate			LOEC:>7.5 NOEC: 7.5	LOEC:>80 NOEC: 80	
Chloroform		LOEC:>10 NOEC:>10			

[a]Cytotoxicity on gill cells of the marine clam *Ruditapes decussatus*
[b]Embryo-larval toxicity on sea urchin *Paracentrotus lividus*
[c]Embryo-larval toxicity on oyster *Crassostrea gigas*
[d]Growth inhibition of the marine diatom *Pheodactylum tricornutum*
[e]Microtox© Bioassay 15 min (Khalanski 2003)

Table 9.11 Results of bioassays conducted on cooling water (CW) samples collected at the Penly and Gravelines power stations

Power station	Bioassay	Date, unit	Intake canal	Discharge basin	$CHBr_3$ (μg/L)
	Sea urchin	11/05/1998	14.0 ± 3.01	18.0 ± 2.78	12.5
Penly	Embryotoxicity	11/05/1998	14.0 ± 3.01	14.0 ± 2.49	14.1
	% Abnormal larvae	08/06/1998	11.6 ± 3.49	11.6 ± 1.58	10.8
	His et al. (1999)	30/06/1998	10.6 ± 1.24	12.0 ± 2.20	7.0
		15/07/1998	12.4 ± 1.58	12.6 ± 1.24	3.84
	Growth inhibition marine diatom	08/06/1998	No inhibition	No inhibition	10.8
	Oyster larvae	09/04/1997		No toxicity	7.0
Gravelines	Embryotoxicity	19/06/1997		No toxicity	20.8
	His et al. (1999)	02/07/1997		No toxicity	23.2
		23/07/1997		No toxicity	39.5
		02/09/1997		No toxicity	25.7

Table 9.12 Chemical properties associated with bioaccumulation processes of the major CBP produced by the cooling water chlorination at marine power stations

	Log K_{ow}	Water solubility (g/L)	Log BCF[a]
Bromoform	2.27–267	0.86–5.0	1.48–1.57
DBCM	2.23–2.24	2.26–4.4	1.74–1.36
BDCM	1.88–2.10	2.9–4.7	1.25–1.47
DBAA	1.22	25.7	0.57
DBAN	1.06	59.2	0.45
TBP	3.92–4.02	0.01–0.07	2.69–2.78

[a]BCF bio-concentration factor, based on QSAR

appears more susceptible for bioaccumulation, but the QSAR evaluation leads to bioconcentration factor of only 600. A bioconcentration factor as low as 1.4 in "edible portions of all aquatic organisms consumed by Americans" is mentioned for 2,4,6-TBP (Grove et al. 1985).

Biomagnification occurs for high Log K_{ow}. It is admitted that the biomagnification factor 1 has to be applied when Log $K_{ow} < 5$ (TGD 2001); thus all the CBPs do not exhibit a significant biomagnification level.

By field data collected on mussels (*Mytilus edulis*), periwinkles (*Littorina littorea*) and mullets (muscle) in the discharge canal and in the effluent plume of the Gravelines Power stations in 1981, the bioconcentration factor of bromoform is between 1 and 3. The depuration of bromoform in mussels was complete in 2 days after the cessation of chlorination. These findings confirm the low BCF of bromoform in marine invertebrates and fish and the rapid depuration of the organisms found in the experiments of Gibson et al. 1980 (Table 9.13).

In 96 h experiments of exposure of the American oyster *Crassostrea virginica* to bromoform, rapid uptake of this THM was observed in the soft tissues to reach a threefold bioconcentration factor. Two days after the bromoform exposure, depuration was complete (Scott et al. 1980). The uptake and depuration of THM are rapid processes and these types of CBPs are not bioaccumulated except in fats where maximum concentrations exceed the average level in soft tissues.

5.8 Study on Ecotoxicity of CBPs on Sea Bass

The biological effects of long term exposure of sea bass, *Dicentrarchus labrax*, to CBPs were studied in relation to power station cooling water chlorination. Parameters considered were bioconcentration of CBPs in fat and histology of muscles and liver. CBPs measured were THMs, dibromoacetonitrile, dichloroacetonitrile and total organic halogens (TOX as Cl/kg fat). Liver tissue was examined by light microscopy to look for abnormalities, necrosis and signs of pre-neoplastic lesions. Commercially cultured fish in the chlorinated effluent of Gravelines power station were used as exposed group. These fishes of the Gravelines aquaculture farm are

Table 9.13 Bio-concentration of bromoform after exposure of marine invertebrates and fish for 28 days

	Water concentration (mg/L)	Body burden (μg/g wet wt.) after 28 days	BCF[a]
Bivalve molluscs			
Crassostrea virginica	0.03	0.00	
	0.09	0.0–0.18	0–2
	0.86	0.22–0.48	0.26–0.56
Mercenaria mercenaria	0.03	0.00–0.03	0–1
	0.09	0.23–0.25	2.6–2.8
	0.99	0.09–0.21	0.1–0.21
Prothotaca staminea	2	1.08	0.54
	19	14.25	0.75
Shrimp			
Penaeus aztecus	0.03	0.26	8.67
	0.05	0.00	0
	0.29	0.37	1.28
Fish			
Brevoortia tyrannus	0.03	0.00	0
	0.04	0.15	3.75
	0.21	0.67	3.20

Data from Gibson et al. (1980)
[a]*BCF* bio-concentration factor

raised in warm water containing CBPs approximately 7 months a year. Comparable cultured fish from farms on the Spanish and French coast were used as controls. Wild sea bass from sites considered uncontaminated on the Atlantic coast of Spain and were used as reference.

Results of this study indicate that long-term exposure to CBPs does not impose an ecotoxicological risk on sea bass. Extensive histopathological study did not show any signs of liver tissue damage that could be attributed to CBP exposure. Bromoform was found in relatively high concentrations in cultured sea bass fat, up to 894 μg/kg (i.e. a bioconcen-tration factor of 40). Bromoform rapidly disappeared from the fat after chlorination was stopped and bromoform concentrations were below detection level (<3 μg/kg fat). Muscle tissue did not show any bioconcentration of bromoform. Other CBPs found frequently in the fat were dibromoacetonitrile and dichloroacetonitrile. TOX levels in fish fat were not positively correlated with CBP exposure. On the contrary, when CBP levels were high (summer) TOX levels were relatively low. TOX levels in wild fish from uncontaminated water were comparable to those in fish from chlorinated water. It can be concluded that for sea bass and probably for most fish species, survival rates are comparable in chlorinated and non-chlorinated water. Long-term exposure to CBPs produced by low-level chlorination (1–2 mg/L TRO) did not impose ecotoxicological stress. It is pertinent to mention here that fish can detect low levels of chlorine and actively avoid areas with higher chlorine concentrations.

5.9 Genotoxicity

This is probably the major environmental and health issue for this type of persistent substances. Some evidences of mutagenic activity were found for CBPs in chlorinated drinking water. Unfortunately, few studies are available on CBPs found in seawater and the interpretation of the results in terms of environmental and health risks are not easy. In a study of the genotoxicity of 14 organohalogenated compounds identified in drinking water, using three bacterial and mammalian cells in vitro, it was found that brominated halomethanes are genotoxic and that bromoacetonitriles are more genotoxic than chloroacetonitriles, suggesting a structure–activity relationship between the number of bromine substituents in the molecules and the genotoxic activity (Le Curieux et al. 1996). In vivo assays based on micronuclei tests in mouse bone marrow cells and unscheduled DNA synthesis in rat liver do not confirm the previous results: bromoform and brominated THMs do not exhibit a genotoxic activity (Stocker et al. 1997). However, it is mentioned in the paper that brominated THMs cause increase of the tumour in rat and mouse but "their mode of action as rodent carcinogens remains unexplained".

In the collaborative research project on CBPs (KEMA, Nuclear Electric, Akzo Nobel, EDF), 12 determinations of mutagenicity were carried out on cooling waters at EDF power stations using the bacterial Mutatox® test. The results of the Mutatox® tests were negative, except in one case on both samples from the intake canal and the outfall 1 of unit 4 at Gravelines.

6 Conclusions

In summary, chlorination of seawater involves, in reality, NOT chlorine chemistry but bromine chemistry. Figure 9.10 presents the salient aspects of the chlorine and bromine chemistry.

6.1 Chlorination in Control Application

It is important to mention that the dosing rates and effective concentrations of chlorine, the formation of CBPs and the potential environmental effects, depend largely on the quality of the surface water used for cooling. The chemical characteristics of the sea water and presence of organic compounds play a major role in chlorine demand and formation of CBPs. Also, the residence time of the water within the system will determine the eventual presence of CBP compounds and concentrations.

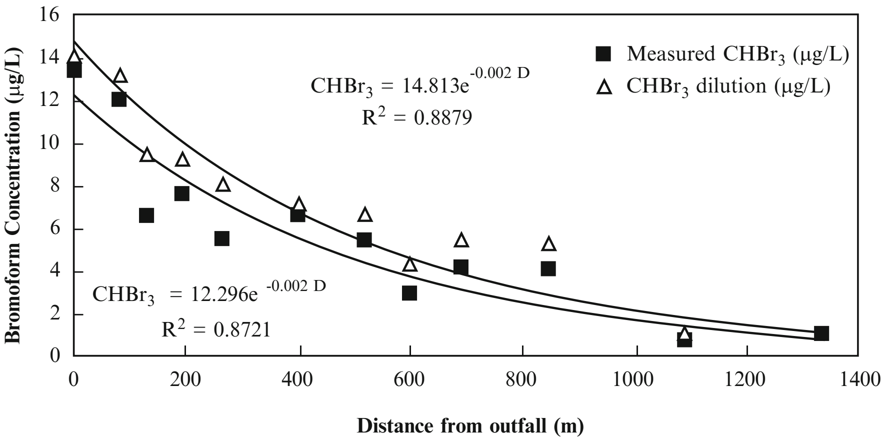

Fig. 9.10 Bromoform decay in the discharge plume of Heysham power station (UK) on 16/07/93. Comparison of measured concentrations and concentrations calculated according to the dilution rate of the cooling water based on water temperature (Jenner et al. 1998)

The acquired experience in the chlorination of the CWS of marine power plants in Europe (Jenner et al. 1998) can be summarised as given below:

- It is necessary to maintain the minimum TRO of 0.2 mg/L in all parts of the CWS to be protected against macrofouling.
- In order to achieve this TRO level, an initial chlorine dosing concentration between 0.5 and 2.0 mg/L, depending on the water quality and the design of the cooling system, is generally required.
- At all sites where the growth rate of macrofouling organisms is high enough to affect the power station operation, it is necessary to use continuous chlorination over the whole period of settlement and growth of the targeted species.
- Pulse-Chlorination® (intermittent dosing at high frequency; 15–30 min on, then 15–30 min off) applied during the continuous treatment period is effective and allows up to 50% reduction in the consumption of chlorine and the associated discharges of CBPs.
- Concerning the risk of chemical corrosion, the initial chlorine concentration in the CW system may not exceed 3 mg/L TRO. This is an absolute safe limit value, which is well above the minimum recommended concentration for effective biofouling control. Potentially dangerous level for corrosion starts at 5 mg/L TRO.

6.2 Impact of Residual Oxidant Discharges on Coastal Marine Ecosystems

Various components explain the oxidant demand in natural waters, responsible for the decrease of TRO in CWS: chemical reaction with ammonia and dissolved organic compounds, consumption by the organic biofilm covering the walls of the cooling system and solar light. Finally, there is generally a residual of 0.1–0.4 mg/L at the outfall for a chlorine dosage of 1 mg/L. During the process of mixing of the cooling water into the discharge plume, the dissipation of the residual oxidants does not follow the dilution of the cooling water. The loss of TRO is more rapid than the temperature decay. At the majority of open coast sites, the formation of monochloramine is excluded by the low ammonia content in seawater ($NH_4^+ \leq 0.1$ mg/L at pH 8.1) and only brominated combined oxidants does exist. In seawaters with high ammonia content, monochloramine is produced at Cl_2/N molecular ratio <1.5. However, monochloramine formed by chlorination of seawaters is much less persistent than in freshwaters.

Brominated oxidants compounds formed in chlorinated seawater disappear very rapidly. Though they are not bioaccumulated, they exhibit short-term toxicity for the marine flora and fauna.

In bioassays involving chlorination, it is almost impossible to constantly maintain a given level of oxidants in the experimental system. Moreover, chlorine measurement methods suffer from poor analytical limits. The current methods measure the residual oxidants as the TRO. The limit of measure of the reference method (Colorimetric DPD) in natural waters is in theory 0.01 mg/L but in practice it does not exceed 0.03 in 0.05 mg/L in turbid (organic rich) waters. These specific difficulties probably explain why, among the large number of short-term and long-term chlorine bioassay data on marine organisms found in the scientific literature, the majority of data concerns toxic effects observed in the range of two orders of magnitude, namely, from 0.05 to 5 mg/L.

An interesting complement to the exclusive use of experimental data is collection of field data for the development of ecological models. Field studies confirmed the experimental data showing the high sensitivity of bacteria and phytoplankton to residual oxidants. Almost total disappearance of living bacteria has been observed in chlorinated water at TRO $\geq$ 0.2 mg/L. At the outlet of the cooling system, a loss of phytoplankton biomass (chlorophyll a) and production to the extent of 50–90% was found at British and French power stations. A progressive recovery of the bacterial and phytoplankton metabolism was observed in the plume area where the TRO decays from 0.05 to 0.01 mg/L.

In conclusion, there are no significant biological effects on the plankton and benthos beyond the mixing zone of the chlorinated effluents, which is limited by the TRO concentration of 0.01–0.03 mg/L. In tidal seas, the exposure of benthos may last half of the time because of the periodical movement of the discharge plume.

6.3 Impact of the Persistent CBPs on the Marine Coastal Ecosystem

As shown on Fig. 9.11, the organohalogens formed by chemical reactions of oxidants with dissolved organic matter are dominated by brominated compounds.

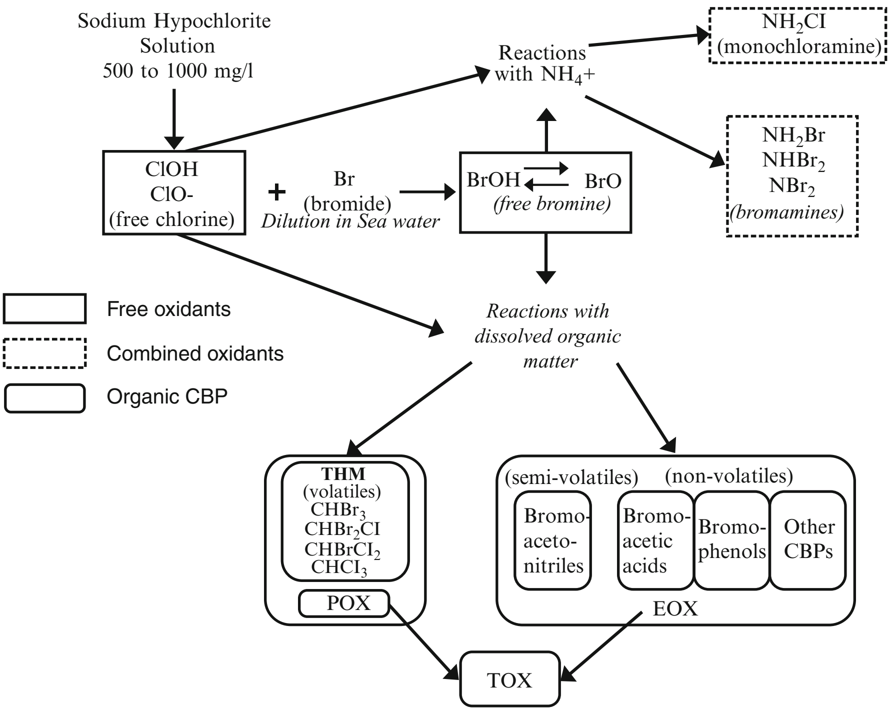

Fig. 9.11 Chlorine and bromine basal chemistry during chlorination of seawater

The main compounds identified in chlorinated cooling waters belong to three chemical categories:

- THM—they are among the most volatile CBPs. Among the THMs bromoform represents ≥95% and about 4–65% of the total measured CBPs. Mean concentrations in the cooling waters: 7–27 μg/L.
- Bromoacetonitriles and bromoacetic acids—mainly dibromoacetonitrile (DBAN), which on hydrolysis forms dibromoacetic acid (DBAA). These two compounds represent 30–60% of the total measured CBPs. Mean concentrations of DBAN + DBAA in the cooling waters: 8–14 μg/L.
- Bromophenols—mainly 2,4,6-tribromophenol (TBP) representing 0.3–0.9% of total measured CBPs. Average concentrations are in the range 0.1–0.4 μg/L.

In the near field of discharge plumes, the decay of the above CBPs follows the dilution rate of the cooling water, even for the volatile THM. CBP concentrations decrease rapidly at the limit of a mixing zone, defined by a dilution of factor 10, to reach about 0.5–5.0 μg/L for bromoform, 1–2 μg/L for DBAN + DBAA and 0.01–0.04 μg/L for TBP. However, in the far field, volatilisation is the main process of decay for the THM.

The annual production of CBPs by the chlorinated cooling waters of all the French coastal power plants in 2000 was estimated to be approximately 210 tons. This value pales in comparison with the natural production of bromoform by seaweeds and planktonic micro-algae in The Channel (estimated to be a few hundreds to a few thousands of tons) and with the production of bromoform in the world ocean (one to two million tons).

Among the various chlorination by-products, only TBP could reach higher bioconcentration factors (600 based on QSAR). The uptake and depuration of THM from marine organisms are rapid processes and the CBPs are not bioaccumulated except in fats, where maximum concentrations exceed the average level in soft tissues.

In the case of most of the CBPs, the acute toxicity threshold for marine many species of biota exceeds 10 mg/L. Even very sensitive bioassays, such as those testing for embryonic abnormalities in oysters and sea urchins, showed that the CBPs present a lesser acute toxicity than the residual oxidant species. However, it appears that the toxicity threshold for DBAN may be as low as 50 μg/L.

Nevertheless, in contrast to the TRO, CBPs are persistent substances and their chronic toxicity constitutes a key question in the impact assessment of these substances. There is lack of sufficient experimental data to precisely assess the chronic toxicity levels of these substances.

As it was mentioned for oxidisers, field studies are an essential complement to experimental data. Long-term field observations can answer the questions regarding the risk of chronic toxicity. From this point of view, long-term ecological surveillance is a valuable tool and it is advisable to develop such programmes at marine power plant sites.

Several organohalogenated substances identified in chlorinated drinking waters are known to be mutagenic and some are suspected to be carcinogenic. Therefore, special attention must be given to the potential genotoxic effects of CBPs in sea water. There is also a lack of knowledge in this topic. Probably, one of the most worrisome by-products is bromate ion, which may form in tanks of sodium hypochlorite, when it is produced by on-site electrolysis of sea water. To avoid the formation of bromate, it is recommended to reduce the storage time of the hypochlorite solution as much as possible.

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Chapter 10
Biofouling Control: Alternatives to Chlorine

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1 Introduction

Knowledge about the fouling organisms in the cooling systems and their implications on the operational efficiency is a prerequisite to the design and monitoring of fouling control strategies in power stations (Whitehouse et al. 1985; Jenner et al. 1998). Several types of antifouling processes, which have been used in large cooling water circuits, fall into two main categories (Rajagopal 1997; Rajagopal et al. 2010a): physical methods, in which there is no addition of chemical substances to the cooling water, and chemical treatments that use injectable or surface-bound chemical toxins (Rajagopal et al. 2010b). The development status of the various methods is quite variable: some are in moderate or even widespread industrial use, others are being tested on site, while many remain for the moment at the level of laboratory research (Claudi and Mackie 1994).

The central focus of this chapter is biofouling and its control in large cooling water systems (CWS) fed with natural raw waters with flow rates exceeding 1 m^3/s. Effective antifouling techniques developed for other types of systems (e.g., ship hulls) are not suitable for industrial applications such as power stations

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(WHOI 1952). In order to achieve economical and operationally feasible solutions, it is important to note that the methods must be appropriate to each type of fouling (bacterial slime, macrofouling organisms, etc.) and to the specific design of the cooling circuit (Jenner et al. 1998; Rajagopal et al. 2010a). While there do exist generic solutions applicable to major categories of organisms, optimizing the procedures requires certain amount of biological knowledge (Rajagopal 1991, 1997). The objective of an economically and environmentally optimized antifouling regime is not total elimination of settlement of organisms within the cooling circuit; in most cases, the goal is to control their settlement and to prevent the growth from becoming excessive (Rajagopal et al. 1996). In operational parlance, a treatment must limit the build-up of fouling in cooling circuits and heat exchangers during the period between two successive scheduled outages, to a point below the threshold at which plant operation begins to be affected. In many cases, antifouling methods at a given site are concerned with only one or two major fouling species, for which generic procedures can be adopted, taking into consideration their periods of larval settlement and their growth rates (Rajagopal 1997; Rajagopal et al. 2002a, 2003b, 2010b). This implies acquiring biological knowledge and carrying out long-term biomonitoring at each site, so as to follow the population development (Rajagopal et al. 1998). Other important elements to be considered are the configuration of the cooling circuits and feed-pump operation (Claudi and Mackie 1994). These determine the hydraulic regime, most particularly variations in discharge and water velocity, as well as areas most favorable to settlement and growth of biofouling organisms (Whitehouse et al. 1985; Jenner et al. 1998).

2 Existing Control Strategies in Industrial Cooling Water Systems

A list of the methods commonly used in the cooling circuits of European power stations is given in Table 10.1. Different methods are currently used in European power stations. The data presented in the table come essentially from experience acquired by power station operators in France, the United Kingdom, the Netherlands, and Italy. The physical methods comprise water filtration, mechanical cleaning, high water velocity, and heat shocks (Claudi and Mackie 1994; Jenner et al. 1998). Among the chemical treatments, chlorination is the most common biocidal approach (Table 10.1). For the purposes of illustration, the fouling control methods infrequently used by different power stations to control bacterial slime and macrofouling settlement are summarized in Table 10.2. More recently, new methods have evolved from the zebra mussel research projects conducted in North America since the introduction of this species at the end of the 1980s (Van der Velde et al. 2006). Ontario Hydro and EPRI programs have played a major role in testing these new methods (Claudi and Mackie 1994). Some have been tested on-site and have proven to be efficient against this particular invasive species (Rajagopal et al. 2010a, b).

Table 10.1 Physical and chemical antifouling treatment methods commonly used in cooling circuits of European power stations (modified after Jenner et al. 1998)

Treatment	Methods		Biofouling target	Remarks
Water filtration	Gross filtration (>1–10 cm)	Grids of water intake generally equipped with trash racks	To remove natural or artificial drifting debris at water intakes	Commonly used in Europe
	Fine mesh filtration (1–10 mm)	Rotating screens band or drum filters at water intakes. Debris filters to protect heat exchangers. Removable grids with screens	To remove natural or artificial drifting debris at water intakes. Stops biological debris arising from the fouled walls of the intake culverts (shells)	Commonly used in Europe
Mechanical cleaning	Manual cleaning	Dry or underwater cleaning of pipes and basins. High pressure water cleaning of removable screens and heat exchangers	To remove settled macro-biofouling. To eliminate bacterial slime on condensers or plate-type heat exchangers	Commonly used in Europe
	Automated cleaning systems	High-pressure water cleaning of rotation screens	To remove drifting debris from the screen	Commonly used in Europe
		Continuous cleaning of condenser tubes by sponge balls	To remove bacterial slime (and some scale)	Widely used in Europe
		Self-cleaning debris filters	To remove biological debris produced by macrofouling	Widely used in Europe
		Cleaning plate heat exchangers (PHE) by vacuum suction processes	To remove biological debris and mineral deposits	Occasionally used
Water velocity	High water velocity	Increasing the water velocity above critical values dependent on the species to be eliminated	To avoid settlement of macrofouling	Commonly used in Europe
Heat treatment	Thermal backwash	Increasing the water temperature by recirculation for a few hours several times a year	To avoid settlement of macrofouling on parts of the circuits with lower water velocities	Some marine and freshwater power stations

(continued)

Table 10.1 (continued)

Treatment	Methods		Biofouling target	Remarks
Chemical treatments	Low toxicity paints and coatings	Applied on parts of the circuits with lower water velocities	To avoid settlement of macrofouling	Some parts of cooling circuits increasingly used
	Chlorination with sodium hypochlorite or chloramines	Continuous treatment at a low dosage (generally ≤1 mg/L). Possibility of semi-continuous injection	To control marine macro-biofouling and bacterial slime. To eliminate Bryozoans in cooling tower basins	Widely used at marine power stations; some use in cooling towers
		Shocks chlorination of cooling tower basins: 8–40 mg/L for 4–6 h	To eliminate green and blue-green algae	Some cooling towers in France and Belgium

Table 10.2 Physical antifouling methods and chemical treatments tested on-site on large industrial cooling circuits

Processes and treatments	Methods	Function	Biofouling target	Uses on large cooling water circuits
Water filtration	Microfiltration (<0.1 mm)	Filters to protect the entire circuit	Stops plankton larvae (zebra mussels, marine mussels, barnacles) to prevent settlement on the walls of the circuit	Tested at the Bergam power station and in Canada at an Ontario Hydro power station against zebra mussels
Other physical methods	Ultraviolet light	Kill macrofouling plankton larvae at the water intake	To prevent settlement of macro-biofouling[a] on the walls of the circuit	Tested in Canada at an Ontario Hydro power station against zebra mussels
	Sound blasts	Remove macrofouling from the walls of some parts of the circuits	To prevent development of macro-biofouling on the walls of the circuit	Tested in the US on power stations against zebra mussels
	Nontoxic paints and coatings	Especially efficient on the parts of circuits where the water velocity is high enough to produce a synergistic effect	To reduce settlement of macrofouling. To facilitate cleaning of fouled walls	Some parts of cooling circuits. Increasingly used in the US and Japan
Chemical treatments[b]	Oxidizing compounds	Chlorine dioxide	To eliminate macro-biofouling and bacterial slime	Tested on power stations in Italy and Spain; used on large cooling circuits in Italy and France
		Ozone: continuous treatment of cooling water	To eliminate macro-biofouling and bacterial slime	Tested on a cooling tower circuit in Belgium, applied at RoCa power station (tower assisted) in Rotterdam, the Netherlands
	Organic compounds	Organic tin in coating or added in solution	To eliminate macro-biofouling and bacterial slime	Tested at some marine stations over 10 years ago. Abandoned for environmental reason
		Fatty amines: short-term (24 h) or long-term intermittent treatment (2 times 20 min a day)	To control macro-biofouling and bacterial slime	Tested at some marine power stations in the Netherlands, France, and Belgium
		Quaternary amines for short-term (24 h) or long-term intermittent treatment (2 times 20 min a day) with Glutaraldehyde isothiazolones	To control macrofouling and bacterial slime. Gluteraldehyde does not eliminate fungi and algae	Widely used in the US. Some use in European countries

[a]Macro-biofouling represented by macroalgae, sponges, hydroids, annelids, bryozoans, barnacles, bivalve shellfish, and gastropod mollusks etc.
[b]KEMA BV listed 13 different organic compounds used as antifouling agents in the Netherlands in 1996; modified after Jenner et al. 1998

Trials have been conducted or research is in progress to test the efficiency of several physical methods or selected oxidizing compounds and organic compounds (Table 10.2). These include microfiltration, nontoxic coatings, UV light, electrolytic currents, cathodic protection, acoustic energy, and use of organic compounds. In European countries, alternatives to chlorination (e.g., chlorine dioxide or ozone) and some organics have been investigated (Jenner et al. 1998). Most have proven efficient in controlling at least one type of biofouling. However, their cost or environmental impacts will limit their widespread use in CWS. Zebra mussel control programs have shown that some methods such as magnetic fields are not effective or suitable for large CWS (Claudi and Mackie 1994). Similarly, bromination and ozonation of seawater generate the same oxidants and by-products as reported for chlorination and are more expensive (Jenner et al. 1998). Finally, some methods can be useful for very specific applications, such as addition of potassium chloride in fresh water cooling circuits to eliminate zebra mussels (Claudi and Mackie 2009). Table 10.3 presents a list of potential antifouling methods currently not used in large cooling water circuits. These primarily include natural repelling agents, natural biocides, toxins, and biological control methods. For these methods, no detailed data are yet available to allow assessment of their efficiency, cost, and environmental acceptability on the basis of actual industrial feedback (Rajagopal 1997). Some, however, are currently used in completely closed circuits or low discharge systems, while others are still in the research phase (Rajagopal et al. 2010a, b). Of these, some appear promising and may, in coming years, find applications in large industrial CWS; others may not prove useful for such applications or will not go beyond the laboratory level evaluation (Table 10.3).

3 Evolution of the Antifouling Strategy

The search for efficient, environmentally sound, and economically viable biofouling control methods for industrial CWS has been going on since the beginning of twentieth century (Jenner et al. 1998; Rajagopal et al. 2010a). The first major report on the different aspects of biofouling problems in cooling conduits of power station was that of Ritchie (1927), followed by the publications *Marine Fouling and Its Prevention* (WHOI 1952), *Marine Boring and Fouling Organisms* (Ray 1959), *Biofouling Control Procedures: Technology and Ecological Effects* (Jensen 1977), *Marine Biodeterioration: An Interdisciplinary Study* (Costlow and Tipper 1984), and *Cooling Water Management in European Power Stations: Biology and Control of Fouling* (Jenner et al. 1998). Works of Woods Hole (1952) and Ray (1959) do not offer useful data upon which to base a marine fouling control protocol for industries that use cooling water (e.g., power stations), where very large volumes of seawater are continuously pumped. However, the value of these two books is in the background information given on the wide variety of compounds investigated in as a part of the search for suitable chemicals, and in the details of the life history, colonization,

Table 10.3 Other promising physical and chemical antifouling methods which are under investigations in industrial cooling water systems (CWS) (modified after Jenner et al. 1998)

Methods	Treatments	Target/objective	Remarks
Toxic metals	Electrolytic generation of copper and aluminum ions	Microfouling and macrofouling	In small CWS (ships, offshore oil, and gas industry)
Settlement inhibitors	Artificial or natural compounds	To prevent settlement of mussel and barnacle larvae	Research in progress in the USA and European countries
Oxidizing compounds	Toxic paints with no toxic releases: Quaternary ammonium grafted on the paint	To eliminate the bacterial film and possibly to prevent settlement of macro-biofouling	Research in progress
	Hydrogen peroxide	To eliminate bacterial slime and algae; probably efficient against macro-biofouling (known to be involved in some natural antifouling processes, by Echinoderms)	Disinfection of swimming pools and in the food industry
Pathogen agents	Paracetic acid	To eliminate bacterial slime and algae; probably efficient against macro-biofouling	Disinfection in the food industry
	Brominated compounds such as BCDMH (bromochlorodimethyldation)	Bacterial slime	Used in small CWS
	Bacterial toxins	To kill macrofouling such as zebra mussels	Research in progress in the USA
Natural biocides	Produced by plants or animals	To kill macro-biofouling such as zebra mussels	Research in progress in the USA

and growth rates of a large number of fouling organisms. Jensen (1977), Costlow and Tipper (1984), Jenner et al. (1998), and Rajagopal et al. (2010a, b) provide state-of-the-art review of biofouling control in industries, as available at the time of their publication. In recent years, continuing efforts have been made in the optimization of conventional antifouling treatments (Rajagopal et al. 1995a, b, 1997a, b, 2002a, b, c, 2003a, b, 2005a, b, 2006a, b, 2010a, b). New methods have also been investigated (Molloy 2002; Molloy and Mayer 2007; Costa et al. 2012; Rajagopal 2012).

To date, the major emphasis for work on fouling control has been in the marine field (Whitehouse et al. 1985). The reasons for this have been well summarized by Mattice (1983) and Jenner et al. (1998). However, it is also clear from experience in Europe and the USA during the last half century that freshwater fouling is also a case of equally serious concern, especially as invasive species, transported around the globe by various anthropogenic activities, colonize new geographical zones and become extremely formidable pest species (Rajagopal and Van der Velde 2012). Excellent examples are the zebra mussel and the Asiatic clam (refer to Van der Velde et al. 2006 for review). Such developments remind us about the need to engage in continuous research to develop novel control procedures. Many studies conducted in Canada and the United States to control the impact of invasion of inland waters by the zebra mussel at the end of the 1980s have given rise to publications of great interest (EPRI 1992; Nalepa and Schloesser 1993; D'Itri 1997; Claudi and Mackie 2009). The last decades represent a new phase of zebra mussel invasions in Europe, with range extensions to other countries such as Ireland and Spain (Pollux et al. 2003; Rajagopal et al. 2009), as well as range expansion to new areas within countries. The latter is probably caused by increased economic and recreational activities, which provide vectors for the dispersal. Recently, up-to-date overview of European experience with zebra mussel fouling and its control in industrial CWS has been reviewed by Rajagopal et al. (2010a, b).

4 Alternatives to Chlorine

4.1 Chlorine Dioxide

Chlorine dioxide is a potential alternative to chlorination because of its effectiveness as a disinfectant (Bernarde et al. 1965) for control of microbial slimes in condenser tubes of inland power stations (Rauh 1979; Mayack et al. 1984) and because there is less production of organohalogenated by-products (Ben Amor et al. 1988; Lykins and Griese 1986). Although the main uses of chlorine dioxide are for pulp and paper bleaching, food processing, drinking water, and wastewater disinfection, its efficacy has been tested on-site in large marine CWS in Italy and Spain.

4.2 Production of Chlorine Dioxide

Chlorine dioxide is a gas and, unlike chlorine, cannot be condensed and liquefied because of the risk of explosive disintegration. For this reason, it has to be produced on-site using sodium chlorite ($NaClO_2$) in two principal ways (Schneider 1997): chlorite oxidation by chlorine gas.

$$2NaClO_2 + Cl_2 \rightarrow 2ClO_2 + 2NaCl \quad (10.1)$$

This reaction requires excess of chlorine to optimize the chlorine dioxide production yield. The second method is acidification of sodium chlorite:

$$5NaClO_2 + 4HCl \rightarrow 4ClO_2 + 5NaCl + 2H_2O \quad (10.2)$$

This is the most common industrial process used for ClO_2 generation for cooling water treatment. To maximize the production yield of chlorine dioxide (up to 95%) and to reduce resulting by-products, large excess of HCl (>250%) is required.

In yet another method, some commercial firms are using hydrogen peroxide to generate chlorine dioxide according to the reaction:

$$NaClO_3 + \tfrac{1}{2}H_2O_2 + \tfrac{1}{2}H_2SO_4 \rightarrow ClO_2 + \tfrac{1}{2}Na_2SO_4 + H_2O \quad (10.3)$$

In this method, aqueous solutions of 40% sodium chlorate and 7–10% hydrogen peroxide are used as precursor chemicals for the production of chlorine dioxide. This method is claimed to be “chlorine-free,” as it does not use chlorine for ClO_2 generation.

As clearly stated by Schneider (1997), there is no such thing as stabilized chlorine dioxide in a canister. These preparations are nothing more than diluted sodium chlorite solutions.

It must be borne in mind that chlorine dioxide gas at air concentrations above 10% is explosive in the presence of a flame (Masschelein 1979). Therefore, gas generators must be designed to eliminate this risk. Chlorine dioxide solutions are explosive above a concentration of 30 g/L and hence the concentration at all points of the production system must be kept safely below 30 g/L. It is also necessary to avoid any accidental mixing of the reagents (chlorite and acid). Acute exposure of workers results in irritation of eyes, nose, throat, and lungs. The short-term exposure limit for people working in chlorine dioxide production areas is 0.9 mg/m^3 (Gordon and Bubnis 1997).

4.3 Chemistry of Chlorine Dioxide in Aqueous Solution

Chlorine dioxide is a gas at ambient temperature. It is very soluble in water and is decomposed by light. It is a powerful oxidant with the following global reduction reaction involving five electrons (Belluati et al. 1997):

$$ClO_2 + 4H^+ + 5e^- \rightarrow Cl^- + 2H_2O \quad (10.4)$$

Unlike in the case of free chlorine, the oxidizing power of chlorine dioxide is pH-independent in a wide pH range (5.0–9.5). In aqueous solutions, chlorine dioxide does not react with bromide ions as do other oxidants like ozone, chlorine, or hypochlorite. This means that it does not produce free bromine in seawater. In a major departure from chlorine-based reactions, it does not react with ammonia to form chloramines and does not chlorinate organic compounds. As a consequence, it does not produce chlorophenols, trihalomethanes (THMs) or, in general, absorbable organohalogens (AOX). Chlorine dioxide oxidizes metals in reduced forms (Fe^{2+}, Mn^{2+}), nitrites (NO_2^-) and sulfites (SO_2^-) and dissolved organic matter (Doré 1989). This process can cause high demand in polluted or eutrophic natural waters. It can also produce deposits of $Fe(OH)_3$ and MnO_2 in heat exchangers.

Inorganic by-products such as chlorite ions (ClO_2^-) and chlorate ions (ClO_3^-) are produced during the generation phase (Lefebvre and Deguin 1997), but chlorite is also formed by the oxidation process itself:

$$ClO_2 + \text{organics} \rightarrow \text{oxidation products} + ClO_2^- \quad (10.5)$$

The chlorite concentration in treated water depends on the demand of the water; it will be >1 mg/L if the ClO_2 demand is higher than 1 mg/L (Gordon and Bubnis 1997). At pH 7, chlorine dioxide solutions are stable but hydrolysis occurs at basic pH to form chlorite and chlorate:

$$2ClO_2 + 2OH^- \rightarrow ClO_2^- + ClO_3^- + H_2O \quad (10.6)$$

Photochemical reactions result in formation of chlorate ions. Some organohalogenated compounds can also be formed by indirect chlorination due to the hypochlorous acid produced by chlorine dioxide reactions on different substances such as phenolic compounds (Doré 1989). Moreover, the US-EPA has identified bromates and aldehydes as by-products that can be formed by chlorine dioxide. The aldehydes include the propanal to decanal series, glyoxal, methyl glyoxal, and benzaldehyde (Richardson 1997). Several analytical methods have been developed to measure chlorine dioxide and its inorganic by-products. The amperometric method (Eaton et al. 2005) determines concentrations of ClO_2, ClO_2^-, and ClO_3^-. This method by difference is, however, subject to major errors, in particular for chlorates (Gordon and Bubnis 1997). Online amperometric systems exist for continuous monitoring of chlorine dioxide levels with a detection threshold in seawater as low as 10 μg/L. Ente Nazionlae Energia Electtrica (ENEL) has developed a continuous potentiometric method with the same detection threshold of 10 μg/L. Among the calorimetric methods (lissamine green B, chlorophenol red, amaranth), amaranth has the best specificity and the lowest quantification limit, at 20 μg/L (Mantisi et al. 1997). Ion chromatography can be used to measure chlorites and chlorates at 10 μg/L level (Gordon and Bubnis 1997).

4.4 Experimental Data on Chlorine Dioxide Efficacy

Experiments performed at a pilot plant fed with Seine river water have shown that to eliminate microfouling and filamentous algae which develop on the packing of cooling towers, a residual dose of 1.5 mg/L chlorine dioxide for 2 h is required. At the 0.3 mg/L concentration, the exposure time required is a few days (Merle and Montanat 1980). With respect to macrofouling in freshwater systems, laboratory data are available on zebra mussels *Dreissena polymorpha* (Montanat et al. 1980; Van Benschoten et al. 1993; Khalanski 1993; Matisoff et al. 1996). It was observed that brief exposure (13 min at 10 mg/L or 3.2 min at 40 mg/L) kills 50% of adult mussels. On the other hand, there was no significant mortality for 6 h of exposure at 2 mg/L. On Lake Erie mussels (Matisoff et al. 1996), intermittent injections of 1 mg/L for 30 min a day for 28 days were not effective. Mortality was significant at 5 mg/L and it took only 4 days of exposure at 40 mg/L to kill 95% of adult mussels. These findings show that intermittent chlorine dioxide dosing at relatively low concentrations, repeated over several days, can kill between 50 and 90% of adult zebra mussels. Chlorine dioxide is, therefore, more effective than chlorine in intermittent treatments at high concentrations.

Continuous treatment with chlorine dioxide kills adult zebra mussels in 8 days at a residual of 0.2 mg/L. The lethal time (LT_{100}), the time required to kill 100% of the exposed mussels, is given by the following relation:

$$LT_{100} = 4.47 + 3.79 * \mathrm{LOG(C102)} = 0.94 \tag{10.7}$$

ENEL has tested the efficacy of chlorine dioxide in seawater in model culverts. No macrofouling development was found on concrete plates at residual concentrations of 0.1–0.2 mg/L and after a month of continuous treatment at 0.1 mg/L. Moreover, there was no microfouling growth on condenser tubes (Ambrogi 1997). Experiments with chlorine dioxide on the Mediterranean hydroid *Laomedea flexuosa* by ENEL (Geraci et al. 1993) showed no significant decrease in hydroids at 0.05 mg/L for 96-h exposure. However, significant reduction was observed at 0.1–0.2 mg/L for 48-h exposure, while total elimination of hydroids was recorded at 0.1–0.2 mg/L for 96-h exposure.

At the Vandellos II nuclear power station site on the Mediterranean coast of Catalonia in Spain, laboratory experiments have been conducted using the marine mussel *Mytilus galloprovincialis* (Belluati et al. 1997). The results showed that chlorine dioxide at a residual of 0.2 mg/L kills the mussels more rapidly than chlorine at a residual of 1.1 mg/L. Experiments have shown that long-term semicontinuous addition of chlorine dioxide at a residual of 0.2 mg/L, 1 h on, 2 h off, is as effective as continuous treatment. To achieve the same effect with semicontinuous addition of hypochlorite, significantly higher residuals (1.0–1.2 mg/L) have been employed. As regards other macrofouling, chlorine dioxide treatment can significantly reduce biological growth when the oxidant is added for 8 h/day (Jenner et al. 1998).

4.5 Industrial Level On-Site Testing of Chlorine Dioxide

Very little data are available on industrial level testing of chlorine dioxide as an antifouling agent, especially for macrofouling control. A few large-scale experiments at cooling circuits of power stations fed with seawater have been conducted in Italy and in Spain. Details of some of the prominent studies are given here.

At Brindisi Nord power station (4,320 MW) located on the Adriatic Sea, biofouling is mainly composed of calcareous tube serpulids, hydroids, mussels, and barnacles (Ambrogi 1997). The condenser tubes are not equipped with a sponge-ball cleaning system. The cooling water intake is located in a sheltered basin of the Brindisi harbor where municipal sewage discharges high amounts of organic matter. Chlorine dioxide produced on-site was continuously added to the cooling water from 1989 to 1992. In 1989, the dosage was 0.22 mg/L. Since 1990, it was reduced to 0.18 mg/L during the summer season and 0.07 mg/L in winter from November to May. This was done to allow for the seasonal variation in chlorine dioxide demand. Chlorine dioxide residuals at the end of the outlet canal were very low (≤0.024 mg/L), while outside the canal the residuals were below the detection limit of 0.01 mg/L. The results showed that experimental panels placed inside the condenser box were invariably clean of both macrofouling and slime.

At the Vandellos II nuclear power station (1,000 MW) located on the Mediterranean coast, a program was conducted to compare the efficacy of chlorination and chlorine dioxide and the production of THMs. Half the cooling water flow (25 m^3/s) was treated with chlorine dioxide, while the remainder was treated by electrochlorination. Antifouling treatment is done for 3–4 months a year, depending on biofouling monitoring data. The dosages adopted were continuous addition of ClO_2 at 0.16–0.20 mg/L (0.04 mg/L residual at the outlet) and continuous hypochlorite addition at 1.1–1.2 mg/L (0.3–0.4 mg/L residual at the outlet). The results showed that both procedures eliminated the macrofouling organisms. However, the cost of chlorine dioxide was estimated to be about 30% higher than that of electrochlorination.

In an experiment carried out at the Leghorn-Livorno power station (2,160 MW) on the Mediterranean coast, short-term injection of chlorine dioxide at 10.2 mg/L for 20 days eliminated serpulid growth in the circuit downstream of the hypochlorite injection point (Jenner et al. 1998).

A few seawater-based steel and petrochemical plants in Italy and France use chlorine dioxide as an antifouling agent. For example, the Taranto steel plant, located in the south of the Italian Peninsula, uses 35 m^3/s seawater for cooling. Here, macrofouling is composed of mussels, barnacles, hydroids, and serpulids, with biomass values of about 60 kg/m^2/year. The chlorine dioxide dosage at the beginning of the treatment was 0.5 mg/L (continuous). However, dosing was changed to intermittent mode afterward: 0.5 mg/L for 9 h/day in winter and 0.5 mg/L for 16 h/day in summer. The residuals were in the range of 0.02–0.05 mg/L. ClO_2 demand in the range of 1.3–1.8 mg/L ensured that all the ClO_2 disappeared prior to discharge (Belluati et al. 1997). Biofouling monitoring (visual and photographic inspection as well as use of fouling collectors) showed no macrofouling development. However, a few juvenile settlements could be observed during the reproduction periods.

At the petrochemical plant in Lavera (Mediterranean coast, south of France), the ClO_2 dosage, depending on the demand, is in the range of 0.15–0.20 mg/L, sufficient to maintain a 0.02 mg/L residual in all parts of the circuit. The residual level is continuously monitored by amperometry (detection threshold of 0.01 mg/L) and the ClO_2 addition is fine-tuned to get the desired residual target of 0.02 mg/L. The method has been reported to offer protection against slime and macrofouling (Jenner et al. 1998).

4.6 Environmental Impact of Chlorine Dioxide Usage

4.6.1 Freshwater Systems

Three types of by-products can be found in natural freshwater systems treated with chlorine dioxide: (1) residual chlorine dioxide ClO_2, which is a powerful oxidant and hence disappears rapidly in the cooling circuit itself or in the discharge plume, (2) weak oxidant ions like chlorites (ClO_2^-), chlorates (ClO_3^-), and possibly, bromates (BrO_3^-), (3) organics, including organohalogenated compounds (THMs, AOX), and (4) aldehydes. The formation yield of these products depends on the on-site production yield of chlorine dioxide and on the chlorine dioxide demand of the cooling water, which in turn is determined by the chemical composition of the water (Jenner et al. 1998).

Production of chlorite and chlorate ions and organohalogenated compounds has been reported in river water (Khalanski 1993; Duvivier 1993; Wasel-Nielen and Baresel 1997). Upon injection of 1–8 mg/L, 40–60% of the chlorine dioxide is found in the form of chlorites. Chlorine dioxide treatment of river water or of a solution of humic acids can produce from 60 to 80% of chlorites (Doré 1989). The proportion of chlorates may range between 10 and 30% of the injected ClO_2. Chlorite and chlorate ions are transformed by anaerobic bacteria into chloride by the chlorite dismutase enzyme as given below (Rikken et al. 1996):

$$ClO_4^-\text{(perchlorate)} \rightarrow ClO_3^-\text{(chlorate)} \rightarrow ClO_2^-\text{(chlorite)} \rightarrow Cl^-\text{(chloride)} \quad (10.8)$$

Chlorine dioxide produces very little THM (<5 μg/L), and forms only 10–50% of AOX in comparison with equivalent treatments with sodium hypochlorite. The toxicity of chlorine dioxide is far greater than that of chlorites, as found in toxicity tests performed in Seine water (Montanat et al. 1980). The toxicity of chlorite is very low when the concentration is below 10 mg/L (Couri et al. 1982). Chlorate toxicity is very low for freshwater organisms (Van Wijk and Hutchinson 1995). In fact, NOECs (No Observed Effect Concentration) range from several tens to several hundreds of milligram per liter for invertebrates and freshwater fish. However, marine brown algae are relatively very sensitive to chlorates; the long-term (6 months) NOEC has been reported to be 5 μg/L (Jenner et al. 1998).

4.6.2 Seawater Systems

As in the case of freshwater, THM formation following chlorine dioxide treatment of seawater is lower than that resulting from chlorination. In fact, in seawater enriched with humic acid, chlorine dioxide dosage in the range of 0.5–2.0 mg/L produces just 3–4% of the THM produced with comparable hypochlorite treatments (Ambrogi 1997). However, at higher chlorine dioxide dosages (20–40 mg/L), THM formation increases up to 58% of the THM formed with chlorine. At a chlorine dioxide dosage of 0.2 mg/L at the Vandellos II nuclear power station in Spain, the ClO_2 residual at the outlet was about 0.04 mg/L and the THM concentration was found to be 3.5 μg/L. In comparison, hypochlorite treatment generated 30 μg/L of THMs. At the Taranto steel plant, intermittent chlorine dioxide treatment (0.5 mg/L for 9–16 h a day) resulted in no measurable THMs and a mussel farm located close to the outlet was not affected by the discharges from the plant (Belluati et al. 1997).

ENEL (Italy) has carried out studies on the toxicity of chlorine dioxide for non-target marine organisms, for example, sperm toxicity and embryotoxicity in the sea urchin *Sphaerechinus granularis.* Sperm inactivation tests showed that 10 min contact at 0.74 mg/L before fertilization of the ovocyte resulted in significant reduction in the percentage of fertilized eggs. At concentrations higher than 2.0 mg/L, the development of embryos was blocked at the morula stage, whereas concentrations of 0.74 and 0.22 mg/L produced no significant effects (Geraci et al. 1993). Acute toxicity of chlorine dioxide for young sea bass (*Dicentrarchus labrax*) showed a 96-h LC_{50} of 20.8 μg/L, while at 15 μg/L there was no significant toxicity after 96 h (Ambrogi et al. 1994). The 96-h LC_{50} for sodium hypochlorite, under similar experimental conditions, was 78.6 μg/L TRO (Saroglia and Scarano 1974).

5 Ozone

Ozone is an allotropic species of oxygen obtained by means of the ionization of oxygen by the action of an electric field. Ozone is produced on-site from air or pure oxygen. Two types of ozone generators are available: plated and tubular generators; the largest units, which can produce 5–10 kg/h, are tubular generators (Duvivier et al. 1996). Recently, Mitsubishi Electric developed a storage system (MABOS), which makes it practical to apply intermittent ozonation to cooling water (Nakayama et al. 1997). This system is tested since 1996 by Ontario Hydro, Canada. Ozone is very volatile compared with other oxidizing biocides. McCoy et al. (1990) compared the volatility of various oxidants in cooling towers.

From this study, the following order of volatility appeared: ozone > chlorine > chlorine dioxide > hypochlorous acid > hypobromous acid. Compared to other oxidizing agents, ozone shows two major specificities. Ozone is a stronger oxidant than chlorine; it can decompose high molecular organic substances like humic acids to produce low molecular compounds such as aldehydes and carboxylic acids. It is thus a very effective sterilization agent whose main appliance is disinfection of drinking water and bathing waters, but also used in food industry. The use of ozone decreases the organic carbon content of water and AOX formation (Duvivier 1993).

On the contrary, this property is responsible for the generation of brominated oxidants in sea water. Ozone oxidizes the bromide ions almost instantaneously to form active bromine, producing the same oxidizing products as those occurring after chlorination. This is why ozonation of sea water is not suitable as an antifouling treatment. Ozone decomposes rapidly in water; its half-life time in pure water is a few hours but in raw waters used for cooling purpose, the half-life is reduced to minutes by consumption with organic matters. The rate of decomposition also depends on the pH, it increases with increasing pH. At acidic pH, the dominant species is molecular ozone (O_3), but at alkaline pH, ozone generates very short-lived (micro-seconds) hydroxyl free radicals (OH^0).

5.1 Experimental Studies

In Switzerland, in a small closed CWS (10–12 m^3/s), a 2-year period continuous treatment with approximately 50 μg/L was found effective against bacterial slime, and total bacteria counts decreased by a factor of about 100 times (Wellauer and Kyas 1987; Wellauer and Oldani 1990). Some corrosion was observed on C-steel materials; corrosion rate was 1.5 times higher when ozonizing water was used, but no corrosion was recorded in the presence or absence of ozone for stainless steel alloys, titanium, and also copper alloys. A pilot plant (1,000 m^3/h) was set up at the EVS Heilbronn coal-fired power station in Germany where the cooling water is conditioned river water. In Canada, experimental data on zebra mussels mortality in ozonized water (Claudi and Mackie 1994) show that mortality rate for adult mussels depends on the water temperature. At the ozone concentration of 2 mg/L, the 90–100% mortality level is reached in 9 days at 40°C and in 5 days at 20°C (Jenner et al. 1998).

Experimental trials have been made on zebra mussels and freshwater snails in Belgium (Duvivier et al. 1996). It was observed that adult zebra mussels (2–3 cm) exposed to dissolved ozone keep their shell open but stop to filter the water. At 21°C, the 100-h mortality rate is observed at a concentration of 0.32 mg/L in 39 days (Duvivier et al. 1996). Ozone is also very efficient in preventing the settlement of mussel larvae and there is no production of byssal threads for ozone concentration in the range of 20–30 μg/L. The fresh water snail *Physa acuta* is more susceptible to ozone than adult zebra mussels: at 21°C, 100% mortality is observed in 10 days for 0.32 mg/L. Duvivier et al. (1996) reported lethal concentration for 100% (LC_{100}) of the tested adult zebra mussels at temperatures of 20–21°C. A power function curve was fitted to the data for exposure time of 2 days: LC_{100} (mg/L) = $17.73 \times t^{-1.1127}$ ($r^2 = 0.91$), with t = exposure time in days.

The young colonies of the bryozoan *Plumatella emarginata* are very sensitive to ozone: $LC_{100} = 0.08$ mg/L with a 4-h exposure. Statoblasts and large colonies are more resistant. Nevertheless, Leynen et al. (1997) concluded that a continuous low level ozone treatment up to 0.1 mg/L is sufficient to eliminate bryozoans and zebra mussels. However, at 20 μg/L, there is no effect on zebra mussels (Duvivier et al. 1996). Intermittent application of ozone has been tested in Canada in a test rig at Lake Ontario Hydro (Nakayama et al. 1997). Addition of about 10 mg/L of ozone leading to a residual of 2–8 mg/L for 6 min twice a day was found efficient on microfouling which was reduced by 94–99%. The zebra mussel mortality was very low (3%), but a 30% reduction in tissue weight was observed. In this experiment, the ozone storage system developed by Mitsubishi Electric was used.

5.2 Ozone Testing at Industrial Sites

On-site studies performed in the USA, at the Bergen power station on the Delaware river, have been clearly negative for ozone (Sugam 1985). Ozone is an efficient biocide against the bacterial slime but it produces deposits of manganese dioxide, and the cost of ozone treatment is much higher compared to chlorine. Ozone was implemented in 1995 at the Mol power station, operated by Electrabel in Belgium: injection in the inlet canal at 0.3 mg/L, at pH 8 ozone half-life is 25 min. The ozone consumption was very rapid, and the effect on zebra mussel was limited in the canal to only the first 50 m.

The use of ozone as a biocide still remains a very expensive method, estimated to 3.8 times the cost of sodium hypochlorite (Duvivier et al. 1996). At the Seraing power station, in Belgium on the river Meuse, ozone dosing is implemented at 1.0 mg/L in the auxiliary cooling system (Jenner et al. 1998). This circuit is the makeup of the main semi-closed cooling system. In this system, the concentration factor reaches 1.8. In the cold water basin of the cooling tower, the ozone residual is as low as 5 µg/L. This treatment kills 100% of bivalves (*Corbicula* and *Dreissena*) in 18 days. Total bacteria decrease below 100/mL and DOC was reduced by 30%. In Germany, the recirculating cooling system of the air separation plant at Höchst is continuously treated by ozone since 1985. This circuit, fed with river Main water, comprises four cooling towers; the recirculating rate is 4,800 m^3/h (Wasel-Nielen and Baresel 1997). Ozone is added at 0.10–0.15 mg/L, and the ozone is measured in the water supply at 0.05–0.08 mg/L. The water is clear and colorless "like a mountain stream." A slight reduction of the AOX was measured in the cooling system compared to river Main levels (5–30 µg/L). Corrosion of copper alloy was stopped by addition of a nonferrous corrosion inhibitor. New systems are ozonized since 1992 with a mean recirculating rate of 12,000–22,500 m^3/h. The ozone level must be at least 0.1 mg/L in the supply water; it is sufficient to eliminate all biological deposits in the heat exchangers.

In the Netherlands, ozonation is applied at a cooling tower-assisted power station (RoCa) in Rotterdam. Make-up water is filtered over sand filters, improving the water quality which enables the use of ozone. A recirculating CWS at a chemical plant is also treated with ozone in the Netherlands. This system is completely made out of stainless steel and fed with demineralized water. The system was put in operation in 1995 and the results have so far been excellent.

5.3 Safety of Workers

The high volatility of ozone causes enrichment of ozone gas in the vicinity of treated waters. The air concentration limit to protect the workers is 0.2 mg/m^3. Ozone generators are presently equipped with removing systems destroying the excess ozone in the air using different processes: thermal destruction, activated carbon, and catalytic systems.

5.4 *Ozone Environmental Assessment*

Although the formation energy of ozone is high, the application of ozone is often referred to as more environmentally acceptable than hypochlorite, since it leads to less formation of THMs and extractable organic halides (EOX). Compared chlorination by-product formation, relatively little attention has been paid to by-product formation resulting from ozonation. Ozonation may however lead to formation of bromate (BrO_3) and aldehydes (Cavanagh et al. 1992). The new WHO guidelines for drinking water (WHO 1993) recommend a limit of 25 μg/L for bromate, and a new proposed regulation in the European Union countries (Ottaviani 1997) and in the USA (Richardson 1997) requires a lower limit at 10 pg/L. The formation of bromates by ozonation can be reduced at pH <7, but the pH of most of the large European waters suitable for cooling purposes is frequently higher. At the Hocht plant on the river Main, in Germany, no bromate was detected in the recirculating cooling system treated with ozone at 0.10–0.15 mg/L, but the detection level for bromate was 100 μg/L (Wasel-Nielen and Baresel 1997). By-product formed by ozonization at a dosage of 6–12 mg/L of effluent from a wastewater treatment plant in La Roche-sur-Yon (France) was investigated by Langlais et al. (1992). Ozonization led to complete or partial elimination of aromatics (e.g., allyltoluene, dichlorobenzene, dimethoxybenzene, etc.) and nonsaturated fatty acids, whereas no significant change on the concentration of long-chain saturated fatty acids was observed. Aldehydes (heptanal, nonanal) and short-chain saturated fatty acids appeared or increased in concentration.

Short-term toxicity tests carried out on the ozonized effluent showed no mortality on fish (*Brachydanio rerio*) and crustacean (*Artemia salina*), but some growth inhibition on the green algae *Scenedesmus subspicatus*. These tests were made with no residual dissolved ozone and the conclusion was that ozonization of wastewater does not generate acute toxicity. Dissolved ozone is very toxic for fish, as shown on juveniles of fresh water fishes. However, the high ozone consumption in river waters can be used to eliminate the residuals by diluting the ozonized water.

6 Other Oxidizing Compounds

6.1 *Bromine*

From an antifouling efficacy point of view, hypochlorite dosing in combination with sodium bromide in freshwater systems (Jenner et al. 1998) may lead to a reduction of the required dose, since free bromine, unlike HOCl, is not totally dissociated at basic pH and bromamines (reaction products with ammonia, which is naturally present in water) are more toxic than chloramines. Therefore, in some freshwater CWS, sodium hypochlorite is dosed in combination with sodium bromide. However, in seawater, with natural bromide concentration of about 65 mg/L, additional dosing of sodium bromide makes little sense. Nevertheless, some coastal power stations such as the Madras Atomic Power Station (India) resort to supplemental dosing of bromide for fouling control in heat exchangers (Murthy et al. 2010).

6.2 Hydrogen Peroxide and Peracetic Acid

Hydrogen peroxide finds application as an algicide or biocide in small recirculating CWS. In a food processing plant using recirculating CWS (fed with demineralized water) in the Netherlands, hydrogen peroxide is dosed continuously at a high concentration of 15 mg/L to keep the bacterial counts very low (Jenner et al. 1998). An advantage of hydrogen peroxide addition in such CWS is that it does not add chloride ions (Cl^-) to the cooling water. H_2O_2 disintegrates easily to oxygen. It does not produce organohalogenated compounds, and there are no known harmful decomposition products. Its use for CWS treatments is mainly limited by its poor antifouling activity at low concentrations and at low temperatures. Moreover, it can be inactivated by bacterial enzymes such as catalases and peroxidases.

