Vertika Shukla · Narendra Kumar
Editors

Environmental Concerns and Sustainable Development

Volume 1: Air, Water and Energy Resources

Springer

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Foreword

Environmental issues emanating from unplanned urbanization and industrialization are of serious concern attracting the attention of scientific community as well as the policy-makers around the world. It has become imperative to monitor and assess the impact of the degrading quality of air, water, and soil in addition to loss of biodiversity and climate change on human health and socioeconomic aspects.

To ensure sustainable development and safeguard our next generations from catastrophic extreme environmental conditions, major environmental issues are required to be addressed using physical, chemical, and biological approaches or a combination thereof. In addition, a conducive regulatory framework ensuring timely policy interventions from the government is the need of the present times.

The proposed book volume covers topics to provide a comprehensive discussion on major topics of prevalent environmental concerns and strategies to accomplish sustainable development, which will be beneficial for students, researchers, scientists, and policy-makers.

I am delighted to see the efforts made by the editors from the Department of Environmental Science, Babasaheb Bhimrao Ambedkar (Central) University, Lucknow, in compiling the book volume.

Tezpur University (A Central University), Tezpur, Assam, India
25th October 2018

V. K. Jain

Preface

Environmental concerns associated with natural (climate change) and anthropogenic changes (resulting due to unplanned urbanization and industrialization) are major environmental issues which require both the continuous assessment of the environmental impact and concomitant upgradation of regulations and policies.

Nowadays, air pollution represents one of the crucial environmental and social issues with far-reaching consequences on an ecosystem and human health. Chapters of the book present a range of regulatory strategies and the use of lower plant groups, algae, mosses, and lichens as an ecosustainable tool for air quality management not only in urban and agricultural ambient but also in remote areas and places hardly available for instrumental applications (e.g., volcanic craters, tunnels) and as stratospheric biomarkers.

The improvement of crop production is utmost important to feed the growing world's population. Crop yield has enhanced with good pest control agents. However, associated deleterious effects for the human and animal health and the environment of pesticides require regulatory guidelines and risk assessment for safe use. Apart from source and effect studies of various pesticides, nowadays, the use of nonexperimental methods during pesticide risk assessment to predict physicochemical properties and biological effects and to avoid tests on vertebrate animals is gaining strength within existing pesticide legislations. Chapters provide details about various chemical and biological aspects of pesticides and potential use of in silico computer-based chemical modeling techniques for pesticide management.

Availability of clean water is the prime requirement of living organisms. Although some of the minerals are essential for our growth and healthy development, excessive buildup of these minerals, namely, fluoride, can pose a great health risk to flora and fauna.

Water security has become an issue of concern with the depleting water levels due to overexploitation of groundwater and deterioration of groundwater quality. There is a need to strengthen the policy and legal framework for regulation and for judicious distribution of water resources.

About 70% of the world's rivers are estimated to be fragmented, exploited, or regulated by hydrologic alteration, with about 50% of the primary watersheds modified by flood defense embankments, impoundments, and the presence of at least one large dam. Globally there is enough room for the improvement of e-flow processes and the dissemination of the knowledge and tools. Developed nations should extend their support to the developing nations in choosing the best suited methodology for water resource management.

RS-GIS-aided monitoring provides relatively cost-effective and high-frequency tool for regional-scale estimation of various monitoring studies. Groundwater depletion rate estimated by GRACE/GLDAS data not only interpolates the observed regional groundwater well data but also is helpful for policy-makers and land use planners.

Among the different sources, industries play a key role and also release heterogeneous toxic chemicals, organic and inorganic matters or sludge, radioactive sludge, sulfur, asbestos, poisonous solvents, polychlorinated biphenyl, lead, mercury, nitrates, phosphates, acids, alkalies, dyes, pesticides, benzene, chlorobenzene, carbon tetrachloride, toluene, and volatile organic chemicals in air and water. These wastes, when discharged into the water ecosystem without adequate treatment, become unhealthy for any type of human and other use. The industrial wastewater is responsible for many diseases such as anemia, low blood platelets, headaches, risk for cancer, and many skin diseases. To prevent such type of issues, effective treatment technologies, adequate waste water treatment, water reuse, desalination, infrastructure repair and maintenance, water conservation, and also strict pollution control law and legislation are required to be implemented.

