Phycoremediation of Emerging Contaminants

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1 Introduction

1.1 Emerging Contaminants

Emerging contaminants (EC) or contaminants of emerging concerns (CEC) cover a broad spectrum of chemicals and compounds which are being recognized as potentially harmful in the last decade or so. These compounds may have been in application for a long period, but their environmental and health impacts are being observed and their hazardous nature identified recently; these might belong to a whole new class of compounds in application for their certain properties. The major concern over these emerging contaminants is the nonavailability of analytical techniques to identify them in the first place within the complex environmental matrices and to quantify them since their concentrations are very low (ranging from μg L^{-1} to ng L^{-1} or even lower). Because of the nonavailability of these protocols for either identifying or to quantify these compounds, regulatory limits are virtually nonexistent. This results in their uninhibited discharge into environment. With the advancement of analytical methods, such compounds are being increasingly identified and quantified. In addition, their environmental hazards are being recognized, thus raising a concern on their continued applications and initiating a search for better alternatives. The endocrine disruption potential is one of the major concerns of many of these products.

1.1.1 Pharmaceutical and Personal Care Products (PPCP)

The continuous and unchecked use of pharmaceutical and personal care products (PPCP) over a long period has resulted in their presence in aquatic bodies all over the world (Li et al. 2013; Yang et al. 2013). These products include, but not limited to, following distinct classes of compounds (Ellis 2006): veterinary and human antibiotics (e.g., trimethoprim, erytromycine, lincomycin, sulfamethaxazole, chloramphenicol, amoxicillin, etc.), analgesics and anti-inflammatory drugs (e.g., ibuprofen, diclofenac, fenoprofen, acetaminophen, naproxen, acetylsalicylic acid, fluoxetine, ketoprofen, indometacine, paracetamol, etc.), psychiatric drugs (e.g., diazepam, carbamazepine, primidone, salbutamol, etc.), lipid regulators (e.g., clofibric acid, bezafibrate, fenofibric acid, etofibrate, gemfibrozil, etc), β-blockers (e.g., metoprolol, propranolol, timolol, sotalol, atenolol, etc), X-ray contrasts (e.g., iopromide, iopamidol, diatrizoate, etc.), steroids and hormones (e.g., estradiol, estrone, estriol, diethylstilbestrol, etc), fragrances (e.g., nitro, polycyclic, and macrocyclic musks; phthalates), sunscreen agents (benzophenone, methylbenzylidene camphor, etc.), insect repellents (e.g., N, N-diethyl toluamide), and antiseptics (e.g., triclosan, chlorophene, etc.). Recent advancements in analytical techniques, e.g., GC-MS, LC-MS, and LC-MS-MS, have lowered their detection limits to parts per trillion (ppt) levels (Oulton et al. 2010a), which has resulted in the increasing observations of these compounds or their metabolites in environmental matrices. The recent interest in these contaminants and their metabolites is due to their possible toxicological nature (including endocrine disruptive potential) to humans and other living organisms which is often complicated by their synergistic effects (Tyler et al. 1998). The sources of these products in aquatic bodies are mainly from wastewater treatment plant effluents and also due to leaching from landfills of domestic/medical garbage or sludge laden with these compounds (Kaplan 2013). Due to their persisting nature in environment, these compounds could affect many generations

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B. Singh et al. (eds.), *Algae and Environmental Sustainability*, Developments in Applied Phycology 7,
DOI 10.1007/978-81-322-2641-3_11

of organisms and produce exposure effects that may be correlated wrongly to other factors (Daughton and Ternes 1999; Kaplan 2013).

1.1.2 Pesticides

The use of pesticides in human civilization has a long history spanning centuries, where earlier pesticides were mainly of inorganic nature such as calcium arsenate and lead arsenate and some fluoroorganic compounds (Battaglin and Fairchild 2002). Since then, numerous new organic compounds have been developed for their application as pesticides. Many such pesticides, viz., DDT (dichlorodiphenyltrichloroethane), remain in the environmental matrices long after their targeted application, mainly due to their persistent nature. This results in their subsequent buildup and provided their toxicological profile for human health; over the years these pesticides have been identified as contaminants of concern. Although, with improved analytical methods and availability of their toxicological profile, many of these pesticides, for example, DDT and endosulfan, have been banned and their application discontinued; environmental matrices are still contaminated with their presence. A major concern is the carcinogenic nature and endocrine-disrupting potential of a majority of these compounds even at low concentrations (at ppb levels). As the information is garnered about these pesticides and their toxicological risks determined, new compounds presumably of lower risks are introduced as a replacement. However, with continued application of these new compounds, more information about their fate and hazardous characteristics are gathered, and new compounds are further searched. Such application of many pesticides through decades results in the buildup of a very complex mix of original compounds as well as their metabolites in environmental matrices and whose interactions are yet unknown and hence a matter of great concern.

1.1.3 Endocrine Disruptors

A normal hormonal function in a living organism is a prerequisite for good health. However, many natural and synthetic compounds mimic and possess similar chemical and biological properties like these hormones and thus disrupt/interfere with their normal functions or organisms. A wide variety of compounds has demonstrated their ability to interfere with the endocrine system and hence is collectively termed as endocrine disruptors or endocrine-disrupting compounds (EDC). These include pesticides (e.g., atrazine), surfactants, dioxins, polychlorinated biphenyls (PCBs), synthetic estrogens (e.g., 17β-ethinyl estradiol), natural estrogens (e.g., 17β-sitosterol, estrone), natural androgens (e.g., testosterone), phytosteroids (e.g., 17β-sitosterol), etc. (Richardson and Ternes 2005). The main complexity in streamlining the study and analysis of these compounds arises due to their highly variable affinities to hormonal receptors and different pathways. Due to these reasons, their endocrine potencies show a huge variability. Continued exposure of organisms to these EDCs may lead to drastic impacts on their health and the overall ecology of the system.

1.2 Major Challenges in Conventional Wastewater Treatment in Removal of Emerging Contaminants

Effluents from conventional wastewater treatment plants are recognized as a major source for these emerging contaminants into receiving bodies, mainly due to the limitations of these plants in achieving an effective removal (Battaglin and Fairchild 2002; Oulton et al. 2010b; Sedlak et al. 2000). This is in part due to the inherent limitations of the conventional treatment processes which are not designed and optimized for these emerging contaminants, for example, secondary treatment is optimally designed for BOD removal and in part due to the specific properties of these compounds which render it very difficult to be removed from water with conventional methods, such as high chemical stability, low biodegradability, low sorption coefficients, etc. Another major factor which complicates the removal of ECs is their highly variable response to a particular treatment process due to the sheer number and diversity of these compounds.

1.2.1 Low Levels and Limited Availability of Protocols for Identification and Quantification

The foremost challenge in the study of the fate of ECs in wastewater treatment plants is the unavailability of appropriate analytical protocols to identify and quantify such compounds and their metabolites at their low levels of presence (Battaglin and Fairchild 2002; Petrović et al. 2003). Without any identification and quantification, these products have not been an area of focus while developing the conventional processes. Hence, conventional treatments are not efficient in their removal because of the inherent design limitations.

1.2.2 Low Biodegradability

Most of these compounds have low biodegradability with conventional microbial populations found in treatment plants under natural conditions. This results in its inefficient removal during such treatments. For example, Ternes (1998) observed only 7 % removal of carbamazepine in municipal sewage treatment plants. Oulton et al. (2010a) also identified the conventional treatment plants to achieve removal efficiencies of all PPCPs not higher than 1-$\log_{10}$. A major reason for such poor biodegradability of these compounds in conventional treatments is the requirement of stable specific microbial culture for them. Since conventional activated sludge systems do not facilitate the enrichment of such specific culture because of their suspended growth and low retention times, which may result in a wash out, the removal efficiencies are low. In comparison, processes such as trickling filters allow the development of a stable microbial culture which could be, with operation, enriched specifically for these endocrine disruptors and hence could perform better in removal of these compounds (Kasprzyk-Hordern et al. 2009).