Peracetic acid, or peroxyacetic acid (CH_3CO_3H), is a weak acid that does not exist as a pure compound. Aqueous solution of peracetic acid is an equilibrium mixture of acetic acid and hydrogen peroxide:

$$CH_3CO_3H + H_2O \rightarrow CH_3CO_2H + H_2O_2 \tag{10.9}$$

Peracetic acid is very corrosive at high concentrations. Its final decomposition products are methane, carbon dioxide, oxygen, and water—acetic acid being a major intermediate compound. Disinfection by peracetic acid is due to the production of oxygen free radicals, which destroy the SH and S–S bonds in the cell membranes and enzymes (Fraser 1986).

For water treatment applications, commercial solutions are available at concentrations of 1–15%. Peracetic acid is used as a disinfectant in the food industry (Swinnen 1995). Though no applications in large CWS are known, it appears to be better than glutaraldehyde or isothiazolones for elimination of *Pseudomonas aeruginosa*, a common slime-forming bacterium, and therefore could find application for biofilm control in cooling towers (Kramer 1997). The recommended dosage in cooling water is in the range of 1–10 mg/L for a contact time of 1–3 h (Jenner et al. 1998).

7 Chemical Treatment with Nonoxidizing Compounds

This category contains mineral or organic compounds having biocidal effects. The composition of the commercial products, particularly in the case of organic products, is generally more complex than that of the "active substance." In this case, the chemical and ecotoxicological properties of the product may differ from those of the active substance. While oxidizing biocides exercise nonspecific biocidal action on the target organisms ranging from bacteria to mussels, organic biocides have more specific action, for example, on weeds (algicides), or molluscs (molluscicides).

7.1 Organic Agents

Toxic compounds for molluscs were produced in the 1960s to combat parasitic diseases, such as bilharziosis, where aquatic snails are intermediate hosts of the causative parasitic agent. Some of these products are very toxic for zebra mussels (Hoestland 1972). In a review of toxicity data on molluscicides used in African continental waters, Dejoux (1988) concluded that they cause mortality of nontarget organisms. For water treatment against macro-biofouling in industrial systems, specific products have been developed. Three major groups of organics currently used in industry to control fouling in CWS can be identified:

(a) Products containing isothiazolones as the toxic substance
(b) Products containing quaternary amines as the toxic substance
(c) Other organics, such as glutaraldehyde, 2,2-dibromo-3-nitrilo-propionamide (DBNPA), 2-bromo-2-nitropropane-1,3-diol (BNPD), methylene bisthiocyanate, 2-dithiobisbenzamide, b-bromo-b-nitrostyrene, etc. The biocides like quaternary ammonium compounds (QACs), isothiazolones, and fatty amines are not detected as toxic by the target organisms. Thus, bivalve molluscs continue to filter the water when the product is added at a non-excessive dosage, and they are exposed to the biocide until the first detrimental effects cause a behavioral response: valve closure, reduction of the water filtration rate

As a consequence, most of these organic agents are effective for short-term applications: 12–48 h, while others require a few days exposure. They are generally used in recirculating CWS and not in once-through systems.

7.1.1 Quaternary Ammonium Compounds

QACs have long been known to have strong bactericidal properties. Some products are particularly used as molluscicides in industrial systems. Examples are as follows:

(a) Clam Trol from Betz, whose active substance is ADBAC (alkyl dimethyl benzyl ammonium chloride), associated with dodecylguanidine
(b) H-130 M, from Calgon, whose active substance is DDAC (didecyl dimethyl ammonium chloride)
(c) Bulab 6002, from Buckman, whose active substance is poly [oxyethylene (dimethyliminio) ethylene dichloride]

Their spectrum of action is wide, ranging from microorganisms to molluscs. The toxic effect is due to destruction of the cell membrane of bacteria or the destruction of branchiae of molluscs. Some of these products act rapidly; others require longer exposure. Their effectiveness is heavily dependent on water temperature, or in other words the physiological activity of the organisms (Petrille and Werner 1993). Treatments are of the "periodic" type, and are applied 1–6 times a year depending on the site and the system, with exposure times of 6–24 h.

QACs are surfactants and are adsorbed on suspended matter in water or on colloids such as humic acids. In order to reduce the concentration of active compounds in the treated water before discharge, clay is added, resulting in immediate detoxification. For example, bentonite concentration required to detoxify the discharged water is in the range of 5–40 mg/L. Degradation of ADBAC has been measured by carbon dioxide production tests; 66% is degraded in 29 days in aerobic conditions with an initial concentration of 10 mg/L (Dobbs et al. 1995). QACs are not metabolized by aquatic organisms; they are accumulated in the consumable parts of fish (factor 40–50); they are immobilized in the soil and do not pass into ground water (Schroenig et al. 1995).

7.1.2 Isothiazolones, Benzothiazoles

3-Isothiazolone compounds exhibit high toxicity toward microorganisms, and are used to control bacterial slime in recirculating CWS. Benzothiazoles are mainly used as vulcanization accelerators for rubber. They also have use as slimicides, fungicides, and herbicides. TCMTB (2-(thiocyano-methylthio)-benzothiazole) is effective against zebra mussels in low concentrations, but requires exposure times of at least 10 days. Krzeminski et al. (1975a) have investigated the degradation process of 3-isothiazolone. They found that these compounds are rapidly degraded in aqueous systems by hydrolysis (at basic pH) and by biological processes. Degradation products have no special toxicity toward aquatic organisms (Krzeminski et al. 1975b). TCMTB also hydrolyzes in alkaline waters and is partially adsorbed on suspended matters. According to Buckman Laboratories, TCMTB is rapidly degraded under aerobic conditions (half-life of 3.7 days). However, the degradation pathway of benzothiazoles is relatively complex, comprising hydrolysis in anaerobic and aerobic conditions, biomethylation, and photolysis. Bacteria such as *Rhodococcus* are capable of growth on the first-stage degradation by-products (De Wever and Verachter 1997).

7.1.3 Filming Agents

Some long-chain alkylamines amines destroy the gill tissues of aquatic organisms acting on the cell membrane, and/or by combination with the mucous layer produced by the gills. TD 2335 (Elf Atochem) contains, as active agent, a dimethylalkylamine salt of an algicide and herbicide compound: endothall. Extensive studies have been made on the degradation and aquatic toxicity of endothall. Endothall disappears rapidly in natural waters, with a half-life of less than 1 day. Thus, TD 2335 offers the dual efficacy of a pesticide and of a filming agent. On-site trials at the Toledo power station (Ohio) showed that 8 h of application at 3.0 mg/L is enough to kill zebra mussels. The decrease in concentration over long stretches including a fly ash pond resulted in low residual concentrations of the active agent, and the absence of toxicity on nontarget organisms (Piccirillo et al. 1994). Mexel 432 is a commercially available compound primarily constituted of long-chain aliphatic amines. In aqueous emulsions, this product forms a film on the cell membranes causing destruction of tissues in a varying proportion depending on the dosage. It can be effective against bivalves on a periodic treatment basis: at residual concentrations of 3.5 mg/L, the product rapidly causes major damage to the gills of zebra mussels and causes death after 19 h of exposure (Khalanski 1993). The efficacy of long-term intermittent treatments on zebra mussels has also been shown in experiments: a dosage of 3 h/day at 6 mg/L kills 100% of zebra mussels; the effective concentration corresponding to the residual was probably close to 3 mg/L (Giamberini et al. 1994). In this experiment, it was also observed that byssus thread formation was reduced or inhibited by intermittent Mexel 432 injections. It has a broad spectrum of action on microfouling and macrofouling in both seawater and freshwater.

Mexel 432 also has anticorrosion and antiscaling properties; the treatment procedure is generally intermittent, intended to renew the film on the surfaces to be protected, but periodic treatments can be more effective on macrofouling. Three processes are involved in the disappearance of Mexel 432 in solution: an immediate demand wherein clays and humic acids play an important role, the effect of stirring the water and injecting air bubbles, and bacterial degradation in aerobic conditions. Isolated bacterial strains in the Seine degrade Mexel 432; one of these degrades 98% of the product in 10 days. A first-order kinetics equation fitted to the experimental results frequently shows disappearance of 60% of the product in 1 day in river water, independent of the immediate demand. This kinetics is close to that of bacterial biodegradation with the most efficient strain (Allonier et al. 1997). Information acquired regarding the toxic effects of the product on freshwater organisms shows rapid disappearance in natural waters of the product in its toxic form, and absence of detectable toxicity during its degradation (Arehmouch et al. 1998).

On the basis of the data now available, acceptable residual concentration thresholds are proposed to protect freshwater organisms exposed continuously to the product: between 1 and 3 mg/L for brief releases (less than 1 h) and 0.25 mg/L for continuous treatments lasting over 36 h (Khalanski 1997).

7.2 Some General Conclusions on Treatment of Industrial Cooling Water Systems with Organics

Organics present certain favorable characteristics for controlling fouling in industrial cooling systems. They are easy to use. The minimum equipment required is an injection pump operated with a timer and an injection device which also mixes the product; this can sometimes be done by the pump used for circulating water in the system. Generally, they have a wide spectrum of action on microfouling and macrofouling, depending on the selected procedure: periodic or intermittent treatments. Some, as can be demonstrated with a filming product, have also anticorrosion and antiscaling properties. The cost of treatments with organic compounds depends on the protocol adopted, as well as on other factors such as the quality of the water to be treated and the characteristics of the target system. The most unfavorable conditions are found when the target species have a lengthy period of larval settlement and a high growth rate, and when particulate matter and colloids consume a large proportion of the product. With respect to environmental acceptability for the products most commonly used in cooling systems, they disappear more or less rapidly in waters due to adsorption on suspended solids and colloids and by degradation involving no production of toxic by-products. Toxicity data on aquatic organisms exist which are consistent with this.

For some QACs and filming agents, it is possible to eliminate toxic residuals at the outlet of the cooling systems by adding clay, which adsorbs the toxic agents. On the other hand, dilution of treated water with nontreated water inside the cooling system can eliminate any residual toxicity at the outlet of the system. In the United States, the EPA authorizes use of QACs in continental waters under two conditions (Schroenig et al. 1995):

– Mixing: discharge in the river in which the release is made must be sufficiently high, which can preclude use of this kind of treatment in open circuit hydroelectric plants
– Detoxification of the effluent by the addition of clay prior to release, for products adsorbed on suspended matter

Even despite this, environmental regulatory agencies are often opposed to the use of organics as an alternative to chlorination; they tend to prefer physical methods which are thought to eliminate the risk of chemical inputs in the aquatic environment. More and more, it will be necessary to prove that the choice of a given method can be justified by a “BATNEC Approach.” In this sense, when physical methods are not applicable or ineffective, certain organic products can provide the best available solution.

8 Metals

The efficacy of coatings containing leachable copper and zinc was presented by Jenner et al. (1998). There is no doubt that these metals have a toxic effect in their immediate vicinity. Devices have been developed to treat water circuits by producing metals in soluble form. These metals must remain in the water in a concentration which is toxic for the target organisms. Most of the commercially available devices are electrolysis systems; the metals are generated by dissolving copper anodes with which, in certain cases, aluminum anodes have been associated. Aluminum is claimed to produce a floc of aluminum hydroxide, forming a complex with copper

(Cu(OH),Cu_2O) which has a coating effect. Davenport et al. (1986) have shown that this floc only inhibits larval settlement in low flow areas where it forms a physical choking barrier, but it is not toxic for biofouling organisms. This technique has been used in seawater since 1960s, essentially in boat cooling systems, but also in cooling systems in factories on land. A copper ion concentration of several dozen milligram per liter is required to eliminate marine biofouling: the long-term toxic concentration for the marine mussel is between 10 and 20 mg/L (Davenport et al. 1986).

To treat high flows, the electrodes must be dimensioned accordingly; it is poor dimensioning which is responsible for the failure of these processes (Mussali 1988). In one device proven effective in circuits with flow upto 3.3 m^3/s, the electrodes are composed of a cathode with copper and aluminum anodes which deliver copper in a concentration of 25 mg/L in the circuit. The current varies between 10 and 250 A in the largest installations. Other systems, also effective against marine biofouling, maintain a copper concentration which varies between 13 and 54 mg/L (Roch et al. 1986). In addition to the investment cost, the cathodes must be periodically changed: consumption of copper can be up to 65 kg/month, for a treated flow of 1 m^3/s. The use of this type of process for direct cooling systems (a few dozen cubic meter per second to a few hundred cubic meter per second) would add several dozen tons of metal per year to the coastal environment. Unlike paints, for which leaching generates but little additional copper, electrolysis processes are not environmentally acceptable for direct cooling systems.

In recirculating cooling systems, with lower flow rates (3–8 m^3/s), metal releases are lower but nonetheless represent an important occasional source in the river. The toxicity of copper in freshwater depends to a large degree on the hardness of the water. The European Union Directive regarding water quality requirements to protect the fish populations sets concentrations as a function of water hardness (Jenner et al. 1998; Turnpenny et al. 2012). In water with a low mineral content, copper is toxic in low concentrations for certain invertebrates and for salmonids. It is thus clear that water quality determines the amount of copper needed to eliminate invertebrates in freshwater: a few milligram per liter in soft water at 25 mg/L $CaCO_3$, as opposed to hundreds of milligram per liter in hard water, with 300 mg/L $CaCO_3$ (Kelly 1988).

The use of copper to combat freshwater biofouling in cooling systems with high flows therefore poses a problem, though tests are being conducted to eliminate the zebra mussel with a concentration of around 10 mg/L (Blume et al. 1994). A biocide combining hydrogen peroxide and silver is used in closed systems for sterilization in the food industry, and poses no particular problems for this type of application. On the other hand, treatment of direct cooling systems and even of recirculating cooling systems, with releases into the environment, is environmentally questionable due to the addition of nonnegligible amounts of metal. Lastly, in this succinct overview, we should list the products which are probably, among those commercially available, the most effective against all types of biofouling: the organotins. Twenty years ago, Tributyl tin oxide (TBTO) was successfully tested on marine power stations in Italy, in the Netherlands, and probably in other European countries. It was found effective against bacterial slime and all kinds of macro-biofouling organisms in very low concentrations (7.5 mg/L in TBTO or 50 mg/L in commercial products).

However, the release of small amounts of organotin from the antifouling paints on pleasure boats was found responsible for a drastic reduction of oyster reproduction in the Bassin d'Arcachon on the southwest coast of France from 1976 to 1981. The extreme toxicity of TBT has been demonstrated on oyster larvae and adults (Alzieu et al. 1980; His 1995), on plankton crustaceans, and on various invertebrates. Sexual disturbances (imposex) are found in marine molluscs with concentrations as low as 0.5 mg/L (Hall 1988). Because of their toxicity, organotins are no longer used in cooling water circuits in European Union countries, and their use in antifouling paints has been restricted by regulations.

9 Oxygen Deprivation

Tolerance of the Asian clam *Corbicula fluminea* and the zebra mussel *D. polymorpha* to chronic hypoxia has been investigated by Johnson and McMahon (1997) and shown to be dependent on water temperature. On the zebra mussel, at the 5% dissolved-oxygen saturation level, the time required to kill 50% of the tested animals (LT_{50}) is 44 days at 5°C, 25 days at 15°C, and only 5 days at 25°C. On the Asian clam, the LT_{50} is 20 days at 5% and 6 days at 25°C. Oxygen deprivation was tested in France on an intake pipe at the Merysur-Oise drinking water processing plant. The test consisted in isolating the pipe and injecting sodium bisulfate (also known as sodium hydrogen sulfate: $NaHSO_4$) to consume dissolved oxygen. The procedure was not effective: it took 2 weeks to consume the oxygen in the long pipe, where mixing of the reductive solution was difficult, and some of the mussels survived the treatment. Hypoxia-based control methods require very low oxygen concentrations and sustained application at water temperatures lower than 20°C. They are only potentially applicable to stagnant or semistagnant waters.

10 Potassium Ions Toxicity to Zebra Mussels

Since the experimental work of Fisher et al. (1991) potassium ion is known to be a specific toxic agent for zebra mussels: LC_{50} 24 h is 138 mg/L at 20°C. Total mortality for 7–11 mm *D. polymorpha* in the Moselle river was achieved for 48 h at 600 mg/L of KCl ($K = 314$ mg/L) (Khalanski 1993). These high concentrations are not compatible with treatment of large CWS but can be a convenient solution for circuits containing stagnant or semistagnant waters, such as fire protection systems. At Bruce B nuclear power station, operated by Ontario Hydro, treatment with potassium concentration of 100 for some days was successfully applied to a fire protection system (Lewis et al. 1997b).

11 Other Physical Methods

11.1 Ultraviolet (UV) Light

Ultraviolet light (<253.7 nm) is capable of killing bacteria in the bulk water of circulating water systems (Gilpin et al. 1985) and is now commonly used by hospitals and food industries for water sterilization purposes. It has become an attractive disinfecting agent for small volumes of drinking water and small recreational pools. However, availability of equipment to treat large volumes of water has led to its use for antifouling treatment in larger systems. Turbidity, suspended solids, and dissolved organic substances reduce the efficiency of UV as a disinfectant. Therefore, water clarity is an important criterion that decides the efficacy of UV as an antifouling method.

11.1.1 Application in Freshwater Systems

Experiments by Ontario Hydro using zebra mussels showed that 40-s exposure to a UV (at a flux of 24 W/cm^2 measured at the lamp surface) significantly reduced larval settlement, though mussels of 2–5-mm length were occasionally observed. These translocators were probably protected against UV light by their shell (Ewans et al. 1992). Plant level tests were also carried out by Ontario Hydro at the Bruce B nuclear power station, located on the shore of Lake Huron, where the water is very clear. UV treatment killed about 85% of the zebra mussel veligers. The results suggested that UV might be effective in preventing the settlement of macrofouling spat, but not the settlement of older stages entering the CWS.

11.1.2 Application in Seawater Systems

Experiments have been carried out in Japan on UV irradiation as a potential alternative to seawater chlorination (Hori et al. 1993) with laboratory experiments by Hori et al. (1990) on nauplius larvae of the barnacle *Chthamalus* spp. Mortality was dependent on the UV dosage, that is, energy density (mW/cm^2) × exposure time (s). Irradiated larvae were killed in 71–75 h at a UV intensity of 5.6 mW/cm^2 for a minimum exposure of 2 min; 4 min of exposure were needed at 3.0 mW/cm^2. The effective dosage is thus 672 mW s/cm^2. Irradiated nauplii lost their swimming capacity at sublethal dosages. Majority of larvae exposed to 85 mW s/cm^2 were unable to swim after 72 h. Cypris settlement was reduced by 40% at 17 mW s/cm^2 and by almost 97% at 30 mW s/cm^2 (Hori et al. 1993).

Encouraged by the experimental results, a UV treatment system was designed and installed at the lsogo (530 MW) power station operated by Electric Power Development Co. Ltd. and located near the mouth of Tokyo Bay. The irradiation system consisted of a panel of low-pressure UV lamps (160 W) attached to the side wall at one of the four intake conduits where the water flow was 4.6 m^3/s. The results of the field test showed about 59% reduction (by wet weight) in macrofouling, mainly due to the decreased mussel and tube worm settlement (Kawabe 1997).

The results of various experiments and field test appear to suggest that the antifouling action of UV light is largely preventive; it may kill plankton organisms (bacteria, larvae) in the bulk water, but cannot kill the populations already settled on the heat exchanger surfaces and other critical areas in the CWS. Moreover, it is important to ensure the clarity of the water for effective penetration of the UV light. In spite of such drawbacks, UV light may be used as a supplemental method for biofouling control due to its environmental friendly nature.

11.2 Electrical Methods

Electric fields (high-energy electric shocks or low-level currents) have been shown to prevent fouling settlement. Theoretically, the efficiency is proportional to the square of the electric field intensity in volt per centimeter. The energy consumption would depend on the salt content of the water: it is inversely proportional to the water resistivity. In order to minimize the energy consumption, experiments have been conducted on pulsed fields; for example, shocks of 0.77 μs with intensity in the range of 1–10 kV/cm have been tested. Barnacle larval settlement was prevented with 0.77 μs shocks at 7 kV/cm, and a more than 90% reduction in settlement was observed at an intensity of 3 kV/cm. Field study performed in river water at Norfolk, VA, showed that pulses of 0.77 μs at 6.5 kV/cm could protect pipes against biofouling. The method was energy-intensive as the consumption in the above trial was about 1 MW to treat a flow of 2 m^3/s (Schoenbach et al. 1997). Experimental results have also been reported on the use of low-level electric currents for biofouling control. Tests conducted at the Nanticoke thermal power station operated by Ontario Hydro used electrode panels placed 5 cm apart and currents of 16–20 V, 1.0–1.9 A, generating a field intensity of 3–10 V/cm. The results showed that the method was effective against settlement of zebra mussels (Fears and Mackie 1997).

Despite such promising results, industrial experience is lacking on the use of electric fields for the control of biofouling in large CWS involving relatively fast flowing water.

Apart from electric fields, cathodic systems have been used to prevent zebra mussel settlement. Cathodic method is generally used for corrosion protection. In this case, higher current densities than required for anticorrosion are used. Studies carried out in the United States and Canada showed that larval settlement was greatly reduced at current densities of 6–9 mA/ft^2 (Lewis and Pawson 1993). Hydro Quebec used special anodes (Cu, Ni, Pt) at a current density of about 13 mA/ft^2 in a large sluice gate. After 5 months, 70% of the zebra mussels settled on steel and concrete walls were removed and probably killed (Serli et al. 1994). Ontario Hydro tested cathodic protection to control zebra mussels on the concrete walls of a pump well at the Bruce B power station. Anode mesh panels were fixed on the walls of the well between trash racks at the inlet and the traveling screens. After 2 years, 90% reduction in the 0.5–2.0 cm age class mussels was observed in comparison with the control wells (Lewis et al. 1997a). The conclusion from this experiment was that current densities of less than 10 mA/ft^2 and potential of 40 V are effective in controlling zebra mussels on steel and concrete walls.

11.3 Magnetic Fields

Magnetic systems are being sold, purportedly able to control scaling in pipes. It has been suggested that biological effect on calcium metabolism would disturb shell deposition in mollusks and thereby can affect their growth. However, there is no experimental evidence for effects. Experimental trials conducted at a Rochester Gas & Electric Corporation testing station showed no significant differences in terms of zebra mussel mortality, shell length, or calcium-magnesium content in soft tissues (Smythe et al. 1997).

11.4 Acoustic Methods

Ontario Hydro conducted experiments on the use of high acoustic energy (173–199 dB) on juvenile mussels in an aluminum pipe (Ewans et al. 1992). During a 4-h treatment, the most effective frequency was in the range of 8–16 kHz (100% mussels not attached). Pulses with a high acoustic energy can remove the biofouling cover from concrete walls and avoid mechanical cleaning in pipes, basins, and wells fed with raw water. A submersible unit has been specifically designed for this purpose, equipped with a sparker unit delivering 5-kJ pulses at 45-s intervals, generating sound intensity of >200 dB. It was tested successfully for 6 months against zebra mussels and biofilm at municipal water treatment facilities.

12 Water Filtration

Different type of filtration devices are invariably used in CWS sourcing water from natural water bodies. Filters of the coarse grid type (about 10 cm spacing) are used as the first line of protection. These filters are located at the water intake point and are generally equipped with trash racks for removing larger debris entrained along with the incoming water. The grid size of the trash rack depends on the drifting debris most common in the area concerned; kelp and other aquatic plants, and anthropogenic debris are examples.

Traveling water screens (TWS) represent the second level of defense against debris and they are used to protect downstream equipment such as heat exchangers.

These generally consist of continuously moving band screens (where the flow rate is <10 m^3/s) or drum screens (for higher flow rates). The screen mesh is in the range of 1 mm to about 1 cm, depending on the type of heat exchangers to be protected. Smaller ones (1–3 mm) are used when plate heat exchangers (PHE) are placed downstream. In a typical PHE, the distance between successive plates is just a few millimeters. Larger meshes (about 1 × 1 cm) are used in circuits with shell and tube type heat exchangers. The TWS while in use are kept in rotation and have automated cleaning systems using pressurized water sprays. The debris sticking on the screens is removed by the water jet and is led to the outlet by mixing with the outgoing cooling water, in other instances. Sometimes the wastes are collected in skips for subsequent disposal. The debris removed by these rotating screens includes seaweeds, aquatic plants, fouling debris released from the intake canal/tunnel, etc. In addition to the TWS, specific debris filters are also sometimes installed to protect the heat exchangers. These are installed just before the heat exchanger. The mesh size is generally 1 mm, and the debris is removed by backwashing or intermittent maintenance. Debris filters are commonly used in the case of plate-type heat exchangers, in order to reduce the frequency of cleaning heat exchangers.

Recently, microfiltration-cum-backwash systems are increasingly being used to remove very small particles (50–100 μm). These fine filters can, to a great extent, get rid of even the planktonic larvae of barnacles or mussels from the incoming cooling water. They can purportedly work even in high flows (up to 4 m^3/s). Test runs have been conducted by Ontario Hydro (Canada) to eliminate zebra mussels from an auxiliary circuit of a power station located on a lake (relatively clean water). However, the availability of such filtering devices can be expected to be low in waters heavily loaded with suspended matter; consequently, the volume of water that can be filtered before clogging occurs is limited. Expectedly, filtration costs for the high flow rates (e.g., from 8 to 240 m^3/s) found in the main cooling system of power stations are prohibitive.

13 Water Velocity

Water velocity and the potentially complex hydrodynamics of circuit design are important factors in the "fouling potential" of a given cooling system. Settlement of larvae and the ability of settled organisms to remain on a given surface depend greatly on water velocity. In the total absence of water circulation, dissolved oxygen becomes the limiting factor and causes death by asphyxia in 1–3 weeks, depending on the temperature. Some species are adapted to quiescent water, while others prefer high flow conditions. Water velocity varies considerably in different parts of the cooling circuit. It is low near filtering devices like traveling screens and in basins, such as cooling tower basins, while it is high in pipes leading to heat exchangers and in heat exchanger tubes. The rapid renewal of water in the cooling systems is an extremely favorable factor for the organisms settled on the walls of the circuit, as it replenishes particulate nourishment and dissolved oxygen and carries away waste products. Therefore, the organisms show faster growth rate in cooling systems as compared to the outside environment (Rajagopal et al. 1996, 1998, 2003a). However, if the velocity exceeds a critical threshold, larvae may not be able to attach and adults may not be able to feed properly; some of them (e.g., mussels) may even get detached from the substratum. It has been observed that in cooling water circuits of some EDF power stations, zebra mussels are very abundant in areas where the water velocity is in the range of 10–50 cm/s, but they are not observed in those parts where the water velocity exceeds 1 m/s. At the Le Havre plant on the English Channel, operated by EDF, colonization of the wall in a conduit with a large circular section (3–5 m^2) by mussels (*Mytilus edulis*), barnacles (*Balanus crenatus*), and hydroids (*Tubularia* sp.) is considerably reduced when the mean velocity is in the range of 1.8–2.2 m/s. Interestingly, dense barnacle fouling has been observed at the Vado Ligure power station in Italy where the water velocity is about 3.0 m/s. Taken together, the available data indicate that the velocity value must be taken very close to the wall, about 1 mm from the surface, rather than the mean water velocity. Consequently, the critical water velocity to avoid macrofouling would depend on the size of the conduit; in large pipes, the velocity must be higher than, say, in small condenser tubes. Accordingly, a velocity of about 1.4 m/s at 1 mm from the walls has been recommended earlier (Jenner et al. 1998). Another factor that must be taken into account is the surface roughness. For a given water velocity, rough surface would favor settlement of larvae more than a smooth surface.

14 Heat Treatment

Application of heat is a very efficient way to eliminate all macrofouling and is adopted in some European and North American power stations. In this method, the cooling water is progressively heated by means of recirculation to a maximum temperature of about 40°C, and the temperature is maintained in the circuit for about 30 min to 2 h. All macrofouling organisms are killed by the heat shock. However, thermal treatment is not effective against bacterial slime, as the temperature level required to control the biofilm on the heat exchangers is much higher (>70°C). Moreover, heat treatment requires that the CWS be designed for hot water recirculation and therefore the design has to be incorporated in the early stage of plant construction. Retrofitting, even if technically feasible, may turn out to be prohibitively expensive. Another factor that must be considered is the power penalty due to loss of generation during the treatment. The advantage of heat treatment over other conventional methods is that it does not involve addition of any harmful chemicals.

In the Netherlands, four seawater-cooled stations (Hoogovens, Ijmuiden, Eems, and Delfzijl power stations) use heating as the only antifouling method (Jenner et al. 1998). In these power stations, blue mussels and barnacles are eliminated by heat treatments 4–5 times a year (Fig. 10.1). However, once or twice a year treatment would suffice for cooling circuits using freshwater. The criterion for the determination of treatment frequency is that mussels killed and detached from the walls should

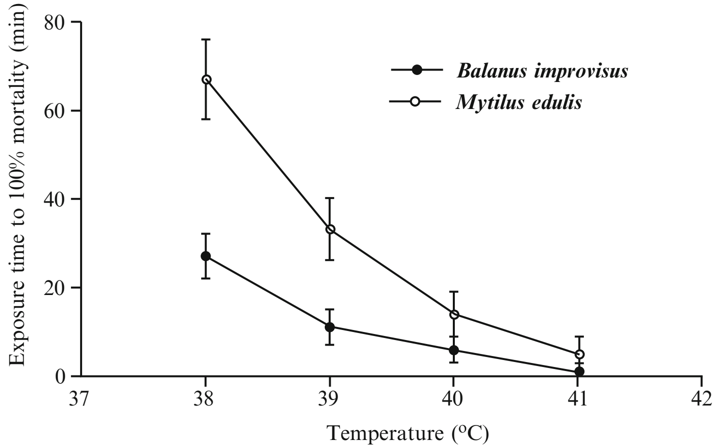

Fig. 10.1 Comparison of exposure times to reach 100% mortality of blue mussel, *Mytilus edulis* (Rajagopal et al. 2005b), and barnacles, *Balanus improvisus* (Rajagopal, unpublished data). Mortality data are expressed as mean ± SD ($n = 60$)

be small enough to pass through the heat exchangers and not be large or abundant enough to clog the filters (Jenner 1982).

Time–temperature–mortality curves of marine bivalves are typically characterized by a steep increase in mortality within narrow ranges of temperatures, the range being typical of the organisms being tested. Jenner (1982) observed that, in most of his experiments on the response of *M. edulis* to temperature, either all animals were killed or all survived. Hence the point of death was fairly sharp defined with little variation from one individual to the other. Similarly, Wright et al. (1983) and Rajagopal et al. (1995b, 2005a, b, c) recorded only small differences between temperatures causing little or no mortality and those producing a complete kill in *Crassostrea virginica*, *Crassostrea gigas*, *Mulinia lateralis*, *Argopecten irradians*, *Mercenaria mercenaria*, *Spisula solidissima*, *Perna viridis*, *Perna perna*, *M. edulis*, and *Mytilopsis leucophaeata*. A comparison of mortality data of different fouling species suggests that the temperature tolerance of oysters, *Crassostrea madrasensis*, is significantly higher than that of the other bivalve species (Fig. 10.2). This higher tolerance to higher temperature is probably related to its distribution in the upper reaches of the intertidal zones (Rajagopal et al. 2003b). The data also indicate a significant size effect on the mortality of the oysters; small oysters are more sensitive to high temperature stress than large ones (Fig. 10.3). This would be advantageous in an actual CWS, since heat treatment can be appropriately timed so as to eradicate oysters before they reach a problematic size.

The temperature difference between intake and outfall (ΔT) is maintained for a certain contact time to ensure mortality of attached fouling animals. However, any potential damage to the environment as a result of the discharge of heated effluents is avoided. Though heat treatment is power intensive (due to production penalty)

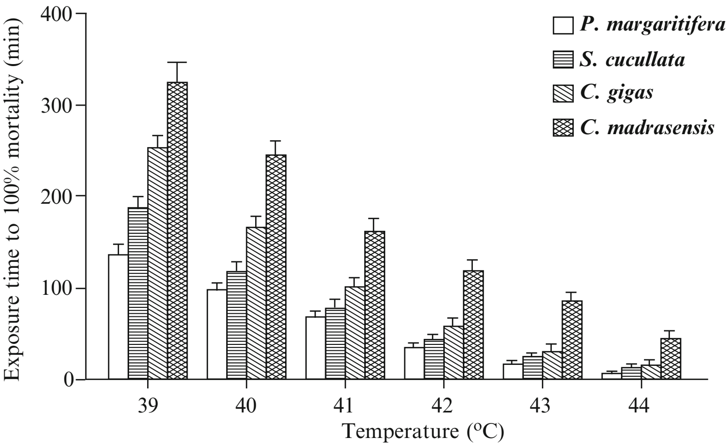

Fig. 10.2 Comparison of exposure times to reach 100% mortality of different species of oysters, *Crassostrea madrasensis* (Rajagopal et al. 2003c), *Crassostrea gigas* (Rajagopal et al. 2005a), *Pinctada margaritifera* (Rajagopal, unpublished data), and *Saccostrea cucullata* (Rajagopal, unpublished data). Mortality data are expressed as mean ± SD (n = 36–60)

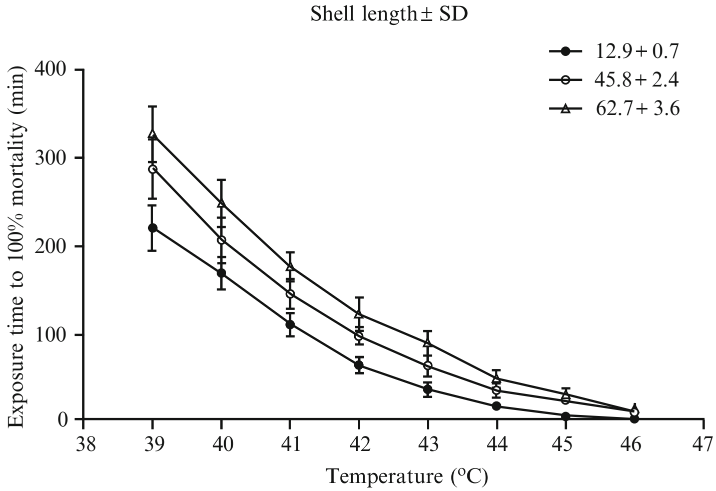

Fig. 10.3 The exposure time required for 100% mortality of different size groups of *C. madrasensis* at different temperatures (modified after Rajagopal et al. 2003c). Mortality data are expressed as mean ± SD (n = 36) of six replicate experiments (n = 6 in each experiment). The criterion for mortality of oysters was shell valve gape with no response of exposed mantle tissues to external stimuli

and retrofitting is expensive, many power stations (San Onofre power station in California and La Spezia power station in Italy) have successfully adopted heat treatment for fouling control (Stock and Strachan 1977; Jenner et al. 1998). Recently, power stations operating with freshwater (Diemen and Moerdijk power stations, the Netherlands; Commonwealth Edison power, Canada) have also successfully adopted heat treatment for fouling control (Claudi and Mackie 1994; Jenner et al. 1998). It has been reported that in all cases, heat treatment is more economical and less damaging to the environment than continuous chlorination (Whitehouse et al. 1985; Jenner et al. 1998; Rajagopal et al. 2010b).

15 Paints and Coatings

Rather than adding toxic substances into the rapid flow of cooling water circuits, it is possible to treat the surfaces on which biofouling develops so as to prevent settlement of larvae and halt the growth of settled organisms. Paints or complex multilayer coatings may be applied at different locations in the CWS: intake conduits, screens, pipes, condenser waterboxes, and condenser tube plates. Two major classes of paints and coatings have been developed: those containing one or several toxic substances and those which contain none and whose action is due rather to their physical surface properties. These products have mainly been developed for treating boat hulls. For use on cooling water circuits, such paints must be selected in the light of four criteria (Ewans et al. 1992):

(a) Ability to resist fouling or to provide an “easy-clean” surface
(b) Absence of toxic releases, or release of toxic substances at an acceptable level
(c) Long lifetime
(d) Applicability to concrete and/or steel

Two other criteria must also be considered: the cost of the product and of product application, and the way in which the coating degrades. To be applicable to CWS, coatings must not detach from the surface at the end of their lifetime, producing fragments which might plug up heat exchangers. The points also have to be applied in the brief opportunities allowed by maintenance programs and outages.

15.1 Toxic Paints and Coatings

Antifouling paints generally contain selected toxic substances, which are progressively released from the paint by a leaching process such as hydrolysis or by surface erosion. Very small amounts of the toxic substances can generate sufficient concentration gradient in the immediate proximity of the surface. These toxins can kill or repel the approaching larva. Among the various antifouling paints, those containing TBTO have been found to be very effective against a wide variety of marine fouling organisms. However, because of its extremely toxicity to marine organisms (e.g., mollusks), TBTO was rapidly abandoned for power station antifouling treatment (Whitehouse et al. 1985; Kawabe 1997). The toxicity of organic tin is now well documented, and severe biological effects have been reported for tin concentrations as low as 1 pg/L or less (His 1995). Therefore, its use as an antifouling paint has been banned. Commercially available toxic coatings generally contain toxic metals such as copper. The efficacy of such paints depends on the leaching rate of copper ions; the paints become ineffective when the rate falls below 10 pg Cu/m^2/day. Field tests performed with paints containing copper oxide have demonstrated effectiveness for about 9 months (Yokouchi et al. 1996). That is, in about 9 months, the leaching rate can decrease from 60 to <10 pg Cu/cm^2/day.

The possibility of antifouling protection by means of electrolytic production of chlorine at an anode was reported by Lovegrove and Robinson (1968). Electro-conductive coatings have been developed in Japan for applications in seawater. As current passes through the paint film, hypochlorite ions are generated by electrolysis of seawater. The power consumption was reported to be low: a few watts per 100 m^2. Field tests have proved the antifouling efficiency of such coatings when tested on the hulls of boats (Usami and Ueda 1993), and four marine power station units have experimented with this type of paint (Jenner et al. 1998). As this process generates very small amounts of chlorine, it can be considered environmentally benign. However, experiments performed on model canals at the Anan power station showed that cracks appeared in the paint after 6 months and that thereafter biofouling would spread rapidly even on previously treated areas (Yokouchi et al. 1996).

15.2 Nontoxic Coatings

This type of coatings has no toxic ingredients incorporated into the paint. The paints function by foul-release principle, whereby the coatings permit biofouling to take place but by facilitating its easy removal by weakening the adhesive bond between the coating and the organism. A particular group of paint that appears to be promising for CWS is the silicone-based variety. Since they do not contain any inherent toxicity, silicone-based coatings are fouled; however, the rate of fouling is lower and it can be removed easily by the cooling water flow itself. Silicone-based coatings are to be applied to perfectly clean and dry surfaces, or to clean and almost dry (5% or less moisture) concrete. Therefore, the coating is difficult to apply in existing systems, where dry conditions are seldom obtainable, than in new systems being built. The coatings are usually applied in layers, although experiments with a single layer have also shown good results. The coatings are susceptible to impact damage and abrasion. Attempts to toughen the paints have invariably resulted in diminished antifouling performance. The development of a coating with good antifouling capability and abrasion resistance, therefore, remains a challenge (Leitch 1994). The estimated lifetime of commercially available silicone coatings is about 4–5 years, but actual data indicate a shorter period of efficacy.

Results in the United States have shown that silicone-based coatings applied to intake pipes accumulate less fouling than those applied to intake walls and other areas exposed to lower flow velocities (EPRI 1989; Gross 1991). In 1990–1991, Ontario Hydro tested different antifouling paints on panels placed at a forebay (water velocity: 7–8 cm/s) of the Nanticoke power station on Lake Erie (Ewans et al. 1992). Some silicone paints showed 50% less coverage of zebra mussel as compared to the control. Moreover, the settled mussels were only weakly attached to the painted surface. Similar findings were obtained by Electricite de France in 1991–1993 in tests at the Cattenom plant on the Moselle, using a silicone epoxy resin which proved efficient against zebra mussels. According to Kawabe (1997), 30% of Japanese marine power stations used silicone-based paints in 1992. Repainting is mostly done every 2 years. Practical experience has been acquired in the Netherlands through a number of pilot trials with exposure panels, inlet culverts, and heat exchanger inlet boxes at Dow Benelux, Terneuzen, Dodewaard power station (freshwater), and Maasvlakte power station. Two commercially available silicone-based coatings have been tested on exposure panels by KEMA for two seasons in fresh, brackish, and sea water. The coatings performed well in freshwater. In brackish water and seawater, fouling developed, although it was less than on the control (PVC) panels. Moreover, the biofouling could be easily removed by hand. The coatings proved to be effective in cooling water intakes, conduits, and the inlet chambers of heat exchangers. The use of nontoxic coatings is encouraged by the US-EPA (1992, 1996). In Denmark at the Esbjerg power station, a marine site with severe mussel fouling, a full-scale experiment with a three-layer silicone coating from a Danish manufacturer was found to be successful during 3 years of operation (Jenner et al. 1998).

Antifouling paints that appear promising for application in CWS are (1) self-polishing paints containing copper oxide and possibly other organic biocides with no adverse ecological effects and (2) silicone-based “foul-release” coatings, whose efficacy depends to a large extent on the water velocity. It is necessary to perform on-site testing of antifouling paints to ascertain their suitability to control biofouling. Quantitative data on colonization, cost of cleaning, repainting schedule, etc. would help in properly assessing their potential application in CWS.

16 Emerging Control Technologies

16.1 Biological Control

In biological control, the targeted species is controlled by favoring the growth of its natural enemy or competitor. Biological agents such as pathogens, parasites, predators, or competitors can reduce populations of the target species. For example, natural aquatic bacteria capable of killing zebra mussels have been isolated from stressed mussels; some have been shown to cause 100% mortality in 5 days. Toxins (polysaccharides and proteins) extracted from these strains have been successfully tested as part of organic coatings (Gu and Mitchell 1997). Parasitic species are generally host-specific as such associations are the result of coevolution processes. Ciliate parasites in the digestive gland of *D. polymorpha* are an example (Molloy et al. 1997).

Pseudomonas fluorescence Pf-CL145A has been shown to be capable of controlling *Dreissena* spp. (Molloy 2002). The bacterium, when ingested, can kill zebra mussels (*D. polymorpha*) and quagga mussels (*Dreissena rostriformis bugensis*). When live or dead cells are ingested by the mussels, a toxin in the bacterial cells destroys the mussel's digestive system. Presence of the bacterial cells in the water does not deter feeding activity in the mussels. This is unlike chlorine, whose presence in the water causes the mussels to shut their valves, effectively blocking chlorine's access to the soft tissues. In flow-through experiments carried out at a hydropower plant, high zebra mussel kill (>95%) was achieved in 6-h treatments at 100 ppm (milligram dry bacterial mass per liter). No bacteria-induced mortality was recorded among any of the nontarget organisms including fish, ciliates, daphnids, or other bivalves. Trials suggested that planktonic larval stages (veliger) of zebra and quagga mussels were also susceptible to the bacteria. The toxin appeared to be a heat-labile, membrane-associated protein (Molloy and Mayer 2007).

Competition for space is a critical factor in the success of sessile benthic populations. It has been observed that zebra mussel populations have declined in some parts of the Rhine due to proliferation of the amphipod crustacean *Corophium curvispinum*, though according to observations in 1996–1997, the two species coexist in the Moselle. Interestingly, zebra mussels are not found on the sponge *Spongilla*, but the latter has a low coverage of hard substrates. The bryozoan *Lophopodella carter* has been observed to reduce the settlement of zebra mussels in the Great Lakes (Lauer et al. 1997).

Competition for food is also very important in the development of biofouling species. Filter feeders consume particles in suspension. In this context, the characteristics of the CW circuits themselves are important. The conditions in CWS are quite favorable to biofouling, and the basic ecological factors (water velocity, availability of food, absence of predators) are extremely conducive for biofouling development. Consequently, ecological factors involving competition and predation are difficult to apply to CWS, though they may play an important role in natural systems. For example, zebra mussels are controlled in many lakes and reservoirs in northeast France by diving ducks. However, such methods can seldom be applied in power plant circuits, which are heavily colonized by this species. Other biological control methods, especially those involving pathogens and parasites, offer interesting prospects for the future. But they are still in various stages of experimental phase and cannot yet be used in industrial systems.

16.2 Use of Elevated Carbon Dioxide in Combination with Sodium Hypochlorite

Though chlorination is an effective means of controlling biofouling in once-through cooling systems, there are disadvantages attached to the use of chlorine as an antifouling agent. Presence of chlorine in the water is readily perceived by mussels, and they close their valves upon sensing chlorine, effectively blocking chlorine's access to the soft body parts. Moreover, chlorine by-products (e.g., halophenols, halo acetic acids) are known blacklist compounds (Jenner et al. 1998) and can be potential pollutants of receiving waters. Viewed in this context, use of chlorine alternatives or chlorine minimization is important steps in the reduction of environmental effects of chlorination.

Carbon dioxide gas has the potential to be used as molluscicide. Relatively small increase in medium CO_2 concentration can induce increase in the body fluid and tissue CO_2 concentration in mussels (Truchot 1987). Increases in body fluid CO_2 concentration drive the carbon dioxide's reaction with water toward HCO_3^- and H^+ (Cameron 1989). Increase in body fluid H^+ concentration results in a corresponding decrease in blood and tissue pH (Truchot 1987). The activity of basic metabolic enzymes is pH dependent. Therefore, even relatively minor reductions in tissue pH (<0.5 pH units) interfere with an organism's basic metabolic function leading to death (Cameron 1989). However, information about its use for fouling control is scanty and so far only a few studies have focused on the effects of CO_2 on fouling organisms (e.g., McMahon et al. 1995 by using N_2). Carbon dioxide has number of advantages and disadvantages as a molluscicide. First, it is a natural compound, readily available in compressed gas bottles, and is relatively inexpensive. It is safe and nonhazardous to human beings. CO_2 is environmentally neutral and discharge into receiving waters will be rapidly removed through fixation into organic compounds by the photosynthetic organisms. However, relatively large quantities are required to induce effective fouling control when compared to presently utilized molluscicides. In some cases, CO_2 can increase metallic corrosion rates due to its acidic nature.

Venhuis and Rajagopal (2010) carried out innovative experiments involving the use of carbon dioxide along with chlorine for the control of mussel (*M. leucophaeata*) fouling. A series of laboratory experiments were carried out to study the effects (mortality and sublethal) of CO_2 in combination with sodium hypochlorite on *M. leucophaeata*. The results showed that at 0.5 mg/L TRO (chlorine alone), 100% mortality in *M. leucophaeata* was achieved after 1,824 h (Rajagopal et al. 2003b). However, the exposure time required for 100% mortality was dramatically decreased from 63 to 6 days when same 0.5 mg/L TRO was applied along with CO_2 (pH reduced to 5.0). The results clearly indicated that CO_2, when used in conjunction with chlorination, has the ability to bring down exposure times necessary for 100% mortality considerably (Fig. 10.4). However, it was not clear from the study how CO_2 achieved this feat; available data indicated the possibility that CO_2 might be acting as a narcotizing agent, undermining their ability to sense chlorine and consequently close their shells, making the soft tissues prone to chlorine damage.

It may be borne in mind that in healthy mussels onset of chlorination provokes an immediate valve closure response, which effectively shuts off soft tissues against chlorine damage (Opresko 1980; Rajagopal et al. 2003b). Exomotive chlorination (Lewis 1985; Jenner et al. 1998), a mode of continuous low-dose chlorination (less than 0.5 mg/L TRO), has been developed by CEGB to take care of this, whereby plantigrades are prevented from settling by creating an unpleasant environment. Subsequently KEMA developed (Jenner et al. 1998; Rajagopal et al. 2003b)

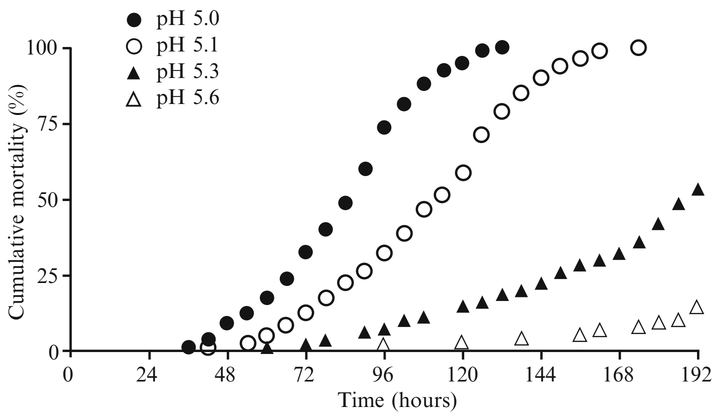

Fig. 10.4 Cumulative mortality (%) of dark false mussel, *Mytilopsis leucophaeata*, at different CO_2 concentrations (pH 5.6, 5.3, 5.1 and 5.0) and 0.5 mg/L TRO. Eighty mussels were used at each CO_2 concentration. Mortality of mussels was monitored at 6-h intervals. The criterion for mortality of mussels was valve gaping with no response of exposed mantle tissues to external stimuli

the Pulse-Chlorination® technique, again to circumvent the shell closure problem. However, this method entails the use of complicated monitoring techniques to keep a watch on the shell opening activity of the mussels. The CO_2 method on the other hand is very simple and can be performed even by unskilled operators. An added advantage is that CO_2, which is a waste product in coal-thermal power plants, can be effectively made use of within the plant itself, without discharge to the atmosphere. Since oceans can act as a sink for CO_2, it would be possible for plant operators to get rid of the green house gas in a most economical and productive manner.

16.3 Microencapsulated Pellets

Chemical-based antifouling techniques have a disadvantage that bulk water contamination is inevitable in their use. This can lead to harmful impact on non-target species residing beyond the precincts of the industrial unit. Such concerns can be addressed if more efficient and selective mitigation techniques based on innovative application of existing biocides can be developed. In this context, a novel, cost-effective, and environmentally sustainable approach to deliver biocidal agents has been developed (Costa et al. 2012). Commercially known as BioBullets, it involves the encapsulation of the biocides within a nontoxic, non-recognizable material, edible for the bivalves. The method exploits the ability of mussels to filter fairly large quantitative of water using their gills. For example, zebra mussels can filter water at rates as high as 570 mL/h/mussel (Elliott 2005). Edible particles (with entrapped toxins) suspended in the water will be taken in by the mussels, effectively overcoming their valve closure response when challenged by repugnant chemicals.

Such pellets, commercially known as BioBullets, represent a Trojan horse approach to control bivalve mussels. It is possible that virtually any biocide can be incorporated in the particles as the active ingredient. BioBullets loaded (25% w/w) with polyquaternary ammonium compounds (polyquat) as active ingredient are available. The size of the pellets can be made to match the size of the food particles typically consumed by the mussels. Results with zebra mussels showed that the polyquat concentration necessary to kill 50% of the mussels (LC_{50}) was reduced by half as a result of encapsulation. LC_{90} was almost 3 times lower when compared to treatment with uncoated material (Costa et al. 2012). Apart from polyquat, potassium has also been used as a selective molluscicide for zebra mussel control in closed systems (Claudi and Mackie 1994; Wildridge et al. 1998; Sprecher and Getsinger 2000). High concentration of potassium can cause mortality in zebra mussels by depolarization of the membranes of the gills, resulting in impairment of cell volume regulation, cellular vacuolation, leading to tissue disruption (Fisher et al. 1991; Durand-Hoffman 1995; O'Donnell et al. 1996). Studies with potassium-loaded pellets showed mortality of about 60% compared to the control mortality of <3%. Microencapsulated pellets as biofouling control agents have the advantage that specific toxin can be delivered directly to the target organism by modulating the size and shape of the pellets to match the target organism. It is environmentally less damaging than the direct application of the chemical as the quantity of the chemical used is significantly less and hence environmental discharge will be minimal.

17 Concluding Remarks

Though chlorination remains the most widely used antifouling technique in industrial CWS, there are alternatives available. Among chemical biocides, both oxidizing and nonoxidizing options are available. Some of the oxidizing alternatives such as chlorine dioxide and ozone have proven capability to control biofouling, but cost is an important hurdle in their wider application. In certain cases, the environmental impact of the chemicals is also not well understood. Physical methods such as electrical and acoustic methods appear attractive from the environmental viewpoint. However, their potential to effectively control biofouling at plant level needs to be demonstrated in unequivocal terms by properly conducted field trials. Filtration and judicious application of water velocity are relatively simpler techniques; but their application is limited due to practical difficulties. Viewed in this context, heat treatment appears attractive as it is a simple and elegant method of achieving good biofouling control, albeit at a production cost. Environmental and cost factors will play very important roles in deciding whether some of these technologies will be finally accepted by utilities as a replacement of chlorination. It is anticipated that green technologies of biofouling control will become more and more relevant in the coming decades. It is, therefore, necessary that emphasis may continue to be placed on research aimed at development of environmentally benign biofouling control technologies.

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Chapter 11
Improved Mussel Control Through Microencapsulated BioBullets

Raquel Costa, Geoff D. Moggridge, and David C. Aldridge

1 Introduction

Biofouling control is a major challenge in the operation and management of industrial cooling water systems. Several aquatic organisms are of concern in this context. Amongst them is the freshwater zebra mussel (*Dreissena polymorpha*), which has been recognised as one of the world's most important pests (Pimentel et al. 2005).

The species is native to the basins of the Black and Caspian Seas. It began to spread across Europe in the late eighteenth century, and currently can be found in countries such as Great Britain, The Netherlands, Germany, Switzerland, Sweden, Italy and Spain (Elliott 2005). Zebra mussel infestations are also a serious issue in North America, where the bivalve was introduced in the mid 1980s, probably as a result of ballast water discharges (Hebert et al. 1989).

Zebra mussels are unusual amongst freshwater bivalves in being epifaunal, attaching to hard surfaces by means of byssus threads. Furthermore, they are highly fecund and have a great dispersal capacity associated to reproduction through free-swimming larvae. These make the species an extremely successful invasive species and a powerful biofouler.

Zebra mussel infestations have several ecological and economic impacts. The species is known to have lead to the extirpation of native populations of unionid mussels by colonising their shells and hindering their burrowing, movement and

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Table 11.1 Summary of zebra mussel control approaches

Type of control method	Description
Mechanical	Aimed at preventing the species from entering the system through the use of screens, strainers and filters
Physical	Involves the direct removal of the mussels from the infested surfaces by scraping or high pressure jet-cleaning
Thermal	Based on flushing with warm water (usually at 34–37°C for 6–24 h); applied in systems where thermal backwash is feasible
Chemical	Application of chemicals with toxic activity
Paints and coatings	Permanently submerged surfaces may be protected by materials with antifouling properties

feeding (Claudi and Mackie 1994). Additionally, as prodigious filter feeders, zebra mussels tend to promote a pronounced decline in the levels of phytoplankton in the invaded ecosystem. The effects of such decline extend to the whole aquatic food web (MacIsaac 1996). Colonising industrial and recreational structures, zebra mussels also cause important economic damage. Water treatment facilities and industrial cooling systems are especially vulnerable to the effects of their biofouling activity (Kovalak et al. 1993; LePage 1993). Pipe and equipment blockage, reduced efficiency of water cooling systems, increased corrosion and plant operation disturbance associated to the need for biofouling removal are some of the problems experienced by freshwater-dependent industries as a result of zebra mussel infestations. The damage caused by this pest and its control costs over $1 billion each year in US alone (Pimentel et al. 2005).

Research into efficient mitigation methods for zebra mussels has been ongoing for several years in the public and private sectors, and currently many control strategies are available. These can be broadly classified into five categories: mechanical, physical, thermal, chemical and paints and coatings (Table 11.1; Post et al. 2000). Methods of all kinds have achieved reasonable success. The most appropriate control strategy for a particular installation depends on various factors that are often related to facility design and operation (Claudi and Mackie 1994; Post et al. 2000). An effective control programme usually involves the integration of several methods.

Typically, the use of chemicals with molluscicidal properties is the favoured approach to zebra mussel control in the industrial environment. Compared with other methods, this strategy tends to be cheaper and more versatile and flexible. A large number of compounds, including oxidising chemicals, such as chlorine and ozone, and non-oxidising substances, such as quaternary and polyquaternary ammonium compounds, aromatic hydrocarbons and metals and their salts, are currently employed in zebra mussel control (Sprecher and Getsinger 2000).

In spite of its advantages, chemical treatment raises concerns related to harmful impacts on non-target organisms and the cost-efficiency of some toxins. These concerns have prompted the development of more efficient and selective mitigation solutions based on new toxins or innovative application strategies for existing biocides.

In this chapter, a novel, cost-effective and environmentally beneficial approach to deliver molluscicidal agents is presented. This approach, commercially known as BioBullets, involves the encapsulation of the biocides within a non-toxic, non-recognisable material, edible for the bivalves. It increases the susceptibility of the animals to the toxin by exploiting their great filtration capabilities and overcoming potential valve closure defensive responses. The principles underlying the design of BioBullets and the benefits they provide are first discussed. The product formulations available and the respective manufacturing process are described next. Finally, some experimental evidence on BioBullets' performance is provided.

2 Principles Underlying Control Through BioBullets

BioBullets are small spheres in the micron size range, in which biocides are coated by a nutritious material, edible for zebra mussels (Fig. 11.1). Two main principles are involved in the formulation of BioBullets for zebra mussel mitigation.

Firstly, BioBullets exploit the considerable filtration capabilities of the bivalves. Zebra mussels are capable of processing water at rates as high as 570 mL/h/individual under natural conditions (Elliott 2005). The mechanism through which the animals sort particles for ingestion from the inhalant water is not fully understood. Particle size seems to be an important variable in this process (Morton 1971; Ten Winkel and Davids 1982; Lei et al. 1996). Zebra mussels have been shown to filter algae with diameters between 0.7 and 450 μm, retaining preferentially those in the size range 5–35 μm (Sprung and Rose 1988). In addition, there is some evidence that the bivalves may complement this size-based selection mechanism with a chemical one that allows them to sort food based on its sensory quality (Morton 1971; Ten Winkel and Davids 1982; Kryger and Riisgård 1988; Pires et al. 2004).

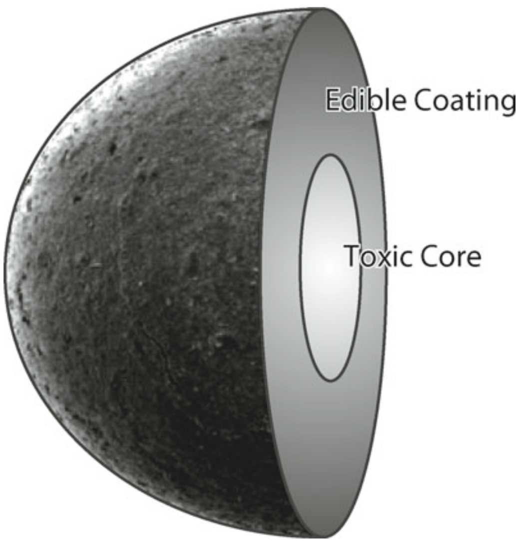

Fig. 11.1 Schematic representation of BioBullets structure

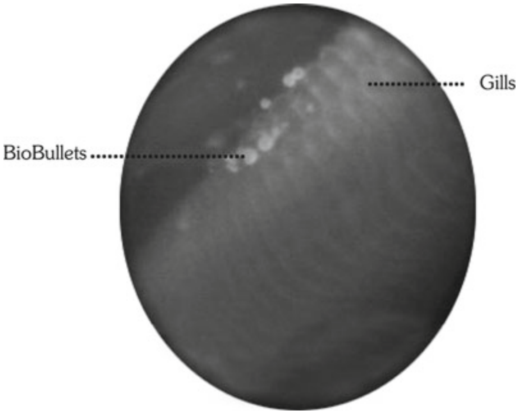

Fig. 11.2 Endoscopic photograph of BioBullets being transported in the gills of a live zebra mussel (Credits: Dr. Paul Elliott, University of Cambridge)

BioBullets have mean diameters below 250 μm and incorporate materials that are not recognised as irritating and are edible by zebra mussels. Thus the bivalves actively filter the particles from the water column, concentrating them within themselves (Fig. 11.2). As a result, the lethal bulk water biocide concentrations necessary to achieve mitigation are reduced greatly.