Chapters provide an insight to the problem of water scarcity and contamination and suggest probable remedial measures; rainwater harvesting and artificial recharge; water conservation measures in agriculture, industrial, and domestic sectors; and adoption of modern irrigation techniques, such as sprinkler and drip irrigation.

As the demand for energy increases, reserves of fossil fuels are steadily declining. Growing consumption of energy is responsible for dependency on nonrenewable energy sources, such as petroleum, gas, and coal. Burning of fossil fuels is increasing the atmospheric emission of greenhouse gases which in turn increase global temperature. Bioethanol, biodiesel, and biogas are the best fuels generated from biomass, and they are also emerging fuels for minimization of overload of nonrenewable fuels and managing the pollution load. Alternative fuels can play a major role in economic growth, biomass waste management, cleaning environment, decreasing gaseous pollutant, and ultimately achieving sustainability. This book also addresses the energy problem, current status of conventional sources of fuels, and role of alternative fuels in the sustainable development.

Lucknow, India Vertika Shukla
Lucknow, India Narendra Kumar
28 September 2018

Contents

1 **Contributions of Computer-Based Chemical Modeling Technologies on the Risk Assessment and the Environmental Fate Study of (Nano)pesticides** 1
Juan José Villaverde, Beatriz Sevilla-Morán, Carmen López-Goti, José Luis Alonso-Prados, and Pilar Sandín-España

2 **Moss Bag Biomonitoring of Airborne Pollutants as an Ecosustainable Tool for Air Protection Management: Urban and Agricultural Scenario** 29
Mira Aničić Urošević and Tijana Milićević

3 **Use of Lichens in Biological Monitoring of Air Quality** 61
Gülşah Çobanoğlu Özyiğitoğlu

4 **Organochlorine Pesticides (OCPs) in Atmospheric Particulate Matter: Sources and Effects** 97
Sushil Kumar Bharti, Shyamal Chandra Barman, and Narendra Kumar

5 **Vehicle-Generated Heavy Metal Pollution in an Urban Environment and Its Distribution into Various Environmental Components** 113
Vidhu Gupta

6 **Antioxidative Response of Water Macrophytes to Changes in the Living Environment During Vegetation Season: An Experimental Study** 129
Tanja Maksimović, Dino Hasanagić, and Biljana Kukavica

7 **Application of Grace Satellite Data for Assessment of Groundwater Resources in Central Ganga Alluvial Plain, Northern India** 153
Anjali Singh and Ashwani Raju

8 Restoring Environmental Flows for Managing River Ecosystems: Global Scenario with Special Reference to India 163
Venkatesh Dutta, Urvashi Sharma, and Ravindra Kumar

9 Water Security Issues in Punjab State, Northwest India 185
K. P. Singh and Naval Kishore

10 Industrial Wastewater Footprinting: A Need for Water Security in Indian Context 197
Shamshad Ahmad, Pradeep K. Majhi, Richa Kothari, and Rajeev Pratap Singh

11 Fluoride Contamination and Health Effects: An Indian Scenario 213
Ganesh Chandra Kisku and Pokhraj Sahu

12 Role of Industries in Water Scarcity and Its Adverse Effects on Environment and Human Health 235
Pankaj Chowdhary, Ram Naresh Bharagava, Sandhya Mishra, and Nawaz Khan

13 Inter-basin Water Transfer and Policies of Water Resource Management 257
Narendra Kumar and Anjali Verma

14 Policy Interventions in Achieving Water Security in India 275
Jaya Tiwari Dubey, V. Subramanian, and Narendra Kumar

15 Conservation of Energy Resources for Sustainable Development: A Big Issue and Challenge for Future 293
Vishal Chand

16 Alternative Fuels for Sustainable Development 317
Chandra Bhan, Lata Verma, and Jiwan Singh

17 Microbial Remediation of Crude Oil-Contaminated Sites 333
Babita Kumari, Kriti, Gayatri Singh, Geetgovind Sinam, and D. P. Singh