1.2.3 High Water Solubility

Many of these compounds, mainly pharmaceuticals, demonstrate high solubility in water. For example, norfloxacin, tetracycline, and fluoxetine have water solubility of 1.78×10^5 mg L^{-1}, 5×10^4 mg L^{-1}, and 5×10^4 mg L^{-1}, respectively. Such high solubility also results in high variability in their levels in the influents. Petrie et al. (2014a) observed acetaminophen to appear at concentrations ranging from 6924 to 492,340 ng L^{-1} in influent wastewater. Such high variability in ECs concentrations complicates the optimization of a process design for their effective treatment.

1.2.4 Solid Phase Partitioning

Another important aspect of dealing with these compounds is its partitioning between solid and liquid phase depending on their sorption coefficients and subsequent hydrophobicity. Many organic pesticides and drugs (e.g., triclosan and triclocarban) are extremely hydrophobic in nature (log K_{ow} of 4.2–4.8) and thus are retained within the solid matrices (e.g., sludge etc.). For example, concentrations in excess of 1 mg kg^{-1} in biosolids have been reported for chemicals such as triclocarban, triclosan, bisphenol A, ciprofloxacin, ofloxacin, etc. (Petrie et al. 2014a). Disposal of such laden sludge is a major source of contamination for these compounds. In addition, the mobility of these compounds in the solid matrices, e.g., soil, is also dependent on many factors and widely varies among all compounds. For example, partitioning of charged endocrine disruptors is highly governed by electrostatic forces (Hyland et al. 2012). pH also plays a critical role in such partitioning behavior within the complex solid-water matrices (Petrie et al. 2014a).

1.2.5 Metabolites

Majority of these compounds are present with metabolites or undergo transformation into its metabolites during conventional treatment, both biological and physicochemical. Serious concerns about these metabolites have been raised recently, since these could reach concentrations highly in excess to their parent compounds and may also be biologically active in nature (Kasprzyk-Hordern et al. 2008; Petrie et al. 2014a). For example, Huerta-Fontela et al. (2010) observed carbamazepine to be present in influent wastewater at concentrations less than 1.5–113 ng L^{-1}, while concentrations of one of its metabolite carbamazepine epoxide ranged from 880 to 4026 ng L^{-1}. In addition, many of these metabolites are more toxic in nature than the parent compound and hence may pose a serious threat (Petrie et al. 2014a). The ability of these metabolites to again form the parent compound within the environmental matrices after treatment is also a concern, and limited information is available. A major limitation is that pathways for these metabolite formations are not yet identified and established for majority of the parent compounds.

1.3 Bioremediation

Bioremediation is a process where biologically mediated treatment of hazardous pollutants with naturally occurring organisms into compounds with less or no toxicity is achieved. The treatment occurs by the uptake of these compounds from environmental matrices by organisms and subsequent utilization for their growth or enzyme-mediated breakdown into other less hazardous compounds that are released into the environment.

1.3.1 Phytoremediation

Various plants have the ability to remove pollutants from environmental matrices and hence in the process provide treatment. Phytoremediation involves this ability of plants and their symbiotic microbes to effectively remove various pollutants from a contaminated site. This process has been successfully implemented worldwide to remediate heavy metals, pesticides, and other hazardous organic compounds from the environment (Ali et al. 2013; Malik 2004). Since it is a lost cost treatment option, phytoremediation is applicable at large contaminated sites where other treatments are not cost effective. Phytoremediation occurs by different distinct mechanisms such as phytoextraction, phytostabilization, and phytotransformation. The direct uptake of a pollutant from environment by plants is termed as phytoextraction. This process directly reduces the level of contaminants in the bulk surrounding medium. Uptake of heavy metals by plants occurs by phytoextraction (Ali et al. 2013). Another mechanism by which plants treat the contaminated sites is by stabilizing and containing the pollutants within the site. Plants do not uptake the pollutants but provide a microenvironment near their root zone, where with the help of symbiotic microbes, sequestering of the pollutants and sorption are supported. Such stabilization reduces the bioavailability of these pollutants and lowers their harmful effects in long term. Plants can also transform various compounds into less toxic metabolites with various enzymes by the process of biotransformation (Ali et al. 2013). However, phytoremediation also suffers from many limitations. Effective treatments of contaminated sites may need long duration depending on selected plant species, contaminants, and level of contamination. Also, plants are able to treat low to mild levels of contaminants in sustainable manner, since high levels of pollutants are toxic for them too. Such phytoremediation also poses a very realistic threat of contaminating the whole food chain and requires proper management (Ali et al. 2013).

1.3.2 Phycoremediation

Pollution abatement from contaminated environmental matrices with the application of algae is termed as phycoremediation. Algae have historically been utilized for domestic wastewater treatment and have led to the development of specific processes (e.g., raceway ponds and photobioreactors). Their ability to uptake heavy metals has also lead significant research on their application for heavy metal removal (Chojnacka et al. 2005; Perales-Vela et al. 2006; Yu and Wang 2004) and other hazardous organic pollutants (Muñoz et al. 2006; Munoz and Guieysse 2006). In addition, algae have been demonstrated as a suitable sink for CO_2 (Jacob-Lopes et al. 2009). The ability of algae to grow on wastewaters in hitherto nonarable land with high productivity makes phycoremediation an attractive subset of bioremediation. The value-added algal biomass can potentially be utilized for extracting many useful products, for example, lipids, proteins, carbohydrates, pigments, etc. (Olguín 2012). The recent focus in phycoremediation is on following sustainable biorefinery approach, where wastewater treatment and removal of other pollutants is complimented with the value extraction from generated algal biomass (Prajapati et al. 2013b; Subhadra 2010).

2 Ecological Fate of Emerging Contaminants

Emerging contaminants are mainly released into the environment due to its unregulated applications. Such applications include domestic or medical discharges of various PPCPs and other compounds, agricultural applications or runoff of various pesticides, or inadequacy of conventional treatment in their effective removal from influent streams and thus discharge into receiving bodies. Once these contaminants enter environmental matrices, they undergo various processes which govern their ecological fate in the system.

Contaminants, as they reach aquatic bodies due to inefficient sewage collection/treatment or leaching from agricultural fields/domestic sources, pose a direct threat to living organisms and the ecology of these receiving bodies. Many of these dissolved contaminants (e.g., gemfibrozil, ibuprofen, ketoprofen, etc.) have shown evidences of undergoing photolysis and effective breakdown into harmless metabolites (Lin and Reinhard 2005). However, the ability of these compounds to undergo photolytic breakdown varies substantially due to their different structures. In addition, such photolytic degradation could also result in compounds of higher toxicity. However, the actual pathways of such degradation for majority of these compounds are still not available and pose a serious limitation in establishing their fate. Indirect photolysis of many such compounds also occurs due to the presence of free radicals in aquatic bodies (Ryan et al. 2011). Also, compounds which are resistant to such degradation persist in aquatic bodies and are more prone for uptake by living organisms and eventually undergo biodegradation or bioaccumulation. This uptake also reflects in the harmful effects on the health of these organisms and ultimately affects the ecology of the whole system.

Those compounds which are hydrophobic in nature get sorbed on various organic solids or sediments present within these matrices and are effectively removed from liquid phase. Such solid phase partitioning results in heavily laden solid mixture which is retained in the matrix where partial desorption may occur eventually, thus releasing these compounds into the aquatic phase. In addition, such solid–liquid phase partitioning is also governed by various environmental factors such as pH and temperature. The widely different characteristics of these compounds also determine the governing mechanism of such phase separation and their relative distributions. For example, charged and uncharged compounds experience different levels of electrostatic forces.

In addition to these major physicochemical processes occurring in the receiving bodies, emerging contaminants also undergo biological transformation during their original use or during their treatment within the treatment plants in both aerobic and anaerobic conditions. For example, Tiwari and Guha (2013b) studied the degradation of endosulfan in both aerobic and anaerobic conditions and established the degradation pathways. Degradation metabolites for acetaminophen and azithromycin have been observed in the effluent from a treatment plant (Gómez et al. 2010). Similarly, Tiwari and Guha (2013a) quantified various degradation metabolites of endosulfan and chlorpyrifos. However, the availability of information about degradation products and the governing pathway is very limited for majority of the emerging contaminants. This results partially due to the nonavailability of analytical protocols for identification and quantification of these products and partially due to the complexity of the environmental matrices and highly variable formation mechanism for a single product from a parent compound. Since many of the intermediate metabolites are more toxic than parent compounds, the degradation actually worsens their impact on the environment. Hence, it is utmost important to focus on these metabolites along with parent compounds while performing their removal and degradation analysis within treatment plants or other environmental matrices.