In addition to taking advantage of the filtration capabilities of zebra mussels, BioBullets also represent a "Trojan horse" approach to control. Zebra mussels are able to sense some biocides in their surroundings and respond by closing their valves for hours to weeks to avoid contact with the noxious chemical. During inactive periods, the animals rely on stored food reserves and anaerobic respiration. This type of avoidance response has been observed in the presence of chlorine (Claudi and Mackie 1994; Rajagopal et al. 2002) and organic pollutants, such as pentachlorophenol (Borcherding and Jantz 1997). The entrapment of the biocides into an edible coating overcomes such a defensive valve closing behaviour.

3 Economic, Operational and Environmental Benefits Provided by BioBullets

The use of encapsulated biocides in zebra mussel control provides economic and operational advantages as well as environmental benefits.

By monopolising on zebra mussels' filtration activity and minimising avoidance responses, BioBullets increase the mussels' susceptibility to the biocides. The treatment dosages and durations required for effective control are thus reduced compared to the direct application of the non-encapsulated poison. This has obvious economic advantages, not only by diminishing the expenditure on biocides, but also by reducing the cost of downstream effluent decontamination processes.

BioBullets offer the possibility of being tailored for specific applications to maximise their performance. For example, the robustness of the particles may be increased to face situations of high turbulence, their ability to sustain the release of the biocide may be augmented for dosing in long pipes and the particles' biocide-loading may be adjusted according to the water temperature at which treatment is to be performed. Additionally, the increase of biocidal toxicity through encapsulation may open the opportunity of using substances whose use as control agents would not be viable if they were applied in their original form. An example of a situation in which this would prove beneficial is that of trying to control zebra mussels by applying a chemical already in use in the plant for other treatment purposes but facing problems related to the moderate sensibility of the bivalves to that compound.

Further operational advantages of BioBullets include the fact that they promote shorter treatment durations with reduced plant operation disturbances and do not present storage or handling issues, contrary to other biocides, such as chlorine dioxide.

BioBullets incorporate harmless food-grade materials as coating and are designed to rapidly degrade before discharge into natural water bodies. These, combined with the fact that the particles provide an actual reduction of the total toxic potential applied, guarantee a more environmentally friendly control.

It should be noted here that the ecological advantages provided by BioBullets increase with the environmental acceptance of the biocide chosen for encapsulation.

4 Formulations and Manufacture of BioBullets

Several formulations of BioBullets are currently available, and others may be tailored to the needs of specific applications.

Virtually any biocide may be incorporated in the particles as active ingredient. A range of organic and inorganic toxins has already been encapsulated. A food-grade mixture of vegetable oils and waxes has been used as coating. This material is non-toxic to humans and aquatic ecosystems in general. It seems to be edible by zebra mussels and does not elicit defensive valve closure responses. Additionally, it effectively coats the biocides and provides an adequate profile of toxin release from the interior of the particles.

The particle manufacturing process largely depends on the active ingredient and coating to be used. The BioBullets formulated so far have been processed by spray chilling (Thies 1996; Lang 2002). In Fig. 11.3, a schematic diagram of this technique is shown. It involves the dispersion of the biocide in molten coating under conditions of controlled shear. The resulting slurry is then sprayed into a cooling chamber, where heat removal occurs to solidify the atomised melt and produce the spherical particles.

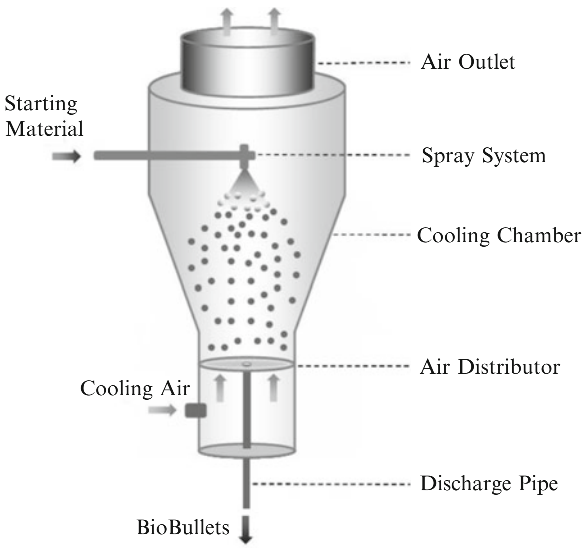

Fig. 11.3 Diagram of the spray chilling process used to produce BioBullets

5 Experimental Evidence on the Performance of BioBullets

The potential of BioBullets formulations has been proved in several laboratory and field scale studies, two of which are briefly summarised below.

5.1 Potential of Polyquat-Loaded BioBullets

Several polyquaternary ammonium compounds (polyquat), many used as coagulants in the drinking water industry, have proved effective as molluscicidal agents (Waller et al. 1993; Sprecher and Getsinger 2000). Having a high cationic charge density and being surface-active, these compounds must exert their toxic effects on adult mussels by adsorbing at the plasma membranes, including in gill tissues, and thus disrupting transfer mechanisms between the cells and the surrounding medium (Abel 1974; Gloxhuber 1974).

A polyquat-loaded BioBullets formulation containing 25% (w/w) of active ingredient is available. The spherical BioBullets (Fig. 11.4a) have a mean diameter of 225 ± 2.4 μm (mean ± SE), thus matching the size characteristics of the materials typically removed from the water column by zebra mussels. The scanning electron micrograph presented in Fig. 11.4b elucidates the internal structure of a fractured particle, revealing a polyquat bead embedded within the vegetable oil and wax matrix.

The retardant power of BioBullets is critical for their performance because the active ingredient release has to be sustained while the spheres travel through the system before being captured by the mussels. The polyquat-loaded particles release

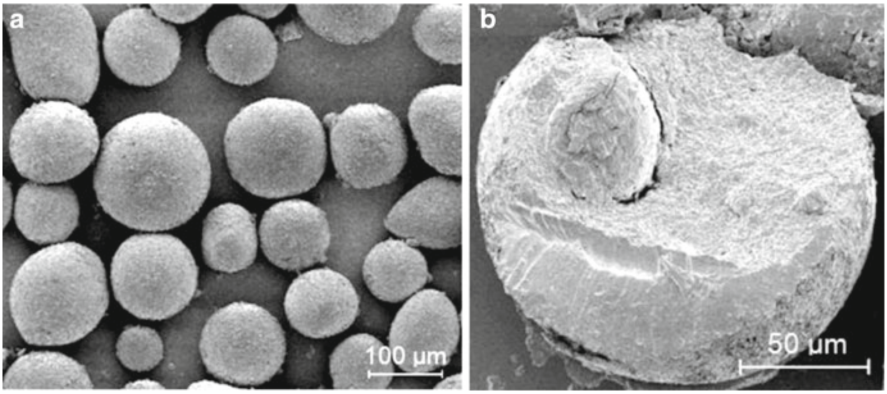

Fig. 11.4 Scanning electron micrographs of polyquat-loaded BioBullets: (**a**) general external aspect of the particles; (**b**) inside of a fractured particle

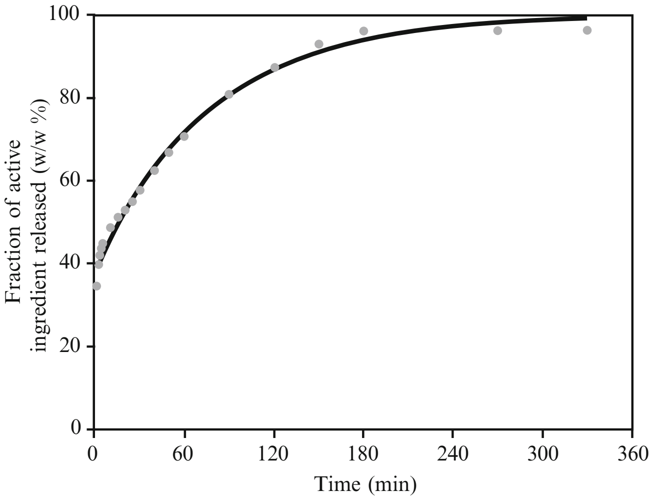

Fig. 11.5 Release profile of a polyquat from BioBullets. Points represent experimental data and the solid line a fitted empirical biexponential model (Washington 1996). The experimental toxin's dissolution kinetics was determined by the conductometrical technique. The standard error in the measurements did not exceed 4%

approximately 50% of their content in 20 min after dispersion in water, but they retain about 10% of the encapsulated toxin for periods as long as 3 h (Fig. 11.5). Note that the dissolution kinetics of the encapsulated toxin and the size of the particles are related, and the optimal product formulation involves a trade-off between these two variables, both decisive to the BioBullets' molluscicidal activity.

The performance of the formulation has been evaluated in laboratory renewal bioassays. Adult zebra mussels were exposed to a series of concentrations of the

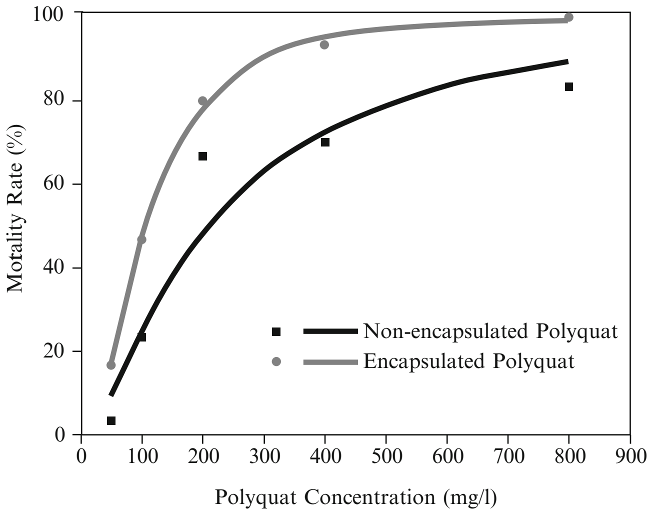

Fig. 11.6 Dose–response data describing the sensitivity of zebra mussels to a polyquat dosed in its original form and as active ingredient in BioBullets. The test organisms were exposed to the biocide for 12 h and then allowed to recover in clean water for 48 h prior to mortality rate assessment. The points represent experimental mortality data and the solid lines models obtained by Probit analysis. The standard error in the mortality rate measurements did not exceed 12.5%

polyquat dosed in both its encapsulated and uncoated forms for 12 h. The BioBullets were kept in suspension by using magnetic stirrers operating at approximately 60 rpm. The test medium was renewed every 3 h to minimise the exposure of the bivalves to toxin-depleted particles, which would hinder the estimation of the product performance under realistic flow-through conditions. The specimens were allowed to recover for 48 h in clean water before the lethal effects elicited by the different polyquat dosages were monitored.

The toxicity tests provided clear evidence of the potentiation action due to biocide encapsulation. As illustrated in Fig. 11.6, the coated polyquat was significantly more effective in mitigating zebra mussels than the original, non-encapsulated toxin (two-factor ANOVA following arcsine transformation of the mortality rate data; $F=14.508$; df = 1; $p<0.001$). The polyquat concentration necessary to kill 50% of the test organisms (LC_{50}) halved as a result of dosing the poison as active ingredient in BioBullets (Table 11.2). The increase of the polyquat toxicity due to encapsulation was even more evident when higher lethal responses were considered. The biocide concentration producing 90% mortality (LC_{90}) was found to be almost 3 times lower when it was applied in the micro-particulate form compared to the dosing of uncoated material (Table 11.2).

Various quaternary and polyquaternary ammonium compounds are claimed to not elicit valve closure defensive responses in zebra mussels (Claudi and Mackie 1994; Sprecher and Getsinger 2000). However, the polyquat used as active ingredient in BioBullets has been observed to induce such type of behaviour when applied

Table 11.2 Toxicity parameters describing the sensitivity of zebra mussels to a polyquat dosed in its original form and as active ingredient in BioBullets

	Median lethal concentration, LC_{50} [mg/L]		Concentration for percentile 90, LC_{90} [mg/L]	
Polyquat dosing form	Estimate	95% confidence interval limits	Estimate	95% confidence interval limits
Non-encapsulated	209.7	161.9–272.8	844.3	573.7–1599.2
Encapsulated	107.0	84.3–131.8	296.0	226.6–450.7

The test organisms were exposed to the biocide for 12 h and then allowed to recover in clean water for 48 h prior to mortality rate assessment. The toxicity parameters were estimated by Probit analysis

at concentrations as low as 2 mg/L (Costa 2008). The fraction of live test mussels with closed shells has been found to triple in the 12 h following the application of this biocide dosage. Thus the increased toxicity of the micro-particulate polyquat must result not only from the exploitation of the mussels' filtration capabilities, but also from the action of the non-recognisable coating in preventing the avoidance response of the animals.

5.2 *Potential of Potassium-Loaded BioBullets*

Potassium is a relatively selective molluscicide that has been suggested as an attractive alternative for zebra mussel control in closed systems (Claudi and Mackie 1994; Wildridge et al. 1998; Sprecher and Getsinger 2000), facilities able to minimise the toxicity of their effluents by dilution or other physicochemical measures (Wildridge et al. 1998), and situations in which the survival of non-target bivalves is not a concern, such as the transport of fish to and from hatcheries (Fisher et al. 1991; Durand-Hoffman 1995). The primary lethal action of potassium on adult zebra mussels is the depolarisation of the membranes of the ctenidial epithelium cells, which results in the impairment of cell volume regulation, cellular vacuolation and, ultimately, disruption of the tissue (Fisher et al. 1991; Durand-Hoffman 1995; O'Donnell et al. 1996).

A BioBullets formulation containing 30% (w/w) of potassium chloride as active ingredient is available. Having a mean diameter of 105 ± 34.4 µm (mean ± SE), the particles are suitable for filtration by zebra mussels. Scanning electron microscopy revealed they are spherical in shape (Aldridge et al. 2006). The formulation retardant power is such that at least 50% of the encapsulated salt is retained within 1 h following dispersion in water, and the amount of biocide released equals 90% of the spheres' content only after approximately 170 min (Fig. 11.7).

The potential of the potassium-loaded BioBullets for adult zebra mussel mitigation has been assessed through field-scale toxicity tests (Aldridge et al. 2006). The experimental facility where such tests were conducted consists of a series of 4-m long open flumes with a basal width of 5 cm. River water flows continuously through

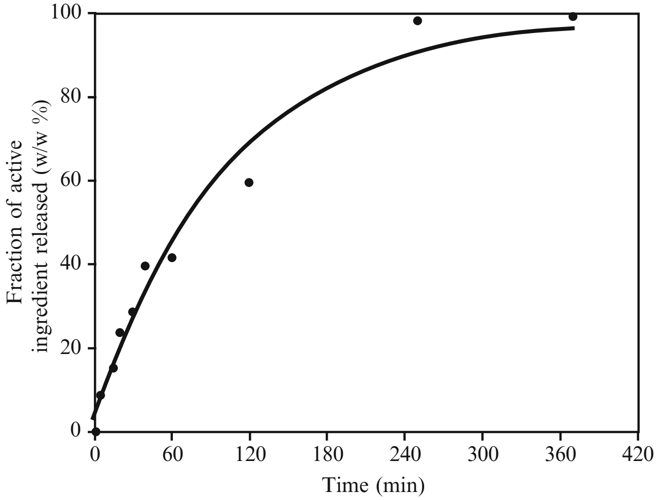

Fig. 11.7 Release profile of potassium chloride from BioBullets. Points represent experimental data and the solid line a fitted empirical biexponential model (Washington 1996). The experimental toxin's dissolution kinetics was determined by the conductometrical technique. The standard error in the measurements did not exceed 4%

Fig. 11.8 Photograph of the experimental facility where the performance of potassium-loaded BioBullets was assessed under field conditions (Credits: Dr. Paul Elliott, University of Cambridge)

the flumes, where the test organisms are held (Fig. 11.8). This facility allows BioBullets performance to be assessed under natural conditions of mussel density, water quality and flow rate. Moreover, by assuring a continuous replenishment of encapsulated product, it reduces greatly the exposure of the test organisms to toxin-depleted particles, and thus promotes an accurate estimation of BioBullets performance. However, contrary to laboratory bioassays, field scale toxicity tests

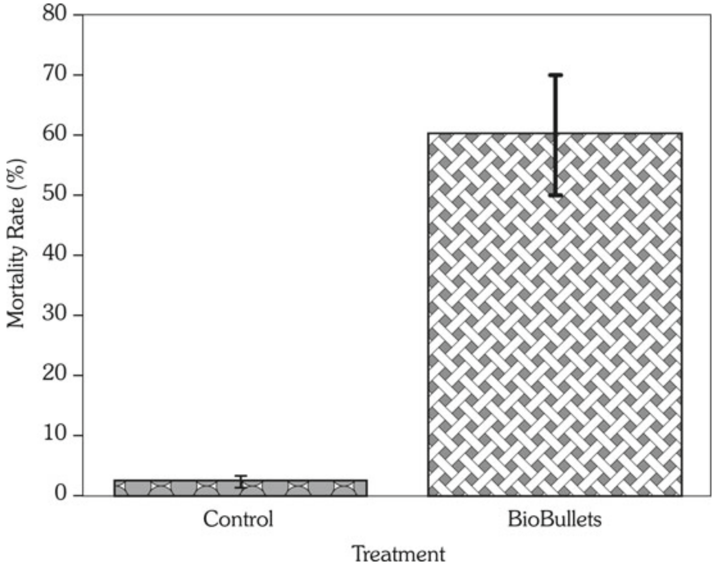

Fig. 11.9 Mortality rates (mean ± SE) produced by control and potassium-loaded BioBullets treatments. Control treatments involved the dosing of 300 mg/L of uncoated potassium chloride combined with 1 g/L of inert calcium carbonate-loaded particles. Potassium-loaded BioBullets were dosed at 1 g/L, equivalent to 300 mg/L of toxic salt. Both treatments were applied for 12 h and the test organisms were allowed to recover in a flow of clean water for 36 h prior to mortality rate assessment

are complex, time-consuming and require increased resources. For these reasons, they do not allow a large number of distinct treatment dosages to be simultaneously evaluated. In these tests, zebra mussels were exposed to 1 g/L of BioBullets, equivalent to 300 mg/L of potassium chloride, for 12 h. Control organisms were treated for a similar period with the same concentration of salt in its uncoated form, combined with 1 g/L of inert particles. Control inert particles were comprised of a non-toxic calcium carbonate core and the same coating as the potassium-loaded BioBullets. The specimens were allowed to recover in a flow of clean water for 36 h before the lethal effects produced by the treatments were assessed.

The toxicity tests clearly revealed the potential of the BioBullets formulation for zebra mussel control. The treatment with potassium-loaded particles was significantly more lethal than the control treatment (Aldridge et al. 2006). The former mitigated approximately 60% of the test organisms, while the mortality rate in the control flumes did not exceeded 3% (Fig. 11.9). This result not only provides evidence of the potentiation effect of toxin encapsulation, but also shows that any of the BioBullets' constituents apart from the coated biocide is toxic.

Potassium does not appear to elicit a significant valve-closure defensive response in zebra mussels (Van Benschoten et al. 1992). Therefore, the increased susceptibility of the animals to the coated salt must be due mainly to the concentration effect promoted by their filtration activity.

6 Concluding Remarks

Biofouling provoked by the freshwater zebra mussel is often a major challenge in the operation and management of industrial cooling water systems. In this chapter, a novel, cost-effective and environmentally friendly approach to control the species has been discussed. Such an approach, commercially known as BioBullets, involves the coating of molluscicide agents with a non-toxic, non-recognisable material, edible for the bivalves. The method monopolises on zebra mussels' filtration activity and minimises their avoidance responses in the presence of certain toxins, which results on an increase of their susceptibility to the biocide. The potential of BioBullets has been demonstrated in several simple and expedite laboratory bioassays as well as flow-though field scale toxicity tests. Some of these trials have been presented here. BioBullets are now available commercially.

So far, the encapsulation of biocides has been explored mainly in the context of zebra mussel control. However, this approach may be applicable in the mitigation of other aquatic nuisances, including other bivalves, such as the blue mussel *Mytilus edulis*, and other suspension feeders, such as sea squirts, sponges, bryozoans and the hydroid *Cordylophora caspia*. Not only may the formulations currently available be directly employed to manage these biofouler species, but also the BioBullets technology may be modified, refined and optimised to the control of these pests. This may be achieved in a number of ways, including:

– Incoporating in the particles species-specific toxins and coatings.
– Producing particles that are size- and shape-specific to the organisms.
– Exploiting the seasonal vulnerability of the target species to refine the dosing regimes.
– Integrating the idea of toxin encapsulation with that of taking advantage of biocides' joint effects, and either combine micro-particulate toxins with other poisons or incorporate more than one toxin in the same particle.
– Increasing the selectivity of the particles for use in natural environments, for example by exploiting the valve-closing response of non-target bivalves and using a coating material that is sensed by them but not by the nuisance species.

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Chapter 12
Pulse-Chlorination®: Anti-Fouling Optimization in Seawater Cooling Systems

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1 Introduction

The marine environment provides many services to the human population of the world's coastal zone. Specifically seawater is a naturally abundant resource that numerous industries can utilize as a cooling medium. For seawater to be efficiently and reliably utilized for cooling a biocide must be added to prevent marine growth. Typical industry practice along coastlines worldwide includes continuous chlorination of the seawater with occasional shock dosing (Fig. 12.1). This practice is not based upon ecotoxicological data of targeted species but rather either a post-hoc observation of anti-fouling efficiency or an attempt to meet regulated discharge to sea of residual biocide concentrations. Shock dosing is applied in the erroneous notion that it stops fouling species from adapting to continuous chlorination. These practices have been identified as major contributors to land-based pollution of the sea, especially within the Arabian Gulf (Khan et al. 2002; Abuzinada et al. 2008). Therefore, opportunities exist for science-based decisions to optimize both site-specific biocide regimes and regulatory discharge limits.

Qatargas is Qatar's first and major liquefied natural gas (LNG) company. As part of the liquefaction process seawater is used as a cooling medium for a number of different heat exchangers (freshwater plate/tube and shell). Currently the operating

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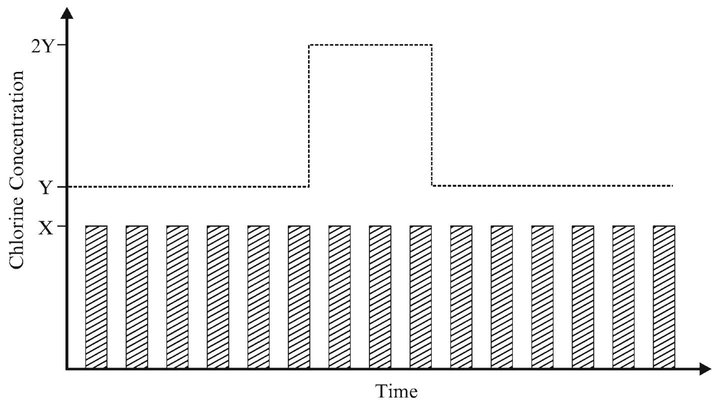

Fig. 12.1 Schematic of typical industry cooling seawater anti-fouling chlorination practice vs. P-C®. *Black dotted lines* represent continuous chlorination at concentration Y with occasional shock dosing at concentration 2Y. *Grey solid lines* represent P-C® dosing at scientifically determined time periods and concentration X. Chlorine concentration X may not necessarily be less than Y

three trains (including sulphur recovery units and utilities of power generation and desalination) utilize 112,000 m^3/h for the cooling demands required by the plant to produce approximately ten million tonnes per annum of LNG. This seawater is pumped from an intake structure (with a debris boom, bar screens and rotating drum fine screens to eliminate entrainment of foreign material) within Ras Laffan Port (RLP) to the plant by three separate glass flaked lined concrete pipelines. After passing heat exchangers the cooling seawater with a lower is then discharged through a back pressure weir into a long open channel ending in a cascade over rock armouring prior to discharge to sea. The total distance of this seawater distribution network is approximately 6 km. Sodium hypochlorite (commonly just termed chlorine) is the only biocide added to the seawater to prevent fouling and is produced on-site within RLP by an ECP.

The issue of environmental impact from residual biocide after the addition of chlorine is localized but common throughout the region at most of the numerous cooling seawater users discharges. It has attracted significant attention from environmentally concerned stakeholders including regulators. The resultant environmental impact of cooling seawater depends upon the operation of each facility that can vary considerably. The effect in the water column also varies if the use of the seawater is solely for cooling or for desalination feedstock. Once-through non-contact seawater typically results in a buoyant plume allowing greater surface water to air exchange of heat and volatilization of residual oxidants and chlorination by-products (CBPs) but affect the pelagic plankton more than the benthic species (Kolluru et al. 2003; Nour El-Din 2004). Cooling seawater associated with desalination can be negatively buoyant thus having reduced atmospheric release creating greater problems for benthic species (Latteman and Höpner 2008).

2 Environmental Regulatory Background

The Qatar Ministry of the Environment, formerly the Supreme Council for the Environment and Natural Reserves (SCENR), had required a free residual chlorine limit in cooling seawater discharges of 0.1 mg/L that was further reduced to 0.05 mg/L in the Executive By-Laws of 2005 of the Environment Law 2002. The SCENR was considerably concerned regarding the environmental impact from cooling seawater chlorination on local marine resources. In addition, the formation of CBPs through the excessive use of sodium hypochlorite has regularly been cited as a significant cause for concern (Khordagui 1992; Azariah 2000; Latteman and Höpner 2008). However, the literature regarding CBPs in the marine environment does not readily support such assertions (Jenner et al. 1997; Khalanski 2002; Quack and Wallace 2003; Gribble 2004; Johnson et al. 2006; Taylor 2006) and indicated their natural production by marine organisms is of equal or greater magnitude. The SCENR standard is significantly lower than the recent International Finance Corporation guidelines of 0.2 mg/L total residual oxidant (TRO) limit (IFC 2008) that updated the World Bank's Pollution Prevention Handbook (World Bank 1999) and other international discharge standards. For example, Taiwan permits a maximum concentration of 0.5 mg/L (Tawain Environmental Protection Administration 2001, cited by Wang et al. 2008).

The residual biocidal effects of 0.05 mg/L are known to be tolerable to many fouling species (Göksu et al. 2002; Wang et al. 2008) and therefore plant operations run the risk of decreased seawater availability for cooling purposes. In addition, the in-field practical quantification limits of equipment utilized for analyzing residual oxidants have been recommended to consider only readings at or above 0.1 mg/L (EU RAR 2007). Furthermore, the actual environmental impact on the marine environment of an efficiently run cooling seawater system's anti-fouling strategy has been reviewed as minimal (Taylor 2006). Sound and sustainable environmental regulator policies and standards have long been acknowledged to be linked to scientific studies (e.g. Khan and Al-Ajmi 1998) such as the case study presented in the paper.

The control and monitoring by industries of residual biocides returned to the sea is warranted and of growing concern internationally (Ma et al. 1998) but has long been acknowledged as should be determined by specific ecotoxicological testing (e.g. Capuzzo et al. 1977) and linked to the carrying capacity receiving environment of the synergistic impacts created by cooling seawater discharges. Multiple species ecotoxicological experiments (e.g. from lethal concentrations to no observable effect concentrations and sub-lethal response) should be conducted on local ecologically, culturally and commercially important species. For example, Wang et al. (2008) calculated the Lethal Concentration TRO for 50% of the test populations over 24 h for 13 species before considering interpretation of cooling seawater discharge targets.

Residual biocide concentration regulations should be based on science and stakeholder engagement (Fig. 12.2). This chapter details the efforts conducted to ensure Qatargas' cooling seawater systems anti-fouling strategy operates at the highest

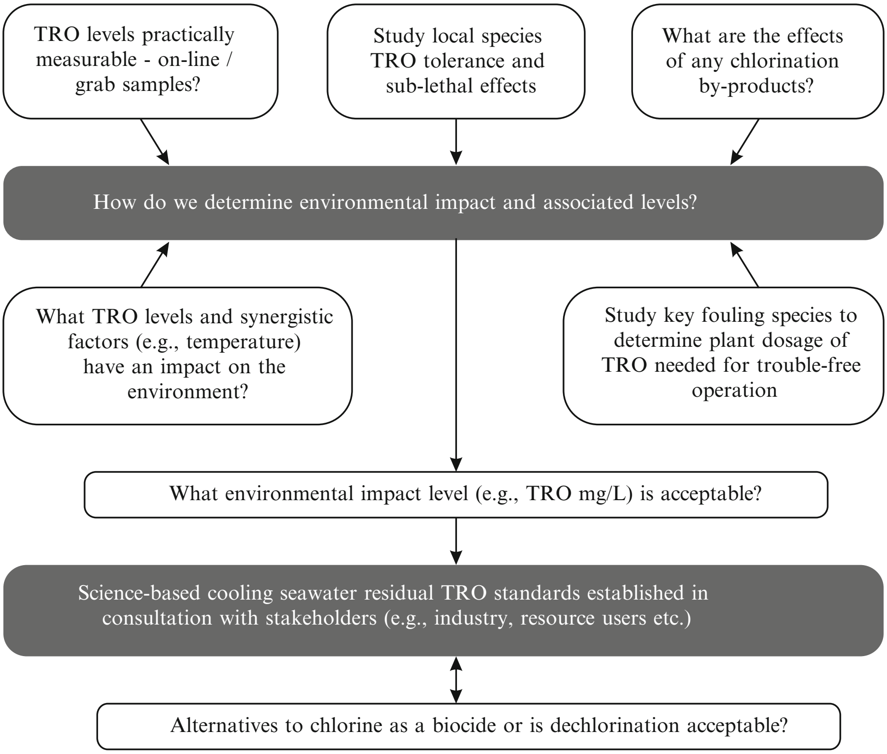

Fig. 12.2 Factors influencing and requiring study to facilitate the creation of a scientifically based cooling seawater discharge residual oxidant standard

level of operational and environmental performance. This level as desired by Qatargas can be defined as the maximum reduction in the cooling seawater TRO discharged to sea whilst maintaining plant integrity. P-C® combines optimal fouling control with minimal chlorine discharge, while retaining safe plant operations. P-C® is the EU Best Available Technology (BAT) for industrial cooling seawater system fouling protection by chlorination (BREF 2001).

3 Methods

To investigate the technical possibilities of using P-C® for anti-fouling optimization, Qatargas ordered KEMA to perform a study to obtain the optimal dosing regime according to the P-C® methodology. The technical details and methodology for P-C® and recent industrial experiences are reported by Polman and Jenner (2002) and Jenner et al. (2003).

The complete study consisted of three phases/reports to bring Qatargas' cooling seawater chlorination up to best practice and can be summarized as follows:

Phase 1: Current and historic fouling problem description, review of current seawater system practices, a literature review of local fouling species and whether P-C® is practically possible and may benefit Qatargas.

Phase 2: On-site research of fouling organism sodium hypochlorite tolerance by ecotoxicological testing with a MusselMonitor® (MusselMonitor® is a biological early warning system for aquatic pollutants that utilizes local bivalve species to determine environmental effect, refer to Kramer et al. 1989 for more details) within a mobile laboratory, including a short-term (few hours) full scale P-C® plant based test.

Based on the tests, measurements and inspections performed on-site during Phases 1 and 2, the optimum hypochlorite injection requirements and monitoring instructions were established. During this time between Phases 2 and 3 Qatargas ran a medium term (10 days) trial to ensure equipment suitability to the required modifications to run P-C®.

Phase 3: Covers the final assessment of P-C® after implementation on a long-term operational basis (10–12 months) over the period July 2007 to July 2008. This evaluates whether P-C® can be a permanent optimization of the cooling seawater systems anti-fouling strategy and suggests further improvements.

4 Brief Description of Pulse-Chlorination® and Its Benefits

In chlorination chemistry a traditional difference is normally made between free (active/available) chlorine and combined chlorine. Free Oxidant (FO) is present as an equilibrium mixture $HOCl \rightarrow OCl^- + H^+$ (hypochlorous acid and hypochlorite). Combined chlorine is available in chloramines or other compounds having oxidizing properties. TRO is defined as the total oxidizing capacity (free and combined) which is available after chlorination. Chlorine demand is defined as the difference between the amount of chlorine added and the FO concentration remaining at the end of a specified contact period.

When chlorine is added to sea water, containing 68 mg/L bromide at full salinity, bromide is oxidized and the hypochlorite is displaced by hypobromous acid (HOBr). This reaction is rapid, with 99% conversion within 10 s at full salinity and within 15 s even at half salinity. Within the Arabian Gulf where salinities are above the normal 35, typically varying in-between 39 and 42 depending upon season in well-mixed deep locations, this would further increase the conversion rate. However, since hypochlorite is produced and stored on-site (10 m^3 tank at approximately 500–2,000 mg/L) prior to dosage there is the opportunity for chlorine-dominated chemistry to produce various by-products.

P-C® is based on the biological observation that bivalves (e.g. oysters, mussels and clams) show a distinct recovery period after exposure to chlorinated seawater for a certain time period. Only after this recovery period do they open their valves

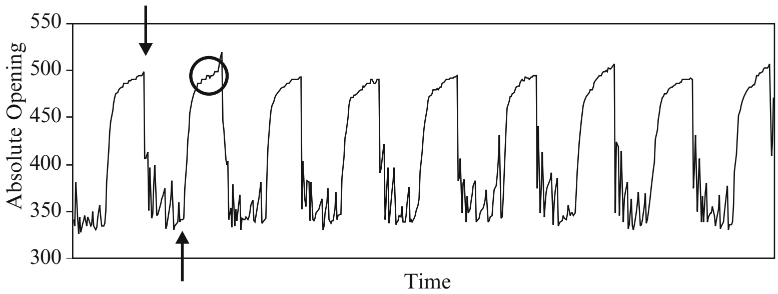

Fig. 12.3 A fouling bivalve's movement behaviour (opening and closing of the valves) detected by a MusselMonitor® during a P-C® regime. *Top arrow* indicates the start ("on"), the *bottom arrow* the timing of stop ("off") of chlorination. The *circle* indicates the recovery period during which the bivalve slowly opens. Normal behaviour would reflect a continuously open valve position allowing respiration and feeding to occur

fully before re-starting filtering water for oxygen and nutrients. P-C® enhances a cyclic mode of hypochlorite dosing (on/off dosing regime), based on the behavioural responses of the specific bivalve to chlorine, thereby taking advantage of this recovery period to delay the re-start of P-C®. By applying P-C®, bivalves will have to switch their metabolic mode continuously between aerobic and anaerobic. In adults this leads to physiological exhaustion and subsequently death. Juvenile bivalves (either free swimming spat or newly settled individuals) are more susceptible to oxidants and typically would move on through the system to a location of lower oxidant concentration (i.e. in the natural marine environment post-discharge). In principle, this dosing procedure does not apply chlorine as a toxicant or oxidant to mitigate against bivalves, but rather as a trigger to force bivalves to switch between their metabolic modes and the bivalves are prevented from re-starting filtration. P-C® results in a more rapid effect, i.e. mortality of the mussels, compared to the conventional continuous chlorination method. For better understanding of P-C®, an example of the valve movement behaviour which shows the reaction pattern of bivalves in general during P-C® is given in Fig. 12.3. Typical behaviour of a bivalve in seawater would be represented by valves being fully open >99% of the time.

During the time that the target organism's valves are closed (and show their recovery period) the sodium hypochlorite dosing can cease. As soon as the target organism's valves have returned to their 100% opening, the dosing can be re-started resulting in the immediate closing of the valves. Thus, the effect of P-C® upon the target organism is based on repetitive exposure to short successive periods of chlorination. P-C® forces the target organism to switch continuously between aerobic and anaerobic metabolism, leading to physiological exhaustion. In this situation the target organism use their own energy reserves (i.e. fat, muscles and glycogen). In this situation bivalves may "survive" for several weeks depending on their physical condition and environmental conditions.

The required effective initial dosage of hypochlorite concentration depends on, first, the target organism's behaviour and, second, the seawater quality parameters at the intake. Qatargas' most significant parameter is temperature as this fluctuates significantly (typically between 17 and 35°C) and a mere 5°C increase in temperature effectively doubles the chlorine decay rate. The chlorine concentration expressed as TRO has to be measured directly in front of the last point of required protection (i.e. heat exchangers). The initial hypochlorite dosing concentration at the intake to achieve the desired concentration TRO in front of the heat exchangers is largely influenced by the chlorine demand of the intake seawater.

It is evident from previous studies that P-C® leads to an improved method for the control of macro-fouling in once-through seawater cooling systems. This is concluded after years of undisturbed operation of power plants in The Netherlands and elsewhere, e.g. Korea and Australia. The application of P-C® provides both economical and environmental advantages. In the case of ECP installations, for the production of sodium hypochlorite, their production requirements are lowered which allows less and quicker maintenance requirements and reduced power consumption. The environmental benefit is obvious, less chlorine in the discharge cooling seawater and subsequently less production of the unwanted CBPs.

5 Chlorination Chemistry in Seawater

Hypochlorite/bromite immediately reacts with suspended and dissolved organic matter within seawater, especially with N-containing compounds. This process is called "chlorine (bromine) demand". Reactions between N-containing compounds and chlorine produce halogenated amines referred to as "bound oxidants". During chlorination in sea- or brackish water, these oxidants provide an extra toxic effect on bivalves by the reaction product bromamines. Bromamines are, in contrast to chloramines, acutely toxic for mussels. Brominated amines are, more or less, as toxic as hypobromous acid. The creation of these chlorinated by-products accounts for using the term TRO in seawater.

Summarized, the effective part of the hypochlorite dosing in seawater is the total toxicity of free (bromine) oxidants (FO) and bound (bromine) oxidants. The latter are defined as TROs. For this reason, the chlorine concentration is generally defined by the amount of FO when used in freshwater and TRO when used for either seawater or brackish water.

6 Results

6.1 Phase 1

In Phase 1, in early 2005, a site survey had been performed to determine the principle fouling species present on site and to obtain all technical information necessary for Phase 2. In addition, a literature study was performed in Phase 1 to obtain information on fouling species found on site. This study showed that the pearl oyster *Pinctada radiata* is the most problematic species and also the most chlorine tolerant among the fouling species present. The only data available in the literature indicate different opinions on the breeding periods of the oyster. Al-Sayed et al. (1993) have recorded continuous spawning of *P. radiata* with peaks in hot summer from Bahrain waters, whereas, the spawning season of *P. radiata* was restricted between May and September in Kuwait (Al-Matar et al. 1993). Based on their recruitment pattern, Mohammed and Yassien (2003) suggested that *P. radiata* was semi-continuous breeder in Qatari waters. However, it was rather difficult to predict the breeding season of *P. radiata* in Qatari waters from the presented data different spawning seasons were reported from nearby areas. All the above studies are consistent with peak spawning season of *P. radiata* during the summer period. Control of the pearl oyster is the leading requirement of this cooling seawater anti-fouling research project. Other fouling organisms observed at location were barnacles, tubeworms and a small "exotic" mussel (*Brachidontes* spp.).

The conclusions of Phase 1 were positive and no serious limitations were found withholding a successful implementation of the P-C® method after finalizing Phase 2. Fouling and target species were known and discussed including the collection of the very limited available literature related to Qatari coastal seawaters. The necessary technical items (location, power supply and telecom) for starting Phase 2 were all on hand or could be, with rather simple adaptations, made operational.

6.2 Phase 2

During Phase 2 a full-scale 4-h P-C® dosing test had been performed, according to a cyclic mode of hypochlorite dosing: 15 min on/15 min off (hence referred to as 15″ on/15″ off), applying the highest concentration possible. These timings were chosen as they were a previously determined P-C® regime, see Polman and Jenner (2002). After management approval, a Qatargas-specific P-C® on/off timings and target concentration were trialled over 10 days to evaluate ECP performance to ensure that the dosing system could handle the cyclical nature of P-C® and to monitor discharge concentrations.

The on-site ecotoxicological P-C® tests have been performed by means of the KEMA Mobile Laboratory to determine the optimum P-C® regime. This laboratory is fully equipped with wet and dry sections and all the necessary equipment to conduct P-C® testing. The main purpose of the test period on-site was to determine the most effective dosing regime and concentration to mitigate the pearl oyster settling in the cooling seawater system of Qatargas. This is implemented through the subsequent optimization of the hypochlorite dosing according to the P-C® principle by integrating process technology, system monitoring and fouling organism biology. Based on the on-site tests, measurements and inspections performed, the optimum injection requirements and instructions were established. These requirements are not reported due to their confidential nature and species—location specificity of the results.

The results of Phase 2 4-h full-scale 15″ on/15″ off test indicated that the desired TRO concentration to be measured at the last critical point for fouling protection can be technically met with the present operation of the electrochlorination plant (ECP). According to the final results of Phase 2, the P-C® dosing regime and pre-set dosing period for Qatargas were defined and advised to be run throughout the year due to uncertainty over the reproductive timing of the pearl oyster *P. radiata*. The operational procedure for the on/off regime is to be determined in practice and re-programmed in the operating electronics of the ECP. It was decided that a 10-day plant trial would be sufficient to determine the practicality of the prescribed on/off timing regime; target TRO concentration was monitored within the plant, and to gauge environmental benefit, the TRO was monitored at point of discharge to sea.

After management approval and regulator concurrence, P-C® was initiated at Qatargas on 4 July 2007 and has been applied continuously. During this time period the chlorine dosing concentrations, over the P-C® dosing time, were carefully monitored at four locations. On-line analysers exist at the common header of the cooling seawater intake and also on each of the three distribution pipelines prior to the point where they are discharged into a weir and common open discharge channel. Manual sampling was conducted at the determined last critical point for fouling protection and, as per required by the SCENR, at point of discharge to the sea. Meetings between operations, engineering and environmental affairs allowed adjustments which were necessary due to changes in seawater temperatures and ECP efficiency.

6.3 Phase 3

The results of the on-line residual chlorine measurements during P-C® implementation, (July 2007 to July 2008) are presented in Fig. 12.4, showing the mean concentrations per month. These readings do not represent discharge to sea concentrations but within plant concentrations and are subjected to aeration and UV degradation prior to discharge to sea. Data before P-C® (2002–2007) are presented to show the achieved decrease in concentrations and a significant reduction of 36% has been achieved. For some of December and all of January and February concentrations were uncharacteristically high. This was due to a separate operational requirement at the seawater intake structure.

7 Discussion

The required initial dosage of sodium hypochlorite for cooling seawater anti-fouling purposes at any facility that does not compromise operational reliability depends on (1) target species behaviour and (2) the seawater quality parameters at the cooling seawater intake. The control of initial dosage modelling or otherwise determining the required concentration to meet regulatory chlorine discharge concentrations

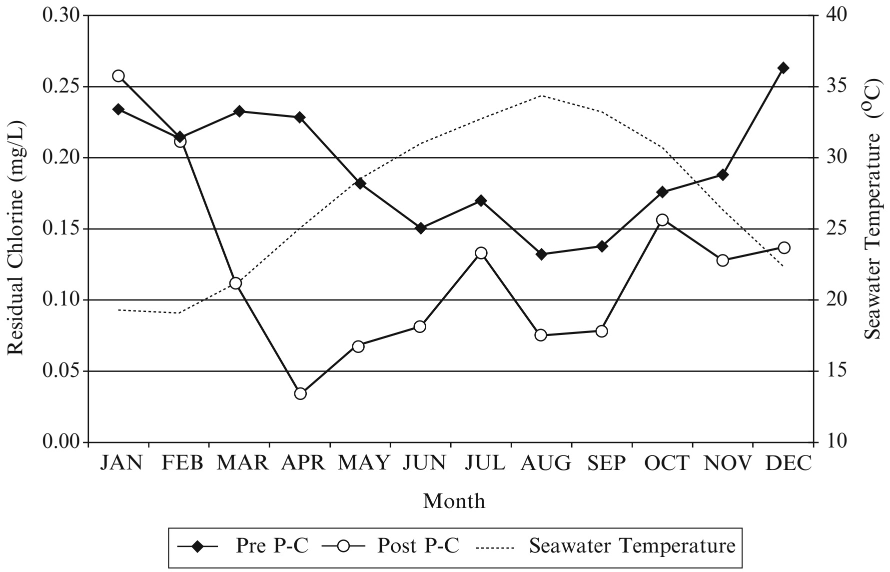

Fig. 12.4 Monthly average data from on-line analysis of residual chlorine in the cooling seawater prior to release through back pressure weir into open channel leading to the sea. Data represent Pre P-C® (2002–2007) vs. post P-C® (4 July 2007–2008). Seawater temperature taken from seawater intake within RLP displayed

(e.g. Wang et al. 2008) allows for potential fouling problems to occur and therefore is not advised.

At Qatargas the target organism for fouling control was documented to be the pearl oyster *P. radiata*. This fouling species is known to have a high tolerance to sodium hypochlorite with a dosage concentration of 1.25 mg/L and a 0.47 mg/L residual causing mortality in 50% of the population within 24 h (Göksu et al. 2002). This exceeds even the IFC recommended 0.2 mg/L discharge guidelines on residual oxidant concentration and indicates that *P. radiata* may be a persistent fouling species reducing cooling seawater systems operational efficiency and thus facility production. A species and locality-specific targeted chlorination regime, P-C®, was subsequently calculated and implemented. Qatargas' most significant seawater quality parameter is temperature as this fluctuates significantly (typically between 17 and 35°C, see Fig. 12.4). Given the nearly 20°C annual fluctuation in seawater temperature then a significant difference in chlorine decay rates may be expected from the seawater intake (i.e. point of chlorine dosage) to within plant residual chlorine measurement. P-C® is based upon achieving a desired minimum TRO concentration measured directly in front of the last point of required protection (i.e. heat exchangers). Due to this fluctuating natural decay rate of chlorine then the initial chlorine dosing concentration at the intake is required to be regularly altered to ensure optimization and minimal residual oxidant discharge into the marine environment.

The experience with implementation of P-C® at the Qatargas facility is so far positive. The current major issues for on-going optimization are modifications of

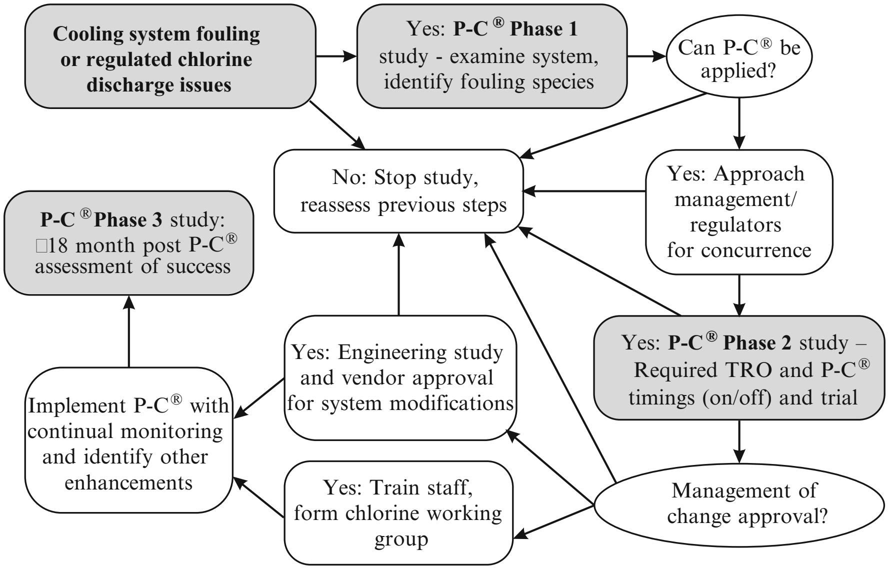

Fig. 12.5 Management of change diagram to illustrate the path taken for the study and implementation of P-C® within Qatargas

the seawater intake structure, chlorine dosage pipe work network and ECP maintenance issues unrelated to P-C®. Problems during implementation were related to equipment issues discovered by the close examination of the system required for P-C® to be adopted. It can be concluded that the implementation of P-C® for Qatargas has been successful through the inspection conducted during a recently scheduled LNG train shutdown. From a marine environmental protection perspective compared to the years before 2007, a reduction of ~56% of hypochlorite added to the cooling water was calculated based upon design requirements. This has a direct effect on lowering the discharge concentration of CBPs to the receiving environment.

The expectation for the coming years is that a lower and more stable measured monthly mean TRO values 0.05 and 0.15 mg/L will occur. These values are at the lowest end of the practical quantification ranges of the available equipment operating under local environment conditions within Qatar. Although some technical aspects and additional monitoring recommended by KEMA are not yet fully operational, already several clear improvements are observed in both fouling mitigation and discharge of TRO, while no problems in heat exchanger operation have occurred. It can be concluded that the objectives set for P-C® study were achieved and the path followed is summarized in Fig. 12.5. Qatargas chlorine discharges are as low as reasonably practical with P-C® and no further environmental risk reduction measures should be necessary beyond those currently practised and proposed to be conducted in the on-going optimization as advised for cooling seawater operation by the EU Risk Assessment Report for Sodium Hypochlorite (EU RAR 2007).

In addition to the P-C® regime, accompanying recommendations were made to ensure continual improvement of fouling control within the cooling seawater system. These recommendations included monitoring of TRO, macrofouling and microfouling within the system. The reduction of TRO discharged to sea can be further improved if an understanding is achieved of the local breeding times of all fouling animals involved. This necessitates a thorough study over multiple years to discount any interannual variability. These data are required to identify specific times of the year when chlorination is critical to mitigate macrofouling and conversely when no fouling species recruits are present, then the applied chlorination regime can be optimized.

Any restriction of the chlorination regime has to allow for mitigating against biofilm formation (microfouling) and possible Microbial Influenced Corrosion (MIC). MIC is an undesirable operational and environmental consequence of inadequate chlorination. Operationally MIC reduces heat exchanger efficiency, corroding parts, etc. and environmentally it is a likely contributing source of the metal contamination found within desalination plant discharges. Qatargas' material choices reduce the likelihood of MIC. With respect to monitoring microfouling, a BioGeorge® monitoring system (for technical details see Bruijs and Venhuis 2001) has been separately trialled. Monitoring microfouling is important with respect to P-C® as the preferred cooling seawater *chlorination* technique to ensure the specific regime applied inhibits microfouling and therefore MIC. However, dead areas within the system may still suffer MIC due to lack of chlorinated seawater circulation.

The issue of cooling seawater residual biocides will only increase and grow in complexity as the industrial development of the region continues. Science-based regulation is required but needs the leadership of industries that aspire to be good corporates to identify the latest trends and potentially pioneer new technologies for the industry/region. Source reduction of biocides (as documented in this paper) is only one approach to reducing the environmental footprint of cooling seawater systems. Internal plant optimization of cooling system design and waste heat recovery are additional options (e.g. Bin Mahfouz et al. 2006). End-of-pipe technologies are also available to remove the residual biocides; however, the various dechlorination agents available must be assessed in terms of not only biocide removal performance but also the net environment benefit, and further research is needed in this field (MacCrehan et al. 2005). Regulatory biocide discharge limits and use of end-of-pipe technology need to be balanced by determining the sensitivity of the receiving marine ecosystems to establish if any impact is derived from the discharge-associated stresses and is not related to natural environmental and/or marine organism fluctuations (Lam and Gray 2001).

8 Concluding Remarks

Qatargas Operating Company Limited (Qatargas) contracted KEMA to advise upon the optimization of their current cooling seawater systems anti-fouling policy. KEMA proposed to adapt for Qatargas' operations a scientifically based sodium hypochlorite dosing regime applicable to local fouling species, termed Pulse-Chlorination® (hence referred to as P-C®). This paper details the study of the suitability of P-C® for Qatargas.

P-C® is the European Union (EU) Best Available Technique for cooling seawater chlorination and has previously resulted in significant improvements in operational costs and discharged seawater quality. After a multidisciplinary study P-C® was implemented at Qatargas on the 4 July 2007. A scheduled inspection of the heat exchangers and strainers in April 2008 allowed a thorough assessment of P-C® performance with respect to fouling mitigation after 10 months of operation. Observations indicated that P-C® had been effective at macro-fouling mitigation. No living fouling species and only a minor number of shell fragments were found. These shells were generally black and brittle indicating that they were probably present prior to P-C® initiation.

Operationally P-C® reduced the demand for sodium hypochlorite production allowing half of the designed electro-chlorinator plant (ECP) to be utilized, thereby reducing the power consumption, maintenance requirements (e.g. manpower, hydrochloric acid) and emissions (e.g. carbon dioxide, hydrogen) from the ECP. Furthermore this reduced production demand allowed provision of equipment redundancy and may extend the life span of certain expensive ECP components. The environment benefit of P-C® compared to the years prior to implementation included a calculated mass-based reduction of ~56% of chlorine utilized. Data during the first year of P-C® operation showed an average decrease in chlorine within the plant of 36% (average 2002–2007 vs. 2007–2008). In addition, reduced CBP formation is predicted. Further discharge concentration reductions are expected with operational and engineering-related improvements at the seawater intake and future environmental studies.

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Chapter 13
Environmental Impact of Cooling Water Treatment for Biofouling and Biocorrosion Control

Eugene Cloete and Hans-Curt Flemming

1 Introduction

Water cooling towers are major users of water worldwide. Industrial development has resulted in an increase in the use of water for cooling tower operations. This has led to an expansion of the demand for water and natural resources, particularly in threshold countries such as China, India and South Africa. It is well known that how we use water in industrial applications will drastically affect water quality downstream. What seems as an isolated incidence often results in a complex interaction and the negative effects may amplify each other. While the challenges for water management increase, there are opportunities to prevent destruction of the environment and the water source and in doing so create a sustainable environment for development and water use.

Cooling water systems cool water by evaporation, leading to an increase in the dissolved solids concentration and at some point the dissolved solids will exceed the solubility limit(s) of the materials present, resulting in adverse operational effects. In order to prevent this, water is discharged from the system (blow down) to restrict the build-up of dissolved solids to levels below the saturation point. Cooling water treatment programmes, therefore, have to focus on controlling fouling deposition, scaling, corrosion, etc. by the addition of a variety of chemicals to the water. These include high biocide concentrations that may increase toxicity in water in some instances that could result in discharge problems. The potential negative environmental effects of all of these chemicals are associated with the blow down.

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Micro-organisms in cooling towers attach to surfaces and are exposed to nutrient rich water. The resulting growth form microcolonies which develop into biofilms. Biofilms accumulate some of the suspended solids resulting in an increase in nutrient concentrations to an extent which interferes with operational requirements (Flemming 2002), providing massive biomass development. Inevitably, anaerobic conditions will develop in deeper layers of the biofilm and facilitate anaerobic corrosion, collectively termed biofouling and concomitant microbially influenced corrosion (MIC) (Coetser and Cloete 2005). A range of bactericidal substances, commonly termed biocides or microbicides, are used in aqueous systems to control biofouling. Biocides are chemicals with an active, and in general toxic, effect on living organisms. However, the biocidal effect may extend beyond the target organism(s) with resulting adverse effects to the environment. Bacteria may for example become resistant to biocides with significant health consequences, should these be disposed of in the environment (Gilbert et al. 2003).

Consequently, new environmental regulations, health and safety concerns, performance objectives and economic consideration have curtailed the use of many microbiocides in cooling water treatment applications. The European Union directive on biocidal products, for example, addresses the dangerous properties of a specific subset of chemicals, which are used against unwanted biological organisms (Directive 98/8/EC 1998).

As discharge requirements become increasingly more stringent, a biocide that decomposes prior to discharge may become one of the few suitable methods for controlling microbes in cooling water systems. This chapter deals with the current chemical biofouling control strategies and their potential impact on the environment.

2 Control of Biofouling and Biocorrosion

Monitoring and controlling microbial growth is an essential part of any comprehensive cooling water treatment programme. Practical experience has led to the development of strategies that minimize microbiological growth and prevent shutdown (Cloete et al. 1998). These include the following:

- Bacteria are chemically killed by biocides
- Bacterial cells are dislodged from surfaces by dispersants
- The biofilm structure is weakened by enzymes or chelating agents of divalent cations
- Biofilms are removed physically by a variety of processes
- Biocide efficacy is enhanced by applying an alternating current or ultrasonic sound across the biofilm

Active substances in biocides lead to the disinfection of water by killing bacteria and viruses in the water. There are an estimated 1,200 active substances on the market at the moment. Since the use of bactericides pose the biggest environmental threat, only these will be discussed in more detail. Bactericides are antibacterial agents used to prevent, inhibit or eliminate unwanted microbial growth. The use of biocides to control biofouling in water systems is a common practice although higher levels of environmental awareness and tighter legislation have placed increased pressure on the water treatment industry to seek alternative means of control (Bognolo et al. 1992). Nevertheless, biocides are still essential for effective control of biofouling. Biocides are categorized as either oxidizing or non-oxidizing.

The above mentioned Biocide Product Directive (BPD) of the European Union is intended to balance the efficacy of biocides in their intended use with their impact on human and animal health and the environment. It legally organizes the process of putting a biocide on the market and harmonizes the regulation of the EU member states. Biocides have to be subjected systematic tests for efficacy and risk before approval. The BPD achieves its aims using a two-stage regime of rigorous evaluation of biocidal active substances and products, to ensure they pose no unacceptable risks to people, animals or the environment. Although this system is complicated and sometimes not completely without contradictions, it is an important and serious attempt to protect humans, animals and the environment from effects of an otherwise unregulated use of biocides, which sometimes are considerably toxic (Flemming and Greenalgh 2009).

2.1 Oxidizing Biocides

Oxidizing biocides are general chemical oxidants that are not selective for living organisms, but react with any oxidizable matter. Oxidizing biocides include oxidizing halogens, peroxides, electrochemically activated water and ozone (Cloete and Atlas 2005).

Peroxides are unstable oxygen compounds which decompose to form free hydroxyl radicals that react oxidatively with organic matter. The peroxides include hydrogen peroxide, peracetic acid, aromatic peroxyacids, persulphates and calcium peroxide. Silver enhances both the stability and antimicrobial effect of peroxide solutions. Peroxide has wide spectrum antimicrobial properties killing both gram-positive and gram-negative bacteria and decomposes to water and oxygen, leaving no toxic waste. Peracetic acid is the best known of the organic peroxides. Like hydrogen peroxide, it forms free hydroxyl radicals, which react with various protein structures and DNA. In addition, the dissociation of peracetic acid leads to formation of acetic acid, which is mildly antibacterial itself. Application of peracetic acid to systems does not leave any toxic by-products behind. Although environmentally safe, peroxides are seldom used in cooling tower applications because of the corrosivity of these chemicals on mild steel (Cloete and Atlas 2005).

Hypochloric and hypobromic acids are excellent biocides within defined pH ranges. Chlorine, chlorine dioxide and hypochlorous acid (HOCl) are the most widely used biocides worldwide. HOCl is a powerful oxidizing agent, oxidizing thiol groups and halogenating amino groups in proteins (Russell et al. 1997) and oxidizing lipids and proteins (Hyslop et al. 1988). The stability and antimicrobial activity of HOCl are dependent on pH. It dissociates at pH greater than 7, and above pH 7.5 it loses its antibacterial activity. It is excellent for biofouling control, as it weakens the extracellular polysaccharide (EPS) structure, leading to sloughing and removal of sections of the biofilm.

Hypobromous acid works similarly to HOCl. It, however, retains its antimicrobial activity up to a pH of 8.5. This makes it more suited for application in cooling waters which are often maintained at a slightly alkaline pH. Certain organic compounds release hypobromic and hypochloric acid slowly when in solution. An example is 3-bromo-1-chloro-5,5-dimethylhydantoin (Pietersen et al. 1995). Such compounds maintain a longer antibacterial level of hypohalous acid in the system treated. Currently, chlorine dioxide is being adopted in several European power stations because of its effectiveness in killing macrofoulants as well as microbial biofouling and lesser formation of organo-halogenated by-products (Walker and Morales 1997). Typical doses of ClO_2 for seawater cooling systems range from 0.05 to 0.1 mg/L (Petrucci 2005).