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About the Editors

Vertika Shukla obtained her M.Sc. degree in organic chemistry and Ph.D. degree (2003) in chemistry of lichens from H.N.B. Garhwal University, Srinagar (Garhwal). Presently, she is working as an Assistant Professor (Contract) in the Department of Earth Sciences at Babasaheb Bhimrao Ambedkar (Central) University, Lucknow. During her more than 17 years research experience, she has been awarded 3 fellowships by DST, New Delhi (two projects were pursued in CSIR-NBRI and one project in BBA (Central) University, Lucknow). Till now she has published 63 scientific articles in reputed national and international journals, mostly in SCI journals, and presented research findings in seminar and symposia with total impact factor 39 and h-index 11. She has authored one book 'Lichens to Biomonitor the Environment' (Springer) and coedited two book volumes of 'Recent Advances in Lichenology (Springer) and 'Plant Adaptation Strategies in Changing Environment' (Springer Nature). Her area of interest includes secondary metabolite chemistry, interaction of lichen with the environment, and role of lichen in bioremediation of atmospheric fallouts.

Narendra Kumar obtained his M.Sc. and Ph.D. degrees in environmental science from the Babasaheb Bhimrao Ambedkar (A Central) University, Lucknow, India. Dr. Kumar also qualified UGC-NET in environmental science. He is an active researcher and academician having almost 16 years of postgraduate teaching and research experience. He started his academic career as a project fellow at the National Botanical research Institute (NBRI-CSIR), Lucknow, UP, India. In 2002, he joined as a Lecturer in the Department of Environmental Science, Institute of Bioscience and Biotechnology, C.S.J.M. University, Kanpur, UP, India. He is working as an Assistant Professor in the Department of Environmental Science, Babasaheb Bhimrao Ambedkar University, Lucknow, from June 2005. Dr. Kumar has published more than 30 international and national research papers. He has published 10 book chapters with reputed national and international publishers. One Ph.D. degree has been awarded under the supervision of him and currently four research scholars are working under his guidance for doctoral degree. In addition, he has guided more than 40 students for their M.Sc. dissertation work.

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Chapter 1
Contributions of Computer-Based Chemical Modeling Technologies on the Risk Assessment and the Environmental Fate Study of (Nano)pesticides

Juan José Villaverde, Beatriz Sevilla-Morán, Carmen López-Goti, José Luis Alonso-Prados, and Pilar Sandín-España

Abstract The improvement of crop production is nowadays of utmost importance to feed the growing world's population. Crop yield is enhanced with good pest control. However, an inadequate use of pesticides with this aim has demonstrated along the history that has deleterious effects for the human and animal health and the environment. Therefore, the use and commercialization of pesticides should be regulated properly, in order to only put on the market pesticides that have demonstrated by their risk assessment a safe use. The use of nonexperimental methods during pesticide risk assessment to predict physicochemical properties and biological effects, i.e., (eco)toxicity of concern, and to avoid tests on vertebrate animals is gaining strength within well-developed pesticide legislations.

With the above background, both the regulations of pesticides for risk assessment and the potential use of *in silico* computer-based chemical modeling technologies are reviewed. Moreover, outlook for current and future trends on these concerns of pressing significance in well-developed pesticide legislative frameworks is analyzed.

European Regulation (EC) No. 1107/2009 promotes the competitiveness of agriculture in this region. Quantitative structure-activity relationships (QSARs) are great accepted tools to be used with classical pesticide risk assessment. In a general way, there are QSAR modeling methods for qualitative or/and quantitative issues. The predictive capability of the resultant QSAR models can only be stabilized by performing an external validation. Quantum chemistry (QC) has shown to be an appropriate tool to characterize the structure and relative stabilities of organic compounds isomers. Degradation processes pathways can also be studied using QC. Quantum descriptors can be an excellent option for QSAR development. However, new technologies used in agriculture such as nanopesticides force a revision of the QSAR and QC suitability.