3 Ecotoxicological Risks of Emerging Contaminants

The main reason behind increasing concerns over ECs is due to their ecotoxicological risks toward humans and other living organisms. Most of these compounds show acute or chronic toxicity depending on their concentrations in environmental matrices or the exposure duration. Main effect is their endocrine-disrupting potential where many of these compounds can mimic the hormonal functions within the body and disrupt/interfere with endocrine system. The toxicity of a particular compound is determined by acute toxicity test on a single organism, and such analyses have been performed for various parent compounds as well as their metabolites. Based on their EC_{50} values, compounds can be classified as harmful (EC_{50} as 10–100 mg L^{-1}), toxic (EC_{50} as 1–10 mg L^{-1}), or very toxic ($EC_{50} < 1$ mg L^{-1}). Petrie et al. (2014b) collated the information about EC_{50} values of different contaminants and analyzed their potential of being very toxic (e.g., erythromycin) to harmful (e.g., trimethoprim) for aquatic organism. However, such toxicity analysis is valid only for test species and is not universal. Other organisms can respond differently than the subject organism. Still, such EC_{50} values provide an indicative baseline for the toxic nature of these compounds. Farré et al. (2008) observed that the concentrations of emerging contaminants such as pharmaceutical products in environmental matrices are 2–3 orders of magnitude lower than their required levels for causing any acute toxicity. These compounds pose a more serious concern due to their potentials to cause chronic toxicity during prolonged exposure to living organisms even at low levels. Another factor which governs the toxicity profile of these compounds is their complex behavior in a mixture. Environmental matrices accommodate a mixture of various such compounds. The toxicological profile of these mixtures might be very complex and synergistic in nature. For example, the mixture of diclofenac, ibuprofen, naproxen, and aspirin showed increased toxicity than their individual effects, thus highlighting the synergistic behavior of these compounds in a mixture (Cleuvers 2004). In addition to the acute and chronic toxicity analysis of these compounds, Petrie et al. (2014b) also highlighted the importance of investigating the toxicological nature of different chiral enantiomers of these compounds which are used concurrently, since there might be a severe difference in their toxicity levels. To analyze and streamline the toxicity analysis of mixture of various such compounds, Eljarrat and Barceló (2003) proposed the concept of toxic equivalency factor to denote the overall toxicity of the whole mixture. However, the ecotoxicological analysis of these emerging compounds while incorporating their synergistic as well as enantiomeric effects remains to be streamlined and standardized for universal applicability and acceptance.

4 Phycoremediation of Emerging Contaminants

As per Chemical Abstracts Service Registry (CAS RN 1649503-59-2), presently, more than 91 million organic and inorganic substances are being formulated and in use, and more than 12,000 new formulations and compounds are being added daily (CAS 2012). All these chemicals and their metabolites are continuously being introduced, disposed, and dumped to various environmental matrices through industrial discharges, agricultural runoff, or inappropriate waste disposal practices and pose deleterious effects to the environment, all living beings, and ultimately to the human health (Daughton and Ternes 1999; Pavlostathis et al. 2003).

In recent years, the occurrence of traces of emerging contaminants such as pharmaceuticals and personal care products (PPCPs), endocrine-disrupting chemicals (EDCs), disinfection by-products (DBPs), persistent organic pollutants (POPs), pesticides, cyanotoxins, etc., in the natural and drinking waters has been reported widely. In aquatic systems, these chemicals get adsorbed and immobilized subjected to various transformations depending upon the biogeochemical processes and prevailing environmental factors. Such chemical contaminants remain available to the benthic microorganisms through the sediment water interface (Perelo 2010). The US EPA (2009) has listed 116 drinking water contaminants in Contaminant Candidate List 3 (CCL3), which have been detected in public water systems in the USA which are of serious concerns. The presence of such low levels of these contaminants in the environment may not stance lethal effects immediately, but in a long term it may pose catastrophic effects on aquatic organisms and human health.

It is now well established that biological remediation is eco-friendly, economically viable, and comparatively less expensive than chemical or physical treatment processes (Herbes and Schwall 1978). However, studies and reports on the phycoremediation of organic pollutants by microalgae and cyanobacteria lag far behind than that of bacterial and fungal biodegradation (Subashchandrabose et al. 2013).

As far as phycoremediation is concerned, microalgae and cyanobacteria have advantages over various species of bacteria and fungi as these species can grow autotrophically, heterotrophically, or mixotrophically in very harsh environmental conditions, i.e., low nutrient level, wide pH and temperature, etc. (Subashchandrabose et al. 2013). Various cyanobacteria and microalgae have been identified for their potential of wastewater treatment especially nutrient removal such as nitrogen and phosphorus and biomass production (Prajapati et al. 2013a; Shriwastav et al. 2014). However, literature on degradation of complex organic compounds such as polyaromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), pharmaceutical, and personal care products is limited.

Previous studies on microalgae-based wastewater treatments have demonstrated that the removal of organic contaminants (EDCs, PAHs, PCBs, pesticides, surfactants, etc.) takes place by virtue of various physicochemical processes which include both biotic transformation through microalgal accumulation, metabolization, and degradation and abiotic transformation through photodegradation, volatilization, sorption, and adsorption (Abargues et al. 2013; de-Bashan and Bashan 2010; Haritash and Kaushik 2009; Matamoros et al. 2015).

Recently, phycoremediation of 26 types of various emerging organic contaminants including pharmaceuticals and personal care products, pesticides, surfactants, anticorrosive agents, fire retardants, etc., in high-rate algal ponds (HRAPs) was reported by Matamoros et al. (2015). The findings of this study revealed 0–90 % removal, based on the nature of the chemical compound which is majorly achieved by photodegradation and biodegradation. However, hydraulic retention time (HRT) and seasonality affect the efficiencies of HRAPs.

Detoxification, degradation, and transformation of organic environmental contaminants by the use of microalgae/bacteria, microalgae/cyanobacteria, or bacteria/fungi consortia has been found to be more efficient and easy in comparison to the individual species (Subashchandrabose et al. 2013). As in microbial degradation of organic compounds, both species act in a symbiotic way. In a consortium, the catabolic degradation of organics by bacteria is done by getting electrons from algae and the mineralization end products being used by algae for their photoautotrophic growth. Figure 11.1 provides an overview of the phycoremediation for various emerging contaminants.

4.1 Pharmaceutical Products

Water streams adjacent to the urban areas receive considerably large amount of wastewater from wastewater treatment plants which contains residues of various pharmaceuticals. In recent years, several studies have been published on the spatial and temporal monitoring of water streams for various kinds of pharmaceuticals such as antibiotics, analgesics, antimicrobials, antidiabetics, antineoplastics, anticonvulsant, antiepileptics (e.g., carbamazepine), antipsychotics, antihistamines, antianxiety, anti-inflammatory drugs, antidepressants, beta-blockers (e.g., metoprolol), beta-sympathomimetics, cytostatics and estrogens (e.g., 17b-estradiol) and hormonal compounds, lipid regulators (e.g., clofibrinic acid), stimulants, X-ray contrast media and antiepileptic drugs, etc. (Adler et al. 2001; Buser et al. 1999; Hirsch et al. 1999; Kuch and Ballschmiter 2000; Sedlak et al. 2000; Ternes 1998). These pharmaceuticals are excreted directly or partially in metabolized form by human beings and passed into the environment through wastewaters, as most of the wastewater treatment systems are not typically designed for the removal of traces of such contaminants. Therefore, the removal of such residues from wastewaters is challenging and of serious concern. Intense research and technological advent is the need of the day for the removal of pharmaceutical residues from water and wastewater.