Ozone is an excellent biocide capable of killing bacteria and algae and of inactivating viruses. Ozone has a very short half-life and therefore has to be generated on site. In distilled water its half-life at 20°C is 25 min. Its solubility in water is 13 times that of oxygen. Upon reaction with organic material, it decomposes to oxygen. Ozonated water is environmentally safe as ozone degenerates to oxygen (Cloete and Atlas 2005).

"Electrochemically activated water" is another option which is based on the effect of various in situ generated biocidal radicals. In order to produce it, water of varying mineralization is passed through an electrochemical cell. The design of the cell permits the harnessing of two distinct and electrically opposite streams of activated water. A negatively charged antioxidant solution (catholyte) is produced and a positively charged oxidant solution (anolyte) is produced. Anolyte consists of low concentrations of a number of free radicals including ozone, chlorine dioxide, hydrogen peroxide and HOCl and has very good biocidal properties against gram-positive and gram-negative bacteria. When added to water, anolyte will result in an increase of the redox potential to above 900 mV. It has been postulated that it is this high redox potential that gives anolyte its biocidal capability. When discharged into the environment, anolyte will revert back to the benign state of water with no environmental impact so far (Cloete and Atlas 2005).

2.2 Non-Oxidizing Biocides

Non-oxidizing biocides include a variety of organic chemical compounds. Their modes of action differ vastly, and their only common denominator is that they are non-oxidizing, organic molecules (Paulus 2005).

2.2.1 Detergent-Type Biocides

Three surface-active antimicrobial agents are commonly used, i.e. anionic, cationic and amphoteric surfactants (Paulus 2005). Anionic biocides are effective at $pH < 3.0$ and include the aliphatic acids such as sodium dodecyl sulphate. The cationic biocides are the generally organic ammonium salts, commonly termed quaternary ammonium compounds. The best known is benzalkonium chloride (*N*-alkyl-*N*,*N*-dimethyl benzylammonium chloride) (Wallhäuser 1995; Paulus 2005).

2.2.2 Biguanides

Biguanides are polymer derivatives of a general guanidine structure. Polyhexamethylene biguanide (PHMB) and 1,6-di-(4-chlorophenyldiguanido)-hexane, better known as chlorhexidine, are the most commonly used biocides (Wallhäuser 1995; Paulus 2005). Both are not corrosive and all are well suited for application in cooling water (Woodcock 1988). They are membrane-active agents and attach rapidly to negatively charged cell surfaces (pH neutral or alkaline). By making use of ^{14}C-radiolabelled PHMB, it has been shown that PHMB 15 absorbed into cells of *Escherichia coli* within 20 s after exposure (Fitzgerald et al. 1992).

2.2.3 Aldehyde-Based Biocides

Formaldehyde and glutaraldehyde represent the aldehyde-based biocides. Glutaraldehyde is the most commonly used aldehyde-based biocide in cooling water applications (Russell and Chopra 1990). It is stable in acid solution but is only active at pH 7.5–8.5, so it must be alkalinified before application (Wallhäuser 1995). Its reactivity is related to temperature; a 2% solution kills spores of *Bacillus anthracis* in 15 min at 20°C, whereas it requires only 2 min at 40°C. In gram positive bacteria it reacts with, and binds to, peptidoglycan and teichoic acid, and is also sporicidal (Russell and Chopra 1990). In Gram negative bacteria it reacts primarily with lipoproteins of the outer membrane, preventing the release of membrane-bound enzymes.

2.2.4 Phenol Derivatives

A range of halogenated phenols, cresols, diphenyls and bisphenols have been developed from phenol. Bisphenols have the highest antimicrobial activity of the phenol derivatives, especially halogen substituted ones. Hexachlorophen and 2,2′-methylenebis(4-chlorophenol) (dichlorophen) fall into this group (Brözel and Cloete 1993a, b). Phenol derivatives are membrane active agents. They penetrate into the lipid phase of the cytoplasmic membrane, inducing leakage of cytoplasmic constituents (Russell and Chopra 1990). 3- and 4-chlorophenol uncouple oxidative phosphorylation from respiration by increasing the permeability of the cytoplasmic membrane to protons (Gilbert and Brown 1978).

2.2.5 Thiol-Oxidizing Biocides

Thiols on amino acids such as cysteine are important groups which influence the tertiary structure of proteins by forming disulphide bridges. Three groups of antimicrobial agents, isothiazolones, Bronopol (2-bromo-2-nitropropane-1,3-diol) and mercury and other heavy-metal compounds react with accessible thiols, altering the three-dimensional structure of enzymes and structural proteins (Collier et al. 1991). Mercury interacts with sulfhydryl groups by complexing with sulphur (Wallhäuser 1995). Bronopol oxidizes thiols to disulphides, reacting especially with the active centre of hydrogenase enzymes (Wallhäuser 1995). Four water-soluble isothiazolones possess antibacterial activity: 5-chloro-2-methyl-3-(2H)-isothiazolinone (CMIT), 2-methyl-3-(2H)-isothiazolinone (MIT), 1,2-benzisothiazolin-3-one (BIT) and 2 methyl 4,5-trimethylen-4-isothiazolin-3-one (MTI) (Wallhäuser 1995). MIT and CMIT are often supplied in a 3:1 ratio. Isothiazolones react oxidatively with accessible thiols such as cysteine and glutathione (Collier et al. 1990). These thiols are oxidized to their disulphide adjuncts which, in the case of cysteine, lead to an alteration of protein conformation and functionality. Isothiazolone is hereby reduced to mercaptoacrylamide, which in the case of CMIT tautomerizes to thioacyl chloride, the latter reacting with amines such as histidine and valine (Collier et al. 1991). Isothiazolones are primarily bacteriostatic and are only bactericidal at high concentrations.

A common feature to all of the non-oxidizing biocides is the development of resistance to these by bacteria (Cloete 2003). This probably poses the greatest health related risk to humans should these resistant bacteria be discharged into the environment (Gilbert et al. 2003). For details, see Paulus (2005).

2.3 Resistance of Bacteria to Biocides

Concern has been expressed that the use of biocides in industrial applications may be a contributory factor to the development and selection of antibiotic-resistant bacterial strains in nature (Gilbert et al. 2003). Resistance has been defined as the temporary or permanent ability of an organism and its progeny to remain viable and/or multiply under conditions that would destroy or inhibit other members of the strain (Brözel and Cloete 1993a, b, 1994; Pietersen et al. 1995, 1996a, b; Cloete 2003).

Bacteria may be defined as resistant when they are not susceptible to a concentration of antibacterial agent used in practice. Traditionally, resistance refers to instances where the basis of increased tolerance is a genetic change, and where the biochemical basis is known. Resistance of biofilm micro-organisms has serious economic and environmental implications in many applications such as cooling water, papermaking, medical implants, drinking-water distribution, secondary oil recovery, metalworking and food processing (Mattila et al. 2002; Flemming 2002; Shirtliff and Leid 2009). The mechanisms of bacterial attachment and the resulting problems caused in the food and dairy industries are also well known (Bagge et al. 2001; Julien et al. 2003; Gilbert et al. 2003).

Antimicrobial substances target a range of cellular loci, from the cytoplasmic membrane to respiratory functions, enzymes and the genetic material. However, different bacteria react differently to bactericides, either due to inherent differences such as unique cell envelope composition and non-susceptible proteins, or to the development of resistance, either by adaptation or by genetic exchange. At low concentrations bactericides often act bacteriostatically, and are only bactericidal at higher concentrations. For bactericides to be effective, they must attain a sufficiently high concentration at the target site to exert their antibacterial action.

It is well known since long that biofilm organisms display resistance to biocides. For their inactivation, sometimes more than two orders of magnitude higher concentrations are required compared to planktonic cells (for review, see Cloete 2003; Schulte et al. 2005). The reasons for this phenomenon are under research and not fully elucidated. Among the mechanisms discussed in terms of increased resistance are the following:

– Influence of abiotic factors such as limited access of biocides to biofilms in crevices or dead legs of water systems and attachment to particles
– Diffusion–reaction limitation, due to the reaction of oxidizing biocides with EPS components (main inactivation factor for chlorine)
– Slow growth rate, which protects dormant organisms from biocides interfering with physiological processes
– Biofilm-specific phenotypes which express, e.g. copious amounts of EPS in response to biocides or enzymes such as catalase, inactivating hydrogen peroxide
– Persister cells, which is the term for the small number of organisms in a population, which survive even most extreme concentrations by mechanisms still unknown

3 Limiting the Environmental Impact of Biofouling Control

3.1 Risk Assessment

It is known that some of the non-oxidizing biocides and also some of the disinfection by-products of oxidizing biocides can act as carcinogens. Furthermore, the environmental impact and biodegradability of many of the non-oxidizing biocides are unknown, although most biocide manufacturers claim the contrary. To a large extent, legislation has led to better understanding of the toxicity of biocides. A similar effort is needed to investigate the environmental impact of the chemicals upon exposure.

The existing programmes on risk assessment of chemicals can efficiently be used to review biocides. The EU Directive on biocides specifically states: "Whereas it is necessary, when biocidal products are being authorized, to make sure that, when properly used for the purpose intended, they are sufficiently effective and have no unacceptable effect on the target organisms such as resistance or unacceptable tolerance, and, in the case of vertebrate animals, unnecessary suffering and pain, and have, in the light of current scientific and technical knowledge, no unacceptable effect on the environment and, in particular, on human or animal health" (Directive 98/8/EC 1998). This directive has been severely criticized and has since been amended a few times. Nevertheless, the basic message stays the same, acknowledging that human exposure scenario data is lacking and will be equally important for estimating the risk of using and disposing of biocides in the environment.

Risk assessment is an important aspect of the regulatory process according to the BPD (Flemming and Greenalgh 2009). In the BPD, it is performed for both the intended use and a reasonable worst-case situation. The risk from a chemical substance is determined from its intrinsic hazardous properties and the likely exposures of humans and the environment throughout its life-cycle. The intrinsic chemical, health and environmental hazardous properties can be quantified as a hazard assessment. The hazard of the biocide is assessed predominantly through toxicological testing in animal models (Annex IIA and B of the BPD). Good quality human data may also be available, perhaps from epidemiological studies. The hazard assessment is combined with an exposure assessment to produce a risk assessment. If the outcome is favourable, the substance will be recommended for Annex I listing. If not, further information on toxicity or exposure to refine the risk assessment may be demanded. If the risk remains unfavourable, a regulatory decision may be taken to implement risk management requirements, such as additional labelling or restrictions to use, to permit product approval.

Exposure assessment is a more complex issue. There are two basic options: measuring or modelling. Modelling can be carried out using generic data for chemical release. Estimates of environmental release are improved by gathering information on the release of biocides from specific processes to develop emission scenarios. Risk characterization is also conducted regarding animals kept and used by humans. The humaneness of biocidal products targeted at vertebrates is also considered, e.g. for biocides directed against rats.

The rule is that biocidal products can only be approved if, when used as prescribed, they do not present unacceptable risks to man, animals or the environment, are efficacious and use permitted active substances. Approval of biocidal products requires that they are used properly at an effective but minimized application rate. The regulatory authority also assesses the packaging, labelling and accompanying safety data sheet.

Acute and repeat-dose toxicity, irritation and corrosivity, sensitization, mutagenicity, carcinogenicity, toxicity for reproduction and the physicochemical properties of each active substance in the biocidal product are considered. If possible, they are also quantified, preferably as dose–response effect. This includes the exposure of professionals, non-professionals and man exposed indirectly via the environment to each active substance in the biocidal product during its lifetime. Only as a last resort, is the use of personal protective equipment taken into account to enable a biocidal product to be used safely. Replacement of hazardous substances by non-hazardous ones is preferred. Biocidal products containing category 1 or 2A or 2B carcinogens, mutagens or substances toxic to reproduction cannot be approved for use by the general public. Carcinogens are defined after the International Agency for Research on Cancer (IARC 1987):

Category 1 is for substances for which there is sufficient evidence for a causal relationship with cancer in humans (confirmed human carcinogen).

Category 2A is for substances for which there is a lesser degree of evidence in humans but sufficient evidence in animal studies, or degrees of evidence considered appropriate to this category, e.g. unequivocal evidence of mutagenicity in mammalian cells (probable human carcinogen).

Category 2B is for substances for which there is sufficient evidence in animal tests, or degrees of evidence considered appropriate to this category (possible human carcinogen).

Ultimately only those biocidal products which contain an active substance which is included in Annex I of the BPD Directive will be authorized for use. Active substances have to be evaluated to ascertain whether or not they will be included in Annex I. This requires industry to submit data which is evaluated by Member States with decisions over Annex I inclusion being taken at the European level. Industry is charged a fee for this process. Once an active substance has been included in Annex I, national Competent Authorities can authorize products containing it in individual Member States (providing that any necessary data have been supplied and any conditions put on Annex I inclusion are met). Once a product has been authorized in the first Member State, it will be possible for it to be mutually recognized and therefore authorized by other Member States (providing relevant conditions are similar). However, there will have to be an application from other Member States, and again there will be a fee for these processes.

4 Water Reuse

Increasingly stringent water discharge limitations worldwide have forced cooling water operators to re-examine their cooling water treatment practices. This is raised the awareness and in many cases the implementation of water reuse. With their high water demand and relatively low water quality requirements, open recirculation cooling water systems are often considered ideal for reusing industrial waste streams. However, contaminants in the waste streams frequently present new and significant challenges in corrosion control, scale control and microbiological control. Reuse will inevitably require an investigation into the various pretreatment options. The optimum combination can result in significant water and limit the environmental impact of discharge.

Making the right decision on how to reuse water and/or water discharge decisions is a challenge to cooling water operators. Cooperation between design and consulting engineers, customers, and water treatment suppliers at early stages of planning for plant water supply has many benefits. Practical approaches include conducting water audits, determining quality of water required for various uses, reviewing areas of supply such as composition of the proposed water source and how it could affect plant equipment or plant processes. This will help to develop sustainable cooling water treatment programmes with a minimal environmental impact.

5 Concluding Remarks

The use of chemicals supporting the smooth operation of cooling water systems will be unavoidable and will increase in the near future. However, it is absolutely worthwhile to develop alternative strategies which require much less of these substances. The biocides play a particularly difficult role among them. A better understanding of the underlying fouling processes allows for quenching their application considerably. In principle, biofouling in cooling water system can be considered as a “biofilm reactor in the wrong place”: micro-organisms attached to surfaces convert nutrients from the water phase into metabolites and further biomass. This is exactly the principle of biological filters. Therefore, nutrients are potential biomass. A biofilm reactor “in the right place”, i.e. ahead of systems to be protected, will remove nutrients and, thus, lead to an operation which requires less biocides. This has been demonstrated successfully for membrane systems (Griebe and Flemming 1998; Flemming and Ridgway 2009). Of course, this cannot be achieved in all situations but certainly much more often than it is done now. It requires nothing but a little shift of perspective. Further measures to limit the use of biocides comprise fouling monitoring (Flemming 2002) which allows for early warning, timely and precise dosing of chemicals at the sites where fouling occurs and for optimizing the countermeasures. A number of appropriate devices have been developed (Flemming and Griebe 2000). It is surprising that the heat exchanger industry still prefers blind dumping of chemicals over precise dosing. Obviously, only legal regulations will be able to change the mindset of the operators.

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Chapter 14
Effects of Power Plant Entrainment on Phytoplankton

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1 Introduction

The growing energy demand in developing countries such as India has led to the growth and development of electricity generating fossil fuel and nuclear power stations that withdraw large quantities of water for cooling purpose. The efficiency of electric power stations is generally between 30 and 35%, which results in a large amount of waste heat being rejected to cooling water in the process of steam condensation (Glasstone and Jordan 1980).

The water requirement of a power station depends on the type of cooling water system installed. Cooling water system mostly in use is of two kinds: (1) direct or once-through and (2) indirect or recirculating. In once-through cooling water system, water drawn from the source (river, lake, sea) passes through the condenser system once for heat transfer and the heated water is discharged back into the original source. Recirculating or closed cycle cooling water system has comparatively lesser water demand. The volume of water withdrawn is 2–3% of that drawn in once-through system (EPRI 2002a). In this system, water drawn from the source, after passage through the condenser is discharged into cooling pond or tower, where the excess heat is lost through evaporation and the cooled water is recycled to the condensers. Table 14.1 details the quantity of water withdrawn by nuclear and fossil fuel power stations with different kinds of cooling water system.

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Table 14.1 Cooling water withdrawal rates of various power stations (adapted from EPRI 2002b)

Power station and cooling system type	Water withdrawal (m^3/MWh[a])
Fossil fueled steam, once-through cooling	75–190
Fossil fueled steam, pond cooling	1.1–2.3
Fossil fueled steam, cooling tower	1.9–2.3
Nuclear steam, once-through cooling	95–227
Nuclear steam, pond cooling	1.9–4.1
Nuclear steam, cooling tower	3–4

[a]*MWh* mega watt hour

Nuclear and fossil fuel power stations, though similar in operation, differ in their energy source and water requirement. Nuclear power stations withdraw 20–30% more water, as they operate at lower temperature and pressure. This results in greater heat rejection and thus requires more water to maintain the desired temperature across the condensers.

Owing to the shortage of fresh water in sufficient quantity, power stations with once-through cooling system often tend to get located on seacoasts to make use of the abundant seawater (Clark and Brownwell 1973; IAEA 1974; Winter and Conner 1978). This large-scale abstraction of seawater for condenser cooling and its subsequent release as heated effluents into coastal areas may cause undesirable changes in natural ecosystem such as thermal enrichment of receiving waters, alteration of water quality, selective cropping of vulnerable species, and enhancement of surviving species, resulting in modification of biotic structure (GESAMP 1984). The undesirable effects are mainly due to impingement of larger biota such as squids and fish on intake structure screens and entrainment of smaller biota such as plankton into the power station cooling circuit.

Planktonic organisms, including phytoplankton, owing to their small size, limited mobility, and free-floating character, are prone to be passively drawn or entrained along with the cooling water into the power station cooling circuit, where they are subjected to various physical (mechanical and thermal) and chemical stresses. As most power stations located on seacoasts operate in a once-through mode, the biota including phytoplankton in the receiving water body may get entrained into the heated effluent plume, even if they do not pass through the cooling circuit. Mechanical stress to entrained plankton is mainly due to the sudden pressure changes along the cooling circuit. The increase in seawater temperature during and after condenser passage causes thermal stress. Chemical treatment of abstracted seawater with antifouling biocides such as chlorine is the main cause of chemical stress. Chemical and thermal stresses, unlike mechanical stress, continue to have their impact even after the seawater has left the power station and joined the recipient water body. Thus, heated effluents from coastal power stations have the potential to impart thermal and chemical stress, posing environmental problems to the receiving waters (Goldman and Quinby 1979; Miller and Brighouse 1984; Krishnakumar et al. 1991). Phytoplankton entrained into the power station cooling circuit experiences a higher magnitude of thermal and chemical stresses as compared to those entrained in the effluent plume. Detailed account of the thermal and chemical stress factors and their effects on phytoplankton is dealt in separate sections later in this chapter.

1.1 Thermal Ecology Studies on Phytoplankton (TESP)

Thermal ecology studies on phytoplankton (TESP) were a part of a major, multi-institutional, coordinated research project on thermal ecology conducted at nuclear power plant sites in India. The main objective of TESP was to study the effects of power station induced thermal and chemical stresses on phytoplankton. One of the study sites was Madras Atomic Power Station (MAPS), located at Kalpakkam on the east coast of India. MAPS consists of two units of pressurized heavy water reactors (PHWR) and uses coastal seawater of Bay of Bengal as tertiary coolant. A monitoring program that consisted of field survey coupled with in laboratory and mesocosm experimentation was organized to understand the effects of thermal and chemical stresses on phytoplankton. The important observations are discussed in this chapter.

1.2 Role of Phytoplankton in Marine Ecosystem

Phytoplankton forms a critical component of the coastal marine ecosystem. They are the primary producers and food source for other planktonic organisms, ranging from unicellular protists to multicellular copepods, forming the base of the food web. Their occurrence helps in oxygenation of water in the euphotic zone (Owens et al. 1969). Any significant disruption of phytoplankton and their productivity due to power station operation may result in energy shortages occurring within higher trophic levels that are directly or indirectly dependent on phytoplankton. These shortages, if severe enough, could possibly affect the survival, growth, and reproductive potential of various organisms within the ecosystem. Hence any harmful effect on phytoplankton may affect higher trophic organisms of the food chain, including those that are commercially and ecologically valuable. Such undesirable effects are likely to occur more in higher trophic organisms in enclosed systems such as reservoirs and small lakes rather than in those inhabiting well-mixed coastal waters.

Phytoplankton is sensitive to changes in the environment. It is well known that phytoplankton biomass and composition are strongly associated with changes in water quality. Hence, monitoring changes in phytoplankton biomass and community composition can serve as an important assessment tool in evaluating the impact of stress factors on the aquatic ecosystem.

2 Mechanical Stress

Mechanical stress is continuously experienced by entrained biota when cooling water is withdrawn and pumped. The extent of the damage depends on power station operating conditions. Mechanical stress effects show less variability than chemical and thermal stresses, which show variation depending on biocide application schedule and thermal exposure regimes. The damage caused by mechanical

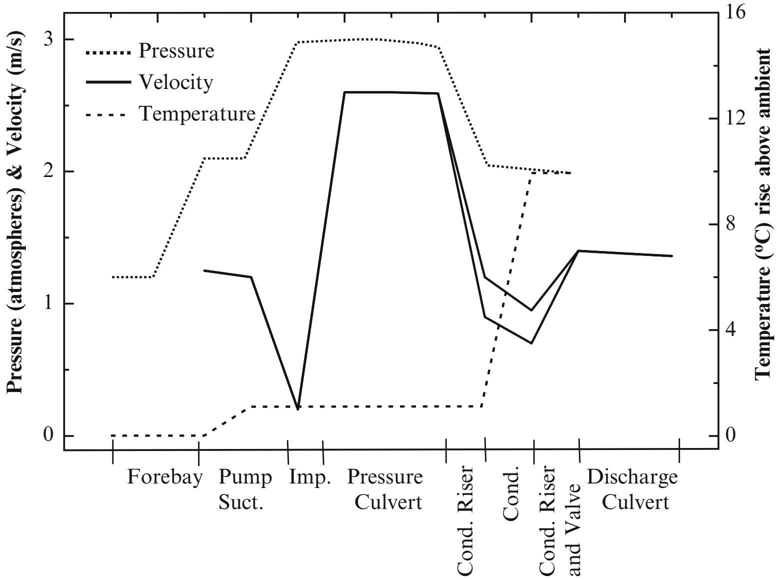

Fig. 14.1 Hydraulic gradient in a direct cooling water system (adapted from Howells and Langford 1982). *Suct.* suction; *Imp.* impeller; *Cond.* condenser

stress is mainly due to the contact of the entrained biota with physical barriers such as intake screens (fixed) at the intake area or traveling water screens at pump house, by sudden pressure changes in pumps, by shear forces due to extreme turbulence, by collision with particles passing along with entrained biota and by forces due to sudden changes in water velocity and direction. Figure 14.1 shows the hydraulic gradient for a typical "direct cooled" cooling water system and the associated changes in pressure and velocity. The effects of mechanical stress on entrained biota have not been adequately studied and assessed at most power stations.

Mechanical stress effects largely depend on the size and fragility of the organisms, the larger and the more fragile being more vulnerable. Bamber and Seaby (2004) in their study on entrainment of three species of marine planktonic crustaceans (shrimp larvae, lobster larvae, and adult copepods) reported that mechanical stress was only deleterious to lobster larvae, as they were comparatively large. It is thought that the impact of mechanical stress on phytoplankton would be less because of their small size and rigidity. Earlier studies by Coutant (1970), Williams (1971), Koops (1972), Knight (1973), Carpenter et al. (1974), Kreh and Derwort (1976); Coughlan and Whitehouse (1977) and Leslie and Moore (1980) observed no significant mechanical damage to phytoplankton that was entrained into power station cooling circuit. However, Gurtz and Weiss (1974a, b) and Bradford and Burns (1977) observed that colonial and filamentous algae were fragmented and therefore were more affected. Mechanical stress is also reported to affect phytoplankton primary productivity. Ahamed (1997) in his study reported that mechanical stress during power station entrainment caused 16–17% reduction in phytoplankton gross primary productivity (GPP). On the contrary, stimulation in productivity to an extent of 17.5–30% was also observed by Smith and Brooks (1971).

3 Thermal Stress

Thermal stress varies in magnitude and duration, depending on the power plant operating conditions and may cause more damage during periods of high ambient temperature. Thermal stress experienced by phytoplankton in the vicinity of power station is of two kinds. Those entrained into the power station cooling circuit along with the incoming water suffer acute thermal shock due to ΔT (increase in temperature over the ambient value) of up to 10°C, during passage through the condenser. Those which do not pass through the cooling circuit are still likely to be entrained into the thermal plume at the mixing point. In the latter case, the ΔT and exposure time are significantly less. Figure 14.1 shows the changes in water temperature in a typical direct cooled cooling water system.

Temperature affects the organisms both directly and indirectly. The direct effect of temperature was classified by Fry (1967) into three main types, i.e., lethal, controlling, and directive. Lethal effect causes death of the organism. Controlling effect causes changes in physiological and biochemical processes. Directive effect causes behavioral changes such as movements and migration. Indirect effects of temperature include the action of temperature on factors such as density, viscosity, vapor pressure, surface tension, diffusion, and solubility of gases, including oxygen. An increase in water temperature results in reduction of its density and viscosity. A decrease in viscosity may result in increased sedimentation. Vapor pressure is an important factor that controls the rate of water evaporation. Dissolved oxygen is essential for sustaining aquatic life. When conditions are normal, the amount of dissolved oxygen in natural waters is inversely related to water temperature and range from 14 mg/L at 0°C to 7.5 mg/L at 30°C. Houston (1982) reported that carbon dioxide was 2.5 times less soluble and oxygen was 50% less soluble at 30°C than at 0°C. Table 14.2 details the physical changes that water undergoes as a function

Table 14.2 Properties of water as a function of temperature (adapted from IAEA 1974)

Temperature (°C)	Vapor pressure (mb)	Viscosity (cρ)	Density (g/mL)	Surface tension (dyn/cm)	Oxygen solubility (mg/L)	Oxygen diffusivity (cm^2/s)
5	8.75	1.519	0.9999	74.9	12.8	–
10	12.32	1.307	0.9997	74.2	11.3	15.7
15	17.10	1.139	0.9991	73.5	10.2	18.3
20	23.45	1.002	0.9982	72.8	9.2	20.9
25	31.77	0.890	0.9970	72.0	8.4	23.7
30	92.56	0.798	0.9956	71.2	7.6	27.4
35	56.41	0.719	0.9940	–	7.1	–
40	74.00	0.653	0.9922	69.6	6.6	–

of temperature change. Thus, the passage of water through the condenser would predictably decrease dissolved oxygen in the receiving water body (Hynes 1960). Apart from direct effects, temperature increase may also indirectly affect the growth of phytoplankton. Sommers et al. (1975) reported that increase in temperature caused increased conversion of nutrients attached to suspended solids to readily available (soluble) forms. Karr and Schlosser (1978) observed that slight increase in temperature above 15°C caused substantial increase in release of phosphorus, due to the exponential increase in conversion rates with increasing temperature.

The rise in ambient water temperature not only affects the physical properties but is also known to have adverse effects on aquatic biota. Temperature is one of the most important environmental variables, which affects the survival, growth, and reproduction of aquatic organisms (Kinne 1970; Langford 1990). Growth rate, reproduction and enzymatic activity of organisms increase with increase in temperature up to a certain level, beyond which adverse effects are manifested (Rose 1967; Kinne 1970; Neill and Magnuson 1974; Jobling 1981). Every organism has a range of temperature that it can tolerate. The tolerance level depends on the genetic makeup and the metabolic functions of an organism and is subject to modification by several environmental variables. Hawkes (1969) reported that diatoms showed optimum growth at a temperature range of 15–25°C.

At most power stations, the rise in temperature of the cooling water is rapid, occurring over a period of a few seconds or minutes, as the water passes through the condensers or other heat exchangers. Thus, the entrained organisms including phytoplankton present in the cooling water are subjected to an acute temperature shock, which is around 8–10°C above the ambient temperature (Coutant 1971; Gibbons and Sharitz 1974). The discharged water from power stations raises the temperature of water adjacent to the discharge point. A maximum discharge temperature of 42°C has been reported in subtropical and tropical regions (Nugent 1970; Thorhaug et al. 1974; Kamath et al. 1975; Kolehmainen et al. 1975). The ambient temperature of the seawater in the tropics is close to the upper limit of temperature tolerance of many marine organisms. It is expected that any further increase in temperature of the surface waters due to the heated effluents may significantly affect the growth and reproduction of phytoplankton at least in the vicinity of power station, causing, in turn, adverse effects on the higher trophic organisms.

Field studies on the effect of temperature on entrained phytoplankton and their productivity showed variations at different sites. Howells (1969) in her study sampled the intake and the discharge water from Hudson River at Indian Point to determine the possible damage to phytoplankton due to passage through condenser cooling system and concluded that there was no significant effect. Morgan and Stross (1969) reported that an increase in temperature of 8°C stimulated primary productivity of phytoplankton when the natural water temperature was 16°C or cooler, but inhibited primary productivity when the natural water temperature was 20°C or warmer. Gurtz and Weiss (1974a, b) reported a decrease in phytoplankton abundance at outfall as compared to intake, but the decrease was not statistically significant. Reetz (1982) in a study at the Fort Calhoun power station on the Missouri River observed differences in phytoplankton cell counts at intake and outfall, which varied from 22% decrease to 25% increase, showing no correlation with temperature. Mallin et al. (1994) observed that direct thermal effects of cooling water discharge on phytoplankton communities were either localized or nonsignificant. Ahamed (1997) in his study observed that increase in outfall temperature up to 38.2°C resulted in increased phytoplankton GPP, while temperature beyond 38.2°C caused reduction in GPP.

3.1 Methods Employed in Aquatic Ecological Studies

Most ecological studies in marine pelagic ecosystem include field observation coupled with laboratory experimentation. In field observations, any observed effect cannot be positively related to a specific environmental parameter due to the variable conditions that operate in the natural waters. In laboratory experiments, an individual component of the ecosystem (such as phytoplankton) is isolated and the changes effected by various parameters of interest are studied. Usually in such experiments, changes are applied to only one variable (or a few variables) at a time and the other variables are kept at optimum levels. Though laboratory experiments are essential to establish the relative effects of temperature, toxins, and other factors, they do not reflect the variable conditions of the natural waters. So, it is often difficult to extrapolate or apply such results obtained in laboratory to the complex natural field situation. In light of this, it has been suggested that controlled aquatic ecosystem or mesocosm experiment on an intermediate scale could bridge the gap (Strickland 1967).

Mesocosm is an experimental system that offers more realistic ecological conditions than a laboratory setup and is a widely practised method in ecological studies (Odum 1984; Cairns 1988; Crossland 1994). A mesocosm experiment has a multitrophic ecosystem, which lasts for a generation's time that is longer than at least the third trophic level (Grice and Reeve 1982). Further, enclosing a suitable volume of water with naturally proportioned biota in a mesocosm provides integrity to the water column and prevents mixing or changes caused by action of currents and tides. Moreover, in these experimental systems, in addition to monitoring the various environmental variables over a period of time, it is also possible to modify or manipulate a single or a number of parameters simultaneously and assess the differential responses of the biota of interest to these environmental variables.

Although a stress factor directly affects an individual organism, its indirect effects may be manifested at all levels of biological organization (viz. population, community, and ecosystem). So there is no single level of organization that can be used to fully understand the effects of a stress factor. Studies at each level provide some information. Therefore an integrated study of the stress factor at all levels of organization is necessary to deduce the full effect of a stress factor. Studies at organism or cellular level are usually carried out in laboratory microcosm. Microcosm is the simplest controlled ecosystem, whose size ranges from a small flask to a large beaker or tank. Mesocosm experiments conducted in controlled environments such as large outdoor tank, artificial streams, ponds, enclosures in pelagic zones, or water

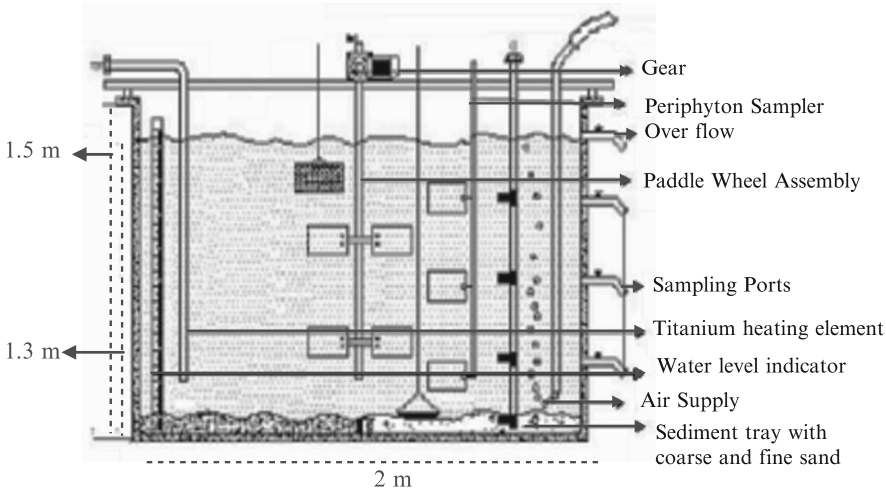

Fig. 14.2 A typical mesocosm facility for thermal stress studies

column captured and separated from a natural water body are usually employed to study stress effects at higher levels of organization. Mesocosm is indeed a small scale functional ecosystem that helps in assessing both the direct and indirect effects of a stress factor simultaneously at different levels of biological organization. Mesocosm studies have been very useful in monitoring phytoplankton bloom dynamics, sinking rates, biogeochemical cycling, species succession, and biological effects of pollutants (Menzel and Steele 1978; Bienfang 1982; Watanabe et al. 1995; Harada et al. 1999; Keller et al. 1999; Kreutzweiser et al. 2002).

In TESP, one such land based mesocosm facility was used to study the effects of power station induced thermal and chemical stresses on marine phytoplankton. The facility consisted of two mesocosm (a control and an experimental) units. Each mesocosm unit was a rectangular tank (4 m^3) made of fiber-reinforced plastic (Fig. 14.2). The water depth was 1.3 m and there was a 10 cm deep sediment bed at the bottom. Mixing of water was aided by a low rpm paddle wheel assembly. Oxygenation in the mesocosm was provided by continuous aeration. The experimental mesocosm unit had titanium heating elements with temperature sensing and control units for maintaining the experimental temperatures.

Mesocosm experiments are especially helpful in short term plankton studies, as the development of plankton community in a mesocosm is qualitatively similar to that of the "free" (natural) community at least for a period of up to 4 weeks (Menzel and Steele 1978). It has been reported that plankton communities exposed to identical conditions inside simultaneously filled mesocosms developed in a comparable manner (Kuiper 1977). It has also been observed that the levels of nutrients and chlorophyll agree well between the enclosure (bag) mesocosms (4 m^3) and the water from which the contents were taken (Brockmann et al. 1977). Thus, mesocosm can be used as an experimental tool to study ecosystem processes in coastal waters. Such studies are extremely important to understand indirect community level changes, functioning, and the effects of pollutants on the natural aquatic ecosystem.

The entrainment mimic unit (EMU) described by Bamber et al. (1994) is another very useful tool for power station entrainment studies. The EMU realistically simulates the conditions of entrainment as seen in the cooling water system of a coastal power station. This apparatus is useful in assessment of the effects caused by four key stress factors of entrainment namely; mechanical effects, pressure, biocide and temperature individually and in combination. Bamber and Seaby (2004) had carried out laboratory experiments using EMU to test the responses of three species of marine crustacean to entrainment stresses.

While conceding that a mesocosm is no substitute for actual field observations, it is nevertheless a generally accepted method for experiments involving a variety of environmental parameters. A good strategy for the assessment of the effects of stress factors in aquatic ecosystem is to couple field studies with experiments involving simulated laboratory and mesocosm facilities.

3.2 *Observations of TESP*

3.2.1 Field Survey

Field survey under TESP was carried out in the vicinity of MAPS and comprised of monthly sampling at the Intake point, the Outfall and the Mixing point (point where the heated discharge mixed with the sea). In addition, water samples were also collected at monthly intervals from areas surrounding the power station discharge by undertaking boat cruises, covering an area of about 2.5 km^2. The sampling stations were fixed using Global Positioning System (GPS).

Field survey revealed that the water temperature was 7.3–9.3 and 3.4–5.9°C higher at the outfall and mixing point, respectively, as compared to the Intake point. Diatoms were the dominant phytoplankton throughout the study period. Phytoplankton biomass (cell counts and chlorophyll-*a*) and GPP were invariably reduced (by 25–80%) during the transit of water from the Intake point to the Outfall. At the Mixing point, the phytoplankton biomass was about 15–50% lower as compared to the Intake, but the values were greater than the values observed at the Outfall. This was due to the mixing of the discharged water with ambient seawater. However, analysis of phytoplankton biomass in the cruise samples collected from stations close to the power station discharge showed that entrainment-induced reduction in biomass was not recognizable even at short distances beyond the Mixing point due to rapid and effective mixing of the discharge water with the ambient seawater. The power station induced effect on phytoplankton was, therefore, relatively localized to a small area near the Mixing point (Poornima et al. 2005). Shannon diversity index of phytoplankton showed little difference at the Intake, the Outfall, and the Mixing point, indicating that the stress factors (mechanical, chemical, and thermal) were not species-specific (Poornima 2005).

Further, field sampling on two occasions, namely when the power station was operating with chlorination and when it was operating without chlorination, suggested that chlorination caused relatively greater damage to phytoplankton biomass

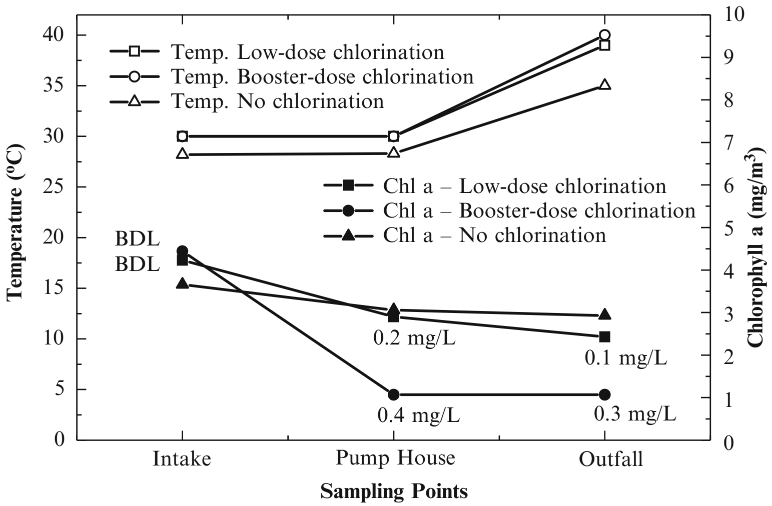

Fig. 14.3 Variation of temperature and chlorophyll *a* at various sampling points during low-dose, booster-dose, and no-chlorination period (*BDL* below detectable limit, numbers indicate TRO levels)

than elevated temperature (Poornima et al. 2006). The reduction of phytoplankton biomass during low-dose continuous chlorination was 43%, while during shock dose chlorination it was 75% (Fig. 14.3). In the absence of chlorination, the reduction of phytoplankton biomass due to condenser passage was <5% (Fig. 14.3).

3.2.2 Laboratory Experiments

Natural phytoplankton assemblage and axenic cultures of diatoms isolated from nonimpacted region of the study site were employed in laboratory experiments of TESP. The following observations were made

1. Axenized cultures of diatoms (*Amphora coffeaeformis*, *Chaetoceros wighami*, and *Cyclotella meneghiniana*) were able to grow between 28 and 40°C, but they showed poor survival at 42°C (Poornima 2005; Rajadurai et al. 2005).
2. Transient exposure of the diatoms (cultured at 28°C) to a temperature shock at 42°C for 15–45-min duration (a treatment designed to simulate temperature increase inside a condenser) caused only a marginal reduction (<10%) in growth and division rates, suggesting that diatoms were unlikely to be influenced by the higher temperature (40–42°C) experienced during condenser transit (Poornima 2005; Rajadurai et al. 2005).
3. Exposure of natural phytoplankton assemblage to 42°C for 15 min caused lesser reduction of GPP (19% reduction) and chlorophyll *a* concentration (<10% reduction) as compared to chlorination. Reduction in chlorophyll *a* was 45–48, 66–69,

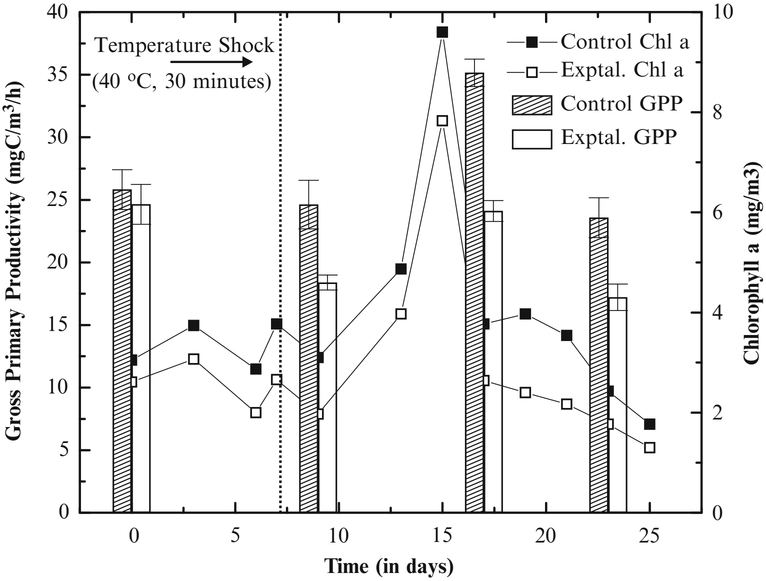

Fig. 14.4 Variation of chlorophyll-*a* and gross primary productivity (GPP) in control and experimental mesocosm (subjected to temperature shock on the seventh day)

and 70–79%, respectively, for applied chlorine doses of 1, 2, and 3 mg/L. Chlorination with a dose of 2 mg/L caused 63% reduction in GPP (Poornima et al. 2006).

3.2.3 Mesocosm Experiment

To study the impact of thermal stress on phytoplankton, temperature shock experiment was carried out in the mesocosm facility. In this experiment, the experimental mesocosm with natural phytoplankton assemblage obtained from the Intake site was subjected to a temperature shock at 40°C for 30 min (to simulate condenser passage), 7 days after initiation of the mesocosm. Appropriate control was maintained and the experiment was terminated after 25 days. The experimental results revealed that temperature shock at 40°C for 30 min caused only marginal (<10%) reduction in phytoplankton biomass and GPP (Fig. 14.4). The data, in fact, confirmed field observation and results of laboratory experiments.

The physicochemical parameters in the experimental mesocosm did not show any change attributable to temperature shock except for a brief 10–15% decrease in dissolved oxygen concentration. The temperature shock affected neither the species composition nor species diversity (Table 14.3), suggesting that phytoplankton is not much affected by short-term temperature rise as experienced during condenser transit.

Table 14.3 Species diversity index (Shannon–Wiener) and similarity index (Sørensen) of phytoplankton in the control and the experimental mesocosm (subjected to temperature shock on the seventh day)

Days	Diversity index		Similarity index between control and experimental
	Control	Experimental	
0	2.37	2.38	0.90
3	2.32	2.20	0.76
6	2.29	2.22	0.88
7	2.23	2.34[a]	0.84[a]
9	2.30	2.33[a]	0.81[a]
13	2.13	2.09[a]	0.91[a]
15	1.98	2.03[a]	0.81[a]
17	1.95	2.18[a]	0.81[a]
19	2.25	2.19[a]	0.86[a]
21	2.18	2.13[a]	0.76[a]
23	2.04	2.14[a]	0.84[a]
25	1.98	2.15[a]	0.73[a]

[a]Values represent post-temperature shock

4 Chemical Stress

Presence of fouling organisms such as bacteria, algae, barnacles, mussels and clams seriously interferes with the functioning of the pipelines and condenser cooling systems, by affecting the cooling water flow and heat transfer efficiency, thereby hampering the process of power generation. In order to maintain the efficiency of the cooling water system, biocides are used to control biofouling. Chlorine (either in its gaseous form or as hypochlorite) is the most commonly used biocide, as it is economical and highly effective on the foulants (Khalanski and Bordet 1980). Chlorine is effective against both micro and macrofoulants in fresh as well as marine waters. The chemical stress experienced by entrained organisms is mainly due to addition of chlorine. Chlorinated effluents may have deleterious environmental effects (Brungs 1973) and it is often difficult to assess the impact of chlorine due to its complex chemistry (Jolley and Carpenter 1981, 1982). The other biocides commonly used against biofouling are chlorine dioxide, chlorophenols, metalloorganic compounds, and quaternary ammonium salts.

The chemistry of chlorine and its interaction with the other physicochemical factors of seawater have not been fully understood (Lewis 1966; Dove 1970; Eppley et al. 1976; Block et al. 1977; Wong and Davidson 1977; Carpenter and Macalady 1978; Carpenter and Smith 1978; Goldman et al. 1978; Hartwig and Valentine 1983; Jolley 1985). Addition of chlorine to water causes the formation of hypochlorous acid. Hypochlorous acid further dissociates to form hypochlorite ion. This dissociation is controlled by pH and temperature. Increase in pH and temperature increases the dissociation. As seawater contains 60 mg/L of bromide ion and bromine being a stronger oxidizing agent, it displaces chlorine to form hypobromous acid and hypobromite ion

(Johannesson 1955; Lewis 1966; Macalady et al. 1977; Sugam and Helz 1977). In the presence of ammonia, hypochlorous acid and hypobromous acid further react to form chloramines and bromamines. Hypochlorous acid, hypochlorite ion, hypobromous acid, and hypobromite ion remaining after demand are together referred to as free residual oxidants, whereas chloramines and bromamines formed due to reaction with ammonia are referred to as combined residual oxidants. The term total residual oxidant (TRO) includes both free and combined forms of chlorine. The aim of chlorination is to create an environment that will discourage the establishment of marine foulants on the internal surfaces of pipelines and condensers. The undissociated hypochlorous and hypobromous acids have better biocidal effect, and chlorination is effective when they are predominant.

In power stations with once-through cooling system using seawater as coolant, chlorination is usually practiced to control biofouling (Yamazaki 1965; Whitehouse 1978; Whitehouse et al. 1985). Intermittent chlorination in which chlorine is injected for 30 min thrice a day with the dosage being 0.1–0.5 mg/L, has been largely discontinued as a method to control macrofouling. It was found to be ineffective where mussels were the major fouling organisms (Turner et al. 1948; James 1967; Rajagopal et al. 1991). Mussels settled between intermittent chlorine injections and were able to resist the subsequent exposures to chlorine (Holmes 1970). The use of continuous chlorination to control mussel fouling is well documented in the literature (Jensen 1982; Jenner et al. 1997). The general practice is to dose chlorine continuously to get a relatively low residual (0.2–0.5 mg/L TRO). The amounts of chlorine dosed and the frequency as well as duration (in the case of intermittent chlorination) vary from place to place and at a given place depend upon the season, biological activity, water quality, and chlorine demand.

Chlorine demand is the difference between the added chlorine (dosage) and the total residual chlorine measured after a given contact time. Coughlan and Davis (1983) observed that there were differences between the effects of similar doses of chlorine at different power stations. This was due to differences in water quality and chlorine demand. From the point of view of environmental protection, it is the general practice to monitor the residual chlorine concentration. Residual chlorine levels vary considerably in power station effluents (Morgan and Carpenter 1978). Coughlan and Whitehouse (1977) reported that a dosage of 0.5 mg/L chlorine in a British power station inlet resulted in residual chlorine of 0.1–0.2 mg/L at the outfall. Table 14.4 shows residual chlorine data reported from a few selected power stations. Beauchamp (1969) suggested that a continuous dose of 0.5 mg/L would keep marine intakes clean and protect the installations from adverse fouling. Once discharged, the residual chlorine levels dropped sharply because of chemical reactions and dilution (Jolley et al. 1978).

There are several reports in the literature about the effects of residual chlorine in discharge waters on phytoplankton and their productivity. Residual chlorine is known to affect the organisms by diffusing through their cell wall and reacting with the cytoplasm, thus inhibiting various metabolic processes (Betzer and Kott 1969; Strauss and Puckorius 1984). Chlorine and its associated oxidants are toxic to

Table 14.4 Residual chlorine levels in discharge of different power stations (adapted from http://www.cpuc.ca.gov/Environment/info/esa/divest-edison/tables/tab4_4_2.pdf)

Power Station	Receiving water	Flow (mgd)[a]	Outfall temperature (°C)	TRO level (mg/L)
Alamitos	San Gabriel River	210.5	40.55	0.2
		389.0	40.55	0.2
		683.1	40.55	0.2
El Segundo	Santa Monica Bay	207	40.55	0.2
Long Beach	Back Channel, Long Beach Harbor	265	40.55	0.2
Mandalay	Pacific Ocean	255.3	41.11	0.2
Ormond Beach	Pacific Ocean	688.2	40.55	0.2
Redondo	Pacific Ocean, offshore	463	41.11	0.2
	King Harbor	674	41.11	0.2

[a]*mgd* million gallons per day

marine phytoplankton at low concentrations (Carpenter et al. 1972; Flemer 1974; Eppley et al. 1976; Goldman and Davidson 1977; Langford 1990). In most field studies, power station chlorination caused inhibition in productivity. Ahamed (1997) in a study on the effects of chlorination on phytoplankton productivity reported that low-dose chlorination (TRO levels of 0.05–0.2 mg/L) caused 30–70% inhibition in gross primary production (GPP), while shock dose chlorination (TRO levels of 1.10–1.50 mg/L) resulted in 83% inhibition in GPP. Morgan and Stross (1969) reported absence of measurable primary production in a tributary of Chesapeake Bay, attributable to chlorination. Eppley et al. (1976) also reported up to 80% depression of photosynthesis, when chlorine was dosed at a rate of 1 mg/L. Lauer et al. (1974) reported 65–90% suppression in productivity when the residual chlorine level was 0.2–0.5 mg/L. The percentage reductions due to chlorination reported by others are 95% (Flemer 1974), 91% (Hamilton et al. 1970), 72% (Gentile et al. 1976), and 57% (Fox and Moyer 1975).

In freshwater systems also, significant reduction in productivity has been observed following chlorination (Brook and Baker 1972; Brooks and Liptak 1979). Brook and Baker (1972) reported 58–90% reduction at a dosage of 2.7 mg/L. Mulford (1974) reported 30–66% reduction in phytoplankton cell counts that was attributed to chlorination. Hirayama and Hirano (1970) in their study on *Skeletonema costatum* cultures observed that the growth rates could not recover after a 5-min exposure to 1.51 or 2.38 mg/L residual chlorine.

Chlorination of seawater also leads to the formation of chlorination by-products that are usually present near the discharge area (Jenner et al. 1997; Allonier et al. 1999). Erickson and Freeman (1978) in their study reported 15 such chlorination by-products. As chlorine and its reaction products are important constituents of many thermal discharges, their role cannot be overlooked while assessing the biological effects of thermal discharges.

4.1 Observations of TESP

4.1.1 Field Survey

At MAPS, two modes of chlorination (continuous low-dose and booster-dose) are employed for control of biofouling. During low-dose chlorination, the chlorine is added continuously so as to provide a TRO of about 0.3–0.5 mg/L. Booster-dose chlorination is employed once a week, resulting in TRO level approximately double that obtained in low-dose chlorination. Field survey revealed that TRO levels at the discharge point mostly ranged between 0.1 and 0.3 mg/L. Occasionally, there were breaks in chlorination due to maintenance work at the chlorination plant. Apart from the regular sampling, phytoplankton samples were collected from various parts of the cooling circuit (intake point, pump house, outfall and mixing point) and analyzed on three occasions: (1) when the power station was operational and low-dose chlorination was going on, (2) when the power station was operational and booster-dose chlorination was being done, and (3) when the power station was operational but no-chlorination was being done. The data from the above observation clearly indicated that chlorination caused greater damage (Fig. 14.3) to phytoplankton biomass than elevated temperature due to condenser transit (Poornima et al. 2006).

4.1.2 Laboratory Experiments

Short-term laboratory experiments on natural phytoplankton assemblages and axenic diatom cultures also showed that decrease in chlorophyll *a* concentration was more due to chlorination than due to elevated temperature. Reduction in chlorophyll *a* as compared to control was 45–48, 66–69, and 79–82%, respectively, for applied chlorine doses of 1, 2, and 3 mg/L. Combined temperature and chlorine treatment showed comparable or even less decrease in chlorophyll *a* as compared to the chlorine-alone treatment, indicating little synergistic effect. Laboratory experiment on phytoplankton GPP using natural phytoplankton assemblage showed that exposure to chlorine dose of 2 mg/L caused 63% reduction in GPP. Combined treatment of temperature (42°C) and chlorine (2 mg/L dose) caused 59% reduction in GPP, as compared to the control (Poornima et al. 2005).

4.1.3 Mesocosm Experiment

To study the impact of chemical stress on phytoplankton, chlorine shock experiment was carried out in a mesocosm facility, as described earlier. In this experiment, the experimental mesocosm with natural phytoplankton assemblage obtained from the intake site was subjected to chlorine shock, 6 days after initiation of the mesocosm. The experimental mesocosm was appropriately dosed with sodium hypochlorite, to obtain a TRO concentration of 0.25 mg/L (representative of the TRO employed by

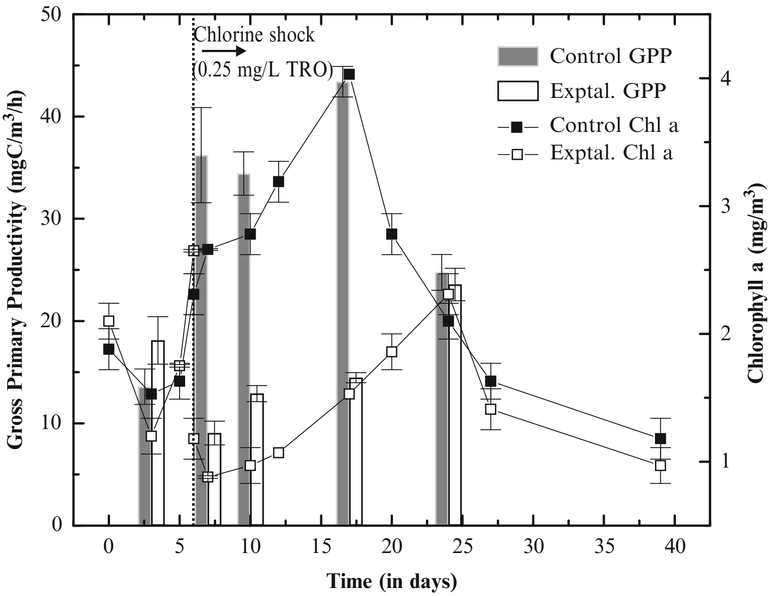

Fig. 14.5 Variation of chlorophyll *a* and GPP in control and experimental mesocosm (subjected to chlorine shock on sixth day)

Table 14.5 Species diversity index (Shannon–Wiener) and similarity index (Sorenson) of phytoplankton in the control and the experimental mesocosm (subjected to chlorine shock on the sixth day)

	Diversity index		Similarity index between
Days	Control	Experimental	control and experimental
0	2.56	2.58	0.91
3	2.54	2.46	0.89
6B[a]	2.48	2.51	0.80
6A[a]	2.48	2.49	0.82
10	2.50	2.49	0.82
17	2.48	2.49	0.82
24	2.34	2.36	0.80
39	2.38	2.39	0.83

[a]6B—before chlorination; 6A—after chlorination

the utility). Appropriate control was maintained and the experiment was terminated after 39 days.

Mesocosm studies essentially confirmed the results of laboratory studies: decrease in chlorophyll and consequent reduction in GPP was inducible more by chlorination than a transient exposure to elevated temperature (Fig. 14.5). Though chlorine shock caused 50% reduction of phytoplankton biomass and GPP, it affected neither species composition nor species diversity, indicating that the stress was not species-specific (Table 14.5). A gradual recovery of phytoplankton biomass and productivity was observed, suggesting that not all phytoplankton was destroyed by chlorination. The phytoplankton that survived chlorination had the capacity to recover.

5 Discharge Criteria of Power Stations

The effects of power station induced mechanical, chemical, and thermal stresses on entrained biota, including phytoplankton, are variable in magnitude and are site-specific. At a particular site, it depends on the topography, size of the source water body, ambient temperature, design and placement of intake and discharge structures, operating condition of power station, chlorination schedule, dispersion rate of heated effluents into receiving water, and type of flora and fauna inhabiting the area. In spite of all these variables, the discharge criteria for power station stipulated by regulatory agencies are generally based on temperature, as it is presupposed to be the most dominant stress factor. Nevertheless, studies including data from TESP support the fact that chemical stress or chlorination may be of equal or even greater importance than thermal stress in reducing plankton population (Fox and Moyer 1975; Flemer and Sherk 1977; Choi et al. 2002; Poornima et al. 2006).

In this context, it is important to point to the excessive significance attached to ΔT (the maximum temperature rise across the condensers) in regulatory regime. As per discharge criteria currently in vogue, the existing power stations (such as MAPS) are permitted to raise the temperature of condenser cooling water by a maximum of 10°C (between the intake and outfall point) but for new power stations the maximum permitted rise in temperature at the discharge site is 7°C above the ambient temperature. A limit on ΔT is specified with the intention of maintaining the natural cycle of temperature variation in the receiving water body. It is arguable whether such a limit on ΔT is warranted in the case of tropical waters, where the annual range of seawater temperature is quite narrow. Scientific studies carried out in temperate regions showed that the grave ecological consequences due to thermal discharges originally predicted for several aquatic populations have not been borne out (Dey et al. 2000; Mayhew et al. 2000; Melton and Serviss 2000). So attempts to bring down ΔT of new power stations from the existing limits (as has been done in India), done with the intention to further reduce thermal effects, may actually result in more environmental damage. For a power station, the total quantum of waste heat load to be rejected to receiving water body remains constant, and therefore, a reduction in ΔT will result in abstraction of a larger volume of water for heat rejection. In this process, the entire cooling water has to be chlorinated to control biofouling, which may result in increased mortality rate to entrained organisms, as chemical stress effects dominate over thermal effects. Moreover, a few studies have indicated subtle sublethal effects of chlorination, such as inhibitory effects on bacterial production and heterotrophic grazing rates, attributable to relatively long lived chlorination by-products (Choi et al. 2002).

Under such circumstances, for tropical sites it may be prudent to stipulate a maximum allowable temperature inside the cooling circuit instead of a specified ΔT, considering the fact that short-term exposure to temperatures up to 40°C seems to be well tolerated by many entrained organisms (Choi et al. 2002; Poornima 2005; Rajadurai et al. 2005). The major advantage would be that utilities will be able to make maximum use of the cooling capacity of the abstracted water, thereby reducing the volume of cooling water abstracted and consequently, the mortality rate due to chlorination. Admittedly, this requires further research before it can be adopted as an alternative. For sustainable use of coastal waters for steam condensation, it is desirable that power station operators and regulatory agencies take into cognizance the relative significance of both the stress factors (thermal and chemical) to entrained organisms.