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1.1 Introduction

Current modern legislations provide high levels of protection to human and animal health and the environment. Their success lie in the use of regulated active substances and plant protection products (henceforth these latter named as pesticides) according to good agricultural practices (Villaverde et al. 2016, 2014a, b). To be commercialized, both active substances and their formulations, i.e., pesticides, should pass a risk assessment of their use, after request of the interested of agrochemical companies. Risk assessment is performed using information from experimental studies provided by these applicants and standard scenarios and models. In this sense, the pesticide (eco)toxicological features and the exposure pattern in all environmental compartments must be delimited, frequently using a huge amount of experimental studies. This allows reducing the uncertainty but makes the procedure very complex, demanding in many cases a high cost, the availability of very specialized and formed personal to assess the information and a delay in arrive the pesticide to the market. The entire process guarantees that pesticides used will not have unacceptable effects on the environment or adverse effects on human or/and animal health if they are used properly, especially within well-established Integrated Pest Management (IPM) practices (Barzman et al. 2015; Booth et al. 2017; Lamichhane et al. 2015). However, this background and the use of the precautionary principle are causing a decrease in the number and availability of approved active substances to combat the pests. A good example is observed in the European Union since adoption of the Regulation (EC) No. 1107/2009 (EC 2009b), where the establishment of (eco)toxicological and environmental classification cutoff criteria for active substances is causing the exit from the market of many active substances due to just the active substance cataloguing. But this loss of tools to combat pests does not always respond to public health issues. In this sense, the difficulty or cost to fulfill specific experimental data requirements during authorization or renewal of the active substances is making that the market strategies of agrochemical companies do not find profitable their placing on the market, although under a correct use they are considered safe.

In this situation, computational chemistry methods are in the spotlight of the most developed pesticide regulations due to their great potential to accelerate advances and knowledge in (eco)toxicological and environmental understanding by *in silico* predictions, reducing the cost, and time required to obtain reliable data to perform risk assessment. Additionally, these prediction tools could also support experimental data or/and provide the necessary proves to discard unnecessary experimental studies, in order to focus the efforts on the really necessary ones. These features could offer a great positive economic impact for the agrochemical sector, facilitating a faster commercialization of safe pesticides and encouraging the productivity and competitiveness of the sector (Aleksandra et al. 2014; Kienzler et al. 2016; Servien et al. 2014).

In silico tools are particularly important in those cases where experimental studies are not acceptable due to ethical motives, e.g., tests with animals (Servien et al. 2014). In that cases where experimental studies could not be viable or are too complex (e.g., focused on long distance transport of pesticides and their by-products derived from biotic and abiotic degradation processes or on the fate of pesticides in the atmosphere), their success would also be guarantee (Clark 2018). Computational solutions to study decurrence of pesticide degradation products (DPs) from drinking water treatments (Lee and von Gunten 2012) and environmental matrices (Villaverde et al. 2018a, b) are also welcomed.

With this background, the purpose of this chapter is to provide a state of the art about the most important concerns of the worldwide regulations for pesticide risk assessment, focusing the attention on the current legislative situation at European level and the importance of computed-based chemical technologies within this legislative framework. The development and use of computational chemistry methods and methodologies for pesticides will focus the attention, especially those approaches on QSARs and QC.

1.2 Regulations of Pesticide: European Union as Case of Study

There is a common agreement among countries to decrease pesticides increasingly in order to diminish their residues in both the environment and food that reaches the consumers. However, pesticide use will continue to be positive until the discovery of viable substitutes for both disease control and feeding of population. With this background, the major part of the worldwide legislations on pesticides agrees that agrochemical companies should prove that pesticides placed on the market and their residues do not have harmful effects. The first objective must be feed population, guaranteeing the maximum level of protection to human and animal health and the environment under good agricultural practices. Once the food and safe use of pesticides are guaranteed, the defense of the agriculture competitiveness of the own territories should be the next step (Villaverde et al. 2016).

Anyway, regulations for pesticide risk assessment arise and evolve following multiple criteria in different countries, so harmonization is a difficult challenge (Villaverde et al. 2014a). For instance, the European Commission is the regulatory body within the European Union (EU). Its decisions are based on the conclusions of the risk assessment performed the by European Food Safety Authority (EFSA). Meanwhile, in the United States of America (USA), the threshold values for pesticide residues are legally enforceable by the United States Environmental Protection Agency (US EPA). Another good example comes from the official guidelines followed to perform the pesticide risk assessment. The EU guidelines are common for all Member States, while the USA ones are set at federal level (US Government 2003; EC 2009b).

The scope of this section could be unapproachable because there are a lot of worldwide regulations for pesticides. Therefore, henceforth the attention is focused on the EU regulation due to the important pesticide trade of this region and because this regulation is one of the most advanced and has supported the development and use of non-animal testing methods based on computational chemistry.