Separation and detection of most of the pharmaceutical residues, with concentrations ranging from few ng/L to μg/L, are two of the major challenges. Nevertheless, these residues exert deleterious effects on aquatic organisms either individually or due to the combined effect of the mixtures. However, due to the unavailability of exact information on mode of action and fate of various pharmaceuticals in the aquatic ecosystem, systematic understanding of their potential ecotoxicological effects is sparse (Cleuvers 2003; Webb 2001). While evaluating ecotoxicological potential of ten prescription drugs, Cleuvers (2003) reported that the acute toxicity of most of the individual pharmaceuticals was moderate, while in combinations it was comparatively more toxic. The concept of independent action should be used for the ecotoxicological risk assessment for the algal tests; however, the acute toxicity of individual pharmaceuticals is very unlikely, therefore chronic combination effects of substances are of concern (Cleuvers 2003).

While assessing the ecotoxicity of three pharmaceuticals and personal care products (ciprofloxacin, triclosan, and Tergitol NP 10) to the natural algal communities of the receiving natural bodies, Wilson et al. (2003) reported marked shifts in the algal community and significant difference in the biomass yield. They also reported the potential influence on the structure and function of algal communities which may result in changes in the natural food web structure.

The phycoremediation of most of the drugs and personal care products is mediated through its cellular metabolism and transformation by mostly cytochromes P450 (P4503A and 2C8 families) in first phase and catabolic biotransformation of such xenobiotics by various metabolic isozymes in second phase (Stresser et al. 2000). Such isozymes facilitate by conjugation of secondary metabolites with reduced glutathione (Stresser et al. 2000; Thomas et al. 1976). Glutathione reductase, responsible for the maintenance of lipid peroxidation and glutathione levels, due to elevated oxidative stress during oxidative biotransformation, also needs to be monitored (Laville et al. 2004; Peakall 1992). Monitoring of metabolic markers such as glutathione S-transferases (GSTs) activity in microalgal and cyanobacterial cells, for the assessment of their phycoremediation potential, can be applied for the screening of suitable species for bioremediation purposes. Vernouillet et al. (2010) investigated phycoremediation potential of a green alga, *Pseudokirchneriella subcapitata*, for an antiepileptic drug (carbamazepine) by monitoring of glutathione-S-transferase (GST), GR activity, and LPO levels. The cellular concentration of carbamazepine in *Pseudokirchneriella subcapitata* was found more than twofold of initial exposure concentration. Such accumulation also results in more than 50 % reduction in cytochromes

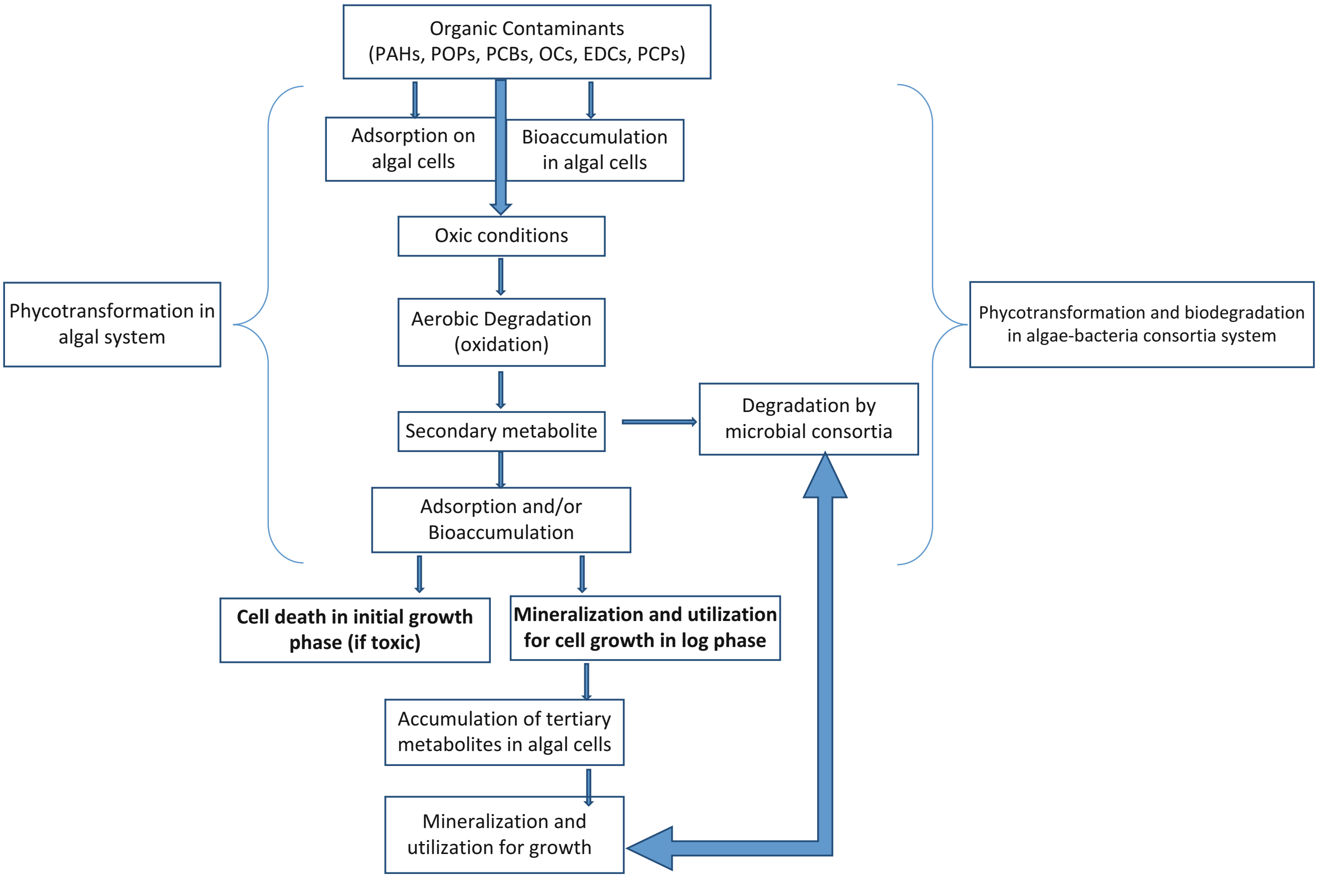

Fig. 11.1 Generalized overview of phycotransformation and degradation of organic contaminants

P450 3A4-like activity in *P. subcapitata*, but glutathione reductase activity was increased up to 40 % which demonstrated that direct exposure to such contaminants results in strong modulation of biochemical biomarkers in aquatic organisms (Vernouillet et al. 2010). In the process of phycoremediation of pharmaceuticals and personal care products, bioaccumulation by algae and cyanobacteria is the primary mechanism. However, it depends on several factors such as toxicity, ionization state, and lipophilicity of the chemical compound as well as sensitivity of tested species (Delépée et al. 2004; Vernouillet et al. 2010; Voutsas et al. 2002).

4.2 Personal Care Products

The ecotoxicological consequences of continuous release and environmental exposure of personal care products (PCPs) are poorly understood. The major contaminant used in PCPs is triclosan (5-chloro-2-(4-dichlorophenoxy)-phenol) (TCS), an antimicrobial compound which has been majorly used in a variety of PCPs such as various cosmetics, soaps, toothpaste, etc., over the last 40 years (Katz et al. 2013). It is also used as a preservative in various consumer products such as textiles, countertops, cutting boards, etc. (Cooney 2010; Savage 1971). Contamination of aquatic bodies and the surrounding environment is resulted through continuous release of inadequately treated domestic wastewaters containing traces of TCS. WWTPs are the major sources of TCS in surrounding water bodies (Fair et al. 2009; Fernandes et al. 2011; Kumar and Xagoraraki 2010). Previous studies have demonstrated that even at very low concentrations, TCS poses serious adverse effects to the phytoplankton, microalgae, cyanobacteria, invertebrates, and fish (Dann and Hontela 2011; DeLorenzo et al. 2008; Jacobs et al. 2005; Perron et al. 2012; Wilson et al. 2003). However, there are various physicochemical and environmental factors such as lower solubility and photolytic degradation and transformation, which regulate the distribution, toxicity, and ecological risk of PCPs (Wong-Wah-Chung et al. 2007) (US EPA 2011). Studies have also demonstrated that TCS easily gets adsorbed to the organic matter thus getting accumulated in sediments (Fernandes et al. 2011; Kumar et al. 2010; Orvos et al. 2002; Ying et al. 2007). In a study of spatial distribution of triclosan, Katz et al. (2013) evidenced that WWTP effluent is an important source of TCS as the annual accumulation rates of TCS in the sediments of Greenwich Bay of Rhode Island, USA, exceeded the calculated annual discharge of TCS from the local WWTP. Therefore, the regulation and control of TCS exposure to the environments can be regulated primarily through the better management of WWTPs.