In most studies, the effects of entrainment were not detectable beyond the immediate discharge zone (Krezoski 1969; Jordan et al. 1983). Recovery of phytoplankton surviving short-term temperature rise either alone or combined with chlorine (power station entrainment) have been reported (Goldman and Davidson 1977; Saravanane et al. 1998). In TESP also, rapid restoration of phytoplankton biomass was evident, though data on the actual recovery of impacted phytoplankton cells was not available. In the field, such restoration of phytoplankton levels (as measured by cell count and chlorophyll-*a*) would be aided by rapid and effective mixing of discharge water with the ambient seawater. The entrainment induced effect on phytoplankton was discernible only in a relatively small area near the mixing point. It may be mentioned that recovery of phytoplankton after stress was observed in mesocosm experiments also, where such mixing with ambient seawater was not possible. Following thermal stress, recovery of the stressed phytoplankton was much faster compared to the chlorine-stressed phytoplankton. However, it is conceded that to understand the complete effects of power station induced thermal and chemical stresses, more data need to be generated on the effects of acute exposure to temperature and chlorine on a variety of entrained organisms other than phytoplankton.

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Chapter 15
Entrainment of Organisms Through Power Station Cooling Water Systems

Roger N. Bamber and Andrew W. H. Turnpenny

1 Introduction

All the organisms in the cooling water (CW) flow taken in at a power station which are small enough to pass through the initial filter-screens proceed right through the CW system. This process is termed entrainment. As these organisms pass through the screen wells, the pump, the culverts, the condensers and thence to the outfall, they are subjected to a number of potentially lethal stressors, which include the following:

- Mechanical and hydraulic stresses in the intake, forebay and screen wells (as also experienced by impinged organisms)
- Exposure to potentially toxic biocide levels throughout the CW circuit
- Rapid temperature increase through the condenser boxes and raised temperature beyond
- Various changes in hydrostatic and hydrodynamic pressure caused by differences in level (altitude) and by pumping
- Hydraulic shear stress, turbulence and abrasion associated with passage through the screens, culverts and small-bore (~25 mm) condenser tubes

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The biota involved in entrainment are predominantly plankton, including the permanent members of the plankton (holoplankton) and the eggs and larvae of species with sessile, pelagic, benthic or infaunal adult life-stages which are temporarily planktonic (meroplankton), as well as juvenile (and other small) stages of pelagic species. The meroplankton has historically been of greatest concern, as it includes the early stages of a number of commercial species of fish, molluscs and crustaceans, inter alia.

In the absence of reliable evidence to the contrary, the simplistic assumption has often been made that all plankton passing through a power station's CW circuit will be killed. In order to gain a more precise understanding of the environmental effects of CW entrainment, a number of studies have been undertaken since the 1970s.

2 Rates of Entrainment

Initial concerns over adverse environmental impacts of entrainment were addressed at potential losses of fish eggs and larvae (ichthyoplankton). In contrast to impingement studies, fewer studies of fish entrainment rates at power stations have been reported. This is principally because entrainment is less visually obvious than impingement and because sampling techniques are more difficult. There has also been a (valid) perception that for fish species, losses of eggs and fry are less important to maintenance of the stock than the capture of more mature fish, which represents a higher value to the population. However, the development in recent years of effective mitigation techniques against impingement mortalities now makes losses owing to entrainment a more significant part of the environmental impact associated with CW abstraction.

Entrainment rates were measured in situ by intercepting a sample of the CW flow with fine-meshed plankton nets. This was achieved using either

- A plankton net placed in part of the intake flow (e.g. in the forebay, if the degree of turbulence allows).
- By drawing water from a tapping on the pressure side of the main CW pumps or screen-wash water pumps (which usually draw from the screen-wells) and passing it through a suspended plankton net.
- By using a purpose-built powered plankton-sampler (pump) lowered into the forebay.

Comparisons of plankton populations involved in entrainment with the community in the surrounding water body are made difficult by the stratification commonly present in the latter, including stratification of the water column owing to temperature or salinity effects, and the behavioural stratification of the plankton itself. Power station intake structures commonly abstract selectively from deeper layers to reduce any recirculation of the buoyant plume and therefore do not draw in a sample representative of the whole water column. This may explain observations reported by Coughlan and Davis (1981) for Bradwell Power Station (Blackwater Estuary, Essex) and Dempsey (1988) for Fawley Power Station (Southampton Water, Hampshire), which showed concentrations of ichthyoplankton entrained to be an order of magnitude less than those found in the open water. In tidal waters, in particular, it is rarely likely that the CW water will be abstracted from the full vertical range of the water column.

A key factor in the success of all of these sampling methods is achieving adequate sample volumes and appropriate diel and seasonal coverage. Developing practice at new sites in the UK has been to specify 24 h sampling periods using sample flow rates of between 10 and 25 $L\,s^{-1}$, where these flow rates are practically achievable. This appears to provide good representation of fish taxa, which are notoriously patchy within the plankton and may otherwise be missed. Sampling is typically carried out at least monthly (sometimes weekly during periods of peak ichthyoplankton activity) all year round, or for a 6-month period from spring to late summer, when the fish are in their planktonic stages.

Other types of plankton entrained will include temporary (meroplankton) and permanent (holoplankton) planktonic taxa, including molluscs, crustaceans and other invertebrates, as well as phytoplankton. The holoplankton is commonly more abundant than ichthyoplankton, and adequate samples can be obtained by the methods outlined above or from much smaller "bucket" samples. However, again these species show marked (and well-documented) seasonality in their abundance in the plankton. Many of the invertebrate meroplankters are of commercial significance (larvae of commercial species of shellfish and crustaceans). These species also show constrained seasonality in their presence in the plankton. Again, it must be appreciated that these taxa too are patchy and are stratified in the water column.

3 Entrainment at UK Inland Stations

Studies at inland stations have been very limited, and confined to investigation of larval fish entrainment. In a brief study at the indirectly cooled Didcot, a power station in the 1970s (see Smith 1998), it was estimated that the station entrained around 1.9×10^6 fish fry annually, but this value did not fully take into account the seasonal variability of entrainment and was therefore considered likely to be an overestimate.

A subsequent investigation at Ratcliffe-on-Soar Power Station on the River Trent undertaken by Smith (1998) between 1994 and 1997, where the dominant species were roach (*Rutilus rutilus*), bream (*Abramis brama*), bleak (*Alburnus alburnus*) and chub (*Leuciscus cephalus*), revealed a strongly seasonal pattern of fish entrainment. This was characterized by influxes of newly hatched "pinhead" fry of coarse fish during the spring and early summer months following spawning, quantities declining throughout the summer as fry numbers in the river decreased (owing to growth and to high natural mortality rates). The overall loss-rate of fish averaged 3.45 to 7.98×10^5 fry per year over the 3 years.

Studies of entrainment at other types of inland water-intake have contributed to an understanding of the effects at power stations. Turnpenny (1999) carried out a desk study of the combined coarse-fish fry entrainment potential of the all raw water intakes on the freshwater Thames (nine in total) based on an extrapolation of data obtained from only one of those intakes. The study concluded that substantial numbers of young coarse fish were likely to be lost to the fishery. As a worst case, if all the intakes were operated at their maximum licensed capacity (around 80 m^3s^{-1} combined capacity), it was estimated that the loss of fish to entrainment could be equivalent to up to 45% of the adult standing stock of the Lower Thames.

All of these studies showed the following common features:

- Proportional losses of stock to entrainment are related to the abstraction flow; cumulatively along a river reach they can represent a significant impact on numbers of fry available for recruitment into the adult fishery;
- Catch rates are seasonal, peaking in the spring, shortly after spawning, but extending through the summer months;
- Entrainment rates tend to be positively correlated with river flows and are highest at night, corresponding with the findings of studies on large river systems which show that fry drift or migrate downstream principally under these conditions as part of their natural distribution mechanism (Pavlov et al. 1978).

The significance of entrainment mortalities to freshwater fish species is not straightforward. Inland water bodies are commonly constrained in size, and thus have a carrying-capacity for their fish populations, which are then limited by density-dependent effects related to intra-specific competition for food, space, etc. A significant reduction in adult stock as a result of entrainment mortalities will only occur when fish stock densities are low enough, or juvenile mortalities high enough, to prevent carrying capacity being reached, assuming that those individuals (or genotypes) lost through entrainment are the same as are susceptible to intra-specific competition mortalities.

4 Entrainment at Estuarine and Coastal Stations

While various studies have tried to estimate the numbers of organisms entrained by power-station CW circuits, greater efforts have been made to determine the actual mortality of those organisms from the stresses of entrainment.

Three main approaches have been used in studying the viability of organisms following exposure to entrainment stressors:

- Power-plant-based entrainment monitoring, where live–dead ratios are compared between the CW plant inlet and outlet points.
- Laboratory-based studies subjecting organisms to the various potential stressors and then trying to extrapolate to the real-life situation.
- Laboratory-based studies mimicking the processes of entrainment under controlled conditions.

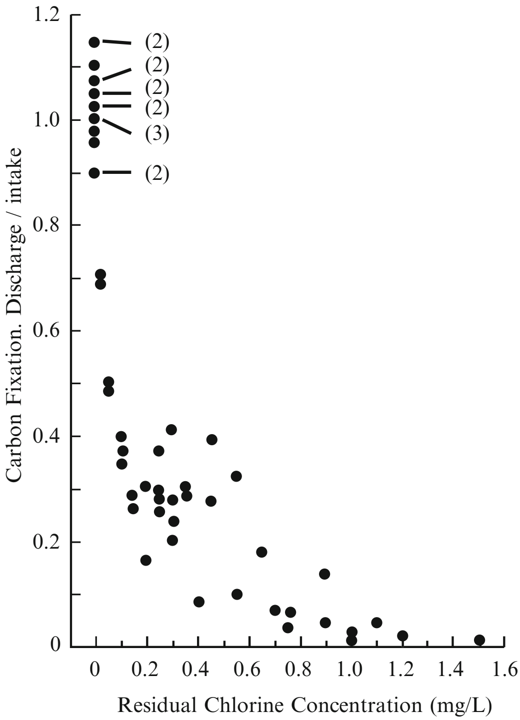

Fig. 15.1 Effect of chlorine concentration on carbon fixation by phytoplankton at Fawley Power Station, Hampshire (redrawn from Davis 1983)

4.1 Power-Plant-Based Entrainment Monitoring

From the late 1970s, Davis (1983) measured phytoplankton productivity at Fawley Power Station as an indicator of entrainment survival. Seawater (10 L per replicate) was sampled from the intake and outfall of the CW system, and incubated with the radioactive carbon isotope C^{14} for 3 h under standard temperature and light conditions. Measurements were made of temperature, salinity and total residual oxidant (TRO). The rate of C^{14} fixation was then compared between intake and outfall samples to give an estimate of the survival rate of phytoplankton passing through the CW system. Phytoplankton productivity fell by 50–60% having passed through the CW system under routine conditions at Fawley Power Station (ΔT 8–10°C, <0.2 mg L^{-1} Cl at outfall). The main cause of mortality was chlorine concentration (Fig. 15.1). Experimentally varying the dosed chlorine level allowed the effect of chlorine toxicity to be assessed. It was concluded that the main cause of mortality (assuming that the rate of C^{14} fixation is a valid proxy of survival) was exposure to the biocide.

Inhibition of photosynthesis by phytoplankton has also been observed in chlorinated cooling-water elsewhere in both estuarine water and seawater (e.g. Carpenter et al. 1972; Khalanski 1978).

Temperature effects were less clear in the study of Davis (1983). Where final water temperature reached up to 23°C, an increase in productivity was observed of up to 15%. Where final water temperatures exceeded 23°C, the productivity decreased by up to 11%. No correlation existed between ΔT and productivity. Trials were also carried out in the absence of chlorination and temperature rise, allowing an assessment of pressure and mechanical damage effects to be made; in both cases, the increase in primary productivity was of the same order as that observed for the temperature rise. It was concluded that the change in productivity observed was owing to heterogeneity in sampling, and that the observations confirmed the views of other researchers that the mechanical effects of entrainment on phytoplankton are too small to be detected in field studies.

As acknowledged by Davis (1983), the wide variation in reported effects of power-plant CW chlorination on the primary productivity of entrained phytoplankton is likely to be caused by differences in the location of the power plants, as well as variations in phytoplankton populations, water quality, operating conditions and sampling or experimental techniques. Davis (*ibid.*) also acknowledged other limitations in his study, such as holding the phytoplankton samples in the chlorinated water for up to 3 h post-sampling. In reality, on return to the sea, chlorine concentrations become progressively lower through processes of demand and decay. This was unlikely to be achieved realistically under laboratory conditions, where TRO concentrations were probably unrealistically high, and thus inhibition of phytoplankton productivity is likely to be lower in reality. It was therefore considered reasonable to conclude that phytoplankton productivity was not as inhibited by chlorination as previous studies had suggested (e.g. Carpenter et al. 1972; Hirayama and Hirano 1970).

Vital staining techniques to analyse entrainment survival of zooplankton were first tried by Heinle (1976) studying copepods at three power stations in the USA. On collection, a vital stain, Neutral Red, was added to the samples; this stain is only absorbed by live organisms (Coughlan and Fleming 1978). This technique is considered more reliable and less time-consuming in the field when compared with monitoring the motility of sampled zooplankton (which must be assessed immediately upon capture) as a means of establishing mortality. Heinle (1976) found poor replication, and inconsistencies which were attributable to stratification of the plankton in the sampled water; numbers of organisms per sample were often below 10. Percentage survivals, measured by those individuals taking up the vital stain, were generally high at both intake and discharge (mostly >80%) with some examples of reduced survival at the discharge during chlorination. However, quantification was not practical. The overall conclusion was that sample sizes (hourly 1-L samples) were inadequate, despite the large amounts of effort and funding such a programme required.

A series of studies on zooplankton survival at French coastal power stations, reported by Khalanski (1978), gave a range of results varying from increased densities of zooplankton at the discharge (vital-staining tests), no differential survival (post-entrainment incubations), holoplankton mortalities of between 30 and 70% (asynchronous post-entrainment densities), and 100% mortality of sprat eggs and 17–61% mortality of sole eggs attributed predominantly to mechanical shock.

In the UK in the 1970s, vital-staining studies were undertaken to examine the survival of entrained phytoplankton and zooplankton at five coastal/estuarine power

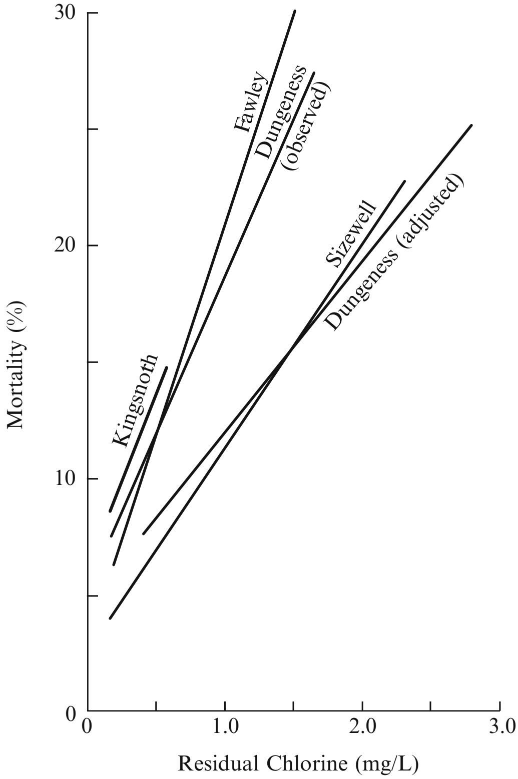

Fig. 15.2 Percentage mortality of adult calanoid copepods within 1 h of entrainment under various chlorination regimes at four different UK power stations (redrawn from Coughlan and Davis 1981)

stations: Fawley (Hampshire), Sizewell A (Suffolk), Kingsnorth (Kent), Bradwell (Essex) and Heysham 1 (Lancashire) (Coughlan and Davis 1981). The zooplankton studies concentrated on adult calanoid copepods, as copepods (holoplanktonic Crustacea) are typically abundant in zooplankton samples. The authors collected zooplankton from 200 L volumes of water sampled with a pump sampler designed to minimize specimen damage, by allowing the plankton to be filtered from the water prior to the water being drawn into the pump. Samples were taken from the power station intakes and outfalls. One hour after collection and staining, the samples were preserved and could later be analysed for live (red) and dead (non-red) individuals.

The studies revealed differences in survival rates depending on geographical location, i.e. whether the power stations were located in estuaries or on the open coast: copepods from estuarine environments incurred greater mortality than those from the open coastal locations. Mortality rates were considered in relation to both seawater quality (i.e. poorer in estuaries) and chlorine concentration (Coughlan and Davis 1981). Although mortality increased greatly with chlorine concentration, it was much lower than had been found for phytoplankton, and under standard power-station operating conditions (ΔT 8–10°C, <0.2 mg/L TRO at the outfall) the survival of adult calanoid copepods in the zooplankton was >90% (Fig. 15.2; Turnpenny and Coughlan 2003).

Attempts have been made to measure the differential survival rates of fish larvae after entrainment through a power station in comparison with those of larvae at the intake of a CW system. Lawler et al. (2001) tested such entrainment survival over 2 years at Brayton Point Power Station, Ma, using induced-flow larval tables. They evaluated 30,000 fish larvae, mainly of bay anchovy (*Anchoa mitchellii*) and American sand lance (*Ammodytes americanus*) for up to 96 h after collection. Despite the large numbers involved, the results found no significant difference in survival at the sample locations for any species except rainbow smelt (*Osmerus mordax*) and sculpins (*Myoxocephalus* spp.), both of which species showed higher survival at the discharge. No relation to exposure temperature was found. It was concluded that it was "difficult" to assess plant effects by this system.

Indeed, between 1970 and 2000, there had been numerous studies in the USA using induced-flow larval tables, from all of which the only conclusion was that mortality of entrained fish eggs and larvae was less than 100% (Mayhew et al. 2000). EPA (2007) reviewed the major known entrainment-effect studies conducted at power stations in the USA; results were highly variable within species (e.g. survival of most fish species at Indian River Power Plant in 1975–1976 ranged from 0 to 100%!), between sites, between seasons and between years. The EPA thus did not consider that any of the results could contribute to valid conclusions.

Despite the practical problems associated with all of these in situ studies, and the difficulty in attributing or quantifying their results, it is evident from them all that entrainment mortality under standard operating conditions is not 100%. Indeed, it is implied that the majority of planktonic individuals entrained may survive.

4.2 Laboratory-Based Studies: Experimental Exposure to Stressors

Difficulties with power-station-based studies are that the range of taxa available for assessment is largely a matter of chance: while it is feasible to study copepods or phytoplankters in general, as some will invariably be present, no particular species can be guaranteed. Further, owing to the sparseness of certain species, including commercially important meroplankton, it may be impossible to sample adequate numbers even if they are known to be present at that time and place. Such studies are only able to test the effects of the totality of entrainment as present at the time, although Coughlan and Davis (1981) were able to vary the biocidal chlorine dosing levels during some of their studies.

Kwik and Dunstall (1985) simply cultured zooplankters in conditions of thermal shock, mimicking entrainment stresses; they generally found that survival was of the order of 90% as long as the test temperature did not exceed 29.5°C, irrespective of ΔT. Obviously, this does not mimic normal operating conditions as only thermal stress was tested.

Schubel et al. (1976) exposed eggs and larvae of three fish species from the Chesapeake Bay region (blueback herring, *Alosa aestivalis*; American shad, *Alosa sapidissima*; striped bass, *Morone saxatilis*) to simulated ΔT effects by simply immersing small pots containing the test animals in water baths at appropriate temperature for between 4 and 60 min, returning them to ambient temperature waterbaths for cooling to background temperature (60–300 min). They found that ΔTs of 7 and 10°C did not significantly affect hatching success of any species, while a ΔT of 15°C significantly reduced hatching success of both blueback herring and American shad; only striped bass larvae could withstand ΔTs up to 10°C with no significant increase in mortality. A ΔT of 20°C resulted in a "nearly total mortality" of eggs and larvae of all three species. Despite finding that the fish eggs were apparently more tolerant of ΔT effects than were the larvae, most response patterns were found to be "complicated". Of course, such buffered thermal impacts do not reflect the actual conditions during entrainment very faithfully.

Other studies in Europe involved simple tolerance tests of stressors (mainly temperature) in culture. These studies were numerous (being easy to set up), inconclusive and were of limited application to the real entrainment situation (e.g. review by EDF 1978).

4.3 Laboratory-Based Studies: Experimental Mimicking of Entrainment

Laboratory-based studies in theory offer the advantage that the entire experimental entrainment process is controlled, including the test animals (guaranteeing results), and the stressors. The apparatus should have a practical advantage of scale, as the flow can be passed through a single (full-length) condenser tube, so that a relatively small and manageable flow of water is used. This means that as few as 30–50 individuals (eggs, larvae, et cetera) can be tested per experimental run, with 100% recapture in the collecting vessel, and no significant handling damage.

Early attempts at experimental assessment of entrainment took too simplistic an approach to offer useful interpretation. Poje et al. (1981) undertook experiments on estuarine fish and arthropods using a condenser-tube simulator; unfortunately, their apparatus was unable to generate the complex pressure profiles characteristic of power-station cooling-water systems. Mortalities of carp (*Cyprinus carpio*) and striped bass (*Morone saxatilis*) were related to effects of absolute (high) temperature rather than to entrainment.

A few simulation experiments were conducted in the USA using condenser tubes to assess the mechanical stresses of entrainment (see Marcy 1975; Cada et al. 1981; review by Jinks et al. 1981). Large differences were observed between species in their response to pipe and condenser passage and, for most species, short-term mortality associated with passage, estimated at <5%, increased with increasing ΔT and/or pumping rate. However, there was commonly no significant difference in survival between test and control organisms.

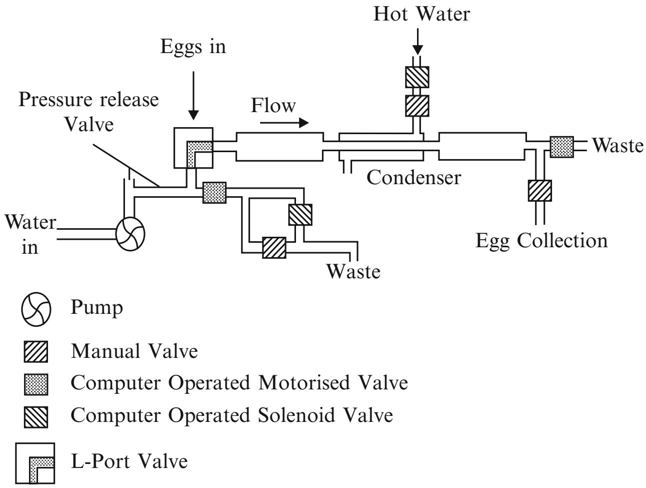

Fig. 15.3 Schematic of the FARL entrainment mimic unit (EMU) (after Bamber et al. 1994)

An Entrainment Mimic Unit (EMU), a laboratory simulator (Fig. 15.3), was developed by Fawley Aquatic Research Laboratories (FARL) in the 1990s for entrainment survival assessment (Bamber et al. 1994). This apparatus was superior to its predecessors in that it was able to mimic the levels and range of the stressors found at an actual power-station, and these stressors could be varied individually and applied alone or in combination, allowing the distinction of their effects, separately, synergistically or antagonistically.

Computer-controlled solenoid and mechanical valves allowed the replication of a complex pressure profile (normally that of a coastal direct-cooled PWR), while controlling the timing of hot-water delivery to allow a range of ΔT. Effects of antifouling "chlorination" were tested by introducing sodium hypochlorite at a range of test dose levels. The mechanical stresses of entrainment (physical abrasion, collisions, etc.) were an inherent feature of the apparatus and as such uncontrollable. Test conditions ranged around typical coastal power-station stress-levels of 0.2 ppm of TRO and 10°C ΔT, normally between 0 and 1 ppm and between 0 and 15°C.

Tests were conducted on the planktonic stages of a range of species, including meroplanktonic eggs and/or larvae of commercial crustaceans (common shrimp and lobster), commercial fish (sea-bass, Dover sole, turbot), a commercial mollusc (Pacific oyster), fouling species (two barnacles, common mussel) and the holoplanktonic copepod *Acartia tonsa*. A summary of the results of entrainment mortality of these species under "normal" power-station levels of stressors is given in Table 15.1, based normally on the condition of specimens 24 h after "entrainment".

What is striking is the wide range of effects between major animal groups, between species and between different life-stages of the same species.

The pressure cycle caused a significant mortality in the copepod *Acartia tonsa*, Pacific oyster larvae, and, combined with the ΔT, inhibited hatching of the flatfish eggs, but affected no other taxa tested.

Table 15.1 Percentage entrainment mortalities of a range of planktonic species under "normal" power-station levels of stressors, interpolated from series of EMU experiments (data from Bamber and Seaby 1993, 1995, 2004; Bamber et al. 1994; Turnpenny 2000)

Species	Stage	%Mortality at 0.2 ppm TRO and ~10°C ΔT (%)	Stressors causing significant mortality
Crustacea			
Acartia tonsa (Copepoda)	Adults	20	Pressure, TRO
Crangon crangon (common shrimp)	Larvae	25	TRO with°C
Homarus gammarus (lobster)	Larvae	8	Physical damage
Elminius modestus (barnacle)	Nauplii	0	
Fish			
Dicentrarchus labrax (sea-bass)	Eggs	46	ΔT
Dicentrarchus labrax (sea-bass)	Larvae	44	TRO, ΔT
Solea solea (Dover sole)	Eggs	7	Pressure with ΔT
Solea solea (Dover sole)	Postlarvae	92	TRO, ΔT
Psetta maxima (turbot)	Eggs	7	Pressure with ΔT
Psetta maxima (turbot)	Larvae	70	Physical damage
Anguilla anguilla (silver eel)	Larvae	52	TRO[a]
Mollusca			
Crassostrea gigas (Pacific oyster)	Larvae	95	TRO
Mytilus edulis (common mussel)	Larvae	0	
Mytilus edulis (common mussel)	Spat	35	TRO

[a]eel larvae were tested at 2 ppm TRO

The physical stresses of entrainment were the only factors to cause the significant mortality in turbot larvae (usually loss of yolk-sac) and lobster larvae (usually loss of abdomen), but affected no other taxa tested (see also Ulanowicz 1975).

The residual from chlorination (Total Residual, Oxidant, TRO) at around 0.2 ppm contributed to the significant mortality of sole post-larvae, sea-bass larvae, eel larvae (elvers), mussel spat, Pacific oyster larvae, *Crangon* larvae and *Acartia* adults, but had no significant effect on any other taxon tested.

The thermal stress was resolved into two factors: the ΔT caused significant mortality to sea-bass eggs and larvae (with an evident synergism with TRO), and contributed to significant mortalities of flatfish eggs and sole post-larvae; the actual enhanced temperature (°C) increased the mortality of *Crangon* larvae in response to TRO in an evident synergism (Fig. 15.4).

The results demonstrate that the majority of individuals of most taxa (other than flatfish larvae/post-larvae and Pacific oyster larvae) survive entrainment. Equally, all the factors examined were found to cause mortality in some, though not all, species, and synergistic effects are observed. However, the causes and degree of mortalities are different for different taxa and for different life-stages, and generalizations, for example for environmental impact assessments, must be undertaken with very great care (or not at all). Interestingly, while the larvae of the potential fouling species (the barnacle and the common mussel) showed 100% survival, the individuals were inactive for the first few hours after entrainment: the function of antifouling chlorination is to prevent settlement of these larvae, not necessarily to kill them, and as such clearly works well.

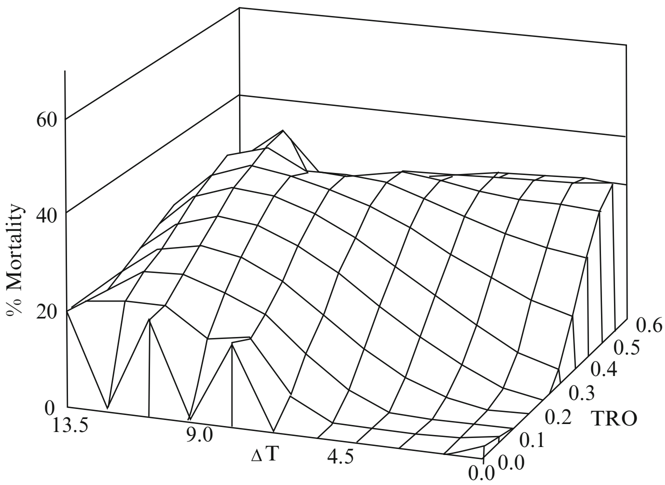

Fig. 15.4 Three-dimensional surface-plot of mean 48 h mortality of *Crangon crangon* larvae in relation to ΔT (°C) and TRO (ppm), generated by bivariate spline interpolation from the results of 32 experiments. As temperature rises, so sensitivity to TRO increases (after Bamber and Seaby 2004)

5 Conclusions

Inevitably, large numbers of organisms are entrained through power-station cooling-water systems. Simplistically, the species involved and their concentrations are assumed to be proportional to the CW flow; in reality, a number of factors, such as seasonality, behaviour and stratification confound this association, and field studies have been unable to confirm it. Nevertheless, sampling at power stations has confirmed the order of densities and diversities involved.

Detrimental effects on the entrained organisms have been demonstrated clearly across a range of taxa, a range of site-configurations, and by a range of techniques. However, despite the complexity of stresses to which the entrained organisms are subjected, all the research has demonstrated that mortality through entrainment is less than 100%. Indeed, in the most comprehensive tests described above, the majority of individuals survive entrainment in most species tested (Figs. 15.1 and 15.2; Table 15.1).

Having said this, there is a lack of understanding of the viability of organisms in the longer term subsequent to entrainment. While ideally the truest measure of entrainment effects would be the number of individuals which survive to produce reproductively viable offspring, this is impractical in any experimental or field situation.

Equally, it is necessary to interpret the significance of any losses that do occur. This significance will largely relate to the proportion of a localized population, and the proportion of the water-body (subject to tidal or spatial replacement), which is entrained.

Holoplanktonic species (both phytoplankton and zooplankton) characteristically show rapid rates of reproduction, and it is reasonable to conclude that mortalities through entrainment, shown above to be less than 50% of the entrained individuals, will be replaced rapidly by reproduction in the local population,

Meroplanktonic species are potentially more at risk. However, the significance of entrainment losses, already tempered by the survival of the majority of entrained individuals and their temporally constrained exposure to entrainment owing to seasonality, will be reduced by any density-dependent control on the population, by the context of the naturally high mortality-rates of these life-stages (planktonic eggs and larvae show a higher rate of natural losses through predation than those found from entrainment) and by the remaining proportion of individuals in the population which are not entrained. The level of fish-entrainment risk is determined by proximity to spawning grounds, and avoiding these and areas where fish eggs and larvae concentrate when locating a CW intake are the main means of minimizing adverse entrainment impacts.

In any assessment of the significance of entrainment losses at a power-station, the answers will be site-specific and species-specific; but losses will be less than 100%, and may be insignificant.

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Chapter 16
Impact of Power Plant Discharge on Intertidal Fauna

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1 Introduction

Water may flow in a thousand channels, but it all returns to the sea

– African proverb.

Oceans are the ultimate sink of much of the waste produced by mankind. Despite the capacity of oceans to dilute, disperse and degrade large amounts of raw sewage, oil and several types of industrial waste, much of the impact of these waste inputs is borne by the coastal areas. Though offshore pollution, especially in the form of oil spills, affects the coastal environment, a large proportion of the pollutants that enter the oceans have their origin from sources on land or land–sea interface. This does not come as a surprise, especially with half the world's population living within 100 km of the coast and expanding at a rapid rate (Miller 1998). The dramatic increase in human population has created considerable demand on every available resource and power generation is no exception.

The industrial revolution of the late eighteenth and early nineteenth century saw the advent of electric power generation and, subsequently, its rapid growth for uplift of human standard of living and creation of national wealth. There has been no looking back since then. With exponential increase in demand for electric power on the one hand and the scarcity of freshwater sources for condenser cooling on the other, the obvious choice of location for an increasing number of power plants has been coastal areas (IAEA 1974; Winter and Conner 1978). In operational terms, site location within close proximity of a source of cooling water would be practical and

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economically viable. However, this comes with a risk, as using coastal waters as heat sink could put the coastal ecosystem under stress.

Despite being the most extensive of coastal systems worldwide, comprising three quarters of the world's shoreline (Bascom 1980), sandy beaches are among the least productive as compared to other coastal systems such as rocky shore, sub-tidal sediments and salt marshes (McLachlan 1983). Despite their low productivity, sandy beaches harbour diverse marine fauna, which depends largely on organic matter and detritus brought in by waves (Whittaker 1975). Nematodes, harpacticoid copepods, platyhelminthes and oligochaetes dominate the meiofaunal groups (McLachlan 1980), while crustaceans, polychaetes and bivalve molluscs constitute the common macroinfaunal taxa (Brown and McLachlan 1990). Considering that exposed sandy beaches are one of the most extended intertidal systems worldwide, in terms of both distribution and diversity, good understanding of the response of organisms to perturbations, natural or manmade, is essential for appropriate system management (Lercari and Defeo 2003).

To assess the environmental impact on the health of an ecosystem, it is impossible to measure all relevant environmental variables and to appropriately integrate the large amount of information into a decision-making process. Therefore, it may be necessary to select environmental "indicators" that could be used to judge the degree to which specified environmental conditions have been achieved or maintained (Cairns et al. 1993).

2 Indicator Organisms

Johnson et al. (1993) defined indicator species as a species (or species assemblage) that has particular requirements with regard to a known set of physical or chemical variables such that changes in presence/absence, numbers, morphology, physiology or behaviour of that species indicate that the given physical or chemical variables are outside its preferred limits. Ideally, indicator organisms are those species that have narrow and specific environmental tolerances. The principal assumption underlying the use of indicator organisms for water quality assessment is that the occurrence of the indicator is a reflection of its environment.

The concept of "indicator organisms" has been employed in a wide variety of applications, ranging from the microbial level to the ecosystem level. For example, coliform organisms have long been used as indicators of faecal contamination in aquatic systems. In the context of the marine environment too, individual as well as groups of organisms have been used as indicators of fluctuating natural conditions or as indicators of anthropogenic disturbances (Soule 1988). One of the classical examples of the use of indicator organisms in marine environmental monitoring has been the "Mussel Watch Programme" of the USEPA (Goldberg et al. 1978). This study demonstrated that the mussel *Mytilus edulis*, a rocky shore inhabitant, possessed several of the characteristics that make an organism a suitable indicator. At the same time, a few types of organisms can serve as indicators for sandy beaches. Potential candidates include interstitial meiofauna, annelids, molluscs and crustaceans (Wenner 1988).

Different meiofaunal groups exhibit differential survivability on polluted and unpolluted beaches. Raffaelli and Mason (1981) and Warwick (1981) used the nematode–copepod ratio to demonstrate the "indicator organism" concept, since nematodes survive better in polluted areas as compared to copepods. It has been demonstrated that macroinfauna too exhibit great potential for revealing variations in habitat quality as a result of environmental impact (Bilyard 1987; Clarke and Warwick 1994). If the structure of a sandy beach were to be seen as a continuum from low intertidal to high intertidal regions, the transition of dominant macrofauna would progress from polychaetes to molluscs to crustaceans (McLachlan 1983). Not surprisingly, all these groups of organisms have been tested as possible indicator organisms. McDermott (1983) and Dexter (1983) have demonstrated the use of polychaetes as indicators in the intertidal region of sandy beaches. Raman and Ganapati (1983) studied the effect of urbanisation and industrialisation on the ecobiology of benthic polychaetes in the Bay of Bengal. However, most species of polychaetes in open sandy beaches inhabit the sub-tidal zone and very often they are too few in number (Ricketts and Calvin 1968) to serve as indicators. Molluscs and crustaceans are the other groups of macroinfauna that dominate the intertidal region of open sandy beaches. Of all sandy shore molluscs, various species of *Donax* have been studied as indicator organisms in the tropics and sub-tropics (Watling and Watling 1983; Gianuca 1983; Penchaszadeh 1983; Sastre 1984).

Despite the potential of the above mentioned taxa to serve as indicators, several authors have unequivocally suggested that crustaceans are the best possible biological indicators of environmental perturbations on sandy beaches (Wenner 1988; Peterson et al. 2000) since they are the most commonly encountered invertebrates of this habitat worldwide (McLachlan 1983; Dexter 1983; Penchaszadeh 1983; Donn and Croker 1983) and therefore offer the greatest number of possibilities in terms of diversity. In addition, they are often available in large numbers and are easy to collect as well.

Phillips (1980) and Wenner (1988) listed several pre-requisites to select indicator organisms for environmental biomonitoring studies and have even suggested that crustaceans possess many of these pre-requisites, which are as follows:

- The organism must be abundant throughout the study area.
- The organism should have a sufficiently long life-span.
- The organism should be of a reasonable size so as to yield enough tissue for analysis.
- The organism should be easy to sample and hardy enough to survive in the laboratory.
- Filter feeding organisms are preferable since they take up more pollutants than other organisms; they do not prey upon one another, making it easy to maintain large numbers in less space in the laboratory, without the risk of cannibalism.

3 Thermal Effluents in Coastal Waters

Water has, for long, been used as the principal industrial coolant in glass-making, metalworking, distilling and brewing and iron and steel, paper and pulp, chemical and petroleum industries, the general practice being the discharge of the heated effluent to the nearest water body. However, it was the growth and development of electric power generation that really brought waste heat as a potential large-scale pollutant (Langford 1990).

Power plants use different energy sources (fossil fuels or nuclear fuel) to produce heat which converts water into steam. Steam at high pressure is used to drive a turbine, which is connected to an electrical generator. Part of the heat energy of the steam is thus converted into mechanical energy which is subsequently converted into electrical energy in the electrical generator. The exhaust steam that leaves the turbine passes into a condenser, where cold water from a nearby source such as sea, lake or river causes the steam to condense to liquid water. However, along with seawater a large number of microscopic and macroscopic organisms are drawn into the condenser circuit. This phenomenon, known as entrainment, causes the organisms to be exposed to elevated temperatures as well as to physical effects like velocity and pressure changes, shear forces and abrasions during their passage through the cooling water circuits (Mayhew et al. 2000). In addition, biocides are added at the point of water intake to control the growth of fouling organisms inside the cooling circuit, exposing the organisms to chemical stress as well.

Most steam electric power plants use a once-through mode of condenser cooling in which ambient water from a nearby source is taken in to cool the condenser, after which it is discharged into a receiving water body which, in most cases, is the same as the source. Power plants with such a mode of condenser cooling, discharge the heated water in one of two ways: either at the surface (surface discharge) or below the surface of the receiving water body (submerged discharge). In the case of the former, the discharge could either be an onshore discharge, in which the discharged water usually flows as a canal before mixing with the ambient water or an offshore discharge, in which the water is taken further into the sea by means of a pipe before it is discharged. An onshore discharge has the potential to directly impact the intertidal belt, while an offshore discharge results in a thermal plume which may or may not reach the shoreline. In the case of a submerged discharge, the effluent water is carried through pipes and is then discharged at a depth using submerged jets or multiport diffusers (Glasstone and Jordan 1990). In such cases, there is a possibility that benthic fauna could be affected.

4 Sand Crabs as Indicator Species

The sand crabs (also known as mole crabs) form a very important component of tropical and sub-tropical sandy beach environments. That they can be used as indicator organisms has been shown in several studies (Sommer 1932; Burnett 1971; Auyong 1981; Siegel and Wenner 1984; Wenner et al. 1985; Lercari and Defeo 1999; Bretz et al. 2002; Ferdin et al. 2002; Powell et al. 2002). These crabs burrow into wave-washed sandy shores and exhibit a high degree of adaptation to this precarious environment. *Emerita* is well represented in beaches characterised by large waves, wide surf zones, fine sands and gentle slopes. The distribution pattern of each species is characteristic in that it is generally limited to long coastlines, although extending to offshore islands. Furthermore, different size classes of *Emerita* have different zonal distribution patterns in the sandy beach. Thus, the smallest individuals consisting of youngest post-megalopae are commonest in the fine sand near the high water mark and the largest specimens are found in the course sand near the low water mark. Specimens of intermediate sizes are distributed between these two zones (Subramoniam 1977a). *Emerita* burrows backward into the loose sand, facilitated by the movements of the anterior pair of legs as well as by the uropods and they come to rest in the sand facing oceanward. Filter-feeding in *Emerita* is accomplished by the antennae, which are modified into a feather-like structure having four rows of diverging setae, armed with inwardly directed secondary setae. When they unfold, the water passing over the animal from behind is filtered through the fine mesh of the setae. The food of the mole crab consists of tiny copepods, protozoans and detritus. *Emerita* has a complex life-history pattern with extended breeding cycle. On the east coast of India, *E. asiatica* (*emeritus*) breeds continuously and hence there is continuous release of zoea larvae all through the year (Subramoniam 1977b). Like many other littoral benthic invertebrates, *Emerita* has a pelagic larval phase, with some species having as many as seven zoeal stages that are spent in the open oceanic waters before metamorphosing into the megalopa stage (Israel et al 2006). The megalopa larvae migrate to the sandy shore for settlement. It is known that larval stages are of considerable ecological significance in the establishment and maintenance of marine communities (Nybakken 1988). They form the dispersal phase of most benthic marine invertebrates and also constitute an important component of the planktonic food chain (McConaugha 1992).

The complex life-history pattern, coupled with primitive filter-feeding and several peculiar features in breeding biology (Subramoniam and Gunamalai 2003), contributes enormously to its adaptation to the harsh exposed sandy beach environment. Evidently, *Emerita* represents the most successful macroscopic interstitial fauna of the sandy beach, making it an important indicator species for monitoring anthropogenic impact, especially pollution, in the beach. The adults of the sand crabs, in addition to being abundant, play an important role in the sandy shore food chain. Their sensitivity to environmental perturbations, combined with their universal distribution, ease of sampling and relatively high longevity (3–4 years), makes them ideal indicators of beach pollution (Siegel and Wenner 1985; Wenner 1988). The fact that both the larval and adult stages are important links in different food chains further underscores their importance as indicator species.

5 Sand Crab Distribution Near a Power Station Outfall

A monitoring study was organised to understand the effects of condenser discharges on intertidal fauna, using the sand crab *Emerita emeritus* as an indicator species. The study was carried out at a nuclear power station operating on the east coast of India.

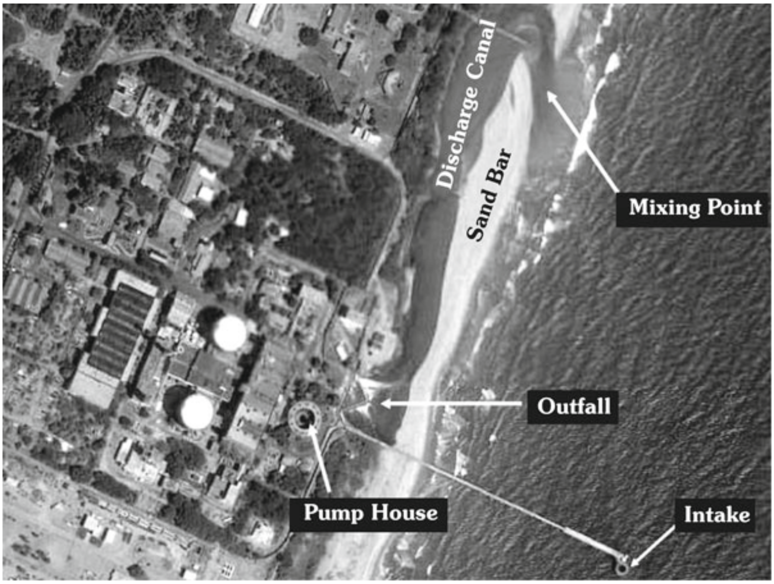

Fig. 16.1 Satellite image of the study site indicating parts of the cooling water circuit of the power station (image credit Google Earth)

Madras Atomic Power Station (MAPS) is located at Kalpakkam (12°33'N and 80°11'E), about 65 km south of Chennai. The station consists of 2 Units of pressurised heavy water reactors (PHWR), each with an installed capacity of 235 MWe, downrated to 170 MWe at the time of study (April 2002–March 2003). It employs a "once-through" system of condenser cooling using seawater as the tertiary coolant at a design flow rate of 35 m^3/s. Coolant water from the condensers and process heat exchangers is released together at the outfall point, located onshore. From the outfall point, the effluent flows as a canal before mixing with the open sea at a point known as the "mixing point" (Fig. 16.1). A unique feature of this study site is that the position of the mixing point shifts on a seasonal basis, owing to the seasonal changes in the length of the sandbar (Fig. 16.2) formed between the discharge canal and the sea (Anupkumar et al 2005). The spatial shifting of the mixing point, which provided an interesting dimension to this study, was attributed to seasonal changes in longshore sediment transport caused by monsoon-induced variations in coastal current pattern (Anupkumar et al 2005). In the steam condensers of the plant, the incoming water temperature is raised (by design) to a maximum of about 10°C above ambient; the increase is about 3°C in the process water heat exchangers (Anupkumar et al 2005). The mixing of the cooling water effluent with the ambient seawater results in a 3–5°C increase in the temperature of seawater at the mixing point. After reaching the sea, the warm effluent flows as a buoyant, shore attached plume.

Previous studies had shown that the region exposed to elevated temperatures (3–5°C higher than the ambient) is limited to an area 500 m parallel to the coast and

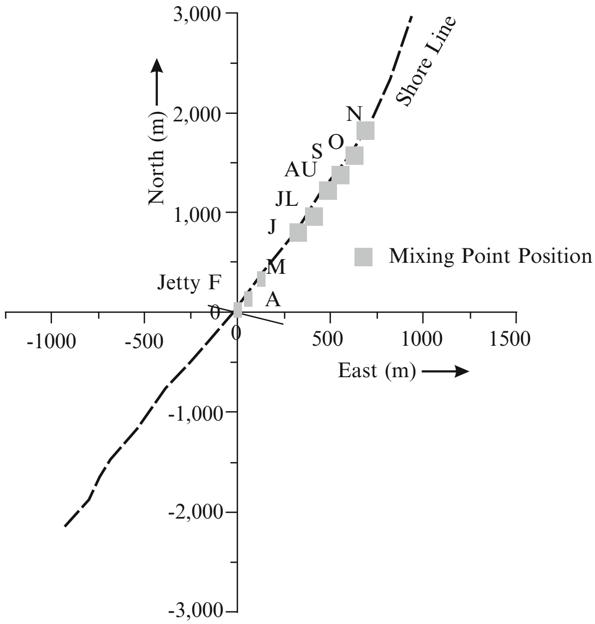

Fig. 16.2 Figure showing position of the mixing point during various months in the year 2002. The spatial shifting was due to changes in long-shore sediment transport caused by the monsoons

200 m offshore from the mixing point. Because of the buoyant nature of the thermal plume, potential damage to organisms present below a depth of 2 m is very minimal. The direction of flow of the thermal plume is determined by the direction of the longshore currents which are in turn governed by the two seasonally reversing monsoons. The predominant Southwest monsoon from March to September drives the longshore currents in the northerly direction while the Northeast monsoon from October to January drives it in the southerly direction. The northerly longshore current is generally stronger with a velocity of 0.2–1.8 km/h while the southerly current is weaker with a velocity of 0.1–0.8 km/h. There are two periods of monsoonal transition—in February and September—during which current reversal takes place and slack currents prevail.

Field studies were carried out during the period from April 2002—March 2003. Fortnightly collections of sand crabs were made at nine stations measuring a distance of about 8 km. Sampling stations were located both to the north and south of the mixing point and their positions were fixed with a GPS using the MAPS jetty (Fig. 16.1) as the reference point. A station located at a distance of 4 km south of the MAPS outfall point and which was never influenced by the condenser effluents, was designated as the control station. Crabs were collected using the quadrate sampling method (McIntyre 1968) from three distinct levels (high, mid and low water marks) at each station in the intertidal region.

The study on the population distribution of the sand crab in the vicinity of the MAPS mixing point revealed a clear pattern of depopulation and subsequent recolonisation. Depending on the thermal plume movement, short stretches of the

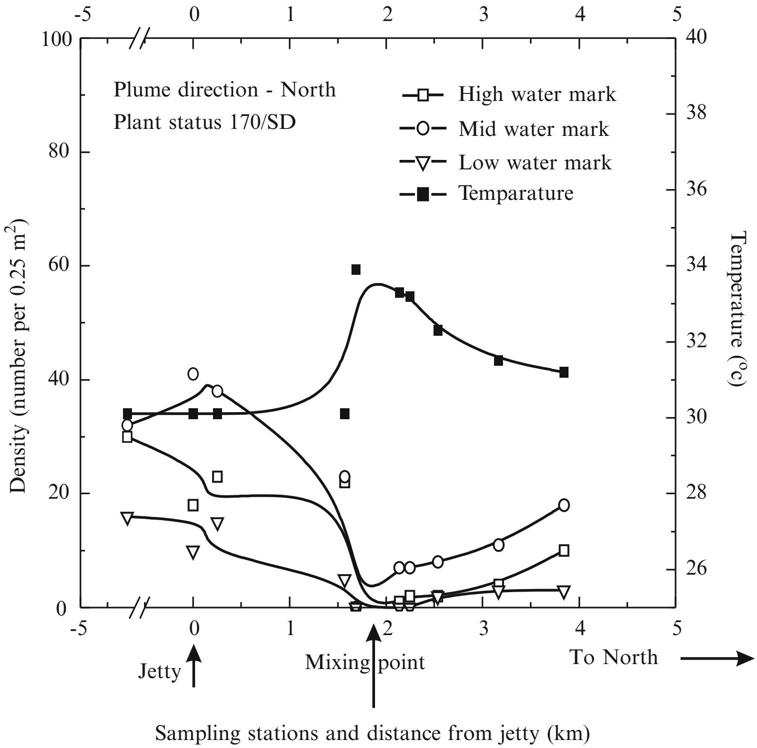

Fig. 16.3 Distribution of sand crabs near mixing point during May 2002 when northerly current prevailed. Crab population on the northern side of the mixing point is affected

intertidal belt immediately north or south of the prevailing mixing point and affected by the thermal plume, were devoid of sand crabs, while their population increased gradually at increasing distances from the mixing point (Figs. 16.3 and 16.4). During the southwest monsoon, the stronger northerly currents carried the thermal plume to longer distances as compared to the weaker southerly currents during the northeast monsoon months. This resulted in an increase in the distance up to which the sand crab population was affected, i.e. up to nearly 2 km north of the mixing point (Fig. 16.3). As the position of the mixing point continued to shift northwards with further progression of the Southwest monsoon season, re-colonisation of sand crab at the erstwhile mixing point locations was observed. This phenomenon of re-colonisation was influenced by the direction and velocity of the longshore currents carrying the thermal plume.

During the northeast monsoon months, when the longshore currents carried the thermal plume in the southerly direction, populations of sand crabs were recorded even at distances as close as 0.5 km south of the mixing point (Fig. 16.3). This could be attributed to the weaker southerly longshore currents which did not carry the thermal plume to any great distances as did the stronger northerly currents.

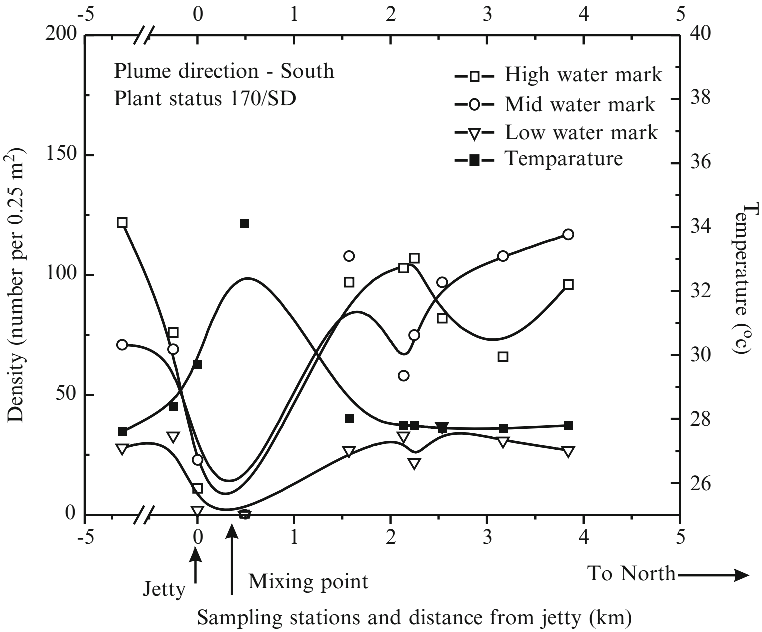

Fig. 16.4 Distribution of sand crabs near mixing point during December 2002, when weak southerly current prevailed. Repopulation of previous mixing point positions (to the north of present mixing point) is clearly seen

At distances further south, the population density was comparable to that at the control station. During the Northeast monsoon, i.e. when the mixing point shifted to the south, regions that were part of the previous mixing points during the Southwest monsoon months showed complete re-colonisation by the sand crabs. The observations, therefore, showed that (1) the sand crab distribution was impacted in the immediate vicinity of the mixing point and that (2) such impact was ephemeral and the effects reversible.

An important factor influencing the distribution of sand crabs in the vicinity of the mixing point was the operational status of the power plant. During periods when the power plant was shut down for maintenance purposes, population density of sand crabs on either side of the mixing point was comparable with that at the control site, irrespective of the direction of the longshore currents (Fig. 16.5). Earlier work by Suresh et al. (1996) on harpacticoid copepod distribution at the same study site had shown that though the copepod population in the vicinity of the mixing point was impacted by the thermal plume, plant shut-down resulted in rapid population restoration. From the available data, it appears that the absence of sand crabs in the impacted region is a transitory phenomenon. Depopulation of regions around the mixing point could be attributed to the increase in the temperature of seawater in these areas. Faunal re-colonisation of previously impacted regions can be attributed to the transmigration of the crabs along the beach and to fresh recruitment of crab

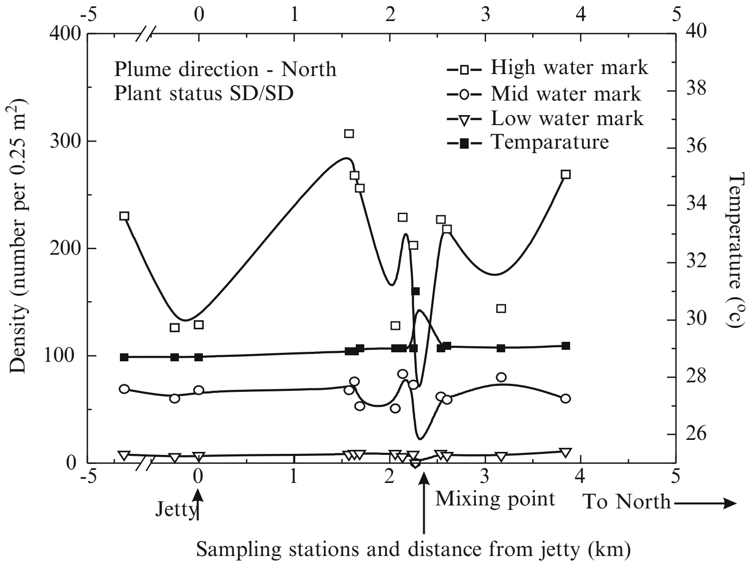

Fig. 16.5 Distribution of sand crabs near mixing point when both units of the power plant were shut down (August 2002; northerly current). Quick repopulation of sites on either side of the mixing point is evident

megalopae. These two phenomena, viz. transmigration and recruitment, can be expected to result in rapid reestablishment of the crab population in the impacted areas, ensuring that no long-term effect persisted as a result of the thermal discharge from the power plant.

6 Laboratory Studies on Sand Crabs

Planktonic organisms and smaller nekton present in the cooling water source are likely to be drawn in to the condenser circuit, where they may encounter elevated temperature and biocides. Zoeal stages of the sand crab, being planktonic, can be expected to undergo such entrainment effects and therefore, there is a need to study the effect of thermal and chemical stressors on larval survival. Laboratory experiments were carried out to study the effect of the exposure of early zoeal stages (I and II) to the stressors, viz. elevated temperature and chlorine (individually as well as in combination), during condenser passage. In addition, studies on the effects of exposure of the megalopa larvae and adults to the stressors, as they would encounter in the thermal plume, were also carried out.

Short term exposure (15 min) of stage I zoea larvae to 38°C (ΔT of 10°C) resulted in about 27% mortality (Fig. 16.6), while stage II zoea larvae exposed to a ΔT of 10°C recorded 29% mortality. However, exposure to a ΔT of 12°C resulted in higher

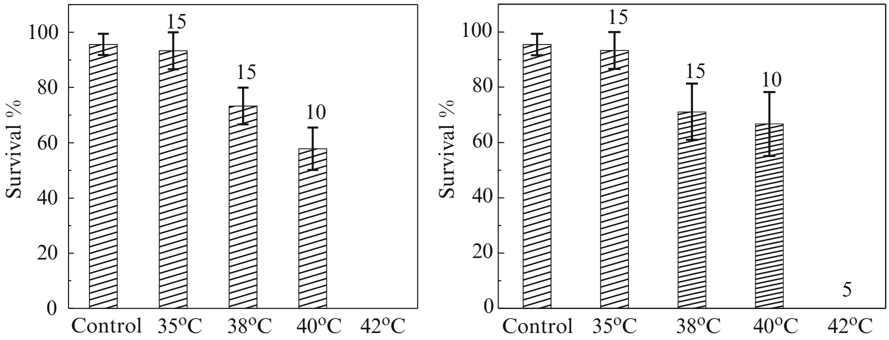

Fig. 16.6 Survival of stage I (*left*) and stage II (*right*) zoea larvae of *Emerita emeritus* exposed to different temperatures (numbers denote exposure time in minutes)

percentage of mortality in stage I larvae as compared to stage II larvae. Adams and Price (1974), observed significant mortality when 61–63-h-old veliger larvae of the red abalone *Haliotes rufescens* were exposed to a ΔT of 13.3°C for 10 min. However, mortality rates were comparable in 41–43-h-old veliger larvae when they were exposed to similar ΔT for 1 min. Kennedy et al. (1974) reported that the early cleavage stages of the hard clam *Mercenaria mercenaria* were more sensitive to short-term exposure to excess temperature as compared to the trochophore larvae, while the later "straight-hinge" stage larvae were even more tolerant. In a previous study, Thiyagarajan et al. (2000) recorded 40% mortality in stage II cirripede nauplii exposed to 40°C (ΔT 12°C) for 45 min as against no mortality for a similar exposure regime in stage VI nauplii. These studies corroborate the observation in the present study that temperature tolerance increased with progression in larval development and that early stage larvae were more sensitive to the temperature stress as compared to later stages.

Exposure to two doses of chlorine (1 and 3 mg L^{-1}) revealed that chlorine, by itself, had little effect on both the early zoeal stages. However, when chlorine was added at elevated temperatures, the mortality percentage increased significantly. Stage I larvae exposed to a combination of 38°C with 3 mg L^{-1} chlorine recorded 60% mortality, while addition of 1 mg L^{-1} chlorine at 38°C resulted in 56% mortality (Fig. 16.7). On the contrary, when temperature was the sole stressor (38°C), 27% mortality was observed (Fig. 16.8), while addition of 3 mg L^{-1} chlorine at ambient temperature (28°C) resulted in 16% mortality, suggesting that temperature (up to a ΔT of 10°C) and chlorine (3 mg L^{-1}), individually had relatively small effect. But addition of chlorine at higher temperatures caused significantly higher mortality. The same was observed in the case of the stage II larvae except that the survival percentage was marginally higher as compared to stage I larvae (Fig. 16.8).