Since the beginning of the second decade of the 21st century, the EU has performed the registration of active substances through a legislation that requires application of IPM practices. In this sense, Regulation (EC) No. 1107/2009 (EC 2009b) of the European Parliament and of the Council concerning the placing of pesticides on the market and Directive 2009/128/EC (EC 2009a) for the sustainable use of pesticides are essential within the current EU thematic strategy on the sustainable use of pesticides (EC 2006b, c). Approval of active substances and authorization of pesticides is regulated through the Regulation (EC) No. 1107/2009 (EC 2009b), while orientations to manage field and promote the sustainable use of pesticides by reducing their possible risks and impacts using IPM practices are provided through the Directive 2009/128/EC (EC 2009a). Member States shall adopt National Action Plans (NAPs) to promote these IPM practices and to control the objectives and measures already completed and compliance with the programmed timetables, in order to reduce the needs on the pesticides use. Prokopy (1993) proposed four levels of IPM in line with their degree of development. The EU aspires to accomplish the requirements fixed in the fourth IPM level. The needed data requirements to perform a full risk assessment of active substances and formulated products are detailed in Regulation (EU) No 283/2013 (EC 2013a) and Regulation (EU) 284/2013 (EC 2013b), respectively. Additionally, Regulation (EU) 546/2011 (EC 2011) establishes the needed uniform principles to perform the authorization of formulated products, since this task is performed at national level. Meanwhile, EFSA and DG Health and Food Safety (DG SANTE) in collaboration with the European and Mediterranean Plant Protection Organization (EPPO) give support to the establishment of debated and agreed guidance documents among Member States to perform the risk assessment of active substances and pesticides.

Currently, the EU pesticide legislative framework is aimed to perform the pesticide risk assessment in the light of current scientific and technical knowledge. Both assessment process and guidance documents are not static instruments within a rigid regulation, just the opposite. Consequently, Regulation (EC) No. 1107/2009 (EC 2009b) calls for continuous improvements in order to integrate the latest advancements for the risk assessment process, allowing to answer the new challenges arising from the new tools aimed at pest control. Among them, nanopesticides require an especial consideration. Excellent review articles dealing with the subject of nanomaterials and nanopesticides provide all the necessary information about the current physicochemical and (eco)toxicological concerns of these relative new tools for crops protection.

Regulation (EC) No 1907/2006 (EC 2006a) named as REACH, which establishes both the European Chemicals Agency (ECHA) and the procedures for collecting and assessing information on the properties and hazards of substances, highlights the importance of nonexperimental methods to avoid tests on vertebrate animals (see recital 47) in similar way than Regulation (EC) No. 1107/2009 (see recitals 11 and 40) (EC 2009b). ECHA has prepared a guidance on information requirements and chemical safety assessment consisting of two major parts: concise guidance (ECHA 2011e, f, 2016d, e, 2017i) and supporting reference guidance (ECHA 2008a, b, 2011a, b, c, d, 2012d, e, f, g, 2013, 2015, 2016a, b, c, 2017e, f, g, h). Moreover, ECHA has several publications where the importance of QSARs is emphasized to avoid animal testing (ECHA 2008a, 2012h, 2016f). Guidance document on the assessment of the equivalence of technical materials of substances regulated under Regulation (EC) No. 1107/2009 (EC 2009b) also considers the use of QSARs under certain circumstances (EC 2012). The European Centre for Ecotoxicology and Toxicology of Chemicals (ECETOC) also acknowledge in a relatively older document but still considered valid that QSARs tools to obtain warnings (ECETOC 2003). ECETOC also highlights that current QSARs tools are more trustworthy for compounds of structural similarity, single mechanistic steps, or common action mechanisms, being appropriate for predicting toxicity but not its absence (ECETOC 2003). Moreover, this European Centre also highlights that current commercial models of QSAR are of low applicability in different degrees for skin and eye irritancy, skin sensitization, acute oral toxicity, chronic toxicity, carcinogenicity, teratogenicity, and in vitro mutagenicity (ECETOC 2003).