Phthalate esters (1,2-benzenedicarboxylic acid) are commonly used as plasticizers and also used in a wide range of products such as pharmaceuticals, detergents, and personal care products. Phthalate esters are known to possess endocrine-disrupting potential for human beings. Babu and Wu (2010) reported the degradation and mineralization of three phthalate esters, i.e., diethyl phthalate, di-*n*-butyl phthalate, and dimethyl phthalate by cyanobacteria *Anabaena flos-aquae* by transesterification on the side chains of phthalate esters instead of de-esterification. In this study, two pathways, i.e., $C_{16} \rightarrow C_{14} \rightarrow C_{12} \rightarrow C_{10} \rightarrow C_8$ and $C_{16} \rightarrow C_{15} \rightarrow C_{13} \rightarrow C_{11} \rightarrow C_9$, following first order kinetics were demonstrated and proposed for phthalate esters degradation by cyanobacteria. Table 11.1 lists some phycoremediation applications for these PPCPs.

4.3 Surfactants

As per estimates, globally more than 1.5–2 million tons of synthetic detergents are produced per year (de Wolf and Feijtel 1998). The extent of environmental discharge of detergents and its degradation by-products depends on the effectiveness of STPs and WWTPs, its adsorption to the sewage sludge and more importantly chemical structure, and the persistence of the detergent molecules (de Wolf and Feijtel 1998; Ojo-Omoniyi 2013). Linear alkyl benzene sulfonate (LAS), alkylphenol polyethoxylates, nonylphenol ethoxylates, alkyl ethoxysulphates, etc., are some of the anionic surfactants most widely used in industrial and domestic detergents. Residual surfactants find their way to the natural water bodies through STPs and WWTPs effluents and enter to the hydro-geological cycle. Biological degradation of LAS is comparatively simpler than the branched, nonlinear alkyl benzene sulfonate (ABS), e.g. dodecylbenzene sulfonates (Gledhill 1974; Nomura et al. 1998; Ojo and Oso 2009). Biodegradation of LAS occurs primarily through w-oxidation of methyl group followed by b-oxidation, i.e., oxidative cleavage of C2 units of alkyl chain (Cook 1998). Sulfo-phenyl carboxylic acids (SPACs) are formed in the primary degradation phases and get further mineralized by desulfonation (Field et al. 1992). Dialkyltetralin sulfonates (DATS) and iso-LAS, which account for 10–15 % as impurities in commercial LAS, are also found to be degraded and being used as a sulfur source by bacteria in various studies (Cook 1998; Field et al. 1992; Kölbener et al. 1995).

Alkylphenols and nonylphenol, which are the precursors of alkylphenol polyethoxylates and nonylphenol ethoxylates, are widely used in detergents and several other industrial products and have been identified to exert estrogenic effects. Nonylphenol (NP) has been identified for its potential endocrine disruptor- and xenoestrogen-like activity (Maguire 1999). While studying the biodegradation of xenoestrogen nonylphenol by *Cyclotella caspia*, Liu et al. (2013) reported 37.7 % removal in 192 h at initial concentration of 0.18 mg/L of nonylphenol. The degradation rate was found to be decreasing with the increasing concentration of the nonylphenol, and at 0.22 mg/L, the degradation reduced to 6.7 % due to its toxicity. In natural seawater, degradation of alkyl ethoxysulfates (anionic surfactants) takes place in two phases. In first phase, cleavage of ether bonds by means of hydrolytic reaction, followed by ω- and β-oxidations of the secondary metabolites in second phase (Sibila et al. 2008). More than 96.5 % degradation of anionic surfactant Empicol® ESB 70/SP was observed after 124 days by Sibila et al. (2008).

4.4 Persistent Organic Compounds

Persistent organic pollutants are ubiquitous in nature due to “grasshopper effect” (Koziol and Pudykiewicz 2001). Moreover, due to two or more enantiomers and chirality, more than 25 % of organic compounds pose serious threat in the biosphere (Williams 1996). The major challenge with the persistent organic pollutants (POPs) to the human being is higher carcinogenic potential of these contaminants. Most of the organohalogenated and organochlorinated compounds such as PAHs, PCBs, and chlorinated pesticides pose serious threat to the flora and fauna and are potentially carcinogenic to the human beings and wild life (IARC 1983). Therefore, once these contaminants find their way to the food chain, they get accumulated to the higher trophic levels and pose serious threats to the human beings. The potential collateral effect of POPs to the nontarget organisms is not well understood as such contaminants behave differently individually, whereas the toxicity increases/decreases several folds due to synergistic and antagonistic effects of co-occurring POPs.

Due to the complexity of the environmental matrices, degradation pattern, and ultra-trace levels of emerging contaminants, the identification and quantification of their occurrences is an intricate process. Though tremendous efforts have been made in the past few decades, the removal of such contaminants has not yet been completely understood by the scientific community. Since most of these parent contaminants and their metabolites have different chemical properties such as molecular weight, normality, polarity, oxidation-reduction state, they follow completely different environmental degradation/removal pathways. Therefore, today the major challenge is the development of suitable techniques for identification and quantification. Moreover, the development of eco-friendly and

Table 11.1 Bioremediation/biotransformation in algae and cyanobacteria of pharmaceuticals and personal care products

Compounds	Nature of compounds	Algae	Remarks	Reference
Carbamazepine	Antiepileptic drug	*Pseudokirchneriella subcapitata*	Bioaccumulation and biotransformation	Vernouillet et al. (2010)
Fluoxetine and its metabolites norfluoxetine, propranolol, lidocaine, and trimipramine	Pharmaceuticals with an aliphatic amine group	*Scenedesmus vacuolatus*	Toxicity of aliphatic amine-based pharmaceuticals toxicokinetic effect rather than toxicodynamic effect	Neuwoehner and Escher (2011)
Tetracycline	Veterinary antibiotics	*C. vulgaris*	Removal of antibiotics through lphotodegradation which depends on shallow geometry of HRAPs	de Godos et al. (2012)
Bisphenol A (BPA; 2,2-bis (4-hydroxyphenyl)propane)	Potential endocrine disruptor	*Nannochloropsis* sp. *C. gracilis*	13–34 % removal by *Nannochloropsis* sp. and was 25–53 % *C. gracilis* in 6 days under light conditions.	Ishihara and Nakajima (2003)
Bisphenol A (BPA; 2,2-bis (4-hydroxyphenyl)propane)	Potential endocrine disruptor	*Chlorella fusca*	85 % degradation under light conditions and production of monohydroxybisphenol A (secondary metabolite)	Hirooka et al. (2005)
Ibuprofen, acetaminophen caffeine	Pharmaceuticals	*Stigeoclonium* sp. diatoms, *Chlorella* sp., *Monoraphidium*	Up to 90 % removal in the high-rate algal pond (HRT of 8 days)	Matamoros et al. (2015)

environmentally sustainable techniques for the removal of such residues from water and wastewater is the topmost priority in the scientific communities.