Carpenter et al. (1974) and Heinle (1976) attributed power plant induced mortality of zooplankton to temperature rather than to chlorine, while Hall et al. (1981) suggested that due to its synergistic effect with temperature, chlorine became more toxic at elevated temperatures, causing increased mortality. Langford (1990) suggested that gradual increase in both chlorine concentration and temperature

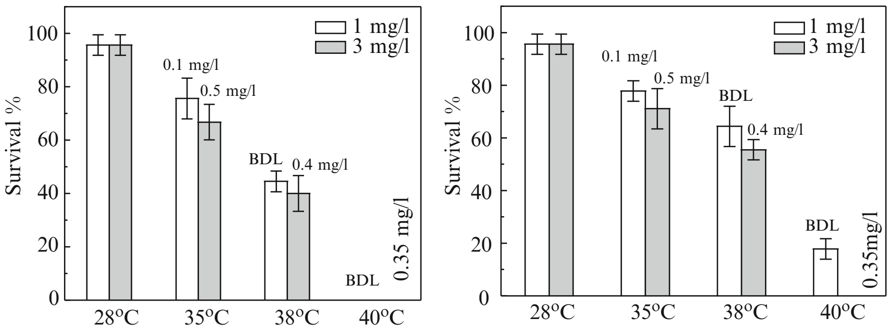

Fig. 16.7 Survival of stage I (*left*) and stage II (*right*) zoea larvae of *Emerita emeritus* exposed for 15 min to 1 and 3 mg/L doses of chlorine at different temperatures (numbers denote the total residual oxidant levels at the end of the exposure time)

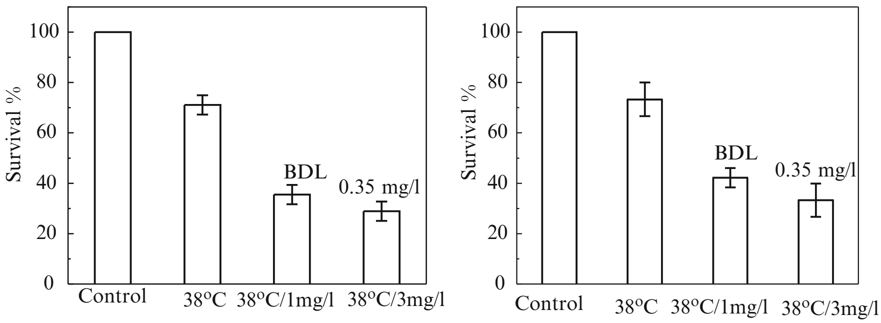

Fig. 16.8 Survival of stage I (*left*) and stage II (*right*) zoea larvae of *Emerita emeritus* exposed for 20 min to temperature alone or temperature and chlorine, followed by ambient temperature exposure for 24 h. Numbers denote the total residual oxidant levels at the end of 1 h

stimulated metabolic activity in animals, followed by an activity peak prior to torpor and ultimate death. A similar trend was observed in the long exposure duration experiments in which the larvae were briefly exposed to 38°C for 20 min and subsequently maintained at 35°C for 24 h. This was done to simulate their passage through the condenser, followed by subsequent longer residence in the discharge canal. The addition of chlorine (3 mg L^{-1}) at 38°C increased the mortality of both stage I and II zoea larvae (71 and 67%, respectively), further confirming the observations made in the earlier experiments (Fig. 16.8). In contrast, Poornima et al. (2005) suggested that chlorine and temperature exhibited little synergistic effect on phytoplankton chlorophyll *a*, as compared to chlorine alone.

Similarly, the impact of temperature and chlorine was studied on megalopae and adult *E. emeritus*. The megalopa stage and adults of *E. emeritus* inhabiting the intertidal region in the vicinity of the MAPS are prone to being subjected to the effects of the thermal plume. Exposure of megalopa to 35°C (ΔT 7°C) resulted in 51% mortality, while the addition of 2 mg L^{-1} chlorine (at 35°C) only resulted in 56%

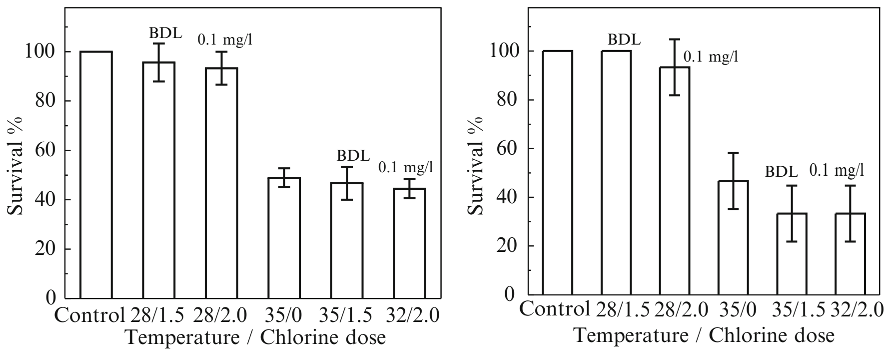

Fig. 16.9 Survival of megalopae (*left*) and adults (*right*) of *Emerita emeritus* exposed to different temperatures (°C) and chlorine doses (mg/L) for 24 h (numbers above bars denote TRO levels at the end of 1 h)

mortality (Fig. 16.9). Addition of 2 mg L^{-1} chlorine at 28°C resulted in 7% mortality, thereby suggesting that temperature proved to be more detrimental to the megalopae and that addition of chlorine either at ambient or elevated temperature had only minor effect. Similar results were obtained in the case of adults but the adults seemed to be marginally more sensitive than megalopa (Fig. 16.9). In an earlier work, Suresh et al. (1995) observed that adult sand crabs succumbed to temperature rise at the condenser outfall site, while those exposed to chlorine alone did not suffer any significant mortality.

Burton et al. (1976) reported no effect of a ΔT of 5.6°C on the blue crab *Callinectes sapidus* and the mud crab *Rithropanopeus harrissi*. Similarly, Hair (1971) observed no effect of temperature on the mysid shrimp *Neomysis awatschensis* up to a ΔT of 7°C for exposure periods of 30 min. However, prolonged exposure to this ΔT resulted in increased mortality. Hall et al. (1979) reported no effect due to chlorine on the adults of *Callinectes sapidus*.

The observations clearly indicate that the adults are more sensitive compared to the megalopae (Fig. 16.10). This was comparable to the observation of Cox (1974), who reported that the larger blue gill *Lepomis macrochirus* was more sensitive to elevated temperature as compared to the smaller ones.

In order to ascertain whether the absence of mole crabs in the intertidal region of thermally affected areas was due to mortality or avoidance, behavioural response of both larvae and adults to elevated temperatures was investigated. Burrowing time of the crabs was used as an index of differences in response between megalopae and adults. It was hypothesised that the longer the crabs remained in the water column following emergence from the burrow, the greater were their chances of being swept by longshore currents away from areas experiencing high temperatures. It was observed that the burrowing time of megalopa stage crabs increased with increasing temperature beyond 32°C (17.8 ± 4.4 s at 35°C). In contrast, the burrowing time in adults remained unchanged irrespective of the water temperature (Fig. 16.11).

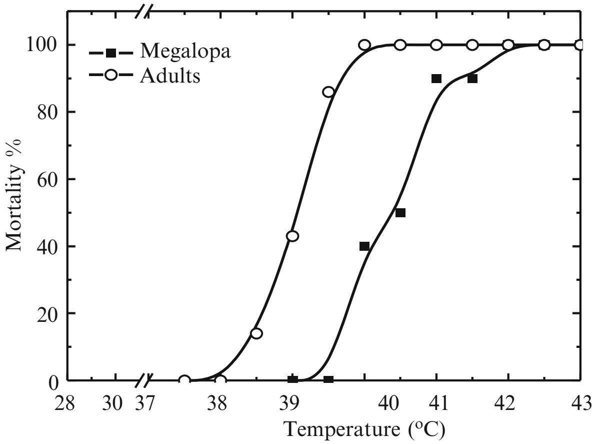

Fig. 16.10 Cumulative mortality of megalopae and adults of *Emerita emeritus* exposed to a graded increase in temperature (rate of increase 0.1°C/min)

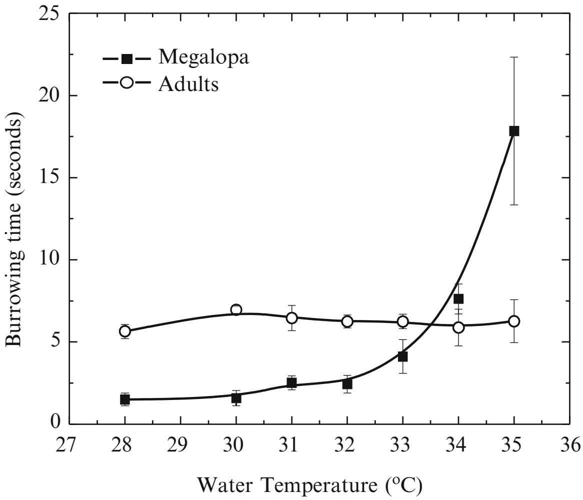

Fig. 16.11 Burrowing time of megalopae and adults of *Emerita emeritus* at different temperatures

Dugan et al. (2000) attributed burrowing rate to the size of mole crabs, with smaller ones burrowing more quickly than adults. The increased burrowing time of megalopae may allow them to escape higher temperatures by means of transmigration with the aid of longshore currents.

7 Conclusion

Crustaceans form the second largest invertebrate group after insects in terms of number, and they are extremely diverse in terms of the habitat they colonise. Therefore, it does not come as a surprise that several studies have suggested their utility as excellent “indicators”. Sand crabs of the genus *Emerita* have been used in several studies as indicator species, as seen from the foregoing account and the present study only serves to emphasise this further. Despite its restricted habitat (the narrow intertidal belt of sandy beaches), characterised by fluctuation in environmental conditions, the sand crab appears to be extremely sensitive to temperature changes, thereby underscoring its utility as an indicator of thermal stress.

Field data collected from the condenser discharge site of an operating power station showed that *E. emeritus* avoids thermally affected areas close to the mixing point. However, they quickly re-colonised the areas once the mixing point shifted as a result of monsoonal changes in longshore currents and littoral drift. Results of laboratory studies using larval and adult stages further showed that, among the two stress factors present in the discharged water, temperature was the greater stressor. This finding appears to be in contrast to earlier studies on phytoplankton, which seem to be affected more by chlorine than by elevated temperature.

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Chapter 17
Fish Protection Technologies: The US Experience

Gregory Allen, Stephen Amaral, and Jonathan Black

1 Introduction

The primary environmental effects of water intakes at thermal power plants are associated with the losses of aquatic organisms. Small organisms (fish eggs, larvae, invertebrates) entrained in the flow are subjected to mechanical, thermal, and chemical stressors. Larger organisms (juvenile and adult fish) are subject to impingement on the racks and screens that are installed to prevent passage of debris. Extensive research has been conducted since the early 1970s in attempts to develop technologies that will reduce entrainment and impingement mortality. As a result, a suite of technologies is available for fish protection at water intakes. Many of the technologies with application at cooling water intakes could also be applied at hydroelectric or irrigation/diversion projects.

Fish protection technologies can be broadly divided into five basic categories based upon their mode of action: (1) collection/transfer, (2) diversion, (3) exclusion, (4) behavioral, and, in some cases, (5) flow reduction. The methods used to estimate a technology's biological efficacy depend upon its mode of action. In addition, the site-specific intake design, operating characteristics, as well as the morphological, physiological, and behavioral characteristics of the organisms involved, will impact the efficacy of a technology.

For collection and transfer technologies (e.g., modified traveling screens), efficacy is measured in two ways: ability to prevent organism passage and ultimate survival. Collection and transfer technologies handle the organisms during the transfer process and return them to the source water body. This handling imparts additional stress to the organisms, which may result in injuries, scale loss, or mortality. At intakes where fine mesh screens (e.g., 0.5 mm) replace coarse-mesh

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screens (e.g., 9.5 mm) to prevent entrainment, the survival of the eggs, larvae, and early juveniles that were previously entrained into the intake becomes important. Survival of impinged organisms is dependent upon their biology (life stage, relative hardiness, etc.) and the screen operating characteristics (rotation speed, spraywash pressure, etc.).

Fish diversion technologies (e.g., angled screens, louvers) bypass fish from the intake flow and return them to the source water body. Since fish are not collected or otherwise handled by these technologies, such systems are inherently less stressful. For diversion to occur, the organisms must have sufficient swimming capability to actively avoid contact with, or passage through, the diversion medium.

For exclusion technologies (e.g., wedgewire screens and barrier nets), the key efficacy factor is organism size in relation to slot width or mesh size. Exclusion can be estimated using the diameter of the eggs or the head capsule depth of the larvae (the widest noncompressible portion of the larval body) targeted for protection. When head capsules are larger than the nominal opening size of the screening material, a larva will not be entrained. With larvae, the orientation of the organism to the screening medium at the time of contact will also influence the likelihood of being entrained. A secondary factor of exclusion technology efficacy is the hydraulic conditions both near the technology and through the technology.

Behavioral devices only provide a benefit for impingeable-sized organisms with reasonable swimming capability. Response to behavioral barriers is species-specific and dependent upon the hydraulic and site-specific physiochemical water conditions. In many species, the sensory structures have not been developed in early lifestages to detect and avoid the device. Also, the swimming abilities of the organism have to be such to overcome intake flow and avoid the device(s). Because of this, it is difficult to assess a priori the level of protection that could be achieved, especially in the absence of performance data for the targeted species at a given facility. Juvenile *Alosa* spp. are the only species showing a consistent response to behavioral barriers (lights and sound). Reducing flow into an intake may be an option for reducing organism entrainment (e.g., pump flow reduction, closed-cycle cooling). It can be assumed that the reduction in entrainment will be roughly commensurate with reduction in flow (USEPA 2004a).

In the remainder of this chapter, existing technologies are discussed by category both from engineering and biological perspectives; cost and operational considerations are also addressed.

2 Fish Collection and Transfer Systems

Conventional traveling water screens were originally designed to prevent debris in the cooling water at thermal power plants from clogging the steam condensers. Beginning in the 1970s, these traveling screens were modified to improve survival of fish during the process of impingement on the screens, spraywash removal from the screens, and return to the source waterbody. The first modifications to traveling screens to protect fish were made at a power plant estuarine portion of the James

River (Virginia, USA) 1976. The Ristroph screen, named for the engineer who designed them, had a screen basket equipped with a water-filled lifting bucket to hold collected organisms as they were carried up with the rotation of the screen (White and Brehmer 1976). Modified screens typically operate continuously to reduce impingement time. As each bucket passes over the top of the screen, fish are rinsed into a collection trough by a low-pressure spraywash system. Once collected, the fish are transported back to a safe release location in the source waterbody. Such features have subsequently been incorporated into through-flow, dual-flow, and center-flow screens.

Advances in Ristroph screen design have been developed through extensive laboratory and field experimentation. Hydraulic buffeting in the fish lifting buckets, identified as injurious to fish by Fletcher (1990), was reduced through improvements in bucket design during the 1980s and 90s. Evaluations of the latest generation of modified traveling screens have generally shown improved survival over previous screen designs (PSEG 1999, 2004; Beak 2000a, b; Fletcher 1990; Consolidated Edison 1996).

Laboratory evaluations by the Electric Power Research Institute (EPRI 2006a) looked at the mortality, injury, and scale loss rates of 10 species of freshwater fish impinged and recovered with a modified traveling screen. Mortality rates did not exceed 5% for any species and velocity tested (0.3, 0.6, and 0.9 m/s). Other modified screen designs, including a rotary disc screen and extruded polymer screens, have shown similar high survival in the laboratory and field (e.g., EPRI 2007a; Hydrolox, unpublished data).

In addition to the fish handling provisions noted above, traveling water screens have been further modified to incorporate screen mesh with openings as small as 0.5 mm to collect fish eggs and larvae and return them to the source waterbody. For many species and early life stages, mesh sizes of 0.5–1.0 mm are required for effective screening. Through-flow, dual-flow, and center-flow screens can all be fitted with fine-mesh screen material. Generally, fine-mesh screen systems have proven to be reliable in operation and have not experienced unusual clogging or cleaning problems as a result of the small mesh size.

A number of fine-mesh screen installations have been evaluated for biological effectiveness at power plant intakes. Results of these studies indicate that survival is highly species- and life stage-specific. Species such as bay anchovy (*Anchoa mitchilli*) and *Alosa* spp. have shown low survival, while other species such as striped bass (*Morone saxatilis*), white perch (*Morone americana*), yellow perch (*Perca flavescens*), and invertebrates show moderate to high survival. Therefore, evaluating fine-mesh screens for potential application at a water intake requires careful review of all available data on the survival potential of the species and life stages to be protected as well as nontarget species. Pilot scale studies at the site of potential application may also be recommended if available data are limited.

In addition to field studies, fine mesh screen survival data is available from extensive laboratory studies (Taft et al. 1981; ESEERCO 1981a; SWEC 1980). In these studies, larval life stages of striped bass, winter flounder (*Pseudopleuronectes americanus*), alewife (*Alosa pseudoharengus*), yellow perch, walleye (*Sander vitreus*), channel catfish (*Ictalurus punctatus*), and bluegill (*Lepomis macrochirus*) were impinged on a 0.5-mm screen mesh at velocities ranging from 0.15 to 0.91 m/s and for durations of 2, 4, 8, or 16 min. As in the field evaluations, survival was variable among species, larval stages, impingement duration, and velocity.

The primary concern with fine-mesh screens is that they function by impinging early life stages that are entrained through coarse-mesh (typically 9.5 mm) screens. Depending on species and lifestage, mortality from impingement can exceed entrainment mortality. In order for fine-mesh screens to offer a meaningful benefit in protecting fish, impingement survival of target species and lifestages must be substantially greater than survival through the circulating water system.

3 Fish Diversion Systems

3.1 Angled Screens

A variety of species have been shown to guide effectively on screens given suitable hydraulic conditions. Angled screens require uniform flow conditions, a fairly constant approach velocity, and a low through-screen velocity to be biologically effective. Angled screen systems have been installed and biologically evaluated at a number of water intakes on a prototype and full-scale basis. Angled screen diversion efficiency varies by species but has generally been relatively high for the many species evaluated (LMS 1985, 1992; Davis et al. 1988). Survival following diversion and pumping (to return fish to their natural environment, as required) has been more variable. Overall survival rates of relatively fragile species following diversion may not exceed 70%. Hardier species should exhibit survival rates approaching 100% (LMS 1985, 1992; Davis et al. 1988).

Angled fish diversion screens leading to bypass and return pipelines are being used extensively for guiding salmonids in the Pacific Northwest (Neitzel et al. 1991; EPRI 2007b). These screens are mostly of the rotary drum or vertical, flat panel (nonmoving) types. Like other angled screens, suitable hydraulic conditions at the screen face and a safe bypass system are required for the screens to effectively protect fish from entrainment and impingement and return to the source water body (Pearce and Lee 1991).

Angled screens can be considered a viable option for protecting juvenile and adult life stages provided that proper hydraulics can be maintained and that debris can be effectively removed.

3.2 Modular Inclined Screen

The modular inclined screen (MIS) was developed and tested by EPRI (EPRI 1994a, 1996; Amaral et al. 1999). The MIS is designed to protect juvenile and adult life stages of fish at all types of water intakes. An MIS module consists of an entrance with trash racks, dewatering stop logs in slots, an inclined screen set at a shallow angle (10–20°) to the flow, and a bypass for directing diverted fish to a transport pipe. The screen is made of flat panel wedge wire with slots aligned parallel with the flow. The module is completely enclosed and is designed to operate at relatively high water velocities ranging from 0.6 to 3.0 m/s, depending on species and life stages to be protected.

The MIS was evaluated in laboratory studies to determine the design configuration which yielded the best hydraulic conditions for safe fish passage and the biological effectiveness of the optimal design in diverting selected fish species to a bypass (EPRI 1994a; Amaral et al. 1999). Biological tests were conducted in a large flume with juvenile walleye, bluegill, channel catfish, American shad (*Alosa sapidissima*), blueback herring (*Alosa aestivalis*), golden shiner (*Notemigonus crysoleucas*), rainbow trout (*Oncorhynchus mykiss*) (two size classes), brown trout (*Salmo trutta*), Chinook salmon, Coho salmon, and Atlantic salmon (*Salmo salar*). Screen effectiveness (diversion efficiency and latent mortality) was evaluated at water velocities ranging from 0.6 to 3.0 m/s and screen slot openings of 2.0 mm. Diversion rates approached 100% for all species except American shad and blueback herring at water velocities up to at least 1.8 m/s. Generally, latent mortality of test fish that was adjusted for control mortality was low (0–5%).

Based on the laboratory results, a pilot-scale evaluation of the MIS was conducted at a hydroelectric power plant on the Hudson River, New York, USA (EPRI 1996; Amaral et al. 1999). The results obtained in this field evaluation with rainbow trout, largemouth and smallmouth bass (*Micropterus salmoides* and *M. dolomieui*), yellow perch, bluegill, and golden shiners were similar to those obtained in laboratory studies (Taft et al. 1997).

The combined results of laboratory and field evaluations of the MIS have demonstrated that this screen is an effective fish diversion device that has the potential for protecting fish at water intakes. Studies to date have only evaluated possible application at hydroelectric projects. Currently, no full-scale MIS facility has been constructed and operated.

3.3 Louvers/Angled Bar Racks

A louver system consists of an array of evenly spaced, vertical slats (similar to bar racks) aligned across a channel at an angle typically between 15 and 35° to the approaching flow and with a bypass at the downstream end. Louver slats are oriented 90° to the flow, whereas bar racks have slats positioned at 90° to the structure. At steeper angles, bar racks can produce similar hydraulic conditions and fish responses typically observed at louvers. However, numerous studies have demonstrated that angled louver and bar racks can be on the order of 80–95% effective in diverting a wide variety of species over a wide range of conditions (EPRI 1986, 1994b; Stira and Robinson 1997; Bowen et al. 1998; Amaral et al. 2002a).

A series of laboratory studies conducted at Alden Research Laboratory evaluated guidance efficiency for several configurations of angled bar racks and louvers with varying approach flow velocities (EPRI 2007b; Amaral et al. 2002a, b, 2003). Species evaluated during these studies included smallmouth and largemouth bass, walleye, channel catfish, golden shiner, shortnose and lake sturgeon (*Acipenser brevirostrum* and *A. fulvescens*, respectively), and silver American eel (*Anguilla rostrata*). With the exception of yearling sturgeon and silver eels, most fish tested were between 75 and 125 mm in length. Guidance efficiencies ranged from about 60 to 100% for louvers and bar racks angled 15° to the flow with approach velocities of 0.3–0.9 m/s. Yearling sturgeon and silver eels had the highest guidance efficiencies. Guidance efficiencies for 45-degree louvers and bar racks were considerably lower (typically less than 60%) than those observed for the 15-degree arrays.

In the Eastern USA, 45-degree angled bar racks have been installed at many hydroelectric projects in attempts to divert downstream migrants (e.g., Atlantic salmon smolts and juvenile clupeids) to a bypass. Results have been mixed, but some installations have experienced guidance efficiencies up to about 95% (Simmons 2000). US resource agency criteria for angled bar racks often include 2-in. spacing of bar slats and approach velocities of 0.6 m/s or less. Louvers have been installed primarily in the Northeast and on the West Coast of the USA, often for guiding anadromous downstream migrants away from water diversion or turbine intakes. Depending on species and hydraulic conditions, guidance efficiencies for louver installations have approached 90% at some sites (Stira and Robinson 1997).

3.4 Fish Pumps

Several pumps have demonstrated an ability to transfer fish with little or no mortality, including the Hidrostal and Archimedes screw pumps that have undergone extensive research (Liston et al. 1993; ESEERCO 1981b; Frizell et al. 1996; McNabb et al. 2003; Weber et al. 2002). These pumps by themselves do not represent a technology for protecting fish. However, when coupled with fish bypass systems, such as angled screens or louvers, fish pumps are biologically effective.

4 Fish Exclusion Technologies

4.1 Cylindrical Wedgewire Screens

Wedgewire screens can reduce both entrainment and impingement at water intakes if the proper screen slot size is selected. These screens are designed to function passively; that is, to be effective, ambient cross-currents must be present in the water body to carry waterborne organisms and debris past the screens.

Wedgewire screens utilize "V" or wedge-shaped, cross-section wire secured to a framing system to form a slotted screening element. In order for cylindrical wedgewire screens to reduce impingement and entrainment, the following conditions must exist: (1) sufficiently small screen slot size to physically block passage of the smallest lifestage to be protected (typically 0.5–1.0 mm), (2) low through-slot velocity (typically less than 0.15 m/s), and (3) ambient currents providing high velocity cross-flow to provide continuous flushing of debris. Where all of these conditions are present, wedgewire screens can reduce entrainment and impingement (Hanson et al. 1978; Lifton 1979; Weisburg et al. 1987; Cumbie and Banks 1997; Ehrler and Raifsnider 1999).

Full-scale cooling water intake structure (CWIS) applications of wedgewire screens to date have been limited to two facilities with large-flow, once-through cooling systems (>20 m^3/s). These two facilities used slot openings of 6.4 and 10 mm to primarily reduce impingement (EPRI 2007b; Blye et al. 2006). In addition to the reduction in impingement, these two installations have also reported some reduction in entrainment. However, it is unknown how much of the reduction can be attributed to moving the point of withdrawal within the source water body. Other sites, with smaller intake flows have demonstrated substantial reductions in entrainment with many different target species using narrow-slot wedgewire screens (Ehrler and Raifsnider 1999; Cumbie and Banks 1997; EA 1986). There are no reports of unusual maintenance problems associated with the use of wedgewire screens.

Based on laboratory evaluation of narrow-slot wedgewire screens, (EPRI 2003), relationships associated with the various factors that affect impingement and entrainment of aquatic organisms were identified. In general, (1) impingement decreased with increases in slot size; (2) entrainment increased with increases in slot size; (3) entrainment and impingement increased with increases in through-slot velocities; and (4) entrainment and impingement decreased with increases in channel velocity. EPRI (2003) identified several biological factors including size and swimming ability of the test organisms.

In the field, environmental variables such as nonuniform flows, debris, and biofouling, could impact the effectiveness of the screens. Field evaluations to look at these effects were undertaken using barge-mounted narrow-slot wedgewire screens (EPRI 2005, 2006b). Test locations included Narragansett Bay (Rhode Island, USA) the Portage River (Ohio, USA) and Chesapeake Bay (Virginia, USA).

A number of general conclusions can be drawn from the data: (1) using a smaller slot width reduced larval and egg entrainment densities; (2) entrainment density was not significantly affected by slot velocity (0.15 and 0.30 m/s); (3) An increase in ambient velocity resulted in an increase in both control and test larval entrainment densities, while egg entrainment densities were unaffected; and (4) entrainment densities decreased with increasing larval length.

In general, consideration of wedgewire screens with small slot dimensions for CWIS application should include in situ pilot-scale studies to determine potential biological effectiveness and identify the ability to control clogging and fouling in a way that does not impact station operation (EPRI 2007b; Smith and Ferguson 1979).

4.2 Aquatic Filter Barrier (AFB)

The AFB is a full-water-depth filter curtain consisting of polyester fiber strands which are pressed into a water-permeable fabric mat. In some cases, the AFB is perforated to increase flow rates. In addition to the small opening size, the AFB uses very low through-fabric velocities to reduce entrainment to 0.04 lpm/cm^2 (10 gpm/ft^2).

There has been one large deployment of the AFB at a cooling water intake. An AFB was installed at a power plant on the Hudson River (New York, USA) in 1994. Early biological evaluations conducted between 1995 and 2001 compared the entrainment rates of a protected intake to that of an unprotected intake. Later biological evaluations conducted between 2004 and 2006 evaluated a full-scale AFB installation by comparing ichthyoplankton densities inside (protected) and the outside (unprotected) of the AFB. During its deployment, refinements in the AFB design increased the exclusion of larval fish. Therefore, the latter data are better representative of the potential biological effectiveness.

Biological monitoring of this expanded AFB system was conducted between 2004 and 2006 (ASA 2004, 2006a, b). Control samples were collected outside of the protected intake, while test samples were collected from inside. Based on the last 3 years of data (2004–2006), the efficacy ranged from 68 to 100%, depending upon species and life stage.

Debris loading and anchoring system requirements must be carefully evaluated at any site considered for possible installation of the AFB system. Given the low flow per unit area required for optimal biological performance, a relatively large and costly deployment area is required near the intake.

4.3 Barrier Nets

Barrier nets have been effectively applied at several power plant cooling water systems, as well as a number of hydroelectric projects. Under the proper hydraulic conditions (primarily velocity less than 0.08 m/s) and without heavy debris loading, barrier nets have been effective in blocking fish passage into water intakes. The mesh size must be selected to block fish passage, but not cause fish to become gilled in the net. Debris cleaning and biofouling control can be labor-intensive (Michaud and Taft 1999; EPRI 2006c).

A barrier net was originally deployed at a power plant on the estuarine Patuxent River (a tributary to the Chesapeake Bay) in July 1981 to combat condenser blockage problems due to seasonal movements of blue crabs (*Callinectes sapidus*) and to reduce impingement of fish and crabs on the traveling water screens. The initial barrier net had poor performance due to fouling and clogging of the net and an inadequate anchoring system. The barrier net system at Chalk Point underwent several modifications, including the addition of a second barrier net in 1984. The system has been successful in reducing blue crab impingement numbers. Clogging and fouling of the net are controlled through regular changing of the barrier net panels (Loos 1986). For the five species that accounted for greater than 1% of total impingement and exhibited a good correlation between impingement numbers and relative abundance (Atlantic menhaden (*Brevoortia tyrannus*), spot (*Leiostomus xanthurus*), white perch, hogchoker (*Trinectes maculates*), and blue crab), the proportionally adjusted estimates of reduction ranged from 82 to 98% (Bailey 2005).

At a pumped storage facility on Lake Michigan (Michigan, USA), a 4.02-km (2.5-mile) long barrier net, set in open water around the intake jetties, has been successful in reducing passage of all fish species that occur near the intake (Reider et al. 1997). The net was first deployed in 1989. Modifications to the design in subsequent years led to a net effectiveness for target species (five salmonid species, yellow perch, rainbow smelt [*Osmerus mordax*], alewife, and bloater [*Coregonus hoyii*]) of over 80% since 1991, with an effectiveness of 96% in 1995 and 1996.

Other facilities have shown similar levels of impingement reduction. Examples include facilities located on: (1) Lake Springfield (Illinois, USA) (90% reduction—Schimmoller 2005), (2) the Hudson River (New York, USA) (91% reduction—Hutchinson and Matousek 1988), (3) the Fox River on the southern end of Green Bay, Lake Michigan (Michigan, USA) (deterrence rate of 98% for some species; no species less than 85%—USEPA 2004b), and (4) Colby Lake/Partridge River (Minnesota, USA) (near 100%—EPRI 2006c).

In conclusion, barrier nets can be considered a viable option for protecting fish provided that relatively low velocities (generally less than 0.08 m/s) can be achieved and debris loading is light. A thorough evaluation of site-specific environmental and operational conditions is generally recommended.

5 Behavioral Barriers

5.1 Sound

Sound has been explored as a fish deterrent for application at water intakes for over 40 years (see EPRI 2007b for reviews of relevant studies). Three types of sound systems have been extensively evaluated: (1) infrasonic (<100 Hz), (2) sonic (100 Hz to 5 kHz), and (3) ultrasonic (>80 kHz). The most successful applications of sound have involved the use of ultrasonic signals (>100 kHz) as a means to repel *Alosa* species (e.g., alewife, blueback herring, and American shad juveniles) (Nestler et al. 1992; Ross et al. 1993, 1996). The strong response of *Alosa* species has been attributed to specialized hearing abilities that are only found in this genus of fish. Strong avoidance exhibited by alewife has led to the installation of permanent, full-scale ultrasonic deterrent systems at some power plants located on the US Great Lakes.

There is no evidence that any species other than those in the genus *Alosa* can hear frequencies above about 4–5 kHz. Consequently, sonic sound signals (typically between 100 and 1,000 Hz) have been evaluated as a deterrent to anadromous salmonids and estuarine and riverine fishes (EPRI 1998; Goetz et al. 2001; Maes et al. 2004; PSEG 2005). Results from these studies have been mixed, but generally sonic sound systems are not considered a viable technology for repelling most riverine fish species and anadromous salmonids at water intakes in the USA. A recent study at a power plant on the Mobile River in Alabama supported this conclusion after it was demonstrated impingement of a variety of riverine fishes was not reduced in the presence of sonic sound signals between 100 and 2,000 Hz (EPRI 1999). Conversely, a sonic system developed by Fish Guidance Systems, LTD has been installed at several cooling water intakes in Europe Based on evidence considerable reductions in impingement can be achieved for estuarine species (Maes et al. 2004).

In the near field, fish response to sound is more related to particle motion than acoustic pressure (Kalmijn 1988). Particle motion is the primary component of sound in the near field and is what fish most likely sense (and respond to) when exposed to infrasonic signals (i.e., frequencies less than 100 Hz). In the first practical application of an infrasonic device, Knudsen et al. (1992, 1994) demonstrated that a piston-type particle motion generator operating at 10 Hz was effective in repelling Atlantic salmon smolts in a tank and at a small diversion channel.

Following the success of the studies with Atlantic salmon smolts, there was a general belief in the scientific community that infrasound could represent an effective fish repellent since there was a physiological basis for understanding the response of fish to particle motion. Based on the results reported by Knudsen et al. (1992, 1994), testing was conducted with anadromous salmonids in the Northwest USA, but the results were mixed (i.e., avoidance varied among species and devices tested; Ploskey and Johnson 2001; Mueller et al. 2001) and were not considered sufficient to support additional testing or the installation of full-scale systems. However, a recent study that evaluated the ability of an infrasonic generator to repel fish at a power plant in Belgium has indicated there may be potential for repelling some freshwater species (particularly cyprinids) with infrasound at cooling water intakes (Sonny et al. 2006). In addition to the mixed results of biological studies, the effective range of infrasound (3–10 m) may be an issue at some power plants where velocities may be too high for fish to respond before being impinged or entrained. Additional testing with other species and at other sites is needed before infrasonic generators can be seriously considered for application at cooling water intakes.

5.2 Strobe Lights

The use of strobe light as a means to repel fish from water intakes has been evaluated during numerous studies over the last 25 years (see EPRI 2007b for reviews of strobe light studies). Avoidance responses have been demonstrated by a variety of fishes during laboratory and field studies. Research efforts have shown that several salmonid species can be repelled by strobe light (Nemeth and Anderson 1992; Amaral et al. 2001; Johnson et al. 2001; Maiolie et al. 2001; Mueller et al. 2001). *Alosa* species have also exhibited avoidance to strobe lights in laboratory studies, as well as at hydroelectric projects (EPRI 1992). Unlike some salmonids and clupeids, avoidance responses of many freshwater fishes have been less evident (EPRI 1998), but several studies have indicated that some riverine species may avoid strobe light (McCauley et al. 1996; Amaral et al. 2001) and that fish passage into intakes may be reduced by this technology (McCauley et al. 1996). However, a recent study at a cooling water intake on the Mobile River in Alabama did not detect any reductions in impingement during strobe light operation for a wide array of species, including blue and channel catfish, freshwater drum, and threadfin and gizzard shad (EPRI 1999). The use of strobe lights in highly turbid water has also been discounted due to the constraints associated with minimal light penetration. Based on the mixed results for some species and poor performance for many others, strobe lights do not appear to have potential for widespread application as a fish deterrent at water intakes.

5.3 Air Bubble Curtains

These curtains generally have been ineffective in blocking or diverting fish in a variety of field applications. Air bubble curtains have been evaluated at number of sites on the Great Lakes with a variety of species. In no case have air bubble curtains been shown to effectively and consistently repel any species. Therefore, the potential for application of this technology appears limited. All air bubble curtains at these sites have been removed from service. It is possible that air bubble curtains combined with other behavioral technologies, such as light sources, might indicate improved potential for this hybrid technology in the future (GLEC 1994; McCauley et al. 1996).

5.4 Mercury Light

Response to mercury light has been shown to be species-specific; some fish species are attracted, some are repelled, and others have demonstrated no obvious response (EPRI 2007b). Therefore, careful consideration must be given for any application of mercury lights to avoid increasing impingement of some species. The use of mercury lights as a primary or sole fish protection device has not been supported by the results of past studies.

5.5 Electric Screens

Electric barriers have been shown to effectively prevent the upstream passage of fish. However, a number of attempts to divert or deter the downstream movement of fish near water intakes have met with limited success (Bengeyfield 1990; Kynard and O'Leary 1990). Consequently, past evaluations have not lead to permanent applications. Given their past ineffectiveness and hazard potential, electric screens are not considered a viable technology for application at water intakes.

5.6 Other Behavioral Barriers

Devices such as water jet curtains, hanging chains, visual cues, and chemicals have been suggested, and in some cases evaluated, as fish protection measures. However, no practical application of these devices has been developed, and they are not considered available technologies for application at water intakes.

6 Flow Reduction

6.1 Reduced Pump Operation

Reduction in pump flow can reduce both entrainment and impingement. However, this option is typically impractical for base-loaded power generating facilities that require full flow to achieve maximum power efficiency and maintain thermal discharge limits. For cycling facilities, the ability to turn pumps off during periods when generation is not required is possible.

6.2 Variable Frequency Drives

Variable frequency drives (VFDs) could be installed on power plant circulating water pump motors to better regulate the cooling water flow without affecting facility generation or the thermal discharge temperature limits. Operating in this manner could reduce entrainment, but the actual level of flow and entrainment reduction would vary by year based on the generation demands and ambient water temperatures. General trends in load demand must be clearly understood to predict periods where running at reduced loads would not affect the reliable energy output of the plant.

7 Closed-Cycle Cooling

Closed-cycle cooling is not a fish protection technology per se. However, closed-cycle cooling could greatly reduce both impingement mortality and entrainment. Mechanical or natural-draft towers require less modification to existing circulating water system piping and less space than dry cooling towers. Natural-draft cooling towers require less energy to operate and have lower annual costs than mechanical draft towers. However, the cost of construction of a mechanical cooling tower is about 60% less than the natural-draft cooling tower. In addition, wet mechanical-draft towers generally have less aesthetic and air quality impacts than natural-draft towers.

8 Selecting a Technology: Engineering and Biological Considerations

The process of selecting a cost-effective technology for application at a water intake requires careful consideration of important engineering and biological factors. The process involves the following: (1) the development of site-specific design, construction, and siting criteria, (2) preparation of conceptual layouts (plans and sections) used to evaluate each alternative to determine whether it will satisfy those criteria, and (3) determination of potential biological efficacy.

For each concept considered, a description of the intake design features should be developed, along with figures showing the basic dimensions of pertinent structures. The conceptual design should also identify all equipment necessary to allow an alternative intake technology to be effective at a site, including components for debris removal and handling, screen cleaning, and fish return. These features can remain somewhat flexible in the conceptual design phase until a preferred technology has been identified. For existing plants, these features define the structural framework around which a technology must be retrofitted. As such, existing features represent a constraint on the potential for practicable and/or effective application of a given technology.

Velocities and flow patterns at existing CWISs may be influenced by the installation of a technology. The velocity through or around a technology which influences the loading for support structures must be sized. For existing sites, velocity measurements should be evaluated, if available. If such information is not available, minimum, normal and maximum velocities should be calculated over the range of plant flows and water levels at critical flow areas in the intake structure.

Appropriate construction techniques for the intake alternatives under consideration must be identified in the evaluation process. For many intakes, the civil works required for installation of a technology can be more extensive than construction of the original intake structure. Some alternatives, such as a shoreline intake with flush-mounted traveling water screen intakes, have to be constructed “in the dry” using earth or sheetpile cofferdams. Other alternatives, such as cylindrical wedgewire screens, can be installed “in the wet” using barge-mounted cranes and divers.

Subsurface conditions are an important factor affecting the construction methods to be used for installation of an alternative technology at a given site. The subsurface materials dictate the method for anchoring structures to prevent sliding, overturning, and flotation. For example, minimizing excavation in hard rock results in more cost-effective structure due the high cost for rock removal. Similarly, soft, clay foundation materials can require deep support piles to stabilize the structure.

Access for construction equipment is another factor that should be evaluated. Shoreline areas near plants may be heavily developed with other industry or may not have available access roads. For offshore intakes (and some onshore intakes), access to the construction site will typically be provided through the use of barge-mounted cranes and other equipment.

The construction season available for installing intakes is another important factor in the evaluation of alternatives. In cold weather regions, contractors may have to demobilize at the end of a short construction season and mobilize several times to complete construction over several seasons. Short construction seasons may require more expensive winter construction techniques to be employed.

Plant outages required to complete installation of an intake alternative at an existing facility are an important consideration in the evaluation of alternatives. Construction methods and sequencing should be designed to minimize the impacts on plant operations during construction.

Operation and maintenance (O&M) requirements of various types of intakes are important factors in evaluating alternative designs. Operating parameters include (1) the electric power (kWh) necessary to operate specific equipment (such as trash rakes, traveling water screens, or screen wash pumps), and (2) the manpower (hours) needed to inspect and operate the equipment in an acceptable condition for effective fish protection. Maintenance parameters that have to be considered include manpower (hours, such as the time and material required to grease rotating elements on a continuously operating traveling screen) and components (spare parts) that are needed on-hand for the performance of routine equipment maintenance.

Technologies are sometimes located remotely from the existing CWIS (e.g., to withdraw water from less biologically productive areas or to provide adequate submergence). The effective open area of the inlet openings and the pipes that are required to convey flow from a new, remote intake to the plant can impact system head losses and water levels at the pumps. System components must be sized to minimize head losses and to maintain adequate suction head on pumps. At existing plants, lower water levels in the pump bay resulting from an alternative technology could reduce pressures in the cooling water system, thereby reducing plant capacity. Therefore, all alternative intakes must provide at least the minimum water level at the pumps that would be acceptable for plant operations. Lost power costs, if any, should be included in the estimated cost of the alternative.

Clogging by debris, sediment, and ice can reduce flow through an intake structure, increase head losses in the system, and increase hydrostatic forces on the intake. If clogging is serious, a structure can become plugged and unable to convey an adequate amount of water to the plant. Therefore, clogging potential is an important consideration in the evaluation of any intake alternative.

The process of developing biological efficacy estimates takes place at the species/life stage level. Species and life stages of concern are typically selected on the basis of their commercial or recreational value, their value to the food chain, and their status as being rare or endangered. Efficacy estimates are derived from available data from other sites of application or other evaluations (e.g., laboratory and pilot-scale studies). Ideally, data will be available for each alternative under consideration at a given site and for each species/life stage of importance. However, this is seldom the case. More often, data are available for some species and technologies and lacking for others. Therefore, the process of estimating potential biological effectiveness of a given technology involves the use of available data in two ways: (1) direct application for those species/life stages for which effectiveness data exist and (2) extrapolation of the available data to other species/life stages for which no data exist.

Direct application is relatively straightforward. For each technology, the available data are reviewed and a "best estimate" of potential effectiveness is derived. The best estimate will be one that is based on results from other sites at which effectiveness evaluations have been performed. In most cases, a range of effectiveness values is available for a given species/life stage and technology as a result of evaluations at more than one site. Therefore, it is necessary to select an estimate within the available range. When the range of values is small (e.g., 10%), it is reasonable to select a best estimate of effectiveness based on a review of the similarity between the site under review and the sites from which data are available (water body type, design and operating specifications of the technology, debris loading, etc.). Within a small range, the degree of uncertainty surrounding the estimate will also be relatively small.

When the range of reported effectiveness is large (e.g., 50% or greater), the accuracy of the estimate selected will be less certain. For example, literature values for mortality of juvenile *Alosa* spp. collected from Ristroph-modified screens can range from 20 to 100%. Again, the process of selecting a best estimate involves a review of all data and the identification of those data that are most representative of the site under review. However, with the larger range of reported values, the uncertainty surrounding the estimate will be greater. In this case, the evaluator must assess the available data and use best professional judgment to develop a best estimate of potential effectiveness.

The degree of uncertainty around an estimated effectiveness value is even greater in cases where there is no data available for one or more of the species/life stages under consideration. Several approaches can be taken in such cases. For technologies that involve handling or other possible sources of physical contact that might injure or kill fish (e.g., collection screens, bypasses, and pumps), one approach is to group species and life stages into categories reflecting their relative "hardiness." Effectiveness values based on survival of other species and life stages in the same "hardiness" category for which data do exist can then be assigned. It has been well documented that species such as shad, herrings, and anchovies are relatively "fragile." That is, they lose their mucous coating and scales and bruise easily, making them more susceptible to immediate mortality and latent stress and mortality resulting from primary and secondary infections and loss of osmoregulatory capability. Injured and stressed fish are also more susceptible to predation by birds, mammals, and other fish species. On the other hand, species such as flat fishes (e.g., flounders) are not as easily injured or stressed and are considered to be relatively “hardy.” Intermediate to these extremes are fish that appear to be “moderately hardy,” such as bass, shiners, and weakfish. Generally, sufficient information is available on the relative hardiness of most fish species that species for which technology effectiveness data are not available can be broadly grouped into one of these three categories. They can then be assigned a best estimate based on professional judgment.

Another approach to developing technology effectiveness estimates for species and life stages for which data do not exist is to examine their morphology (size and shape), physiology, and relative swimming capabilities for comparison to other species with similar characteristics for which data do exist. The earliest life stages, eggs and early larvae, have little or no motility. Therefore, they will interact passively with fish protection technologies. If the technology is designed to protect these life stages passively, then they will be relatively effective given that all other design and operational requirements of the technology needed for biological effectiveness have been met.

Older larvae begin to develop swimming capabilities that vary by species. The size and swimming capability of developing larvae will determine whether larvae of a given species will interact passively or actively with a given technology. Examination of morphology and swimming capabilities can thus be used in a comparative manner to extrapolate data from past studies of technologies to species that have not been previously studied. The technology itself also interacts with larval size and swimming capability to influence the potential for biological effectiveness. For example, both traveling fine-mesh screens and cylindrical wedgewire screens act as a physical barrier to fish. While later larvae will actively swim in front of a fine-mesh screen located within a screenwell structure, the usual outcome of the interaction with this technology is impingement. The same larvae interacting with a submerged, cylindrical wedgewire screen can avoid impingement for the short period needed for it to pass around the screen to safety.

As a worst case, it may be determined that there is insufficient data of any kind to develop a best estimate of potential biological effectiveness of a technology. New technologies or technologies that are considered to be experimental due to limited evaluations to date could fall into this category. In such cases, it is likely that some type of laboratory or pilot-scale field study will be needed to obtain the data necessary to predict effectiveness. Such studies have been common in the past and have advanced the state-of-the-art in fish protection.

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Chapter 18
Fish Impingement and Prevention Seen in the Light of Population Dynamics

Maarten C. M. Bruijs and Colin J. L. Taylor

1 Introduction

Power plant and other industries that have once-through cooling water systems withdraw large amounts of surface water from adjacent water bodies such as rivers, lakes, estuaries and coastal areas. Electricity generation accounts for over 50% of all water usage in the industrialised countries and for almost 75% of industrial usage (Turnpenny and Coughlan 2003). Thermal power plants require 40–60 m^3/s cooling water per 1,000 MWe. The cooling water intake structures are specifically designed to provide this amount of cooling water under all circumstances, and many different types of configurations have been developed since the early beginning of electricity production.

Organisms that are not able to overcome the water current by their swimming capacity are withdrawn along with the intake water (kelso and Milburn 1979). This specially holds for ichthyoplankton and juvenile fish. In many cases, >80% of the impinged fish population has a size of <20 cm (Turnpenny 1988).The impingement of fish rarely leads to problems with power plant operation, i.e. clogging of screens. Only ingress of large amounts of jellyfish, debris or algae may endanger the power plant operation by clogging of cooling water filter screens. Damage and mortality among impinged fish is undesirable from an ecological perspective. Ingress of fish and following mortality may have a significant impact on the natural fish population in the water body from which the water is withdrawn. In Europe, European legislations, such as the Water Framework Directive (WFD), Integrated Pollution

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Prevention & Control (IPPC) (EIPPCB 2001), Habitat Directive and new national cooling water guidelines, are, more or less indirectly, requiring new national rules to address the impingement and entrainment of fish by cooling water intake systems. These regulatory developments are leading to stricter measures to improve the ecological water quality. Large industrial intakes may not impair the goals set out in the WFD, i.e. reaching a Good Ecological Status in European water bodies.

Since many years cooling water intakes have been identified as having potential adverse impact on fish due to impingement/entrapment and entrainment (Langford 1983; Kennish 1992; Hadderingh and Jager 2002). As a result, to measure the magnitude of this impact, many studies have been undertaken over the last 3 decades. The effects of cooling water intakes of thermal power station are well studied in comparison to other industrial water withdrawals.

2 Fish Impingement and Entrainment

Fish are withdrawn as ichthyoplankton, as juvenile fish or adult fish. Before the intake cooling water is pumped through the cooling water system, it is mechanically screened to remove flotsam, debris, fish and other organisms. When fish are drawn in with the cooling water, they can become impinged or entrained. There are many factors involved in this (Taft et al. 2000, see Table 18.1), and the importance and combination of relavant factors can differ strongly between locations.

Impingement occurs when fish is entrapped on mechanical barriers, i.e. trash racks and fine screens that are installed to protect the downstream equipment suchs as pumps and condenser from damage or clogging. Survival of impinged fish depends on biological factors concerning the environmental conditions and the fish, technical factors with respect to the location and layout of the cooling water intake as well as the operation of the screens. When the impingement continues for a long time, the fish may suffocate because the water current prevents gill covers from opening. If the fish is impinged for a short period and removed, it may survive; however, it may lose its protective slime and/or scales through contact with screen surfaces or from the high pressure water jets designed to remove debris from the screens. Juvenile and adult fish are in general able to withstand the cooling water velocity when approaching the trash rack, provided the velocity does not exceed the fish swimming capacity. Fish eggs, larvae and 0+ fish are in general drawn in passively as they are more or less present as plankton mostly during the night when fewer predators are present.

Entrainment occurs when small-sized fish such as ichthyoplankton (eggs, larvae and postlarvae of fish) and small fish (usually 0+) are able to pass the fine mesh screens and are pumped through the entire cooling water system. There, they are subjected to numerous sources of stress. These include mechanical damage by physical contact with surfaces of pumps, pipes and condensers, pressure damage, shear damage by complex water flows, thermal damage and toxicity damage by biocides. From a population perspective, ichtyoplankton and juvenile fish are the

Table 18.1 Summary of factors affecting involvement of aquatic species with the intake resulting in impingement and entrainment and factors affecting impingement and entrainment mortality (after Taft et al. 2000)

Involvement factors		Mortality factors	
Impingement	Entrainment	Impingement	Entrainment
Location of the intake relative to areas of fish concentration	Location of spawning and/or nursery areas in relation to the cooling water intake	Species sensitivity to physical stresses	Organism sensitivity to physical stresses of entrainment
Species seasonal occurrence and non-random vertical and cross-sectional distributions	Seasonal occurrence of species, including occurrence in relation to seasonal changes in power plant operation	Fish behaviour (both in avoiding the intake or when encountering the intake)	Organism sensitivity to thermal stresses
Species swimming ability	Vertical distribution and movements of species	Intake screen type and operation	Acclimation temperature
Species exposure to physiological stresses	Cross-sectional distribution of species	Deployment of other fish protection technologies	Salinity of the source water body
Intake design features	Swimming ability of species and life stages		Losses due to biofouling predation
Water quality	Growth rates and factors affecting growth		Transit time through the cooling water system
Velocity and related hydraulic phenomena	Species-specific morphometry		Losses due to biofouling treatment
	Far-field hydrologic/hydraulic conditions that determine the probability that organisms will be transported into the zone of an intake's hydraulic influence		

organisms of primary concern, because they have relatively long generation times. However, for some fish species, the intake represents a double jeopardy situation where the same population is subject to increased mortality through entrainment of eggs and larvae and additional mortality to juveniles and adults through impingement.

The extent to which fish are drawn in is dependent on, among other factors, the age and length of the fish. Fish larvae drift passively with the water current. Fish larvae and juvenile fish are drawn in because they can hardly withstand the water current and are passively drawn in with the intake water. The main ingress occurs during the night because they cannot orientate themselves in the water current during dark periods. It was found at the Bergum power station in the Netherlands, that the number of fish impinged during the night is 5–10 times higher than during the day. Only at a later developmental stage when their sideline organ is fully developed they can sense differences in water currents. The fish will then show more resistance against the cooling water flow. Fish older than a year are only impinged to a small extent. Owing to their length, fish larvae are able to pass the cooling water screens, pass the condenser and are discharged with the heated cooling water. Mortality among entrained fish is mainly due to mechanical stress and temperature shock in the condenser or because of impingement against mussel sieves. As the fish become larger during the growth season, part of the fish get impinged against the screens. Also, as the fish become larger their swimming capacity increases as thus their ability to withstand the water current increases.

2.1 Seasonality

In the Netherlands, the most important species that are withdrawn at power station located at fresh water systems, are roach, bream, pike perch, perch eel and smelt (Hadderingh and Van der Stoep 1986). At coastal power station it mainly concerns herring, sprat and gobies. The extent to which fish are impinged depends to a large extent on the developmental stage of the fish. The major part of impinged fish exists in individuals younger than 1 year, i.e. 0+ fish: fish larvae with a length of 6–12 mm and juveniles with lengths up to 8 cm. About 90% of the impinged fish are younger than 1 year and have a length of 4–10 cm. The number of fish that is impinged can vary strongly between locations. At eight monitored power stations in the Netherlands, the estimation of the yearly ingress of fish varied between 14×10^3 at the Maas power station and 16.10^6 at Bergum power station. The amount of fish is firstly determined by the species composition and population density of entrainable organisms in the vicinity of the cooling water intake. This can vary strongly from one location to another and from year to year due to spawning success and other environmental factors. Next to this, at each particular site the ingress of fish is determined strongly by the technical design and location of the intake. Foremost among them, the location, depth of water intake, water velocity and flow direction are important factors.

The pattern of fish ingress is mainly correlated with the development of young fish. Most fish are impinged during the spring (fish larvae) and the summer period, which is mainly caused by the presence of massive numbers of young fish in these periods. The rest of the year the number of impinged fish is relatively low due to natural decrease of the population of young fish and increasing swimming capacity of the fish. In the Netherlands, most freshwater species spawn in the period April–May. The fish larvae with a length of 6–12 mm are abundant during the period May–June. This life stage is often impinged in very large numbers, and due to the small size, this life stage will pass through the meshes of the screens. After the fish have reached a length of 3 cm during the second half of June (or earlier or later, depending on water temperature), fish get impinged against the screens. Hereby, the ingress of fish becomes visible. The peak of fish impingement is in the period July–August. In some years, significant number of fish are also found in September, depending on the yearly varying biological conditions and water temperature.

2.2 Behaviour

The behaviour of fish, which differs between species and age classes, in the environment from with the cooling water is withdrawn, is an important factor that determines the chance of impingement (Taft et al. 2000). The vertical distribution and movement of fish in the water column in relation to the vertical position of the cooling water intake influences the risk of impingement. Many of the fish that are important with respect to impingement, are not randomly distributed over the water column. The distribution of fish is mainly caused by habitat preferences of the fish, but there are also clear differences in vertical distribution between seasons and even daily differences occur. Some fish species mainly occur near the bottom, the benthic species. Other species occur at higher levels, pelagic species, which also often show schooling behaviour. At most cooling water intakes, the pelagic species are of highest concern.

3 Survival of Impinged Fish

The survival of impinged fish varies strongly between 0 and 100%. The survival of the physical stress during impingement also depends on size and life stage of the individual fish. The main factors determining survival are the design of the intake and operational conditions that influence the physical stress. Continuous operation of the screens, proper wash-off systems and fish return gutter with debris separation increase survival of the impinged fish. However, many intakes are not fitted with such features, or have implemented these under sub-optimal conditions, such as long distances between the cooling water inlet and outlet. An indication of the survival of marine fish species on cooling water screens is provided by Travade and Bordet (1982) (Table 18.2). The differences between fish species are clear.

Table 18.2 Survival percentages of several marine fish species at the Blayais power station at the river Gironde, France (Travade and Bordet 1982)

Resistance to damage	24-h survival (%)	Fish species
High	100	Paling, adult flounder, prik, bass
Reasonalbe	60–80	Juvenile flounder, sole, adult mullet, stickleback
Low	50	Shrimp
Sensitive species	10	Gudgeonl
Very sensitive species	0	Sprat, herring, Alosa, smelt, juvenile mullet, juvenile zeenaald

Survival chance (effectiveness of the screen installation) depends on biological factors and and configuration of the screening installation itself. The main factors are as follows:

Fish species: for example, smelt and *Alos* sp. are very sensitive, sticklebacks and eel are strong species
Length of the fish: small fish are often more sensitive that large fish
Water temperature: at higher temperature mortality is higher
Water jets and return system: a low pressure wash-off (10–15 psi) and smooth return gutters
Contact time: when the screens are standing still for longer periods, the chance increases that fish, due to the approach velocity in front of the screen, are pressed against the screen. Such physical stress and subsequent damage and mortality are lower when the screens are operated continuously.

4 Effect on Fish Populations

Mortality of fish that are impinged on the inlet screens or entrained with the cooling water has a negative effect of cooling water withdrawal. Adverse aquatic environmental impacts occur whenever there is entrainment or impingement damage as a result of the operation of a specific cooling water intake structure. The potential population-level impact depends on several factors including location of the intake structure, adjacent habitats, flow rates and intake velocities as well as seasonality and tidal state. The critical question is whether the population-level impact is significant. The impact of impingement and entrainment mortality on fish population levels is generally not known and is difficult to assess. Several parameters have to be estimated, among others the species-specific impingement throughout the year, the consequent mortality, the estimated population abundance and the natural mortality. Also, the magnitude of impact should be estimated both in terms of short term and long term impact. Important factors are the absolute number of fish impinged or larvae entrained on a monthly or yearly basis, the percentage of fish or larvae in existing populations which will be impinged or entrained, the absolute and percentage damage to any endangered species or commercially valuable and/or sport fisheries yield. Also, it is important to determine whether the impact would jeopardise the protection and propagation of a balanced fish population in the water body from which the cooling water is withdrawn (long term impact).

An example of a large scale study is provided by Hadderingh and Jager (2002), in which they conclude that it is far from simple to estimate the effect of impingement on estuarine fish populations. Most of the impinged fish are not of commercial interest and do not have long-term catch statistics. Hadderingh and Jager (2002) made an attempt for the herring impinged at the Eems power station (the Netherlands). The juvenile herring originate from the spawning populations at the Dogger bank and the English Channel, which consist of an estimated number of 4×10^{10} 0-group individuals (Corten 1996). The impingement in 1996/1997, consisting of 0- and I-group herring (<16 cm), was 5×10^{6}, which is about 0.01% of the herring recruits. For flounder, the impingement in 1993 can be related to the abundance of the 0-group on the tidal flats in the Dollard (Jager 1998). The latter was estimated at 2.4×10^{6}. The estimated impingement of flounder was 6,000 in 1993, which is about 0.25% of the juveniles in the Dollard. However, flounder is susceptible to bycatch in the shrimp fishery which takes place in the Ems estuary. No comparison of the relative impact of both anthropogenic factors can be made because quantitative data of the bycatch are lacking. Hadderingh and Jager (2002) furthermore mention that special attention is needed for those fish species whose populations are under threat. Red List species are the eel, twaite shad, lamprey, lampern and salmonids. Of these, the twaite shad is probably the most vulnerable to impingement.

5 Assessing Population-Level Effects of Impingement and Entrainment

The effect of fish mortality on populations depends on ecological aspects on which there are many uncertainties with respect to population dynamics. These aspects include the following:

- The number of impinged fish
- The survival rate of impinged and entrained fish
- The population size in the adjacent water body
- Ability of the population to recover
- Presence of other threats to the population
- Presence of sensitive species
- The natural mortality in a population

During the early 1970s and 1980s, several studies have been performed on the effect of impingement on local fish populations in the Netherlands. The results of these studies are shortly listed below.

During 1979/1980, Van Densen and Hadderingh (1983) investigated the effect of fish mortality by the Bergum Power Station on the fish population in the Lake Bergummermeer, the Netherlands. They found that during the spring, the mortality among larvae of pike perch and smelt (length 6–15 mm) was, respectively, 5 and

14% of the entire larvae population in the lake. They estimated that this mortality equals the natural mortality. In principle this can be regarded as a high impact. However, the mortality is compensated by the influx of larvae from other areas. In the period July–September, the mortality of fish (length 5–8 cm) at the power station was estimated to be 0.2% per 24 h, thus a strong reduction.