It should also be taken into account that novel tools in agriculture for pest control as those derived from nanotechnology question the validity of the use of "classical" QSAR with them. Indeed, ECHA has published specific guidance documents focused on the nanomaterials risk assessment, highlighting the existing difficulties on the use of QSARs for nanomaterials/nanopesticides (henceforth named as nano-QSARs) (ECHA 2012a, b, c, 2017a, b, c, d). Therefore, it is necessary to develop nano-QSARs specific for nanomaterials/nanopesticides (see Section 1.3 for further details).

Further information on the QSARs use within the European framework of risk assessment was provided by the European Chemicals Bureau (ECB) (ECB 2003) before the ECHA was born. The Join Research Centre (JRC) also supports the development of software tools that are potentially useful for regulatory purposes (EC 2018).

1.3 Quantitative Structure-Activity Relationships (QSARs)

Currently, QSARs are the most common approach used by agrochemical companies to obtain a nonexperimental good approximation to the physicochemical and biological properties and the environmental fate of pesticides and their degradation products. Moreover, this approach is achieving to be recognized by the pesticide regulatory authorities.

Table 1.1 Considerations for nano-QSAR models development

Needs on nano-QSARs
Specific descriptors for nanoparticles are needed since conventional ones for QSAR are not suitable
Data sets should be well-described and of high quality for structurally related but differently sized nanoparticles
Currently, comprehensive empirical and experimental data are scarce to fully assess the endpoints
In comparison with traditional chemicals, nanoparticles are large compounds, and their structural variety is highly limited
Structural- and size-dependent descriptors for modeling nanoparticle activity are needed

There are three main components in a QSAR/nano-QSAR: the known and unknown physicochemical or biological (e.g., (eco)toxicity) data, i.e., endpoints; the data of measured or calculated molecular parameters, i.e., molecular descriptors; and the modeling methods linking the two data sets (Schultz et al. 2003). The quality and amount of these components define the accuracy of the QSAR results (Nicolotti et al. 2014). Basically, QSARs interpolate the unknown properties of a part of a group of compounds from some molecular descriptors of the whole group, using appropriate statistical methods. However, the causal mechanisms are usually unknown.

Important difficulties in the nano-QSAR models development arises from the lack of knowledge about the complicated biological effects (e.g., (eco)toxicity) and environmental behavior of these nanoentities as a consequence of their chemical composition and morphology and the current small amount of applicable nanodescriptors. Other key obstacle in the development of nano-QSAR models arises from the wide variety of nanoparticles. The current followed approach consists in built nano-QSAR models for nanomaterials/nanopesticides according to their category. Nevertheless, there is not a full-accepted criterion to perform this classification. The Organization for Economic Co-operation and Development (OECD) developed a QSAR toolbox to build chemical categories (OECD 2009) according to a method based on nine stages (OECD 2014). However, many authors do not consider enough the OCDE proposal to address the concern about the categories with nanomaterials/nanopesticides, recommending alternative categories based on nanoparticle properties and structure (Maynard and Aitken 2007), nanoparticle geometry (Shevchenko et al. 2003), nanoindividuals (Córdoba and Zambon 2017), etc.

Finally, Table 1.1 displays the most important specific issues to take into account during development of nano-QSAR models. These issues entail a great change in comparison with the standard QSARs, but the required amendments are already ongoing (Jagiello et al. 2017; Javaid et al. 2017; Wang et al. 2017).

Let's see key concepts for each one of the three components of a QSAR/nano-QSAR.

Endpoints Their definition must be clear and unambiguous. The data normally come from standardized assays measured in a reliable way and with low experimental error.

The database TETRATOX of growth inhibition of the aquatic ciliate *Tetrahymena pyriformis* is considered to be a high-quality data set for the specific purpose of QSAR construction and validation (Bradbury et al. 2003). For more than 20 years, this database has been developed in a single laboratory and using a single protocol. Therefore, toxicity assessment is very precise, and database is excellent in terms of quality, size, and molecular diversity. However, even under these conditions, there is an experimental error. In fact, Seward et al. (Seward et al. 2001) observed that the reactive chemicals have the greater variability in the measured growth inhibition of *T. pyriformis*. Other good extensive databases, developed explicitly for QSARs, are the US EPA fathead minnow database (Russom et al. 1997), guppy database (Konemann 1981), and *Vibrio fischeri* database (Kaiser and Palabrica 1991).