4.4.1 Polyaromatic Hydrocarbons

In aquatic systems, several microorganisms such as bacteria, fungi, protozoa, and some of the microalgae species possess the bioremediation potential for PAHs, PCBs, and other POPs such as chlorinated organic compounds and utilize these compounds as a source of carbon and energy (Brusseau 1998). However, in the degradation of complex aromatic hydrocarbons, asphaltenes is very slow due to its low hydrophobicity; moreover, the shorter- (<C10) and longer-chain alkanes (C20–C40) remain difficult to degrade (Brusseau 1998; Guiliano et al. 2000; Yuste et al. 2000). Studies have demonstrated that certain microalgae species possess some enzymes which facilitate and enhance the degradation potential of microbes. Study of Tang et al. (2010) is in accordance with the above statement. While studying the biodegradation of aliphatic and aromatic hydrocarbons, Tang et al. (2010) observed significant degradation of alkanes (46 %), alkylcycloalkanes (51 %), and monoaromatic alkylbenzenes (33 %) by *S. Obliquus* GH2. Enhanced degradation of PAHs (81 %) of crude oil with the consortia of four bacteria (*Sphingomonas* GY2B, *Burkholderia cepacia* GS3C, *Pseudomonas* GP3A, and *Pandoraea pnomenusa* GP3B) and axenic *Scenedesmus obliquus* GH2 was clearly demonstrated.

In recent years, various studies have demonstrated bioaccumulation, biotransformation, and biodegradation potential of several algal species for various organic contaminants. However, majority of literature is available of microalgal bioaccumulation of organic and inorganic pollutants, and limited studies have been done of phycoremediation of such contaminants other than nutrient removals. Selective phytoplankton, diatoms, and microalgal species have shown the potential of biodegradation of organic contaminants, especially biotransformation of the complex organic compounds in lower carbon compounds. Such secondary or tertiary metabolites are easily degraded by resident consortia of microbes such as bacteria and fungi (Walker et al. 1975). Jacobson and Alexander (1981) reported the degradation (meta-cleavage) of dehalogenate 4-chloro-3,5-dinitrobenzoic acid to 2-hydroxymuconic semialdehyde by non-axenic cultures of *Chlamydomonas* sp. Such transformation is not possible with the only bacterial consortia, which clearly indicates that phycotransformation plays crucial role in the biodegradation of complex organics. Walker et al. (1975) also reported significant degradation of saturated aliphatic hydrocarbons (38–60 %), aromatic compounds (12–41 %) of crude oil by *Prototheca zopfii*. In a recent review, Semple et al. (1999) summarized various studies on catabolic sequences of degradation pathway in phycoremediation of organic contaminants. They highlighted the phycoremediation potential of microalgae for polyaromatic hydrocarbons. At high initial concentrations, PAHs get accumulated in algal cells and pose toxicity at initial growth phases, but in log phases it becomes ineffective, whereas, on exposure of lower concentrations, algae and cyanobacteria are capable of phycotransformation of PAHs (Cerniglia et al. 1979, 1980; Soto et al. 1975). The 1-naphthol, 4-hydrox-4-tetralone, cis-naphthalene dihydrodiol, and trans-naphthalene dihydrodiol are the major metabolites of microalgal phycotransformation of naphthalene (Cerniglia et al. 1979, 1980). *Scenedesmus obliquus* was found to possess the ability to desulfonate the 1-naphthalene which releases sulfonate naphthalene sulfonic acids and being used as sulfur for growth (Luther 1990; Luther and Soeder 1987), whereas amino substituents of aminonaphthalenes and amino and nitrobenzoates are used as nitrogen sources by chlorophyte algae. Such studies clearly indicate that algal bacterial consortia are well capable of phycotransformation and accelerated the degradation of polyaromatic hydrocarbons. Tikoo et al. (1997) reported pentachlorophenol mineralization and degradation by three *Chlorella* species. Various studies have reported mineralization of exogenous phenol in aqueous medium (Ellis 1977; Semple and Cain 1996; Semple et al. 1999). Phycoremediation by conversion of phenols to the corresponding catechols by eukaryotic alga *Ochromonas danica* was reported by Semple and Cain (1996). They observed further degradation of these intermediate compounds by the meta-cleavage of aromatic ring in axenic culture of eukaryotic alga *O. danica*. Pinto et al. (2002) reported up to 70 % removal of phenolic compounds by two green algae, *Ankistrodesmus braunii* and *Scenedesmus quadricauda.*

From above examples it is clear that in phycoremediation of PAHs, algae produce various kinds of exudates and enzymes such as dioxygenase and cytochrome P-450 monooxygenases which oxidize or hydrolyze and/or transform the aromatic compounds in various secondary or tertiary metabolites. Such metabolites either get accumulated in algal cells itself or undergo further degradation by other microorganisms of the native environment (Cerniglia et al. 1979, 1980; Schoeny et al. 1988; Warshawsky et al. 1995). It has been observed that the degradation of complex organic compounds by consortia of algae and other biodegrading microbes is more effective in the removal in comparison to the algal systems alone (Meulenberg et al. 1997).

Degradation of crude oil is reported in various studies. Walker et al. (1975) reported extensive degradation of mixed hydrocarbon and n- and iso-alkanes of crude oil by *Prototheca zopfii*, isolated from the crude oil-contaminated matrix. Various algae species (green, red, and brown), diatoms, and cyanobacteria have shown promising biodegradation potential for organic contaminants. Cerniglia et al. (1979) and Cerniglia et al. (1980) did extensive studies on the degradation of naphthalene by various green, red, brown algal species and diatoms. The results revealed that most of the studied species have degradation potential; however, the extent of degradation mechanism is not fairly understood (Leahy and Colwell 1990). A detailed review compiled by Semple et al. (2009) on aromatic compounds biodegradation by microalgae is recommended for elaborated reading.

4.4.2 Polychlorinated Biphenyls (PCBs)

PCBs are relatively refractory to the biodegradation and are highly toxic, carcinogenic, and ubiquitous in the environment. Microbial and microalgal degradation of these contaminants are very difficult and depend on the extent of halogenation and location of halogen atom in such compounds (Campbell 1977; Saeger and Thompson 1980). It has been established that degradation of chlorinated benzenes and PCBs is done through reductive dehalogenation of such compounds under aerobic conditions (Bouwer et al. 1981; Colwell and Sayler 1978). Degradation of PCBs also mostly occurs via reductive dehalogenation/dechlorination and accelerated by photochemical transformation (Cerniglia et al. 1980; Matsumura and Benezet 1978). Dai et al. (2002) reported that orthochlorinated PCBs suppress dehydroxybiphenyl oxygenase, which is the key enzyme responsible for the microbial degradation. Lynn et al. (2007) reported significant alteration in the PCBs (2,2′,6,6′-tetrachlorobiphenyl) uptake by phytoplankton (diatom, *Stephanodiscus minutulus*) due to nutrient availability which directly affects its trophic transfer. However, such trophic transfer mainly depends on various factors such as algal species, type of organic compound, its environmental circulation, geochemistry, and bioavailability. Moreover, nutrient limitation significantly affects the trophic transfer of such contaminants in the aquatic environment. Removal of PCBs by uptake and accumulation in lipid stores by various algae and phytoplankton has been reported widely (Fitzgerald and Steuer 2006; Lara et al. 1989). Replantation of benthic microalgae in the natural systems accelerate the growth of aerobic microorganisms thus the aerobic activity in the biota (Yamamoto et al. 2008). Such condition leads conversion of anoxic sediment to oxic condition, and in turn the synergy of algae and aerobic bacterial system facilitates aerobic decomposition of organic contaminants. Uptake- and accumulation-based removal of several chlorinated hydrocarbons by marine phytoplankton has been reported widely (Harding and Phillips 1978). Commonly the major constrain in the in situ biodegradation of polychlorinated biphenyls is the lack of effective electron donors which can promote the degradation pathways (Chun et al. 2013). An application of an electric potential in to the PCB-contaminated soils or sediment matrix was found effective for enhancing electron donors/acceptors to the microorganisms (Chun et al. 2013). Therefore, an amalgamation of physical and biological approaches could be a cost-effective and environmentally sustainable option for the in situ remediation of PCB-contaminated sediments and soils. Table 11.2 lists some phycoremediation examples of these hydrocarbons.