A similar study was performed at the Flevo Power Station at the Lake IJsselmeer, the Netherlands during the period May–June in 1974 and 1975. The species found mainly were smelt, percids and cyprinids, but also sticklebacks and eel. Based on calculations, a total damage percentage of 2–4% at population-level was expected, depending on the larvae distribution in the Lake IJsselmeer. The long-term effects were not investigated. If the total mortality of the impinged fish was 100%, the total damage would be 3–5% of the population. The average natural mortality during May and June is, however, much higher and can be >90% for the ichtyoplanktonic phase.

Greenwood (2008a) has recently published data from a long-term monitoring study of impingement at the Longannet Power Station (Forth estuary, east Scotland), the largest estuarine or coastal electricity generating station in the UK. The study investigated fish mortality on the cooling-water intake screens in 1999–2000. This study revealed that more fish die at Longannet Power Station than at any other single British estuarine or coastal power station, in accordance with the station withdrawing more water than any other power station. High numeric losses of commercial species' juveniles potentially translate into high losses of equivalent adults compared to other locations. However, the estimated future loss to commercial fisheries through mortality of juveniles at Longannet is minimal compared to the losses attributable to the fisheries themselves, whether through landings, discards or by-catch. Of greater relevance is the fact that the losses of all species occur in a relatively limited geographic area. Natural interannual variability in population size meant that changes in fish abundance through reduced impingement (or entrainment) mortality generally could not be detected from long-term trawl data. In addition, the monitoring through trawling and of cooling water intakes proved to be a valuable tool for estuarine fish sampling (Greenwood 2008b; Greenwood and Maitland 2008).

To exactly assess the effect on fish populations on a large geographical or small local is a complicated, difficult and costly effort. In general, only little quantitative data are available on the population level mortality of fish due to specific factors. Although much research is done, available data are often scattered such that it is not possible to assess the impacts at a national level. Also, when data are available, this must be related to existing fish populations and information on that is largely lacking for most species.

6 Modelling Entrainment and Impingement

Modelling of the magnitude of entrainment and impingement loss is typically based on sitespecific information on the density of susceptible life stages in the vicinity of the intake, or on measured rates of entrainment and impingement, and the mortality rates associated with the entrainment and impingement processes. Where necessary, information on the life history characteristics and population dynamics of a representative species can usually be obtained from the scientific literature for the same or for closely related species. The range of prospective methods extends from relatively simple to highly sophisticated quantitative models of population dynamics.

In order to estimate the impact of impingement and entrainment at population level, several modelling approaches have been developed. Such models are used to determine the relative importance of impacts on different life stages by translating them into impacts on adult abundances and harvest levels (Newbold and Iovanna 2007). The variety of methods to evaluate power plant intake effects that has been developed reflects the many differences in power plant locations and recource settings. MacCall et al. (1983) made a review of various approaches and divided them into those offering a judgement on the presence or absence of impact and those that describe the sensitivity of populations to varying operational conditions. Impact assessment approaches that are generally used include methods used in estimating the calculation baseline, such as annual estimates of total individuals impinged and entrained and annual estimates of total biomass impinged. Methods for evaluating the effects of cooling water intake structures and cost benefit analyses include adult-equivalent loss (AEL) (Horst 1975; Goodyear 1978), fecundity hindcasting (FH) and production foregone (PF) (Rago 1984). Methods for evaluating population-level effects and estimating appropriate restoration effects include empirical transport models (ETM).

These models can be divided into two general approaches: demographic models rely on species life history information such as the equivalent adult model (AEM) that includes AEL and fecundity hindcasting (FH) and models that estimate the conditional mortality on a population resulting from power plant cooling water intake structure operations such as the ETM.

6.1 Assessing Effects of Impingement

Impingement mortality studies in general estimate the rates, i.e. number and biomass of fish per volume water flowing per time into the plant. Annual impingement estimates are calculated by extrapolating the impingement rates measured during normal operations over the survey periods. The impingement mortality estimates for each survey period are added to provide annual estimates for each species. These annual estimates can be combined with estimates of equivalent adults from entrainment to provide total impact assessment. The demographic models used to calculate such estimates are limited to species for which sufficient life history information is available.

6.2 Assessing Effects of Entrainment

Estimates of daily and annual larval entrainment are generally calculated from data obtained from entrainment stations. Estimates of entrainment loss, in conjunction with available demographic data collected from fisheries literature, will permit

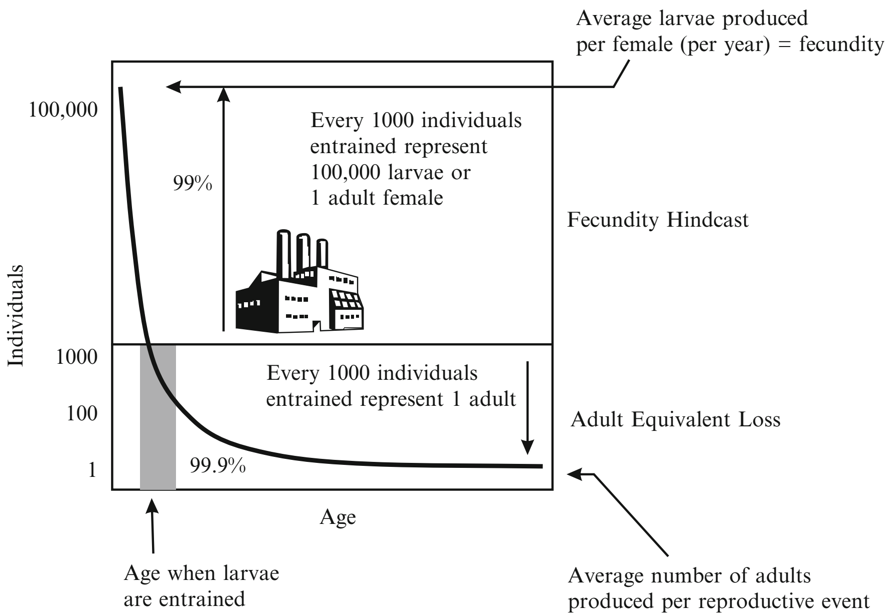

Fig. 18.1 Estimation of adult entrained and impinged fish losses in industrial cooling water systems

modelling of AEL and fecundity hindcasting (FH) (Fig. 18.1). Data from sampling of the potential source populations of larvae can be used to calculate estimates of proportional entrainment (PE) that are used to estimate the probability of mortality due to entraiment using the ETM.

The EAV (equivalent adult value) method, as described by Turnpenny and Taylor (2000), is a procedure where the numbers of fish of any age are standardised to the number that would be expected to be alive at the age when 50% of the stock would mature. Thus, if a fish matures when 3 years old, many millions of eggs or larvae may represent a single “equivalent adult”, and the EAV will be a tiny fraction of unity, whereas a fish older than 3 years will have an EAV of greater than one. The purpose of the EAV method is to allow fish captured at any stage of their life cycle to be compared on an equal footing with fish of commercial size. It is important to note that the EAV method does not take into account density-dependent factors (such as rates of predation, parasitism, feeding success) that might tend to increase the survival, growth and reproductive rates of individuals left in the population when some of their competitors are removed. The values given should therefore be regarded as overestimates.

An example of the application of EAV method (Horst 1975) is provided by Turnpenny (1988). He considers the significance of impingement mortalities at estuarine sites in Britain for six commercially important species: cod (*Gadus morhua*), whiting, (*Merlangius merlangus*), plaice (*Pleuronectes platessa*), dab (*Limanda limanda*), sole (*Solea solea*) and herring (*Clupea harengus*). Life tables are used to establish expected survival trajectories for each species and to compute reproductive potential. Each fish killed on intake screens is then considered in terms of the fraction of the reproductive potential of a single adult at maturity, and is ascribed an "adult equivalent" value. Total catches of mixed juveniles and adults are then presented as "adult equivalent" values. The results are then compared with commercial landings data. The results show that catches by power stations are trivial in comparison with commercial landings.

Newbold and Iovanna (2007) describe a general modelling framework for evaluating the population-level impacts of cooling water withdrawals, applying the framework to 15 harvested fish stocks. The model used is a generalised age-structured model written in descrete time and it can incorporate density dependent survival in one or more of the sub-adult life stages. For the model, they apply life history parameters and information on reproductive rates and historic harvest levels for each species. The results show that the effects of cooling water withdrawals appear to be minor for most harvested fish stocks, but may be severe for a few. Although for some stocks the effects seem to be minor at a large geographical scale, the results do not rule out the possibility of higher impacts in local areas. If no cooling water withdrawals would take place, the changes in equilibrium of fish stocks sizes was estimated to be less than 1% in 10 of the 15 cases and 20–80% in three cases. The results show to be robust for fish stocks with minor impacts, but the results for fish stocks with severe impacts are uncertain. The results indicate that the population level impacts of cooling water withdrawals may be negligible for many fish stocks, but could be severe for a few.

Cakiroglu and Yurteri (1998) discuss a mathematical model that predicts the long-term effects of once-through cooling water systems on local fish populations. The fish life cycle model simulates different life stages of fish by using appropriate expressions representing growth and mortality rates. The heart of the developed modelling approach is the prediction of plant-caused reduction in total fish population by estimating recruitment to adult population with and without entrainment of ichthyoplankton and impingement of small fish. The model was applied to a local fish species, gilthead (*Sparus aurata*), for the case of a proposed power plant in the Aegean region of Turkey. The simulations indicated that entrainment and impingement might lead to a population reduction of about 2–8% in the long run. In many cases, an impact of this size could be considered rather unimportant. The authors concluded however that in the case of sensitive and ecologically valued species facing extinction, necessary precautions should be taken to minimise or totally avoid such an impact.

Turnpenny and Taylor (2000) have made an assessment of the effect of the Sizewel A and B Nuclear Power Stations, which are located on the Suffolk coast of East Anglia, on fish populations. Both power stations are direct cooled with a total flow of 80 m^3/s. The entrained fish are removed by mechanical screening systems ("drum" screens) to avoid CW condenser blockage. The entrained ichthyoplankton passes through the entire cooling system and is discharged back to sea along with the heated water. The later life stages of fish and other material that become impinged upon the drum screens are removed from the water. At Sizewell B, provision is made to return the more robust species of fish back to the sea alive. Between 1981 and 1982, the Central Electricity Generating Board (CEGB), then owner of the the Sizewell site, and the Ministry of Agriculture, Fisheries and Food (MAFF) carried out a joint study of the fish catch after it was announced by the CEGB in the late 70s that Sizewell B would be built. The study showed that the losses on the A station of commercially important species, including plaice (*Pleuronectes platessa*), sole (*Solea solea*), dab (*Limanda limanda*), cod (*Gadus morhua*), whiting (*Merlangius merlangus*) and herring (*Clupea harengus*), amounted to 66 tonnes per year, then valued at £28 000 per annum. This estimate included an allowance for the potential yield of fish which were below the statutory minimum landing sizes when captured, assuming that the rates of growth, mortality and exploitation would have been similar to those experienced by other fish within the North Sea fisheries. The catch rate was summarised by observing that it was "less than that of a single small, inefficient trawler" and therefore of minor significance. It was also concluded that no impact on local fisheries could be defined, as stocks within the North Sea tend to migrate over large distances. Nonetheless, it was agreed between CEGB and MAFF that a number of reasonably practicable opportunities existed for reducing the catch of the B station, such as appropriate location and design of the cooling water intake and the incorporation of the "trash" return system. It was also agreed that, following commissioning, the predictions on fish catch would be validated and the relative success of the various mitigative measures assessed.

From 1991 onwards, the original survey data were re-analysed to assess any likely changes resulting from trends in North Sea stocks. Assessments were made of losses due to ichthyoplankton entrainment at the A station. Experimental studies were undertaken to determine mortality rates of ichthyoplankton passing through the CW system; on the commissioning of the B station, catch rates were compared with the A station to determine whether design and positioning improvements in the B station intake were beneficial. Survival rates on passage through the fish return system on the B station were measured. Comparisons of losses of juvenile fish due to the power stations with those due to other sources, such as the East Coast shrimp fisheries, were undertaken, to provide an alternative context within which to view the findings. An expert system known as PISCES was used to make estimates of impingement rates for other English East Coast power stations, so that the combined effects of these stations acting in concert could be determined. Other fish-related studies were undertaken to determine, for example, any possible impact of fish losses on the availability of food for fish-eating birds at the neighbouring Minsmere nature reserve. The results of these studies are presented in terms of EAVs. The main conclusions of this study are as follows:

- Comparison of the predicted losses of commercial fish species due to impingement and entrainment at Sizewell A and B Power Stations with commercial landings from adjacent waters (ICES area IVc) shows that the power stations losses amount to about half of 1% (0.54%) of the recorded UK and international landings when expressed in Equivalent Adult terms. Of the individual species, Equivalent Adult losses of only sole (1.5%) and herring (5.8%) exceeded 1% of the commercial landings figures.
- The commercial value of the losses due to both stations is estimated at £0.52 million per annum (1994 values), with the bulk of this value being ascribed to

losses of sole (£304,425: 93% as entrained eggs, remainder impinged), whiting (£83,821; 100% as impinged juveniles or adults) and herring (£116,227: 24% as entrained larvae and post-larvae, remainder impinged).
- The commercial value of the loss due to the B station (£305,853) is estimated to be only 40% higher than that due to the A station, despite the fact that the CW demand is twice as large. This reflects improvements in intake design and location, and the successful operation of the trash return system on the B station.
- All of the above estimates are based on the Equivalent Adult evaluation method. This does not take into account possible density dependent population regulation mechanisms, which may serve in practice to reduce the predicted levels of effect. The figures should therefore be regarded as overestimates.
- The trash return system at Sizewell B allows viable return to sea of several of the more significant species involved. Flounder, plaice, sole, dab and bass all have been shown to have high survival rates through the system (80%), and whiting a lower rate (48%). The system also returns brown shrimp, at a survival rate of 90%. Survival of these species without the return system would be zero.
- Trials of an acoustic deterrent system associated with the on-shore intake at Hartlepool Power Station on the Tees estuary have shown that significant reductions in impingement rates (16–80%, depending on species) can be achieved. An acoustic system could have benefits at Sizewell but the practicability of establishing and maintaining a wide spread of permanent seabed acoustic sources around such an offshore intake is considered to be low. Given the proven success of the existing mitigative measures at Sizewell B (relating to intake design and position, and the return system), an acoustic system is not recommended as a priority at this particular site.

7 Guidelines on Fish Impingement

Withdrawal of cooling water from surface water systems, i.e. lakes, rivers and coastal waters, is regulated by a permit system. Existing (inter)national legislation and guidelines in European countries, such as the WFD and IPPC (BREF Industrial Cooling), however do not provide clear guidelines for the evaluation of fish impingement and entrainment (i.e. assessment of significant effect on fish populations), nor do they provide guidelines and Best Available Technologies to reduces the population-level effects.

7.1 Regulations

7.1.1 Europe

The European WFD (EC 2000) has the goal to achieve a good ecological status (GET) or good ecological potential (GEP) for the European waterbodies. This status is partly defined by the fish community. Because fish migrate over short to very long distances, the migration possibilities play an important role, as well as the quality of spawning and nursery areas.

Further, the European Habitat Directive determines whether the "activity" cooling water withdrawal from protected areas, i.e. Natura2000 areas, has effects on population of species mentioned in its annex II (effects in sea- and brackish water systems). In theory, the license applicant must provide details on fish impingement, evaluation fish impingement and preliminary conclusion. The legislator evaluates and determines a final conclusion. When a significant effect is found, a new license application is only possible after implementation of measures. In practise, the licensing process is much more complex. There is no proper procedure available for evaluation of the data. Also, population dynamics of fish and dynamics ecosystems are difficult to elucidate. Furthermore, the Habitat Directive provides no definition for "significant effects". So, evaluation of the results of monitoring or modelling is very difficult.

British legislation covering operation of power stations is represented by the 1989 Electricity Act. Schedule 9 §3(3) requires electricity generators to "avoid, so far as possible, causing injury to fisheries or to the stock of fish in any waters". However, the definition of "injury" is clearly open to interpretation (Greenwood 2008a).

In the Netherlands, there is a new cooling water assessment guideline (CIW 2004) for discharge of heated cooling water in the Netherlands. The regulation also provides some guidelines for withdrawal of cooling water. For cooling water withdrawal from channels, (tidal) harbours and rivers, no significant effects are allowed and the screening installation must contain a functioning fish return system. Also the amount of cooling water withdrawn, i.e. the cooling water flow, should be kept as low as possible. For cooling water withdrawal from the North Sea and estuaries, companies must strive to withdraw least amount of cooling water as possible and withdraw from outside spawning grounds, nursery areas for juveniles and migration routes. Within the CIW-Guidelines the emphasis is on prevention of effects, i.e. keeping the ingress of fish and impacts on a population-level as low as possible. There is however no further detailing of how to deal with impingement and entrainment. There is, however, a clear difference between the reduction of entrainment or impingment mortality, or a reduction of entrainment or impingement itself. Also, no clear definition of significant effect is provided, which makes it difficult to asses the need for measures.

7.1.2 The USA

In the USA, the EPA developed regulations under section 316(b) of the Clean Water Act (USEPA 1977) which are of great significance to the owners and operators of many power plants. To minimise adverse environmental impact, section 316(b) requires that the location, design, construction and capacity of cooling water intake structures reflect the best technology available (BTA). Development of the regulation takes place in three phases: Phase I, which was completed in late 2001, applied to new facilities. Phase II, which was issued in February 2004, consists of regulations applicable to existing large facilities, defined as those withdrawing more than 2 m^3/s cooling water. This law requires that the BTA is used to minimise impacts on marine life and requires that impingement is reduced by 80–95% and entrainment by 60–90%. Phase III consists of regulations applicable to small existing facilities that withdraw less than 2 m^3/s. In January 2007, the US second Circuit Court of Appeals decided in Riverkeeper, Inc., v. EPA that many parts of the Phase II rule were invalid or needed to re-evaluated by EPA. Thus, as of March 20, 2007, the Phase II rule was suspended.

8 Strategies to Reduce Fish Impingement and Entrainment Mortality

Because of the stringent legislations, there is a great deal of interest in studying the effects of cooling water withdrawal and research on mitigation technologies, with the aim to implement operational and/or technological measures to reduce impingement and entrainment mortality. Unlike in the USA where the EPA through the CWA section 316b requires a clear reduction of impingement, in Europe the legislative authorities demand more information on the possible effects and power plants must implement measures to reduce population-level impacts of fish ingress when the effect is significant. However, as mentioned before, to asses the significance of fish mortality due to cooling water withdrawal on a population level is very difficult. Also, European legislation and guidelines do not provide a clear definition of significance. A general and unequivocal assessment method is not available.

For the cooling water intakes of new installations, the IPPC-Directive requires the application of Best Available Technologies (as described in the BREF Industrial Cooling guideline), for the design and operation of cooling water intakes. These guidelines also hold for existing installations, but implementation of these measures is often not cost-effective. However, there are no specific BATs describe to prevent the ingress of fish. For all once-through cooling water system it is needed that they are designed optimally and foreseen with protective measures and a fish return system. As BAT approach it is mentioned that studies are performed on the biotope, as well as migration and spawning and nursery areas. If and in what way ingress of fish is to be mitigated is location specific and must be determined through investigations on site. In consultation with the legislator, it must be discussed which cost-effective measures are applicable, both economically and technically.

The technical possibility to reduce fish ingress, as mentioned in the BREF Industrial Cooling, is to optimise the construction of the intake with respect to flow velocities (approach velocity in front of the trash rack of 0.1–0.3 m/s maximum), continuous operation of the fine screens, functional fish return system and increase of the mesh size of the fine screens (>5 mm). Optionally an acoustic or light system can be implemented to reduce ingress of fish.

Thus, as a first step it is important to design the cooling water intake in a "fish-friendly" way. This is possible by taking into account the guidance of the BREF Industrial Cooling (EU-IPPC Directive BAT Reference Document). In addition to the above, the UK Environmental Agency has published a best practice guide (EA 2005) on screening for intake and outfalls, which provides best practices for different fish protection methods.

8.1 Trash Rack

For the trash rack, the important aspects are bar width (distance between the bars) and approach velocity. Fish have a natural hesitation to pass through trash racks. If the approach velocity is low enough (<0.3 m/s) and the bar width is proportional to the fish dimensions, the fish will not pass the trash rack. Large bar widths of >10 cm must be avoided, about 5 cm or even smaller (the trash rake system still needs to fit between the bars) would be better. However, a small bar width increases vulnerability to clogging with debris. A proper cleaning facility (trash rake system) must be designed for quick removal of the debris.

8.2 Filter Screens

The type of fine screen (band screen, rotating drum screen, etc.) is a technical choice, but several features must be taken into account. The requirements for optimal effect on the survival of fish are as follows:

- Continuous operation of fine screens (includes removal of debris, fish/jellyfish and washing).
- Using two water jet types, one "soft" jet for the removal of fish from the screen, and a second high pressure water jet to remove any debris.
- The fish return system gutter must have smooth walls and no sharp bends to avoid clogging of the gutter and fast flow through.
- The water for the jets and flushing the gutter must be retrieved from behind the filter screens so no debris is in the water. Preferably the water is non-chlorinated.

UK Environmental Agency best practice guide (EA 2005) includes a Design Best Practice of fish return systems. For the fine screens it mentions that it is important when specifying band or drum screens, which are to be used for fish return, to ensure that the design of the fish buckets in particular has been optimised for fish handling and evidence of this should be sought from the manufacturer. Other key points in fish return system design according to EA 2005 are the following:

- The screens should be capable of long-term continuous operation: intermittent operation is unsuitable for fish return. This means, in particular, that bearing life should be considered.

- The screen meshes should be smooth and "fish-friendly". Certain types of woven stainless mesh are commonly used for this purpose.
- The mesh size should be as small as is practical, and of no more than 6 mm aperture.
- Low-pressure backwash sprays (≤1 bar) should be used for fish removal; higher pressure jets may be used at a later point in the cycle to wash off debris.
- The geometry of the collecting hoppers should be checked to ensure that fish that are washed off the screens cannot fall back into the screenwell (an issue mainly on drum screens).
- Biocides should be applied downstream of the screens, unless it can be shown that the toxic risk is negligible.
- Fish return gullies should be smooth, with any joints properly grouted and finished. They should be a minimum of 0.3 m diameter; 0.5 m diameter or larger is preferred for long runs (>30 m).
- It is beneficial to enclose or cover fish return lines to avoid algal growth. Suitable access hatches or rodding points should be provided to facilitate maintenance.
- Where bends are required, swept bends of radius >3 m should be used.
- Dedicated fish return lines which discharge well blow the low water mark are preferred. Return on power plants via the heated water discharge should only be used where it can be demonstrated that survival rates will be acceptable.
- A continuous washwater supply should be provided that will ensure sufficient depth to keep fish immersed and moving along the return line.
- At coastal sites where there is a risk of occasional inundation by schools of pelagic fish, provision may need to be made for diverting the catch to collecting baskets. This can be necessary to avoid the risk of discharging large quantities of dead fish onto neighbouring bathing beaches.

In order to reduce the impingement and entrainment, a variety of fish protection technologies have been developed and operational measures are available (EPRI 1999). Depending on their mode of action, fish protection systems can be split into different categories: physical barrier, collection systems, diversion systems, behavioural barriers (Taft and Cook 2003). They can be applied singly or in combination. The available technologies can be divided into two main categories: first, measures that prevent the ingress of fish, for example, by applying an optimal design (e.g. low velocities, location, vertical position) of the intake and additional technologies that include diversion systems that actively guide fish to bypasses (e.g. angled screens and louvers), physical barriers that passively prevent fish passage (e.g. wedge-wire screens, submerged weirs and barrier nets), and behavioural barriers that take advantage of natural behavioural patterns in fish to cause repulsion or attraction (e.g. sound and strobe lights), such as light and/or sound to deflecting fish from the direct vicinity of the intake, and Second, measures to improve survival of fish that have become impinged, such as optimised screening systems (e.g. fine screens, low pressure washing jets, fish buckets) and a fish return system. The application of the technologies is very site-specific, depending on the technical possibilities determined by the layout of the intake structure, cooling water flows, characteristics of the water system from which the cooling water is withdrawn and the fish species and life stages involved. These aspects must be investigated and used in the design of the cooling water intake.

9 Concluding Remarks

Thermal power stations and industries with once-through cooling water systems withdraw large volumes of surface water for cooling. The withdrawal of cooling water has the potential to cause environmental impacts due to impingement and mortality of organisms, primarily fish, on screens that protect the intake system, and through entrainment and mortality of small organisms, primarily fish eggs and larvae, that pass through those screens and through the plant's entire cooling water system. At many power plants field studies have been undertaken to determine impingement and entrainment mortality. Such field studies have not been able to elucidate the effects on population level. The application of models to assess population level effects is a potential (alternative) method to assess the impact on fish populations or commercial fish stocks. However, it is difficult to fully apply such models for most species as specific data on many fish species and population dynamics are required. Specific data are available only for commercial species. Although many fish are drawn in, the results of many studies undertaken, mostly at estuarine power stations, indicate that the impingement and entrainment mortality do not affect natural fish populations significantly, nor do they affect the future fish stock available for commercial fisheries. The application of surface water from lakes, rivers or coastal waters for cooling is regulated by a permit system, which also covers the environmental effects such as the ingress of organisms. Existing (inter)national legislation and guidelines in European countries however, do not provide clear guidelines for the evaluation of fish impingement (i.e. assessment of significant effect on fish populations). This is, however, a necessity to be able to objectively assess the impact of fish ingress at any site and to justify the often expensive mitigation technologies.

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Chapter 19
Cooling Water Discharge Guidelines in the Netherlands: Recent Developments Through Advanced 3D Modelling

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1 Introduction

The average temperature rise of river Rhine at the border with Germany was found to be 3.3°C during the last 100 years, caused by canalisation, narrowing of the river bed, expending use of industrial cooling water and the overall temperature increase due to climate change. During summer, the background river water temperature of the rivers Rhine and Meuse passing the Dutch border rises up to 26–28°C. In fact, in the Netherlands a temperature drop in the range of 1–2,5°C is measured before the river water is discharged in the North Sea despite all heat discharges during its course to the sea.

Forecasts with respect to climate change show an increase of the surface water temperature in summer time and also unpredictable large fluctuations in river flow especially with low river discharge during dry periods in the summer. Also, forecasts with respect to the future electricity demand show an increase of 80% in 2030. Figure 19.1 shows the occurrences of heat waves in the Netherlands of 1900–2006. During the summer of 2003, which was a very hot summer with low river discharge, the danger of a shortage in electricity supply arose. The summer of 2006 was again a very warm period with the hottest July month in 300 years.

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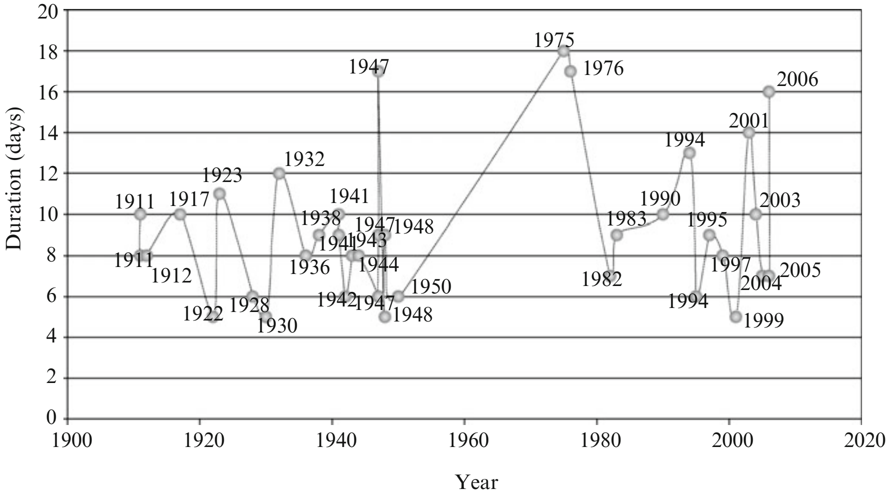

Fig. 19.1 Duration and occurrence of heat waves 1900–2006 in The Netherlands

Power plants and other industries are often applying once-through cooling water systems to remove the excess heat from the condensers. Although cooling water discharges in rivers were normally not critical in terms of environmental impact, the recent combination of low volumetric flow rates in the rivers combined with relatively high water temperatures showed the limitation of once-through cooling in a changing climate and the need for a renewed approach concerning the guidelines and consents for the industry. This novel approach should seek for possibilities for the industry to continue its activities on the one hand, but on the other hand aquatic life should be prevented from excessive thermal effects.

Another important point is that the Dutch water authorities have a zero-tolerance policy on permit exceeding. The former guideline was formulated by the Algemene Beraadsgroep Koelwater (ABK) (i.e. the General Commission for Cooling Water Issues) in 1975 and existed largely in emission- This regulation was, however, inadequate to cope with extreme summer conditions. As a consequence, from 1991, it was common practice to tolerate discharge temperatures >30°C due to "stage-4" conditions. In the Netherlands, new guidelines for thermal discharges have been developed in a more than 2-year intensive consultation with all those concerned (water authorities, power generation and large petrochemical and steel industries), resulting in a rather novel approach which is incorporated in a new law in 2006. The main items were: preserving a free gateway for migrating fish by accepting stratification of the heated water as best solution and an obliged 3D modelling for complex situations of the discharge area for evaluation of the cooling water discharge dedicated on the former item of fish migration and overall heating of the surface water.

The new immission guidelines (Rijkswaterstaat 2004) have been developed by a working group of the Commission for Integral Water Management. They are based on information from available literature and followed the CIW-immission procedures for substances (EC 2000). In order to realise this aim, literature studies have been performed in the area of effects on the aquatic environment due to discharge of heat. Also 3D-modelling studies on the distribution of discharged heat have been performed. From these studies the test criteria for the evaluation systematic have been derived for intake, outlet and mixing zone. The guidelines provide a table for channels, tidal harbours, rivers, North Sea and estuaries. For lakes, it is proposed to derive one generic criterion, as it holds that situations are mostly very different and in itself are difficult to compare. The new cooling water discharge guidelines are attuned to the new European legislation, i.e. the Integrated Pollution Prevention and Control guideline (IPPC) (EC 1996) (including the European IPPC Reference Document on the application of Best Available Techniques to Industrial Cooling Systems 2001) and the Water Framework Directive (WFD) (EC 2000). These regulations and guidelines request for adequate instruments to assess and control emissions and surface water quality of which 3D cooling water models showed to be a real support in the conceptual set-up for each industry.

The effects of impingement, exposure to the cooling water circuit and heating of the receiving environment have been studied for different aquatic organisms. It was found that fish are the most sensitive organisms to these stressors. For the determination of criteria, fish are therefore chosen as the main target organism.

Discharges impact of are assessed by the extent of its influence on the water system, both locally and at the aquatic system level. From literature studies, it follows that the restriction of cooling water discharge is important for the protection of the aquatic environment, but also that uncertainty exists with respect to the effects on population level, as well as to the standard that should be applied for the assessment.

Starting point is that significant effects due to the withdrawal of cooling water may not occur. In the new guidelines the generic temperature limit for cooling water discharge has been dropped. Instead of the temperature limit, the criterion of mixing zone has been introduced. Fish larvae and juvenile fish are highly abundant in spawning and nursery areas during the biological spring. Due to there small dimensions, these organisms are vulnerable to being drawn into the cooling water system. For fresh water systems the biological spring is the period from the first of March to the first of June. For marine water systems, next to the biological spring from the first of February to the first of May, the biological autumn from the first of September to the first of December is also of importance. Large scale withdrawal of cooling water from spawning and nursery areas during these periods is not desirable. In this respect the location and design of the cooling water inlet is important. When choosing a new (power) plant or industry this should be taken into account.

2 New Cooling Water Guidelines

The criteria mentioned in the table apply according to the outlines. For the full overview refer to the appendix 2 of the guideline (Rijkswaterstaat 2004) (Table 19.1).

1. The criteria mentioned in the table apply according to the outlines. For the full overview, the reader is referred to the appendix 2 of the guidelines.
2. Permitted heating: 3°C for cyprinid waters, 2°C for shellfish water and 1.5°C for salmonid waters.

Table 19.1 Old and new heat discharge guidelines which include three criteria: (a) withdrawal at the inlet, (b) mixing zone at the outlet and (c) elevated temperatures in the receiving surface waters

Parameter	Old ABK-guidelines		New guidelines
Emission-demands (*generic*)			
T cooling water	Fresh water: ≤30°C		
T cooling water	Marine water: ≤30°C		
ΔT cooling water	Fresh water	≤7°C (summer)	
		≤15°C (winter)	
	Marine water	≤10°C (summer)	
		≤15°C (winter)	
Heating	≤3°C		≤3°C in relation to background temperature to a maximum of 28°C
Immission demands (*water system related*)			
Channels/tidal harbours			
Withdrawal	–		No significant effects in spawning and nursery areas of juvenile fish, proper fish return system, reduced cooling water flow (optimisation)
Mixing zone (T > 30°C)	–		<25% cross section
Rivers			
Withdrawal	–		No significant effects in spawning and nursery areas of juvenile fish, proper fish return system, reduced cooling water flow (optimisation)
Mixing zone (T > 30°C)	–		<25% cross section
North sea			
Withdrawal	–		Striving for the least possible withdrawal, not in spawning and nursery areas of juvenile fish or migration route, proper fish return system
Mixing zone (T > 25°C)	–		The mixing zone may no touch the sea bed
Estuaries			
Withdrawal			Striving for the least possible withdrawal, not in spawning and nursery areas of juvenile fish or migration route, proper fish return system
Mixing zone (T > 25°C)	–		<25% cross section

3. Heating is related to the background temperature on the border of (parts of) the water system.
4. Maximum temperature: 28°C for cyprinid waters, 25°C for shellfish waters and 21.5°C for salmonid waters.
5. The part of the water system (in the vicinity of the point of discharge), that due to the discharge of heat is brought to a temperature of ≥30°C and is bounded by the spatial 30°C-isotherm (fresh waters) or the 25°C-isotherm (marine waters).
6. Exceptional case at high background temperatures (>25°C): during one continuous period of maximal 1 week in July/August, the temperature at the border of the mixing zone is allowed to be 32°C. If this approach leads to problems with its practical implementation, the administrator can make a reasoned deviation.
7. The administrator can, based on specific information with respect to the considered water system, make a reasoned deviation.
8. For fresh water particularly important during the biological spring (March 1–June 1) and for marine waters during the biological spring (February 1–May 1) and the biological autumn (September 1–December 1). Quantitative, generic criteria for withdrawal cannot be provided. For new situations, it must be assessed through EIA-procedures whether, based on local specific information, the activity can be allowed or not.
9. The background temperature is assumed to be 22°C.

The second ministerial Indicative Long-range Plan for water (Indicatief Meerjaren Programma (IMP)-water), states that the objectives for water quality do not apply within the mixing zone in the vicinity of the point of discharge. For this aspect, the evaluation systematic relates the volume of the mixing zone with the level of Ernstig Risico (ER) (i.e. the level of Serious Risk), which is analogous to the immission procedures for substances. Based on the literature study, the ER-level for heat has been established at respectively 30°C for fresh water and 25°C for marine waters. The mixing zone is furthermore bounded by the maximum cross section of 25% of the total wet cross section of the water system. The mixing zone determines the maximum allowable discharge temperature at a given water system discharge and cooling water discharge, provided that the criteria for heating and withdrawal are also met. From calculations it appears that the "cross section criteria" also limits the volume of the mixing zone for discharges with a temperature ≥30°C. For this reason, the criterion of mixing zone volume has not been incorporated in the evaluation systematic separately.

The literature study on the effects of heat discharges on fresh water environments indicates that in exceptional situations, when the (natural) background temperature of the surface water increases above 25°C, the temperature at the boundary of the mixing zone is allowed to be 32°C during a period of maximum 1 continuous week per year. The frequency of this allowed exceeding is strictly limited to 1 week per year to provide the ecosystem enough time to acclimate.

The way cooling water is discharged may influence the behaviour of fish in the receiving waters. The discharge velocity and the angle to the water flow determine the spatial dimensions and temperatures within the plume. In Table 19.2 the

Table 19.2 Comparison of cooling water discharge aimed at mixing and stratified cooling water discharge

Way of discharge	Influence on plume	(Indirect) effects
Discharge with relative high velocity, aimed at maximal mixing in initial mixing zone	ΔT = small (gradual T-transition)	Lower T in plume: small chance on exposure to extreme T-levels
	Area that in which the T is increased is relatively large	Due to gradual T-transition: no deterring effect: attracting impulse may dominate, and fish might remain within area with less proper conditions
		Cooling in far-field is less than with stratified discharge
Stratified discharge: discharge with low velocity, whereby the discharge velocity equals the river velocity	ΔT is larger (higher T in plume)	By sharp, relative large T-difference between the plume and the receiving water system, a deterring effect is created for fish to pass this T-barrier. Fish will less often enter the plume and there is a sufficient volume of water of a lower T-level nearby (better escape possibilities)
	Remaining volume of water system (outside plume) is less influenced	Cooling down in the far field is better: smaller reciprocal influence of discharges
	Escape area for fish is nearby and of a lower T-level	

discharge aimed at mixing is compared with stratified discharge in which the warm water “floats” on top of the cool receiving water.

In accordance with the EU-Directive on the quality of fresh waters for fish (EC 1978, 2006) heating is also incorporated as a criteria, for limitation of heating at both local and water system level. The heating is determined compared to a reference point, the background temperature at the boundary of a basin area or water system.

For lakes it holds that situations are mostly very different and in itself are difficult to compare. Following the ABK-guidelines, it is proposed to derive one generic criteria for lakes. In the Netherlands, large scale heat discharges into lakes only occur at the IJssel Lake and Lake Bergumermeer.

3 Consequences

One needs to consider whether the withdrawal criteria have possible consequences for the location choice and can possibly be limiting for the cooling water flow. Based on the criteria of mixing zone, the new evaluation systematic may, compared to the ABK-guidelines, lead to increased spatial space for the discharge of heat, provided enough discharge and cooling surface are present. The dimension of this space is dependent on the receiving surface water. For fast-moving water systems (such as rivers), this space shall be larger due to the larger mixing than to the slow-moving, (semi-)stagnant water systems. Whether the extra space will actually be present, also depends on the parameters of heating and withdrawal. For channels, application of the new evaluation systematic, based on the parameter heating, leads to a limitation of the allowable heat load. For existing situations, for these circumstances a realistic transitional period can be determined, in which for the parameter heating the old ABK-criteria can be followed, provided that the experience with respect to water quality justifies this procedure.

Because in the new evaluation systematic, next to the heating criteria, the mixing zone criteria directly limits a heat discharge through the discharge of the water system, the meaning of discharge is more prominent in the new systematic compared to the old ABK-guidelines. This means that the water distribution and regulation of discharge (if possible) may have further consequences for the actual allowable heat load. Wherever the discharge can be regulated by the local water authorities, choices and consideration in this matter can have an effect on the available cooling capacity and, therefore, an effect on the available electricity production capacity of power plants or production capacity of process industry. In order to perform an assessment of cooling water discharges by means of this new evaluation systematic, the local water authority needs to have sufficient knowledge on the water system. This applies to data with respect to water quality, year-round surface water temperatures and water quantity and the year-round discharge. The assessment results in a maximum heat load, whether or not related to the momentary discharge and temperature. This means that the water authorities also need access to adequate momentary data of the water system.

For such precise criteria simple approaches are not sufficient to evaluate whether the discharge match the criteria. The complexity of the transport and mixing of the cooling water is high due to buoyancy, which determines the hydrodynamics of both the discharged water and the ambient water, and due to the heat exchange with the atmosphere.

Commonly three zones around the cooling water conduit are defined:

- The near-field, where the transport is dominated by turbulent entrainment of the incoming buoyant jet.
- The intermediate field, where buoyancy forces in the plume are dominating.
- The far-field, where the cooling water is transported passively by the ambient currents.

The trajectory of the jet in the near-field is governed by the ambient flow and stratification. The spreading buoyant plume interacts with the currents in the intermediate field, while the stratification in the plume suppresses the ambient turbulence. The accurate description of the jet near the outfall is complicated due to the often non-hydrostatic character of the flows and geometry of outfall. The heat exchange with the atmosphere plays only a role in closed and semi-closed water bodies such as lakes, harbours and canals, but less in river systems, estuaries and coastal waters.

4 Conclusions of the Literature Study and 3D-Modelling Studies

Literature studies on the effect of heat discharge on the aquatic environment and 3D-modelling studies of heat discharge distribution brought up new insights:

- With the new guidelines, a full shift is made from emission policy to immission, conforming to the European Directives.
- Stratification of the heated discharge water by dedicated designed outlet constructions is to be encouraged to avoid vertical mixing.
- Mortality of zooplankton/phytoplankton >30°C recovers in <14 days.
- Direct fish mortality is not or hardly found, indirect effects exist: attraction of fish to the heated water plume and fish can detect heated water quite well and take refuge if necessary.
- Due to shifts in spawning seasons of fish species at elevated temperatures, there is an increased potentiality for the occurrence of hybridisation and a mismatch between nursery period and food availability.
- Higher cross-plant temperature rise and lower cooling water intake flow for a given thermal discharge rate are preferred to lower entrainment and impingement.
- As part of the procedure to achieving a tailored consent, cooling water discharge of both existing and new power plants is being modelled (3D) to investigate the available heat capacity of the receiving surface water and compliance with the new guideline demands.
- The results of 3D modelling of power plant cooling water discharges in the Netherlands carried out as worst-case scenarios (hot and extreme hot summers conditions) have shown exactly where problems can be expected but in most case no problems were encountered with complying to the new guideline demands at different surface waters, i.e. estuaries, lakes, canals, harbours and rivers in the Netherlands.

5 Epilogue

The discussion on heat and background temperature shows that foreign influences are, as reflected in the temperature at the border, in the river Meuse at Eijsden and in the river Rhine at Lobith, to a very large extent qualifying for the possibility to, under hot summer conditions, meet the water quality objectives in the Netherlands. It is highly desirable to pay attention to “heat-discharge issue” during the negotiations to achieve international harmony for basin areas with accompanying discussion on establishing the basin area-based standards for the Water Framework Directive.

There is more insight into the effects on organisms due to ingress into cooling water intakes (impingement and entrainment) than into the effects on the aquatic environment on a population level. Also, field studies paid little attention to the influence of a mixing zone on migration possibilities for fish. Additional research in these areas is necessary.

Proper execution and enforcement of the new evaluation systematic in practice asks for implementation of a monitoring network in which data with respect to water temperature and discharge are registered online.

As part of the Water Framework Directive, several actions need to be taken in the coming years. With respect to heat discharge, these include the following:

– Attention for heat issues, both national and international. The subject needs to be put on the agenda of the Water Framework Directive (WFD) and International Commission for the Protection of the Rhine (ICPR).
– Per water system of parts of a water system, it must be stated whether is it is a "natural water", "heavily modified water" or "artificial water", which is important with respect to the final standard.
– For each area, specific limiting conditions with respect to temperature need to be determined to meet the Good Ecological Status or the Good Ecological Potential as mentioned in the Water Framework Directive. To attune this on an international level is a necessity.
– In order to guarantee proper compliance with the limiting conditions with respect to temperature in the Netherlands, and to achieve harmonisation of area-based standards, positioning the heat problem from a Dutch perspective is of great importance.

It is proposed to thoroughly evaluate the new evaluation systematic after, for example, 5 years, for which the new perceptions from the Water Framework Directive are taken into account. Experience from EIA-studies, in which considerations are based the new evaluation systematic, can play a role in this. Based on the information, completed with information derived from the ongoing development of the Water Framework Directive implementation, the aim is to give further area-based content to the standards. Possibly, an evaluation of the experiences gained with the new evaluation systematic is already meaningful on short term. In order to perform a proper evaluation of the systematic, a proper monitoring of the problems is a necessity. This would include the (preferably) online monitoring of temperature and discharge and the establishment of monitoring campaigns, possibly combined with IR-scans by means of planes.

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Chapter 20
Regulatory Aspects of Choice and Operation of Large-Scale Cooling Systems in Europe

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Abbreviations

AOX	Adsorbable organic halogens
BAT	Best available technique
BD	Birds directive
BEP	Best environmental practices (for diffuse sources)
BPD	Biocidal products directive
BREF	BAT reference document
CIRCA	Communication information resource centre administrator (for WFD)
CIS	Common implementation strategy
DSD	Dangerous substances directive
EIAD	Environmental impacts assessment directive
ELV	Emission limit value
EMR	Eel management regulations
EQS	Environmental quality standard
FFD	Freshwater fish directive

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FGD	Flue gas desulphurisation (De-Sox)
HSD	Habitats and species directive
IED	Industrial emissions directive
IPPCD	Integrated pollution prevention and control directive
ISO	International organisation for standardization
List I/list II	Lists of substances within dangerous substances directive framework
MAC	Maximum acceptable concentration
MSFD	Marine strategy framework directive
OSPAR	Oslo and Paris commission/convention
PHS	Priority hazardous substance
POM	Programme of measures
PS	Priority substance
RBMP	River basin management plan
REACH	Registration, evaluation, authorisation, and restriction of chemical substances regulation
SCR	Selective catalytic reduction (De-Nox)
SWD	Shellfish waters directive
WFD	Water framework directive

1 Introduction

The operation of large-scale power plant and other industrial cooling systems is regulated in European Union (EU) through the interplay of a number of Directives and Regulations. These influence the choice, design, development, permitting process, construction and operation of such systems. Ultimately, the authority to construct and operate a cooling system subject to appropriate constraints is manifest through one or more permits.

This review focuses on the principal issues within the regulatory process. It does not deal with the myriad of details which can and does influence installation-specific outcomes. At its heart is the way in which EU-driven Regulation requires the balancing of the many environmental and societal benefits associated with use of water for cooling, derived from the superior thermal efficiency it provides, albeit with its consequences for the aquatic environment, compared with the non-water environmental and societal consequences associated with alternative cooling options.

Of central importance is the interaction of the Integrated Pollution Prevention and Control Directive (Codified version 2008/1/EC, IPPCD) and the Water Framework Directive (2000/60/EC, WFD), since together these deal with the operational emissions to water, air and land from many of the installations equipped with large cooling systems. Given the relatively long life of installations with large cooling systems (say, 30–70 years), issues associated with operation will tend to take precedence over those associated with construction, provided that the construction impacts are nonetheless acceptable. For the first time at EU-level, WFD has led to the requirement for prior authorisation of abstraction, though in many Member

States this has been required for many years. Such is the scale of installations with large cooling systems that their development will in most cases trigger a requirement for Environmental Impact Assessment (85/337/EEC as amended 97/11/EC and 2003/35/EC) which requires consideration of a wide range of impacts, including all operational issues (related to emissions and abstraction) as well as construction, land use and wider amenity and societal issues.

In order to assess the potential for impacts associated with the cooling system it is necessary to consider the nature of the receiving waters. An extensive set of receptor-based legislation has evolved over time to afford protection to particular aspects of or uses of the aquatic environment. Examples include the following:

- The Freshwater Fish Directive (FFD) (2006/44/EC, to be repealed 2013).
- The Shellfish Waters Directive (SWD) (2006/113/EC, to be repealed 2013).
- The Abstraction for Drinking Water Directive (75/440/EEC, repealed 2007).
- The Habitats and Species Directive (HSD) (92/43/EEC).
- The Birds Directive (BD) (79/409/EEC) and most recently.
- The Eel Management Regulation (EMR) (1100/2007/EC).

The establishment of objectives for surface waters is a key element of WFD and the protective function of the first three of the above will be through the Protected Area Register of the River Basin Management Plans (RBMP) required by WFD. These Directives have been or will be repealed. The WFD objectives established for each water body within the RBMP lead to chemical, physical and biological standards for that water body.

The Marine Strategy Framework Directive (2008/56/EC, MSFD) will play a similar role to WFD in protecting European seas. It uses similar approaches to WFD and its geographic extent overlaps with WFD though its implementation in practical regulation is yet to be felt. Nonetheless, its potential requirements must be considered.

The management of the combinations of pressures aimed at achieving the quality objectives or conservation status of the receiving water body can lead to constraints on the choice of cooling system and limitations on the operational window of that cooling system.

Despite the numerous relevant Directives, the body of EU legislation is not prescriptive for cooling water systems. Rather, it leads to a "combined approach" requiring the simultaneous consideration of controls on techniques, controls on emissions and controls on changes in the environment, which together provide the flexibility to take into account the wide range of environmental conditions and installation circumstances occurring across Europe. Moreover, the precise regulatory regime, though compliant with the EU Environmental Acquits, can differ substantively between Member States, depending on how the European law has been transposed and any additional Member State or more local Regulations. There are no hard and fast rules governing cooling system regulation!

In the following sections of this chapter, the principal regulatory requirements relevant to cooling water systems arising from EU Directives are considered with particular emphasis on commercial power plants. Examples of recent developments in four Member States on the regulation of thermal discharges are considered. Environmental regulation has been rapidly evolving over the last 10–20 years, a trend that will doubtless continue. It is, therefore, appropriate to conclude with some speculation on future directions of relevant regulation.

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2 European Legislation

2.1 Overview

The regulation of large cooling water systems in Europe is delivered through the process of applying for, determination of and monitoring compliance with a number of permits. In essence, these govern the following:

- The choice of cooling system. This requires judgement on the balance of the range of effects that different systems can have on the aquatic environment, in other media and on wider societal considerations, including the benefits that derive directly and indirectly from the superior thermal efficiency that results from use of water for cooling compared with air-cooled systems (see Table 20.1 below).
- Aspects of the functional design and mitigation for the permitted cooling system such as the placement and nature of intake and outfall, intake screening arrangements (e.g. physical exclusion and/or behavioural systems, fish return systems).
- The operational window for the chosen system—to provide appropriate environmental protection (typically including constraints on abstraction flow, discharge flow, thermal and chemical emissions).
- Monitoring and reporting requirements (e.g. locations, frequencies and determinants) to ensure compliance with the permitted operational window and possibly, in the early days for a new installation, to confirm that predictions and assumptions used to support the choice of cooling system and leading to definition of the operational window were sound.

In the following subsections, the principal EU legislation governing the permitting is reviewed.

The implementation of the EU legislation differs between Member States and it is the Member State regulation which will be the primary concern. In addition, where the European and/or Member State legislation allows, there may be Guidance, Codes of Practice or Voluntary Agreements produced or promoted by Member State Authorities, which lead to differences in process and possibly outcome.

Table 20.1 Indicative comparison of the principal pros and cons of common large cooling systems for fossil-fired power plant (after Turnpenny and Coughlan 2003)

Aspect	Once-through cooling	Large natural draught tower cooling	Low profile mechanical draught hybrid tower cooling	Air cooling
Overall process thermal efficiency	Highest	Medium	Medium	Lowest
Water abstraction (gross and net resource use and entrainment/impingement)	High	Low	Low	None
Visible atmospheric plume occurrence	None	Moderate	Reduced	None
Ground fog	None	None	Possible	None
Visual impact of structures	None	High	Some	Some
Noise	Low	Low	Moderate	High
Water discharge (including chemical and thermal discharges)	High	Low	Low	None
Fuel use/energy supplied	Least	Medium	Medium	Highest
Production of emissions to air/energy supplied	Least	Medium	Medium	Highest
Site space requirements	Least	Medium	Medium	Highest

The assessment of the relative significance of the above and other aspects such as technical feasibility and costs of the range of options are case-specific. Depending on circumstances, even aspects indicated as "low" can assume significant importance. A similar table appears in EIPPCB (2001, Table 3.1) though not all aspects are IPPCD

The manner in which the necessary permitting is achieved differs between Member States. In England and Wales a single permit (EPR) delivers all the permitting requirements of IPPCD regarding emission to all media. However, in other Member States, this requirement may be met through the use of several separate permits.

One possible simplified regulatory process[1] for assessing the cooling system aspects of an installation proposal, where the developer is considering use of water for cooling, might be as follows:

- Initial consideration of the installation-specific circumstances leads to identification of the preferred cooling option(s), taking into account the overall balancing of environmental impacts across all media.
- Identification of the applicable water quality standards and objectives for the relevant water bodies, taking into account any potentially affected specific receptors and all applicable legislation.
- Assessment of the effects of the preferred cooling option(s) on the relevant water bodies (supported through appropriate combinations of modelling, monitoring, literature review, formal impact assessment, etc.).
- Determination of the acceptability or otherwise of the preferred cooling option(s), taking into account the range of standards and objectives applying and any specific receptors.
- Identification of any non-intrinsic options for mitigation of residual impacts (including the definition of the operational window).
- If the residual impacts of the proposed cooling system are deemed acceptable, determination of appropriate permit conditions which may be derived in part by reference to the environmental quality standards (EQSs) and modelling/field measurement.

Such a process includes extensive input and review by stakeholders and can be iterative in that information obtained later in the process may cause earlier judgments or assumptions to be revisited. In executing such a process the full range of regulatory requirements is considered at all stages, it is not applied sequentially. As the process advances the operator may refine the proposed installation characteristics affecting the preferred cooling option(s). In practice, commercial considerations will preclude complete knowledge of the installation characteristics at the commencement of the process.

Whilst the choice of cooling system is important in any sector, because of the coupling between the cooling system and the main process, it has implications in the power sector for wider societal considerations associated with security of electricity supply. In particular, when thermal efficiency is reduced in conditions of high ambient temperature, for most power plant this will be manifest as reduced energy supplied (since the maximum fuel input is fixed by the installation's characteristics).

[1] IPPCD requires consideration of the installation as a whole and since the cooling system can affect the overall emissions, efficiency and resource requirements of the entire process; in practical regulation, the cooling system is not separated from the assessment/permitting process of the installation.

Since power plant thermal efficiency degrades less rapidly with ambient temperature for once through cooling compared with wet tower-cooling and for wet towers compared with air-cooling, the use of water for cooling offers potential advantages. However, the potential for operational constraint of water-cooled plant in such conditions needs to be borne in mind.

2.2 The EU Integrated Pollution Prevention and Control (IPPC) Directive (2008/01/EC) and Associated BAT Reference Documents (BREFs)

The principal Directive dealing with emissions from cooling water systems is the IPPCD since most installations using such systems are covered by IPPCD, though there are important exceptions such as nuclear power plant. However, when considering cooling systems used in sectors other than IPPCD, the Regulatory authorities may still choose to have regard for IPPCD-related considerations and guidance. Key relevant aspects of IPPCD are as follows:

- Requirement for prior authorisation (use of permits).
- Requirement to use BAT (Best Available Techniques)[2] (art 3.1.a).
- Requirement to prevent "significant pollution" (art 3.1.b).
- Requirement for energy to be used efficiently (art 3.1.d).
- Requirement to return the site to a satisfactory state on cessation of activities (art 3.1.f).
- Permits should:
  - Include measures (e.g. conditions such as emission constraints) to achieve a high level of protection for the environment as a whole (i.e. holistic consideration of air, land and water environments) (art 9.1)
  - Use conditions which are installation specific, i.e. recognising the technical characteristics of the installation, its geographic location and the local environment (art 9.4)
  - Set out monitoring requirements
- General Binding Rules can be used to set out requirements, instead of requiring them in every individual permit (art 9.8).
- Where an EC EQS requires the meeting of conditions stricter than what BAT delivers, additional measures can be set in the permit (art 10).

[2] "Best Available Techniques", "Techniques", "Available Techniques" and "Best" are all defined in this context within IPPCD art 2. Together, these definitions promote consideration of prevention and reduction of emissions to the environment *as a whole* (i.e. not focussing on specific media) subject to commercial and technical viability at the scale required. IPPCD Annex IV provides a list of items for which "special consideration" should be given. Of particular relevance for present purposes is item 9 (consumption of raw materials, including water, and energy efficiency).

What may constitute BAT at a particular installation is informed through Guidance Documents, chief among which are the BAT Reference documents (known as BREFs) compiled by the European Commission in order to promote information exchange between Member States, as required by article 17 and contributing to delivery of article 11. Under IPPCD, the BREFs are simply information on which Member States may base their judgments. For cooling systems, EIPPCB (2001) is the most important. Other BREFs (such as the EIPPCB (2003), EIPPCB (2009) and sector-specific BREFs such as EIPPCB (2006a)) are also relevant. In addition the BREF on "Economics and Cross-Media Effects" (EIPPCB 2006b), is especially apposite, since fundamental to the choice of cooling system is the balancing of the benefits and disadvantages across all media and in wider societal considerations of the range of feasible options, taking account of the superior thermal efficiency arising from use of water for cooling.

Indicative extracts regarding the principal BAT aspects explored within the Industrial Cooling BREF (EIPPCB 2001) are given in Table 20.2. However,

Table 20.2 BAT approaches (from EIPPCB 2001)

Issue	BAT discussion
Overall process energy efficiency	For some processes, in particular power plant, the performance of the cooling system has a significant influence on the process as a whole. Consideration of internal and external heat use opportunity is necessary
"Level of Dissipated Heat" (essentially temperature at which process heat is rejected)	25–60°C Site-specific focus on energy efficiency <25°C water cooling, site specific selection with focus on energy efficiency
Consideration of cooling system requirements and site specifics	Includes meteorology (especially, wet and dry bulb temperature), water availability and temperature range, site-space restrictions, residual impacts on receiving waters, consideration of local non-water sensitive receptors For coastal waters and plant >10 MWth, once-through cooling is the primary BAT approach Where surface water availability is restricted, recirculating systems is the primary BAT approach For recirculating systems where vapour plume reduction is required, hybrid tower system (i.e. including both (wet and dry elements)) is the primary BAT approach
Application of BAT	BAT considerations apply in the design phase for new plant; for existing plants they apply primarily in optimised operation though technological measures can be BAT in certain circumstances
Increased overall energy efficiency	Various measures are listed for different systems along with the declaration reproduced in full below
Reduction of water use	Recalls that water cooling is the most efficient for achieving the best overall energy balance. Use of optimised cycles of concentration for wet tower systems can reduce gross water use (but not net). Consideration of options for new plant is required

(continued)

Table 20.2 (continued)

Issue	BAT discussion
Entrainment/Impingement of organisms at intakes	Though perhaps not strictly an IPPCD, issue since it is not primarily related to emissions, it is a relevant issue in selecting cooling options and in cooling water intake location and design. Suggests that intakes should be positioned and designed on a site-specific basis, taking into account the range of physical and behaviour-based techniques available
Reduction of emissions to water—heat	Notes that limitation on thermal discharges will be achieved through meeting EQS (FFD is explicitly cited) outside mixing zones. Whilst techniques that reduce thermal emissions may be available, the overall energy efficiency for the process as a whole needs to be considered. There is no prescription on temperature or temperature rises at the point of discharge
Reduction of emissions to water—chemical	The appropriate chemical control measures are strongly influenced by system design choices (type, location, materials, provision of mechanical cleaning systems, etc.), all of which affect the propensity to scale, biofoul and corrode in combination with water body chemistry. BAT must, therefore, be considered on a site-specific basis. Consideration of other Directives (e.g. Biocidal Products Directive (98/008/EC)) and increasingly, though not mentioned in the EIPPCB (2001), REACH (Regulation 1907/2006/EC) will influence feasible choices of chemical products. It is explicit that CCA (Chromated Copper Arsenate) or TBTO (Tributyltin oxide) for wood treatment (e.g. in tower structures) is not BAT and that cooling water treatment using chromium, mercury, organo-metallic substances or shock treatment with biocides other than chlorine, bromine, ozone or hydrogen peroxide is not BAT. There is explicit primary BAT Guidance on oxidant emission concentrations from once through cooled systems. In particular concentration of free residual oxidant (FRO) at the outlet ≤0.2 mg/L as 24 h-average[a] for both continuous and intermittent and shock chlorination of sea water and 0.5 mg/L as an hourly average. Continuous chlorination of freshwater once-through cooled plant is not BAT. For tower-cooled plant the guidance is not explicit on emissions but deals with aspects of operational control
Reduction of emissions to air (from the cooling system itself)	Measures relating to wet cooling towers covering tower height and positioning, visible vapour plume incidence reduction. Includes explicit primary BAT Guidance on performance of drift eliminators (leading to loss of <0.01% of the tower recirculating flow)
Reduction of noise emissions	Variety of potential measures for natural and mechanical draught towers with indicative associated noise reduction levels
Reduction of leakage risk	Some process and design options are indicated with particular relevance to systems in which hazardous substances are cooled (for which indirect cooling is the primary BAT approach, leading to a reduced thermal efficiency)[b]

(continued)

Table 20.2 (continued)

Issue	BAT discussion
Reduction of biological risk	A variety of design and operational measures are indicated as contributing to control of biological risk (including that related to *Legionella pneumophila*). Optimised chemical treatment and monitoring are examples. Good maintenance and avoidance of scale and corrosion are highlighted. Particular attention should be paid to periods of outages and start up

[a]Not stated but presumed as Cl_2 using DPD (Diethyl-p-PhenyleneDiamine)
[b]For cooling systems associated with steam cycle power generation, the pressure occurring is such that the risk is primarily that of the cooling medium leaking into the high quality process water rather than any leakage risk to the environment

care should be taken in interpreting the information in any specific situation. For example, what can be expected of a well-maintained and operated plant, built 20 years ago over a period of operation of several years may be different from that of a new plant. Moreover, in many installations it would not be cost effective (or even technically feasible) to change fundamentally the type of cooling system once the construction had commenced. The full BAT discussion can be found in EIPPCB (2001, Chap. 4). It will be noted that in most cases, and in contrast to other BREF documents, the Industrial Cooling BREF does not propose emission limit values (ELVs). The final BAT solution is site-specific (EIPPCB 2001). This assertion is expanded in EIPPCB (2001, Preface.5), particularly including the following: "Even the single objective of ensuring a high level of protection for the environment as a whole will often involve making trade-off judgments between different types of environmental impact, and these judgments will often be influenced by local considerations".