Molecular Descriptors There are four categories of descriptors according to their dimensionality, from the 0D (zero-dimensional) to the 4D (four-dimensional) (Grigor'ev and Raevskii 2011; Kholgade and Savakis 2009; Roy 2017). Figure 1.1 states their meaning. Traditional QSAR studies use generally ad hoc descriptors, such as molecular refractivity and molecular weight, which define, for example, physicochemical properties. These descriptors can be used to assess the environmental fate of chemical substances (Wang et al. 2009). Although determination of these descriptors is easy, they show low capacity to quantify modifications in the electronic structure of the particles and sometimes involve abundant experimental work. However, QSAR models can overcome these problems by means of precise theoretical descriptors obtained by the use of QC, such as frontier orbitals energy and electrostatic potential. Unlike empirical methods, quantum methods provide an accurate and comprehensive explanation of electronic effects. Until today, quantum chemical descriptors for development of QSAR models have been used predominantly in the pharmaceutical drugs field. In fact, to our knowledge quantum chemical descriptors have not been used to develop QSAR models aimed at the pesticide risk assessment (De Benedetti and Fanelli 2014). Taking into account the great potential of quantum chemical descriptors for development of suitable QSAR models for pesticide risk assessment, further information is provided in Section 1.4.2.

Modeling Methods There are QSAR modeling methods for qualitative or/and quantitative purposes. In the same vein, these kinds of endpoints are considered at legislative level during risk assessment of pesticides (Table 1.2). Therefore, the QSARs are usually built using modeling methods appropriate to solve qualitative or/and quantitative issues in line with the target endpoint. On the other hand, currently, a universal QSAR modeling method for all systems is impossible. To find methods that model relations of molecular descriptors with endpoints is highly dependent not only on easeness of use but also on the capacity of the modeling methods to fit nonlinear interactions without overfitting risk and their ability to use small data sets and obtain significant and comprehensible results. Moreover, sensitivity of the modeling method should be low toward changes in the model parameters. Methods should also display an easily interpretable structure and include an option to both to identify the most significant descriptors and to exclude the redundant ones. Transparency is usually required, so black boxes are not

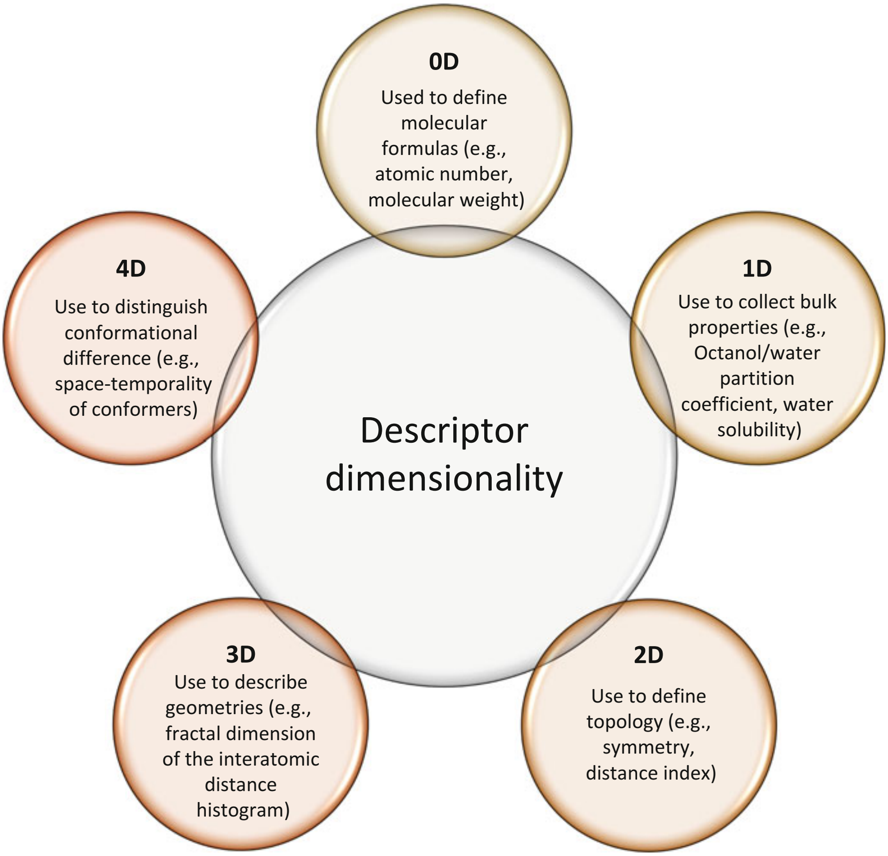

Fig. 1.1 Classification of molecular descriptors according to their dimensionality. (Grigor'ev and Raevskii 2011; Kholgade and Savakis 2009; Roy 2017)