4.4.3 Pesticides

Most of the organochlorine pesticides (OCPs) are persistent and highly toxic to flora and fauna, including human beings and wild life. “*According to the Stockholm Convention on Persistent Organic Pollutants, 9 of the 21 persistent organic chemicals are pesticides.*” The main mechanism of biodegradation of pesticides is the reductive dehalogenation/dechlorination, which is accelerated by photochemical transformation in autotrophic microorganisms and has been reported widely (Cerniglia et al. 1980; Matsumura and Benezet 1978; Miskus et al. 1965). In such reductive dehalogenation processes, microorganisms facilitate electron transfer from reduced organic compounds for the oxidation-reduction which results in the removal of halogen atoms from the complex halogenated compounds (Esaac and Matsumura 1980; Kobayashi and Rittmann 1982). In gen-

Table 11.2 Bioremediation/biotransformation in algae and cyanobacteria of hydrocarbon

Compounds	Nature of compounds	Algae	Remarks	Reference
14c Naphthalene	Aromatic hydrocarbon	*Agmenellum quadruplicatum*	Catalysis of cis hydroxylation of aromatic hydrocarbons	Cerniglia et al. (1979)
R-endosulfan and its oxidation product endosulfan sulfate	Cyclodiene insecticide	*Chlorococcum* sp.	95–99 % degradation in 30 days	Sethunathan et al. (2004)
		Scenedesmus sp.		
BaP		*Selenastrum capricornutum*	Metabolizes BaP to cis-dihydrodiols using a dioxygenase enzyme system to todiols, and quinones	Warshawsky et al.
Polyurethane		*Protothecazopfii*	Removal by immobilized and free cells	Ueno et al. (2008)
Fluoranthene		*Chlorella vulgaris, Scenedesmus platydiscus, Scenedesmus quadricauda, Selenastrum capricornutum*	Species-specific removal	Lei et al. (2007)
Pyrene				
Phenanthrene		*S. costatum* and *Nitzschia* sp.	Higher removal of mixture than the single compound.	Hong et al.
Fluoranthene			The presence of any PAH compound in the matrix enhances the degradation of the other PAH compounds	

eral, similar principle also works for algal degradation or transformation of chlorinated pesticides (Matsumura and Benezet 1978; Matsumura and Esaac 1979). However, in algal system, electrons required for the reductive dechlorination are produced and transferred from photosystem. Esaac and Matsumura (1980) reported that the reductive dechlorination of chlorinated compound mainly depends on its degree of chlorination and occurs only at 0.35 V and/or lower oxidation-reduction potential of a medium.

Other than carcinogenicity to the human beings, some of these contaminants, e.g., endosulfan, are also potential endocrine disrupters. In last few decades, various studies have been done on bioremediation of OCPs especially endosulfan by individual or mixed culture of bacteria and fungi (Guerin 1999; Kullman and Matsumura 1996; Sutherland et al. 2000). However, studies on phycoremediation of such compounds are scanty. Shivaramaiah (2000) reported the bioremediation potential of *Anabaena* sp., a blue-green alga for endosulfan. While studying biodegradation of a cyclodiene insecticide, α-endosulfan, Sethunathan et al. (2004) convincingly demonstrated that high-density cultures of *Chlorococcum* sp. or *Scenedesmus* sp. were capable of the biosorption and biotransformation of this α-endosulfan. It was noted that such phycoremediation process includes transformation of R-endosulfan to endosulfan sulfate and endosulfan ether. These metabolites were further removed by sorption in the algal cells. In this study, 60–70 % degradation was recorded in 20 days, whereas up to 99 % degradation of endosulfan was achieved in 30 days. Such type of phycotransformation coupled with phycosorption makes algae potential candidate for bioremediation of organochlorine pesticides. Kobayashi and Rittmann (1982) compiled interaction of eukaryotic algae with pesticides and reported that algae are capable of biotransforming of some of the organic contaminants.

Time-dependent environmental risk assessment is very important in the evaluation of algal biodegradation and biotransformation of pesticides, as some of the degradation byproducts or transformation products are more toxic to the biota than the parent chemical compounds. Cai et al. (2009) observed a significant biotransformation of an herbicide, diclofop-methyl, which gets hydrolyzed to diclofop after absorption in the cells of *Chlorella vulgaris* and further degraded intracellularly to 4-(2, 4-dichlorophenoxy) phenol. It was found that the 4-(2, 4-dichlorophenoxy) phenol was more toxic to *C. vulgaris* in comparison to the diclofop-methyl. Significant biotransformation of diphenyl ether herbicide by *Chlorocorrum* sp. of an algal bacterial consortium was reported by Wolfaardt et al. (1994). These studies have clearly demonstrated that in algal microbial consortia, other than bioaccumulation in the cells, most of the microalgal species perform biotransformation of the complex organic compounds to the simpler or low-carbon compounds and ultimately facilitate their degradation by other microbes present in the consortia/biota. Though there is no concrete evidence available, however, it can be hypothesized that in natural conditions the autotrophs such as algae and cyanobacteria provide oxic conditions during photosynthesis and nitrogen fixation which facilitate growth of a wide range of other microorganisms, and in turn these bacteria and fungi accelerate degradation in harmony with these autotrophs (Rao and Burns 1990; Sethunathan et al. 2004). Table 11.3 lists some examples of phycoremediation of pesticides. Figure 11.2 provides a generalized overview of phycotransformation and degradation of PCBs and OCPs contaminants.

Table 11.3 Bioremediation/biotransformation in algae and cyanobacteria of pesticides

Compounds	Nature of compounds	Algae	Remarks	Reference
Monocrotophos	Organophosphate insecticides	*Chlorella vulgaris, Scenedesmus bijugatus*	Degradaton	Megharaj et al. (1987)
Quinalphos		Cyanobacteria: *Synechococcus elongatus*, *Nostoc linckia*, *Formidiumtenue*		
Methyl Parathion				Megharaj et al. (1994)
DDT (1,1,1-trichloro-2,2-bis (p-chlorophenyl)ethane)	Organochlorine pesticide	*Anabaena* and *Nostoc*	Transformed to DDD [1,1-dichloro-2,2 bis (p-chlorophenyl)ethyl]benzene	Megharaj et al. (2000)
DDT (1,1,1-trichloro-2,2-bis (p-chlorophenyl)ethane)	Organochlorine pesticide	*Chlorococcum* spp.	Transformed to DDE (1,1-dichloro-2,2-bis(p-chlorophenyl) ethylene)	Megharaj et al. (2000)
Fenamiphos (ethyl 4-methylthio-m-tolyl isopropyl phosphoramidate)	Organophosphorus pesticide	five different species of cyanobacteria and green algae	Transformation into oxidation product fenamiphos sulfoxide (FSO)	Cáceres et al. (2008)
Organophosphorus pesticide, fenamiphos (ethyl 4-methylthio-m-tolyl isopropyl phosphoramidate) and its metabolites fenamiphos sulfoxide, fenamiphos sulfone, fenamiphos phenol, fenamiphos sulfoxide phenol, and fenamiphos sulfone phenol	Organophosphorus pesticide and its metabolites	*Chlorococcum* sp. *Pseudokirchneriella subcapitata*	Biotransformation and bioaccumulation	Cáceres et al. (2008)
DDT, dieldrin, and photodieldrin	Organophosphorus pesticide	*Ankistrodesmus amalloides*	Metabolism of DDT to DDE and DDD	Neudorf and Khan (1975)