The following statement has particular importance for power sector applications (EC 2001, art 4.3.2):

In an integrated approach to cooling an industrial process, both the direct and indirect use of energy is taken into account. In terms of the overall energy efficiency of an installation, the use of once-through systems (*sic*) is BAT, in particular for processes requiring large cooling capacities (e.g. >10 MWth). In the case of rivers and/or estuaries, once-through can be acceptable if also:

- Extension of heat plume in the surface water leaves passage for fish migration.
- Cooling water intake is designed aiming at reduced fish entrainment.
- Heat load does not interfere with other users of receiving surface water.

For power stations, if once-through is not possible, natural draught wet cooling towers are more energy-efficient than other cooling configurations, but application can be restricted because of the visual impact of their overall height.[3]

[3]In interpreting this statement, it should be noted that earlier in the BREF (EIPPCB 2001 4.2.1.4) it is stated that for large capacity systems in coastal areas once through cooling systems is the primary BAT approach.

2.3 The Water Framework Directive (WFD) (2000/60/EC)

The WFD (“A Framework for Community Action in the Field of Water Policy”), sets out a comprehensive and holistic framework for managing Europe’s waters allowing a balance to be struck between anthropogenic use of water and protection of the water environment. It places particular emphasis on biological and ecological measures of quality, in contrast to the more traditional flow and chemical quality measures. Work has been undertaken within the Common Implementation Strategy (CIS) to allow definitions which are consistent across the range of Europe’s waters of high, good, moderate, poor and bad ecological status. These depend on a number of water body type specific biological, hydromorphological and physico-chemical quality elements (WFD Annex V).

Once the water body objectives are determined in line with WFD art 4, the Competent Authority is required to manage water bodies to achieve the corresponding quality element standards as EQSs. Hence, the requirement to achieve the standards for river flow, temperature, temperature rise, chemical concentrations, diversity and abundance of biological species, etc. may influence choice and operational windows of cooling systems.

Chemical standards arise through consideration both of chemical elements supporting biological elements (including oxygenation, acidification, nutrients, salinity) and specific pollutants (which include both priority substances (PSs) and “other substances discharged in significant quantities into the body of water”). In the case of PSs, EQSs are set at EU level, whereas for other specific pollutants (sometimes referred to as Annex VIII substances, though this provides only an indicative list of groups of substances), Member States are required to derive their own standards in line with a protocol set out in WFD. In many cases, such substances would be those up until now are regulated through the Dangerous Substances Directive (76/464/EEC).

Where a water body is established to be artificial or heavily modified, the objectives relate to ecological potential rather than status, recognising that the societal “need” which is served by the modification cannot be provided otherwise. Many large industrial cooling systems are sited in water bodies with a long history of use by man and which may have been extensively modified physically to support that use. Thus, consideration of “potential” rather than “status” will often be required. However, unless there is impoundment for purposes of ensuring supply of water for cooling, it would not be expected that the presence of a large cooling system would lead to classification of a water body as artificial or heavily modified.

The geographic scope of WFD includes all designated “water bodies” and extends offshore to Member State defined limits, typically 1 nautical mile. Central to the WFD is the requirement for the drawing up of a RBMP, through a participatory and inclusive approach, for each defined River Basin District. The RBMP sets out the water body definitions, their individual objectives and the principal measures to be adopted to meet them. Whilst not including prescriptive requirements relating to cooling systems, there are many aspects of the WFD which have the potential to influence cooling system choice, operation and regulation. Key aspects include the following:

- Establishment of Objectives
  - Target status for each defined water body.[4]
  - "No deterioration" target (in terms of water body status).
  - Phase out/cessation objectives for discharge, emission and losses of Priority/ Priority Hazardous Substances (PHSs).
  - Incorporation of standards and objectives for Protected Areas arising from other Regulation (e.g. FFD, SWD).
- Recovery of Costs for Water Services.
- Controls on emissions—the combined approach of emissions controls relating to BAT, ELV and, for diffuse sources, best environmental practices (BEP) arising from other legislation along with limitation on emissions in order to meet EQSs or objectives.
- Establishment of Programmes of Measures defined in order to achieve the established objectives. The measures contributing to a programme could include changes in law, changes in charging for water use, promulgating codes of practice, carrying out physical environmental remediation, education, awareness building, carrying out investigations and research and development. Measures should not be allowed to lead to increased pollution[5] of surface waters, though this requirement does not apply where it would result in increased pollution of the environment as a whole, thus explicitly introducing consideration of consequences for other media. Of particular interest for large cooling systems is that WFD leads to permitting requirements:
  - Requirement for prior regulation for discharges (e.g. permits including emission controls).
  - Promotion of efficient and sustainable water use (e.g. via permit conditions, General Binding Rules).
  - Requirement for prior authorisation for abstraction and impoundment of fresh surface water and groundwater.[6]

[4]The process for this is integral to the holistic nature of WFD. In essence it requires consideration of what packages of measures would "bridge the gap" between current status and the WFD "default" objective of good ecological status by 2015, judging the most cost-effective package of measures and then considering whether technical feasibility or disproportionate cost considerations would render it impossible or inappropriate to seek to achieve the default objective, in which case an alternative timeframe or less stringent objective may be set.

[5]"Pollution" is defined in WFD art2(33).

[6]WFD art11.3(e) in itself introduces no requirement for prior authorisation for abstraction from salt waters, and no definition of "fresh" is provided.

- Adopting measures aimed at the progressive reduction of pollution from PS and ceasing discharge, emission and losses of PHS
  - A list of PS and PHS was determined and a daughter directive (2008/105/EC) was adopted which establishes annual average EQSs for all and maximum acceptable concentration (MAC) EQSs for some of these substances. It also gives Member States the ability to designate mixing zones if they so wish (i.e. extents of exceeding EQSs which do not affect compliance of the remainder of a water body). Of the current PS and PHS, only trichloromethane (chloroform) and nickel are directly relevant to emissions from cooling systems, trichloromethane being a possible by-product of chemical control of biofouling in freshwaters and nickel being present in some condenser materials. The daughter directive also requires the establishment of Member State inventories of emissions. Progress towards the emission-related objectives of WFD will be judged in 2018 through reference to this set of inventories.

Clearly, as a possible measure, any permits granted and any operational constraints they provide to ensure environmental protection can be reviewed in order to contribute to achievement of the established objectives.

In order to promote common approaches to WFD across Europe, a CIS workstream has been set up. The published Guidance is available through the WFD CIRCA web site.[7] Of most interest among those currently available are No. 1 on Economics, No. 7 &19 on monitoring and No. 20 on Exemptions.

2.4 The Dangerous Substances Directive (76/464/EEC, DSD, Discharge of Dangerous Substances to the Aquatic Environment and Its Daughter Directives, in Particular 86/280)

The dangerous substances directive (DSD) and its daughter directives have been the primary means of regulating in the water environment many substances potentially relevant to cooling system operation. These include substances such as copper, nickel and zinc, which may be released from some cooling system surfaces in operation, emissions from application of chemical biofouling control (trichloromethane), substances which may be present as trace contaminant in cooling water system treatment bulk chemicals (mercury and cadmium) and substances potentially present in industrial process or power station effluent streams, which may be discharged via the cooling water system. DSD introduced permitting requirements for point discharges and set EQSs for List I substances. It required member States to define EQSs for List II substances. These EQSs could influence the permitting of cooling

[7] http://circa.europa.eu/Public/irc/env/wfd/library?l=/framework_directive/guidance_documents&vm=detailed&sb=Title.

system operation. However, the function of the DSD has been subsumed within WFD and the DSD is to be repealed in 2013, though transitional provisions apply.

2.5 The Freshwater Fish Directive (FFD) (2006/44/EC, Codified Version Originally 78/659/EEC)

FFD sets imperative and/or guideline standards for a variety of determinants in those waters designated by Member States under the FFD. Member States should "endeavour to respect" guideline values. Two classes of designation are possible, referred to as "salmonid" and "cyprinid", depending on the nature of the fish populations the waters support or are capable of supporting. Separate guideline and imperative standards can apply to each. Derogation is possible for certain determinants on the basis of exceptional weather or special geographic conditions. Determinants directly relevant to cooling system operation are:

- Maximum temperature—thermal discharges must not cause the temperature downstream at the edge of the mixing zone to exceed 21.5°C (salmonid) or 28°C (cyprinid). In addition, when cold water species require such conditions for breeding, maximum temperature is to remain less than 10°C (imperative standards as 98%iles with derogations possible).
- Maximum temperature rise—thermal discharges should not lead to temperature rises exceeding +1.5°C (salmonid) and +3°C (cyprinid) at the edge of a mixing zone expressed relative to waters unaffected by the discharge (imperative standards with derogation possible in some circumstances, weekly sampling).
- Dissolved oxygen (different guide and imperative standards are specified in salmonid and cyprinid waters).
- Suspended solids (25 mg/L guide only, derogation possible).
- Total residual chlorine (imperative 0.005 mg/L as measured using DPD method and expressed as HOCl at pH 6, with higher TRC concentrations permitted if pH is higher than 6, monthly sampling).
- Zinc (total) 0.3 mg/L (salmonid), 1 mg/L (cyprinid) (imperative, at 100 mg/L hardness as $CaCO_3$, with other values for other hardness).
- Copper (dissolved) 0.04 mg/L (guideline, at 100 mg/L hardness as $CaCO_3$, with other values for other hardnesses).

There are other standards relating to determinants which may be influenced by other process or effluent streams and may be discharged via the cooling water system. These include: pH, BOD_5, phosphorus, petroleum hydrocarbons, ammonia and ammonium.

In the past, where relevant standards were not existent, some Member States have sought to apply values based on FFD to non-designated waters, including estuarine and coastal waters. However, the function of the FFD has been subsumed within WFD and the FFD is to be repealed in 2013. Standards should, therefore, derive from the WFD objectives.

2.6 The Shellfish Waters Directive (SWD) (2006/113/EC Codified Version, Originally 79/923/EEC)

SFD sets imperative and guideline standards for a variety of determinants in those waters designated by Member States under the SFD. Member States should "endeavour to observe" guideline values. Derogation is possible for certain determinants on the basis of exceptional weather or special geographic conditions. The exact sampling point is to be set by the Member State Competent Authority.[8] Determinants directly relevant to cooling system operation are:

- Maximum temperature rise—thermal discharges must not cause the temperature rise to exceed +2°C compared with waters unaffected by the discharge (guideline, quarterly monitoring, 75% compliance).
- Dissolved oxygen (guideline 80%sat, imperative 70%sat average, monthly sampling, 95% compliance).
- Salinity (guideline 12–38 ppt, imperative ≤40 ppt and no more than 10% increase compared to waters unaffected by the discharge, 95% compliance, monthly sampling).
- Suspended solids (imperative, quarterly, no more than 30% increase compared to waters unaffected by the discharge, 75% compliance).

There are other standards relating to determinants which may be influenced by other process or effluent streams discharged via the cooling water system. These include:

- pH, BOD_5, petroleum hydrocarbons, organo-halogenated substances, metals (specific suite including copper, zinc, nickel, mercury, cadmium).

The function of the SFD has been subsumed within WFD and the SFD is to be repealed in 2013.

2.7 The Habitats and Species Directive (HSD) (92/43/EEC) (on the Conservation of Natural Habitats and of Wild Fauna and Flora)

The aims of the Directive are …*to contribute towards ensuring biodiversity through the conservation of natural habitats and of wild fauna and flora in the European territory of the Member States to which the Treaty applies* (Article 2.1); and …*to maintain or restore, at favourable conservation status, natural habitats and species of wild fauna and flora of Community interest* (Article 2.2).

[8]Selection of an appropriate monitoring location (e.g. relative to a point of discharge, at the surface, bed or mid-depth) is not straightforward and its choice leads to a de facto mixing zone (see e.g. Turnpenny and Liney 2006).

The HSD provides for the designation and protection of a network of sites (Special Areas of Conservation, SAC) and protection of designated species and habitats. Where the construction and operation of an industrial cooling system is judged by the Competent Authority to have the potential to affect such a protected site, species or habitat, it will be necessary to assess the potential for those effects in the context of the interest features of the relevant site. This may result in a requirement to provide information (e.g. through combinations of monitoring, modelling, literature review, etc.) which allows the Competent Authorities to determine whether or not the impact of the cooling system alone, or in combination with other activities, could affect the conservation status and the integrity of the site (in respect of the interest features, rather than a geographic area). Experience suggests that consideration of potential impacts on SACs can lead to requests for more detailed information and a commensurately greater detail in scrutiny by Competent Authorities, Conservation Agencies and stakeholders in discharging their responsibilities under HSD than would be the case for developments not impacting SACs.

Whilst Member State Competent Authorities may have developed their own guidance on what constitutes a "likely significant effect" (which, despite the terminology, simply triggers the need for subsequent Appropriate Assessment with no presumption of implied outcome), there appears to be no quantitative statement at European level of relevant quality standards. Thus, in practice, the means of and information for assessing these aspects is likely to be determined in the permitting process and on a case-specific basis with participation from relevant stakeholders including regulators, conservation agencies and other interested parties.

2.8 The Birds Directive BD 79/409/EEC (on the Conservation of Wild Birds)

The BD requires the protection of birds in part through the establishment of Special Protection Areas (SPAs) to protect potential bird habitats. The HSD states that SPAs and SACs together form part of the Natura 2000 network of protected sites. Although not required by the HSD, a Member State may have chosen to extend the protection afforded to SACs to SPAs designated under BD and the permitting process described under HSD similarly applied. UK is one such Member State.

2.9 Ramsar Convention on Wetlands of International Importance Especially as Waterfowl Habitat (1971)

Many Member States will have designated wetlands under the Ramsar Convention which will lead to particular receptor considerations in permitting industrial cooling systems. Some may have chosen to treat such sites similarly to Natura 2000 sites (see BD).

2.10 Berne Convention: Convention on Conservation of European Wildlife and Natural Habitats (Bern Convention, 1979)

The Berne Convention is implemented within the EC though HSD and BD and ratified by individual Member States leading to receptor considerations as above.

2.11 Bonn Convention: Convention on the Conservation of Migratory Species of Wild Animals (Bonn, 1979)

The Bonn Convention has led to a number of subsidiary agreements on species or species groups which may be relevant for the permitting of some installations.

2.12 OSPAR: The Convention for the Protection of the Marine Environment of the North-East Atlantic (Paris, 1992)

Oslo and Paris commission/convention (OSPAR) includes consideration of the protection of the maritime environment from land based sources. There have been many recommendations, decisions and other agreements within OSPAR. Of relevance for current purposes are some which relate to industries which may make use of cooling systems with discharges to water and some which relate to the setting up of networks of marine protected areas. Although much of the emission related agreements would be covered within IPPCD, some may be relevant to particular industries.

2.13 The Eel Management Regulation (EMR) (1100/2007/EC)

The Eel Management Regulation requires Member States to develop eel management plans for appropriate river basins[9] to "reduce anthropogenic mortalities so as to permit with high probability the escapement to the sea of at least 40% of the silver eel biomass relative to the best estimate of escapement that would have existed if no anthropogenic influences had impacted the stock". As of 31st December 2008, Member States have submitted plans to the European Commission and are awaiting approval.

[9] Which need not necessarily coincide with WFD River Basin Districts.

Although details are not yet clear, it is possible that measures within such plans may include review of the potential for some cooling water intakes to contribute to eel escapement reduction through entrainment/impingement.

2.14 Environmental Impacts Assessment Directive, EIAD, 85/337 (as Amended by 97/11/EC and 2003/35/EC) (on the Assessment of the Effects of Certain Public and Private Projects on the Environment)

The Environmental Impact Assessment Directive requires that the environmental effects of certain projects be assessed prior to consent being given. The qualifying projects include thermal power stations and other combustion installations with heat output greater than 300 MW(t), nuclear power stations, refineries, iron and steel industries and chemicals industries, all of which may include use of a large cooling system. Moreover, environmental impacts assessment directive (EIAD) allows Member States to require environmental impacts assessment of a wider range of projects, including many which may use a cooling system, if they consider it appropriate. Thus, different Member States may use different criteria for requiring environmental impact assessment for those projects which are not directly required to be assessed through EIAD itself.

The scope of assessment is required to include direct and indirect effects on a case-specific basis on the following:

- Human beings, fauna and flora.
- Soil, water, air, climate and the landscape.
- Material assets and the cultural heritage.

For a project requiring use of a cooling system, the environmental impact assessment can include consideration of the balancing of the potential impacts between the receptors listed above both locally to the intended site and more widely, taking into account alternatives. Whilst initially there may be some consideration of the appropriate cooling system type (e.g. once-through, recirculating tower-cooled, dry cooling), once the appropriate type has been established, there may be variants within that type (e.g. options for combinations of cooling water flow and corresponding temperature rise in the case of once-through cooling).

EIAD as amended by 2003/35/EC requires that the public should have access to relevant information and opportunity to participate in the environmental impact assessment process.

In practice, the EIA process can be extended over quite some period of time, possibly several years in the case of a complex IPPC installation. The timing of applications for individual relevant permits may be linked to this process. As the process develops, information regarding the potential impacts of possible project variants and various stakeholder views on the significance of impacts will be obtained. Together, these may influence choices made by the developer. In some cases the nature of the cooling system to be used and the influence of that choice on the impacts of the project as a whole, both environmental and on wider society, may be one of the major issues explored within the EIA.

2.15 REACH (Registration, Evaluation, Authorisation, and Restriction of Chemical Substances) Regulation 1907/2006 Corrigendum 29 May 2007

The European Chemicals Agency (ECHA[10]) administrates the delivery of REACH. The Regulation requires the phased registration over the period 2008–2018 of chemical substances and products as a means of ensuring their appropriate use. Only registered products will become available in the European market. Operators of many large industrial cooling systems may use chemical products within such systems and within the processes occurring within the wider installation. The regulations place no registration requirements on users of chemical products but rather put registration requirements on their suppliers. Operators will be required to ensure that their use of any chemical products is consistent with the uses described in the product registration (as set out in the safety data sheets and exposure scenarios which suppliers are required to provide). "REACH requires that the operational conditions and risk management measures described in the exposure scenario match the actual conditions of use at the downstream user level" (ECHA 2008).

2.16 Biocidal Products Directive BPD, 98/8/EC (Concerning the Placing of Biocidal Products on the Market)

Biocidal products directive (BPD) imposes requirements on authorisation of biocidal products, some of which may be used within cooling systems for biofouling risk management, which pre-date REACH requirements. Products authorised under BPD are regarded as having met REACH pre-registration requirements.

2.17 Additional Relevant Member State Regulation and Guidance

The feasible choices of cooling system in a particular location and application may be limited through other considerations of the aquatic environment. Common examples include regulations delivering flood protection and safety of navigation (which may limit or preclude the placement of new structures in parts of

[10] http://www.echa.europa.eu/.

water bodies). Whilst some of these regulations may derive ultimately from EU Directives and Regulations, their definition (e.g. Harbour Bye-Laws) and action can be highly site-specific. Also, there are other regulations (e.g. relating to the integrity of civil engineering structures, health and safety, etc.) which influence the way that cooling systems are operated, monitored and maintained.

There are some uses of large cooling systems that are outside the scope of IPPCD, for example in nuclear power plant. However, these systems are within scope of appropriate Member State Regulation and a similar range of issues to that discussed above would be expected to be factors within the regulatory process.

Member States may evolve Guidance to promote consistency of regulation, good practice and improve knowledge of all relevant stakeholders within that State, particularly where the European or Member State regulation allows flexibility in delivering requirements. One example relevant to cooling systems is Turnpenny and O'Keeffe (2005), which discusses Best Practice in screening arrangements for intakes and outfalls, including those used for cooling water. Another is Environment Agency's Guidance for the Combustion Sector (EA 2005), an example of Member State IPPC Guidance for a particular sector, which includes consideration of cooling systems and effluent streams found in combustion installations.

2.18 Typical Permit Elements in Practical Regulation of Cooling Systems

Table 20.3 provides an indicative list of parameters which may appear as constraints, guidelines, thresholds for operator action and/or monitoring requirements within permits relating to cooling systems. In some cases, a permitting element's prescribed constraint value(s) may be linked to another permit element or to an environmental variable (water temperature, river flow, water quality element concentration, etc.). The permit may prescribe for each element:

- The location of applicable constraint (point of compliance assessment).
- Constraint value(s) (either numerical values or determined through a defined relationship with other parameters).
- Constraint nature (maximum, period average, period percentile, etc.).
- Monitoring type (continuous/sampling frequency, etc.).
- Analysis method (for some determinants the laboratory analysis method, e.g. ISO or national standards reference).

The specific elements appearing in permits for a given installation will be determined by the Competent Authority having regard for the Member State applicable law, the information provided by the applicant and the characteristics of the receiving waters, etc. For some determinants it may be necessary to monitor both abstracted and discharged water. The permit elements, the monitoring and the reporting requirements may be varied over time, in line with the principles of risk-based cost-effective regulation.

Table 20.3 Indicative permit elements

Permitting element	Comment
Intake characteristics	Description of location and type. May include outline of screening and other measures to be provided for protection of aquatic biota
Outfall characteristics	Description of location and type
Abstraction volume flux, m^3s^{-1}	May be linked to installed operational pump capacity (note that for reliability the installation may be constructed with spare pump capacity)
Discharge volume flux, m^3s^{-1}	May be linked to installed operational pump capacity (note that for reliability the installation may be constructed with spare pump capacity). Volume flux may be used for some purposes to provide an upper limit on heat or mass flux of a substance. This upper limit may be precautionary since it may not be technically possible or would be statistically rare for maximum volume flux to occur in combination with maximum temperature, temperature rise and emission concentration
Discharge temperature rise (compared with ambient or intake), °C or K	Will act to limit the net thermal emission (in combination with volume flux). Can restrict installation operation
Discharge temperature, °C	Will act to limit the thermal emission (in combination with volume flux). Can restrict installation operation with a varying severity linked to ambient conditions
Net thermal emission, MWth	For some installations flexibility on cooling water volume flux and temperature rise may be permitted subject to a limit on the net thermal emission to the receiving waters. Could be alternatively expressed as product of volume flux and temperature rise, $°C.m^3s^{-1}$
Discharge oxidant concentration, mg/L	Oxidising component of chemical biofouling control. Could be specified as free, combined or total (relating to the chemical form of the oxidant)
Discharge of selected chlorination by-products concentration, mg/L	The particular substances are likely to depend on the nature of the biofouling control used and ambient water quality. Could include a surrogate such as AOX (adsorbable organic halogens)
Cooling system materials related substance concentration, mg/L	May be included if there is reason to require constraint or monitoring depending on proposed cooling circuit chemistry conditions and cooling system surface material type (e.g. copper, nickel, zinc)
Ambient water quality related substances, mg/L	Typically used for tower-cooled circuits in which concentration of non-volatile substances occurs. Substance(s) will depend on ambient quality and local receptor sensitivities
Substances used for recirculating tower circuit scale and corrosion control management, mg/L	Depends on the circuit control strategy. Will often include pH, for acid dosing will include sulphate or chloride
Other process effluents or potential fugitive emissions, mg/L	Depends on the other process effluents using the cooling system discharge. Many installations will have requirements to monitor for pH, oil and suspended solids in the cooling system discharge

3 Examples of Member State Standards and Guidelines on Water Temperature

European law is transposed within individual Member States through national legislation. In some cases, this allows a degree of customisation to fit Member State and local circumstances. For example, water temperature standards being developed under the WFD may be expected to vary between Member States and possibly within a Member State, reflecting differences across Europe in the nature of water bodies and their associated biology. In the following, the current positions of some example Member States are reviewed.

3.1 Overview

While reviewing existing regulations on warm-water discharge worldwide, Turnpenny and Liney (2006) sought feedback from local experts on effectiveness of the discharge guidelines. Interestingly, the experts selected (mainly one per country without further details on their expertise) widely varied in their response from "thermal discharges are not perceived to be of concern" (Sweden) to "too stringent and that there may be more scope for discharging heated water" (The Netherlands) and "too high for salmonids" (Switzerland).

The summary of the key numerical temperature standards used in the countries reviewed by Turnpenny and Liney (2006) revealed a general consistency in regulations aiming to protect the following:

1. Spawning temperatures for coldwater species (10–13°C maxima).
2. Maximum allowable temperatures for the water body after mixing.
3. A maximum temperature change (uplift).

Some countries also limit the maximum temperature of the discharge water in thermal effluents. Most European countries follow the FFD, distinguishing between salmonid (cold-water) and cyprinid (warm-water) habitats, with temperature maxima of 21.5° and 28°C, respectively, and allowable temperature rises of 1.5° and 3°C, respectively. Germany and Switzerland differ in specifying a 25°C maximum temperature for cold-water habitats (Guderian and Gunkel 2000; Turnpenny and Liney 2006). To cite Turnpenny and Liney (2006): "The review of European standards gives little suggestion that regulations in any of the countries questioned have developed beyond the FFD position, nor indeed does it seem that they have been subject to any rigorous scrutiny".

Most large European rivers are summer-warm, with an average longitudinal temperature increase of 0.09°C km^{-1} (Torgersen et al. 2001). However, in Germany and other countries heated effluents were not considered as a significant environmental pressure within the implementation of the WFD (Interwies et al. 2004; Kampa and Hansen 2004; Borchardt et al. 2005; Naumann et al. 2008).

3.2 France

In France, each power plant has a decree governing water abstraction and discharge, which imposes constraints such as the maximum temperature of the water discharged from the installation, and seasonal adaptation of the thresholds for temperature rise and the maximum temperature in the river downstream of the discharge point (Table 20.4). These thresholds are sometimes critical for industrial operation in years with a high frequency of heat episodes.

3.3 Germany

The first warm-water pollution plans ("Wärmelastpläne") were developed in the early seventies (River Rhine 1971, River Elbe 1973, River Weser 1974) for existing as well as planned warm-water discharges. They are available for the rivers Rhine, Main, Mosel, Neckar, Weser, Elbe, Danube and Isar. This work was coordinated by the Bund-Länderarbeitsgemeinschaft Wasser (LAWA). The most recent warm-water pollution plan has been published for the tidal part of the River Elbe in December 2008. It allows a maximum temperature of 28°C and a maximum temperature increase of 3 K at the end of the mixing zone which is to extend a maximum of 500 m downstream discharge point (Projektgruppe Wärmelastplan Tideelbe 2008). The maximum temperature may be exceeded in exceptional cases for 2% of the time annually. Within the mixing zone, the temperature (28°C) may be exceeded by up to 3 K in one third of the fluvial cross section. Finally, in the mixing zone it was suggested to limit the maximum temperature to 30°C and the maximum temperature increase to 6 K in summer and to 7.5 K in winter as suggested by the Projektgruppe Wärmelastplan Tideelbe.

These values correspond to the requirements of FFD, the Directive 2006/44/EC of the European Parliament and of the Council of 6 September 2006 on the quality of fresh waters needing protection or improvement in order to support fish life (OJ L 264, 25.9.2006, p. 20–31), allowing for similar temperatures and temperature increase in cyprinid waters. All large German rivers belong to this water type. The corresponding LAWA guideline is in a revision process. The new guidelines are expected to be in place late 2009. The existing regulation allows for maximum temperatures of 28° and 25°C in Summer-warm and Summer-cold waters, respectively, and for 18°C in salmonid waters (Guderian and Gunkel 2000), which is well below the EU reference value of 21.5°C for salmonid waters. The temperature increase is limited to 5 K in Summer-warm and 3 K in summer-cold waters. To fulfill these thermal limits, the following maximum discharge values have been set up, depending on the cooling system (Guderian and Gunkel 2000):

All mentioned discharge criteria for the different river systems (except the River Elbe) have been developed on the basis of the LAWA guidelines for warm-water discharge and allow for a maximum 28°C and 5 K temperature increase in the large

Table 20.4 Thermal thresholds for the nuclear power plants on the Loire and the Rhône (Souchon et al. 2008)

River	Loire	Rhône			
Power station	All 5 sites	Bugey	St Alban	Cruas	Tricastin
T_{max} in the discharge	No	30° and 34°C in summer[a]	no	no	30° and 34°C in summer[a]
T_{max} calculated in the downstream flow	No	24°C	28°C	no	25°C
		26°C summer[b] (280 periods of 3 h) and 27°C if heat wave			27°C summer[a] (20 days) and 29°C if heat wave
ΔT	+1°C	+7,5°C	+4°C if <22°C	+1°C if <27°C	+7°C
	+1.5°C if <15°C	+5.5°C summer[a]	0°C if >28°C but +3°C in summer[b]	28-T upstream if 27–28° and 0°C if >28°C	+3°C if heat wave
		+3°C if heat wave and <26°C			
		+1°C if heat wave and <27°C			

[a]Summer = 01/07–15/09; [b]Summer = 01/06–30/09

Table 20.5 Maximum temperature limits for cooling water discharge in Germany

Cooling system	Maximum temperatures and temperature increase	
Once through cooling	Maximum discharge temperature	30°C
	Exceptionally permitted	33°C
	Maximum temperature increase	10 K
	Exceptionally permitted	15 K
Extra (discharge) cooling tower or "Ablaufkühlung"	Maximum discharge temperature	33°C
	Maximum temperature increase	10 K
	Exceptionally permitted	15 K
Recirculation cooling	Maximum discharge temperature	35°C

river sections. However, today most European countries, including Germany, regulating warm-water discharge have adopted the FFD (2006/44/EC) and use the threshold values given there (Table 20.5).

3.4 The Netherlands

In the Netherlands, new guidance on cooling water discharges has been formulated in 2004 (Rijkswaterstaat 2004). The former guideline was formulated by the Algemene Beraadsgroep Koelwater (ABK) (i.e. the General Commission for Cooling Water Issues) in 1975 and existed largely in emission-limits. This regulation was, however, inadequate to cope with extreme summer conditions. As a consequence, from 1991, it was common practice to tolerate discharge temperatures >30°C to prevent shortage in power supply. The hot summer scenarios increased the need for a new guideline for heat discharges. The Dutch Commission for Integral Water Management (CIW) developed a new approach to regulate heat discharges. From literature studies on the effect of heat discharges on the aquatic environment and 3D modelling studies of heat distribution, three test criteria have been derived: abstraction, mixing zone and heat discharge. It concerns channels, tidal harbours, rivers, North Sea and estuaries. For lakes, it is proposed to derive one generic criterion, as it holds that situations are mostly very different and in itself are difficult to compare.

With the new guideline, a shift is made from discharge standards (emission) to EQSs (immission) to conform to the European Directives. Also, higher cross-plant temperature rise and lower cooling water intake flow for a given thermal discharge rate are preferred. As part of the permit system, cooling water discharge of both existing and new power plants are being modelled (3D) to investigate the available heat capacity of the receiving surface water and compliance with the new guideline demands. The results of 3D modelling of power plant cooling water discharges for worst-case scenarios (hot summers conditions) have shown no problems with complying to the new guideline demands at different surface waters, i.e. estuaries, lakes, canals, harbours and rivers in the Netherlands. The new Cooling Water Discharge Guidelines fit with the new European legislation, i.e. the Integrated Pollution Prevention and Control guideline (IPPC) (96/61/EC) (including the European IPPC Reference Document on the application of Best Available Techniques to Industrial Cooling Systems) and the WFD (2000/60/EC).

Table 20.6 Proposed boundary values (Turnpenny and Liney 2006)

	Normative definition boundary positions			
Typology	High/good (°C)	Good/moderate (°C)	Moderate/poor (°C)	Poor/bad (°C)
Cold water	20	23	28	30
Warm water	25	28	30	32

Table 20.7 Maximum allowable temperature uplift and drop for all normative definitions (Turnpenny and Liney 2006)

	Normative definition classes				
Typology	High (K)	Good (K)	Moderate (K)	Poor (K)	Bad (K)
Cold water	2	3	3	3	3
Warm water	2	3	3	3	3

3.5 The UK

Turnpenny and Liney (2006) used the concept of "thermal niche" by Magnuson et al. (1979) that most fish will spend two-thirds of their time within ±2°C and all time within ±5°C of their temperature preferendum, which can be used to derive normative boundary values for the ecological status according to the WFD for use in the UK. The upper limit of the ±2°C thermal niche has been defined as class boundary between "high" and "good", the upper limit of the ±5°C thermal niche as class boundary between "good" and "moderate" (Turnpenny and Liney 2006). The class boundaries between "moderate" and "poor" and "poor" and "bad" have been set at the lower and upper limits, respectively, of the lethal temperature range. These proposed absolute standards were based on the 98 percentiles at the boundary of the mixing zone. It was further proposed to use a 2°C uplift limit for waters of high ecological status and a 3°C uplift limit for all other waters (Turnpenny and Liney 2006, see Tables 20.6 and 20.7).

These values correspond well to the existing warm-water discharge regulations for large rivers in Germany and show only minor deviation from the criticised (Turnpenny and Liney 2006) FFD in cold waters.

3.6 Other Effluent Streams

The primary focus of this chapter is on cooling systems. However, at any installation there may be several other systems with liquid effluents. In many cases, the cooling water discharge is likely to be the largest discharge (by volume flux), and depending on the nature of the other effluent streams and the installation layout, it may be advantageous to discharge some of the other streams via the cooling system, since this will reduce the maximum concentrations occurring in the receiving water for a given emission load. In such circumstances, the regulator may choose to designate the individual system discharges as points for regulatory control (either for emission control or monitoring purposes or both) or, having regard for BAT for the individual systems, choose to place emission controls on the final cooling water discharge point alone. In such cases, there may be a wider set of determinants controlled at the cooling water discharge point than would be the case for a "simple" cooling water discharge.

This is illustrated in Table 20.8 for the case of a modern fossil-fired power station below. Each of the sub-processes would be required to be consistent with installation-specific BAT (as a result of permitting under IPPCD) which may involve the use of a range of intrinsic and operational techniques and pre-discharge emission abatement processes such as oil interception, pH adjustment and precipitation,

Table 20.8 Other effluent stream potentially using the cooling water discharge

Sub process	Indicative possible substances of regulatory interest	Information sources	Indicative control techniques
Flue gas desulphurisation plant (Limestone-gypsum)	Chloride, metals, suspended solids, pH, COD	EIPPCB (2006a), Tables 4.71 and 6.45 gives emission levels associated with the use of a BAT-FGD waste water treatment plant as a representative 24 h composite sample	Intrinsic within overall installation processes (e.g. gas stream measures) FGD waste water treatment plant
Flue gas desulphurisation plant (sea water process)	pH, sulphate, [COD[a]], metals	EIPPCB (2006a)	Intrinsic within overall installation processes (e.g. gas stream measures)
Selective catalytic reduction (SCR) or other deNOX techniques	Ammonia (from reagent) possible effects on partitioning of trace elements in flue gas stream may affect emissions to water depending on gas stream controls	EIPPCB (2006a)	To reduce ammonia concentration if necessary, air stripping, or precipitation, or biodegradation
Ash lagoons/mounds	Suspended solids, pH, trace metals, boron, sulphate	EIPPCB (2006a) EIPPCB (2006c)	Mound/lagoon management, collection, settlement

(continued)

Table 20.8 (continued)

Sub process	Indicative possible substances of regulatory interest	Information sources	Indicative control techniques
Coal stock run off	Suspended solids, pH, traces metals, PAHs	EIPPCB (2006a) indicates <30 mg/L suspended solids EIPPCB (2006c)	Stock mound management, collection, settlement
Site area and storage area run off	Suspended solids, oils, others dependent on nature of storage areas	EIPPCB (2006a, c)	Collection, settlement, oil separation
Boiler water make up water treatment plant effluent and regeneration discharges	Dissolved salts present in source water Bulk chemical components and impurities	EIPPCB (2006a)	pH adjustment, sedimentation and neutralisation
Boiler water blowdown and condensate polishing plant effluent	Boiler water chemical control residues (e.g. trace phosphates)	EIPPCB (2006a)	pH adjustment, sedimentation and neutralisation
Intermittent major cleaning activities	Substances likely to be present in fouling material Chemical cleaning agents and breakdown products	EIPPCB (2006a)	Collection, monitoring Treatment or disposal off-site
Desalination plant	Concentrated brine—which influences the chemical composition and density of the discharge if load is sufficiently large compared with cooling water flow		Outfall location and design dependent on the desired initial mixing characteristics
Discharge from district heating systems	Depends on nature of network		

[a]Whilst of regulatory interest in the permitting process, the monitoring of COD in seawater presents practical difficulty and may not appear in the permit

settlement, filtration, etc. Information on such techniques is provided in EIPPCB (2006c) for the Large Combustion Plant sector. For each stream, appropriate monitoring (e.g. continuous or prior to release from batch or contained intermittent discharges) contributes to control measures.

In line with the principles of IPPCD, where feasible and where appropriate in terms of volumes and concentrations of contaminants and final treatment requirements, effluent from one sub-process may be re-cycled or re-used in another process. In such cases, the effluent from a sub-process may contain traces of residues from another sub-process, which would not otherwise be expected to occur. Given the wide range of installation configurations occurring in regulating emissions to the water environment from any particular installation, it is necessary to undertake a case-specific analysis of the circumstances of that plant.

For other chemical sectors, EIPPCB (2003) provide information on techniques for wastewater and waste gas treatment/management but they are potentially applicable in many sectors This is under review as of October 2009. There is a wide range of BREFs covering other sectors available from EIPPCB.[11] In some cases, these give emission concentrations for the sub-process associated with BAT. There are large cooling systems in use within nuclear power plant which are not within scope of IPPCD.

4 Directions in Future Regulation

As of October 2009, it is possible to foresee some directions in future regulation relevant to cooling system selection and operation. However, experience of the last 20 years or so suggests that relevant environmental regulation will continue to evolve rapidly in response to changing societal perspectives and challenges. It is likely that issues connected with energy, water and climate change adaptation and mitigation will be central to the challenge.

4.1 The Marine Strategy Framework Directive (MSFD) (2008/56/EC) (Establishing a Framework for Community Action in the Field of Marine Environmental Policy)

The MSFD will provide a similar approach to the protection of marine waters to that the WFD provides for inland, estuarine and coastal waters and requires the achievement of good status by 2020. Its scope includes marine waters outside the territorial limit and also coastal waters covered by WFD in so far as any aspect of the protection of the marine environment is not already addressed. Thus, aspects of water use by coastal cooling systems may be relevant to both WFD and MSFD. In the MSFD Member States, marine strategies play a role analogous to RBMPs in WFD, and there is a provision for promoting co-operation between Member States.

[11] http://eippcb.jrc.es/reference/.

The Programme of Measures (POM) anticipates spatial protection measures, recognising SPAs and SACs as set up in line with HSD and BD, including the establishment of marine protected areas in line with regional sea international agreements (e.g. OSPAR). In considering measures, Member States are obliged to give due consideration to sustainable development and socio-economic impacts of the measures. A discussion of the MSFD is provided by Mee et al. (2008). Much of the detail regarding definitions of status and Programmes of Measures remains to be worked out.

4.2 Industrial Emissions Directive (IED)

The industrial emissions directive (IED) is expected to supersede the IPPCD in the next few years. However, similar provisions related to BAT are expected to apply. IED will integrate several existing Directives, though none deal explicitly with cooling systems. However, the Waste Incineration Directive (WID) includes some controls on emissions to water from flue gas emission abatement systems which may be discharged via cooling system discharges in some installations. One possibility under discussion is that the BREFs, which simply provide information under IPPCD, may assume greater legal status. However, the details of this are unresolved as of Oct 2009. It is by no means clear that any such provision would necessarily apply to BREFs drawn up under the IPPCD regime.

4.3 Water Framework Directive

Whilst WFD was signed as long ago as the year 2000, many technical details which influence the way in which its provisions and those of its Daughter Directives will be applied in practical regulation remain to be established. In many cases such technical detail will be left to Member States though guided by outputs from the CIS programme.

It is anticipated that Guidance on Mixing Zones for Priority and PHSs will be published in 2010. Within the current substance lists, only tricholoromethane (chloroform) and nickel would be expected to be directly relevant to some cooling systems, though in some installations with other process effluents that are liable to contain PS and PHS being discharged through the cooling system discharge, its provisions may also be relevant. However, the PS list will be reviewed from time to time in line with the provisions of WFD. Moreover, once published, Member States may look to this source for guidance in other regulatory settings (e.g. Annex VIII specific pollutants[12]) which may be relevant to cooling systems.

[12] Annex VIII provides lists of substances or groups. Member States derive their own candidate Specific Pollutants and set EQSs based on whether or not their discharge is in "significant quantities".

Other CIS activity is likely to result in further guidance such as:

- "River Basin Management in a Changing Climate" is anticipated to be published in 2010 which will provide guidance on how climate change issues are to be integrated into WFD Cycles 2 and 3 (i.e. covering the period 2015–2027). This may include discussion of management of scarcity and drought and WFD reference values underpinning the definition of status boundaries in the context of committed climate change.
- Further output from the CIS on the relationship between monitoring and status is anticipated.

4.4 Climate Change Adaptation and Mitigation

The European Commission is very active in the Climate Change arena. There is considerable activity on mitigation (measures to reduce related emissions) and adaptation. The Commission White Paper (EC 2009) identified the priority to be given to reducing the EU's vulnerability to climate change. Prominent within this adaptation discussion is consideration of protection of the water environment and increasing the resilience of production systems, including energy security. Whilst Member States will also develop and apply their own policies, the Commission is keen to ensure policy coherence and is proceeding in two phases:

- 2009–2012: Phase 1
  - Improving knowledge base
  - Integrating adaptation into key policy areas
  - Employing a variety of instruments to deliver adaptation
  - Promoting international co-operation
- Beyond 2013: Phase 2
  - Comprehensive adaptation strategy framework

It can, therefore, be anticipated that issues of climate change adaptation and mitigation will feature ever more prominently in practical regulation, reinforcing the fundamental issue in cooling system choice and operation, i.e. striking the balance between the benefits of superior thermal efficiency resulting from use of water for cooling and its consequences in the water environment compared with the range of merits, demerits and impacts of alternative cooling options.

4.5 Member State Regulatory Initiatives

Member States can be expected to take action in line with their own strategies. Whilst these may ultimately trace back to EU WFD, MSFD or Climate Change drivers, they will reflect the Member States specific circumstances. Areas of activity which may influence choice of cooling systems include:

- Regulation of temperature, temperature rise or thermal discharges.
- Regulation on use of water resources or allocation of water use rights or the use of economic instruments (e.g. water use pricing, water allocation pricing or water rights trading).
- Climate Change Adaptation
  - Including risk assessment of security of supply/infrastructure robustness
  - Market based instruments for ecosystem services
- Climate Change Mitigation measures
  - Development and implementation of Carbon Capture and Storage technologies
  - Further development of market based instruments

5 Concluding Remarks

Choice and operation of cooling systems is a vital consideration for many sectors, none more so than in the power sector. Over the next 10–20 years or so, there will be substantive investment in new power plant across Europe each with design lifetimes of between 25 and 60 years. Integral to this development will be choice of plant type and location. Such choices are fundamentally linked to judgements on the potential for access to water for cooling and the reliability of that access (including both the physical availability of water and any regulatory limitations on its use). Developing a plant, therefore, requires taking a view on the likely regulation of that plant throughout its design life. Unforeseen restrictions on the plant's operational window, resulting from constraints on cooling system operation, could have major implications for the commercial viability of that plant–location combination.

In choosing cooling systems, weighing up the pros and cons of the range of effects on the water environment, other media and on wider societal factors, taking account of the superior thermal and process efficiency which use of water for cooling provides, will remain as important over the next generation of industrial installations as it has been historically. Choices made in the near future will influence the efficiency and security of Europe's energy infrastructure for the next two generations.

Whilst the regulatory context for decision-making will continue to evolve and continue to differ in detail between Member States, access to sound science on the environmental consequences of the operation of cooling systems, as provided by the preceding chapters, is an essential ingredient to enable regulation to deliver sound outcomes for society as a whole.

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Chapter 21
Cooling Water Systems: Efficiency vis-à-vis Environment

Sanjeevi Rajagopal, Vayalam P. Venugopalan, and Henk A. Jenner

1 Introduction

Human beings use water for different purposes. Among the various uses, industrial use is by far the largest single class of use, especially so in developed countries. Among the various industries, power generation industry ranks as the largest user of water, where water is used mostly as a cooling fluid. A large 2,000 MWe direct cooled plant requires about four million cubic metres of water daily for cooling. This huge requirement is met from a suitable source such as river, lake or coastal sea and returned, fully or partially, depending on the type of the cooling water circuit. Therefore, it must be borne in mind that this water is not consumed in the process; it is simply abstracted and then returned to the source water body.

It is known that less than 0.2% of the earth's total water resource is available to mankind as freshwater. What is equally important is that most of this is located at remote locations, away from major centres of population. In such a situation, proximity to source of water becomes an important criterion in the choice of location of an industrial unit that requires cooling water. In the case of a power plant, two other major criteria are proximity to load centres and proximity to sources of fuel. Coal plants, for example, need large amounts of coal (over three million tonnes per year

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for a 1,000-MWe plant) to be transported and this is an important factor in the choice of its site of construction. Nuclear power plants, on the contrary, have the advantage that the quantity of fuel required is comparatively very small and hence they can be easily located at coastal locations so as to use seawater for once-through cooling.

In thermal (coal) or nuclear power plants operating on steam cycle, the cooling water is used to remove surplus heat from the steam circuit. Unfortunately, in the Rankine cycle based on which these plants operate, there is a loss of about two thirds of the energy produced due to inherent limitations of converting heat into mechanical energy. The actual amount of heat discharged would depend on the thermal efficiency of the plant. Thermal efficiency is dependent on the difference in temperature between the internal heat source and the external environment where the surplus heat is dumped; the larger the difference, the greater the efficiency. In simpler words, colder the cooling water, higher the thermal efficiency of the plant, provided all other things are equal. Indirectly cooled plants (recirculating type with cooling towers) have slightly lower overall efficiency compared to plants cooled by once-through systems. Nuclear power plants generally have a thermal efficiency of about 34–36%, while typical coal plants have slightly higher efficiency, with the newer plants approaching efficiency of 40%. Many nuclear power plants, as mentioned earlier, have once-through cooling systems, as their location can be chosen based on the availability of water rather than proximity to the fuel source. It can be anticipated that with increasing restriction on carbon emissions, there will be renewed thrust on nuclear power in many countries and locating more and more plants at coastal locations could place coastal ecosystems at risk from large-scale abstraction and discharge of cooling water.

2 Operational Problems

Abstraction of large amounts of cooling water on a continuous basis presents large number of problems to the plant operator (Venugopalan and Narasimhan 2008). Organisms, both planktonic and benthic, which are normally present in the water body gain entry into the cooling water system (CWS). While the former group largely transits through the system, the latter extends its habitat into the various components of the CWS, given that the conditions (substratum, flow, food availability) inside the CWS are more or less ideal for survival (Venugopalan et al. 1992; Rajagopal et al. 1998). The ensuing phenomenon of biofouling interferes with the operation of the plant in several ways—flow restriction or even blockage, reduction in heat transfer efficiency and enhancement of corrosion of metals and alloys (Fig. 21.1). Biofouling is a universal problem in CWSs of power plants, with its severity dependent on factors such as type of water body, flow, temperature conditions, CWS design, etc. Macrofouling, especially in tropical marine conditions, is an extremely formidable problem because of the inherent diversity of the species involved. In typical cases more than about 100 species have been observed to be

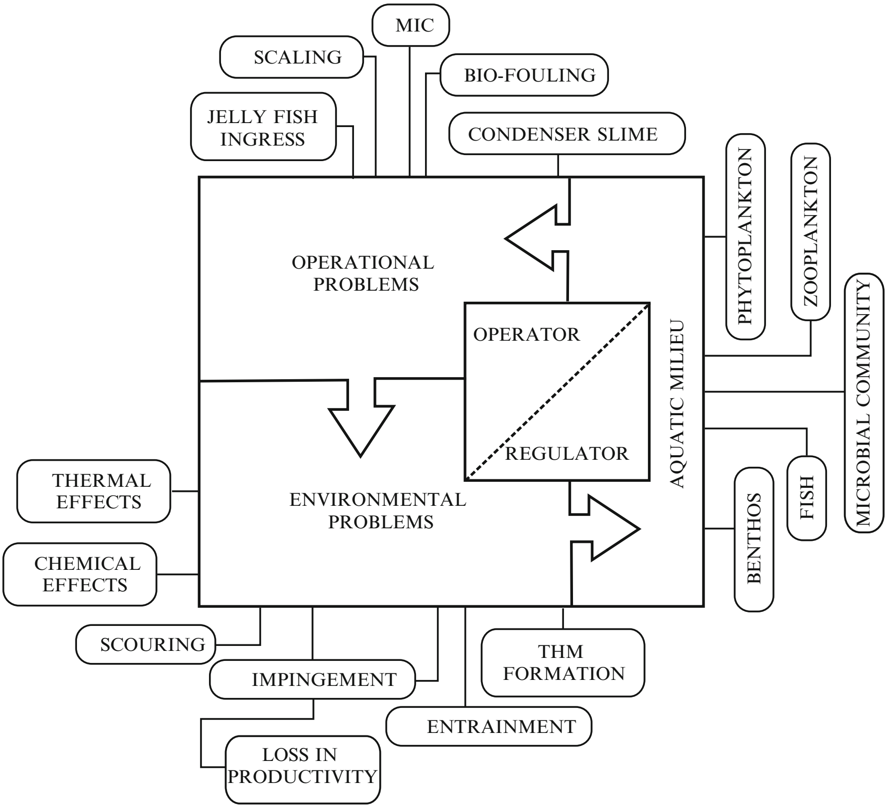

Fig. 21.1 A snapshot of the operational and environmental issues emanating from large-scale cooling water abstraction and discharge

involved, although the ones that actually impact the operation of the plant may be just a handful. It has also been observed that problems could be site-specific with plants located in similar geographical conditions presenting very different fouling scenarios (Venugopalan et al. 1994). The above factors make biofouling control a challenging task, given the fact that the operator is constrained to use antifouling measures that should effectively control the organisms inside the cooling water circuit, but at the same time not adversely impact those residing outside it.

The type of antifouling method used by any affected industry depends on the system being fouled. Shipping industry, for example, largely resorts to application of antifouling paints which are either toxic or non-toxic (e.g., foul-release type). For CWS operators, the antifouling method of choice has been use of injectable biocides, though in recent times, in situ generation of biocide is becoming more and more common (e.g., electrochlorination). Chlorine still remains the most commonly applied biocide because of its relatively low cost, ease of application and broad-spectrum activity. It is applied in the form of gaseous chlorine, hypochlorite or electrolytically generated chlorine. However, chlorine suffers from several disadvantages such as safety issues of storage (of gaseous chlorine), frequent downtime in the case of dosing systems and production of harmful chlorination by-products. Interestingly, severity of some of these problems can be reduced and efficiency of the method increased by resorting to advanced dosing protocols such as Pulse Chlorination (Macdonald et al. 2012). Apart from chlorine, other oxidising biocides such as chlorine dioxide are also gaining acceptance due to their advantages such as low chemical demand and reduced by-product formation (Petrucci and Rosellini 2005). Alternative antifouling methods such as ozonation, UV treatment, use of ionising radiation, use of electrical or acoustic methods, biological control methods, etc. are being studied mainly at laboratory scale; most of them have not yet been employed on commercial scale (Rajagopal et al. 2012). Among the various alternative options, heat treatment has been found to be an attractive alternative control strategy and is being routinely employed by a few power stations (Rajagopal et al. 2012). An interesting strategy involving encapsulation of a toxic substance within edible material has been proposed as an environmentally benign method to combat bivalve fouling (Costa et al. 2012).

3 Environmental Effects

Irrespective of the condenser cooling method used (direct or indirect), CWSs have their own environmental and societal impacts and are, therefore, subject to regulation (Fig. 21.1). The environmental impacts are largely due to the very act of abstraction of water (entrainment, impingement) and due to the discharge of heated effluents (thermal and chemical effects). Societal impacts emanate from the unsightly presence of huge cooling towers and problems (e.g., plume or ice formation) associated with their operation. All electrical power plants that are cooled by water drawn from natural water bodies are under regulatory control regarding the temperature of the outgoing water or the difference between the inlet and outlet temperatures (ΔT).

Coastal waters, as mentioned earlier, are increasingly being used as source of cooling water for a large number of new plants being set up. However, many ecologically sensitive areas such as inland seas, bays, estuaries, marine sanctuaries, coral reefs and mangroves may fall under the above category and are generally avoided as heat sink of power plants. In many countries such as India, no discharge is permitted in such ecologically sensitive areas as estuaries, mangroves, reefs and breeding grounds of aquatic animals.

In general, the environmental effects of CWS on the fauna and flora of the receiving water body could be classified as direct or indirect. Direct effects impact the organisms directly (lethality or effects on physiological functions) and include such effects as mortality of organisms inside the cooling circuit, mortality at the discharge site, delayed mortality, decrease in phytoplankton productivity, changes in behaviour/physiology, reproductive changes, displacement of fauna or flora and changes in species composition. Indirect effects may be more subtle and caused by changes in the external milieu brought about by the discharge of water, such as effects caused by changes in hydrographic conditions, increased predation and incidence of parasitic infections. Detailed studies on the impact of CWS are required for quantification of actual impact and for development of predictive capabilities. Precise quantification will also help in refinement of regulatory stipulations, as systematically carried out long-term studies can provide valuable database that can be used as the basis for further fine-tuning of regulatory standards. Such long-term ecological data, as stated by Langford (1990), would be a major economic and ecological asset. It is extremely difficult to assess the impact on the whole suite of organisms present in the receiving water body. Hence researchers may employ the concept of indicator organisms, which, if selected after careful analysis, can provide valuable information about the potential impact of CWS on receiving water bodies (Israel et al. 2012).

There are several levels at which the effects on organisms can be studied. Studies at molecular and cellular levels provide information on the threshold levels at which detrimental effects are manifested and on the mode of action of the stress factors. However, one also needs information about the impact at population, community and even ecosystem levels. It is quite impossible to collect all such information from laboratory level experiments. Mesocosm and field level experiments are very valuable in this respect (Poornima et al. 2012). However, it must be borne in mind that complexity of the experimental systems increase as we go to higher levels of organisation and consequently there would be a corresponding decrease in reproducibility.

Ecological studies at power plant sites need to look at the broad picture of the ecosystem as a whole and accordingly, have to include studies on temperature distribution, distribution of other hydrographic parameters, general circulation patterns, coastal currents and tides, local bathymetry, nutrient (especially N, P and Si) dynamics and sediment movement characteristics. Unfortunately, not many studies have attempted to comprehensively address all these issues. The data gap is especially glaring in the tropics, which, by virtue of their high ambient temperatures, are particularly at risk arising from further thermal enrichment and the resultant ecological perturbation.

The impact of cooling water abstraction and discharge are borne largely by (1) the flora and fauna entrained along with the cooling water, (2) larger organisms such as fishes that are impinged, (3) intertidal organisms inhabiting the discharge zone (in the case of shore discharge) and (4) those entrained into the thermal plume in the receiving water body. Entrainment mainly affects planktonic (both holoplankton and meroplankton) organisms, which are smaller than the screens employed to prevent entry of organisms in the CWS. The organisms are subjected to mechanical, chemical and thermal stress during their passage through the CW circuit (Capuzzo 1980). Their survival rate has been reported to be a function of their size, shape and body constitution (Bamber and Seaby 2004). Ahamed (1997) reported that ichthyoplankton entrained into the cooling water circuit of a coastal power plant in India suffered mortality depending on the stress involved: mortality due to low dose continuous chlorination was 1–8% and mortality due to mechanical effects was 31–42%, while mortality due to thermal effects was in the range 7–16%. Recently, observations of the effect of phytoplankton and productivity have been discussed by Vinitha et al. (2010) and Poornima et al. (2012).

Impingement mostly affects juvenile and adult fish. There have been studies to find out the magnitude of biomass lost in these processes (see Bruijs and Taylor 2012). Ahamed (1997) reported that the daily loss of fish due to impingement was roughly equal to the amount of fish caught by an ordinary fishing boat operating in the area. His studies, carried out at a tropical coastal power station, showed that mainly four types of fishes were impinged on the travelling water screens: shoaling fishes, ribbon-shaped fishes, foraging fishes and small fishes. Obviously, body size, shape and behavioural patterns appear to be important in impingement phenomenon. Ahamed (1997) also observed that impingement varied with time of the day and water transparency, indicating that visual clue played a very important role, enabling the fishes to avoid impingement. This kind of information can be used to design fish protection devices that can be incorporated into CWS design for minimising fish impingement (Bruijs and Taylor 2012).

4 Concluding Remarks

While considering the general impact of abstraction and discharge of water for CWS, (1) it should be borne in mind that the ambient water body (at least in the case of discharge into coastal waters) is substantially larger compared to the discharge, (2) inorganic chemical constituents of water mostly remain unchanged due to abstraction and discharge, (3) dissolved oxygen is affected by a number of factors but the levels in outgoing water are generally sufficient to support life, and (4) the CWS provide large surface area for colonisation of micro and macro organisms, due to the activity of which, chemical and biological characteristics of the water could undergo significant changes. Studies relating to ecological impact of CWS on receiving water bodies generally show that a small area close to the discharge zone bear the maximum brunt with respect to changes in physical, chemical and biological characteristics. In this context, it is important to understand the concept of mixing zone. Mixing zone is a relatively small area (more precisely, volume) at the discharge zone, where the effluents mix with the receiving water and where there would be relatively large temperature change. The designated water quality criteria (e.g., ΔT) are generally applicable at the boundary of the mixing zone. Delineation of a mixing zone permits the utility to have a definite buffer zone where the perturbations due to cooing water discharge can be contained. However, a mixing zone is not permitted universally and in many countries such a concept is non-existent. Thermal ecology studies carried out at Kalpakkam (India) near a nuclear power plant site have shown that the volume of water impacted (by a ΔT of 2–3°C) is less than 0.5% of the volume of water abutting the power plant site (Thermal Ecology Studies 2004). Delineation of a legally recognised mixing zone makes economical and ecological sense because it allows the plant operator to contain the impact within a stipulated zone and benefits the environment by making the impact zone as small as possible.

The increased use of coastal waters for industrial cooling has been more or less matched by an increased concern regarding the impact of such activity on the receiving water body. Research efforts must be continued so that neither industrial progress nor ecological sustainability need be compromised. The focus of research should be to reduce the environmental impacts (especially impingement and entrainment) of once-through cooling through reduced water usage, use of green water treatment methods and development of advanced cooling technologies. It is hoped that the fruits of industrial development can be enjoyed by all without putting the environment to unacceptable risk.

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