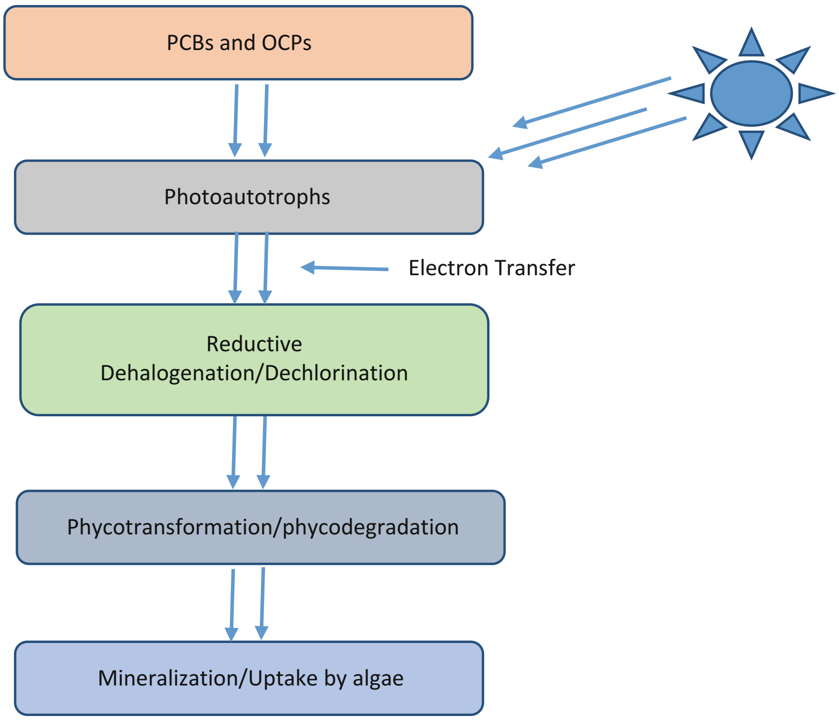

Fig. 11.2 Generalized overview of phycotransformation and degradation of PCBs and OCPs contaminants

5 Phycoremediation: Limiting Factors

The algal biotransformation and degradation, i.e., phycoremediation of emerging contaminants depend on various factors such as physiology of the selected species, their survival and growth, species density, tolerance potential, and prior exposure to the specific xenobiotic compound. The synergy and compatibility of selected species with other resident-competing microflora and fauna also play very important role (Corner 1981; Horvath 1972; Rosenzweig and Stotzky 1980). Various studies have demonstrated that the consortia of algae and bacteria were found to be more effective in biotransformation and mineralization of the organic contaminants in comparison of individual algal or bacterial degradation (Chekroun et al. 2014; Horvath 1972; Kobayashi and Rittmann 1982). Other than the physiology of algal sp., the concentration, physical and chemical properties i.e. hydrophobicity, solubility and volatility of the xenobiotics are also important and need to be considered while accessing the phycoremediation (Gibson 1978; Kobayashi and Rittmann 1982; Steen et al. 1980). The susceptibility of hydrocarbons degradation depends on their chemical form as well. Polar and high molecular weight compounds are less liable to degradation, whereas light aromatic and saturated compounds are comparatively more susceptible for degradation (Leahy and Colwell 1990). In case of petroleum hydrocarbons, physical state and the contaminated matrix both play crucial role in its biodegradation. In natural water system, petroleum hydrocarbons easily get dispersed, resulting the formation of a thin slick due to the action of wind and flow current, tidal oscillation. Such thin slicks provide high surface area thus higher degradation. In contrast thick slick or large mousse of hydrocarbons either in water or in soil inhibits the biodegradation due to low surface area (Colwell and Sayler 1978; Cooney 2010). In general, algal mineralization and degradation is proportional to the concentration, water solubility. Degradation of low molecular weight aromatic hydrocarbons such as toluene follows the Michaelis-Menten kinetics (Boethling and Alexander 1979; Pfaender and Bartholomew 1982), whereas the same is not applicable for insoluble hydrocarbons such as naphthalene and phenanthrene, having high molecular weight (Thomas et al. 1986; Wodzinski and Coyle 1974). The octanol-water partition coefficient for the organic compound is also crucial for degradation (Gibson 1978) (Fig. 11.3).

As far as halogenated complex and persistent organic contaminants are concerned, the degree of halogenation, number of halogen atoms, and their bioavailability and toxicity have direct potential effects on the phycoremediation process (Colwell and Sayler 1978; Gibson 1978; Kobayashi and Rittmann 1982; Leahy and Colwell 1990). There are several environmental factors such as temperature, light duration and intensity, pH and oxidation-reduction potential, salinity, and dissolved oxygen of the medium, which directly or indirectly affect the feasibility and success of phycoremediation process either by limiting growth and survival of the microalgae or by changing the geochemistry of the medium (Colwell and Sayler 1978; Gibson 1978; Kobayashi and Rittmann 1982). For example, temperature plays very important role in in situ biodegradation of PAH; therefore, the optimal degradation varies seasonally. Moreover, the solubility of the PAHs is temperature dependent (Bamforth and Singleton 2005). The solubility, thus the bioavailability, increases with the increase of the temperature (Kobayashi and Rittmann 1982; Leahy and Colwell 1990; Margesin and Schinner 2001). pH also plays critical role in the algal degradation of polyaromatic hydrocarbons. Degradation of PAHs is higher in acidic to neutral pH range in comparison to basic range (Wong et al. 2002). PHAs degradation is also affected by oxygen. Therefore, the rate of aerobic and anaerobic degradation of PAHs is greatly affected by the influence of oxygen (Bamforth and Singleton 2005).

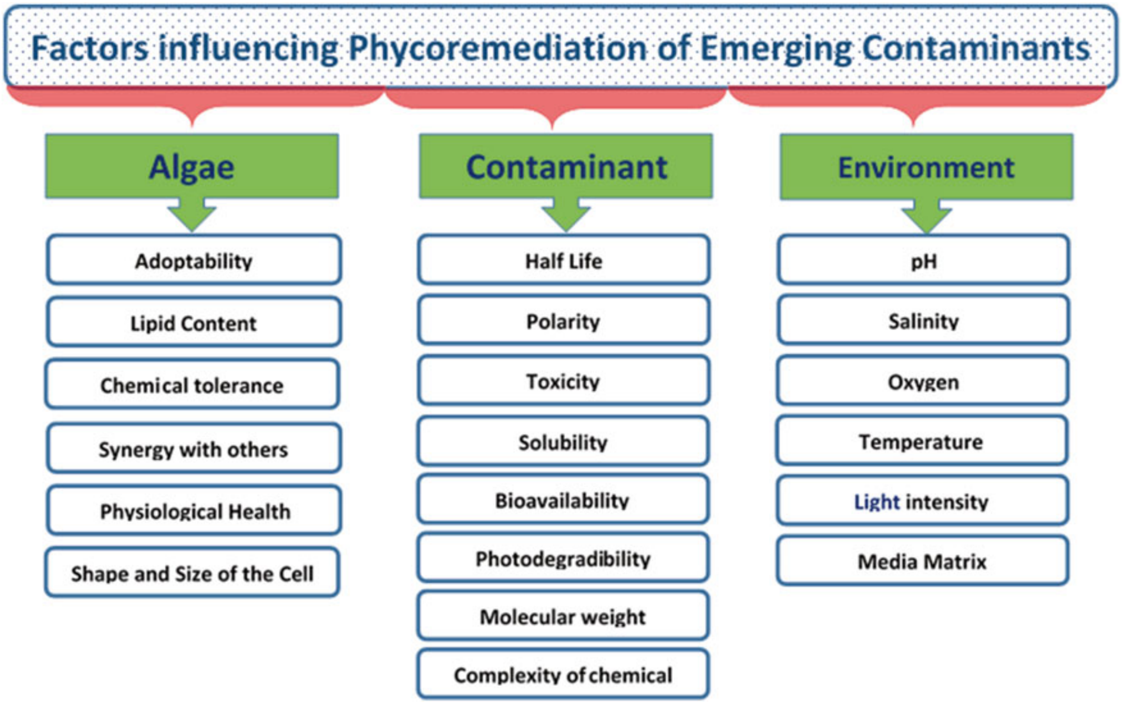

Fig. 11.3 Generalized overview of factors influencing phycoremediation of emerging contaminants

6 Conclusions

Though several incidences are available to date on degradation of various organic contaminants by individual algae and cyanobacteria or in conjugation of other native microbes such as bacteria and fungi, however, such mechanistic understanding of algal degradation pathways for individual type of contaminants needs to be elucidated. The biodegradation potential of mixotrophic cyanobacteria and microalgae species should be identified, and efforts should be made to improve the biodegradation potential of selected species by employing genetic engineering. Microbial consortium engineering by functional genomics, metabolic profiling, and other genetic engineering tools can help in improving the biodegradation potential of such microorganisms (Subashchandrabose et al. 2011, 2013).

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