Table 1.2 Examples of quantitative and qualitative endpoints considered at legislative level during risk assessment of pesticides

Properties	Endpoints	
	Qualitative	Quantitative
Physicochemical	Classification as oxidative, explosive or/and flammable	Vapor pressure, Henry's law constant, boiling point, melting point, density, surface tension, partition coefficients
(Eco) toxicological	Classification as carcinogenic, mutagenic or/and toxic	IGC_{50}, EC_{50}, LD_{50}, LC_{50}

recommended (Arkadiusz et al. 2006; Chen et al. 2015; Dearden et al. 2009; Polishchuk 2017; Walker et al. 2003). In this sense, the modeling methods which are more useful for in the development of QSAR models are shown in Fig. 1.2.

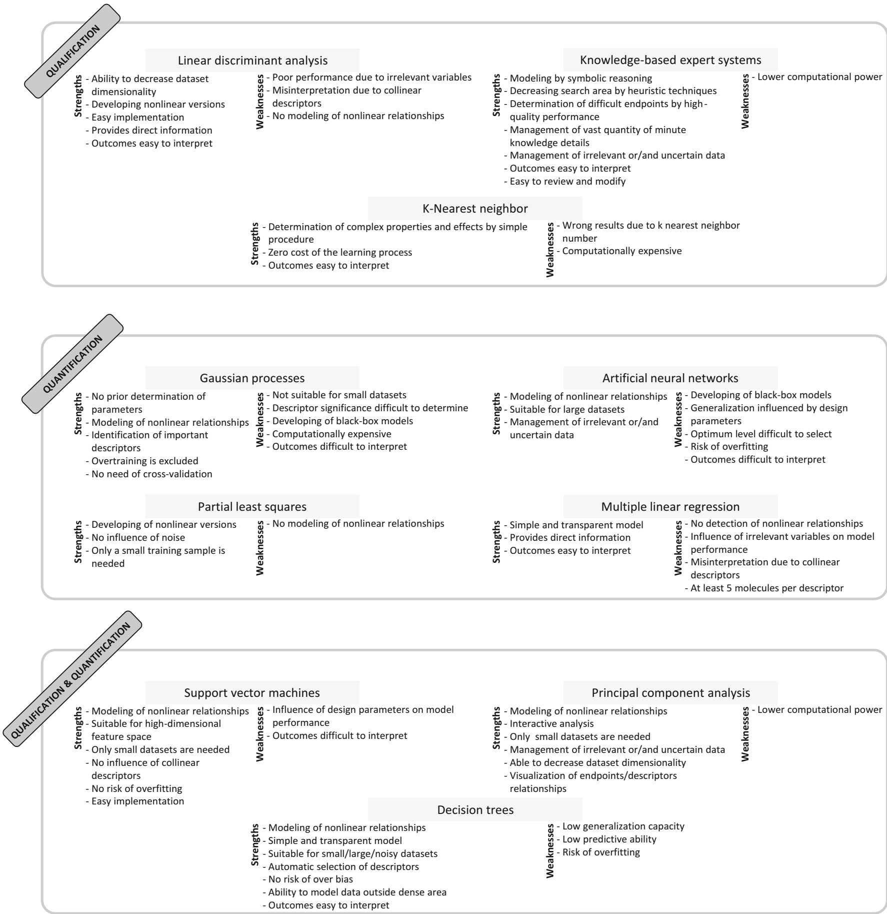

Fig. 1.2 Main modeling methods for QSAR construction attending to their purpose, i.e., qualification or/and quantification. (Biau and Devroye 2015; Hanrahan 2011; Henseler 2010; Judson 2009; Liang et al. 2011; McLachlan 2005; Rasmussen and Williams 2006; Rokach and Maimon 2014; Sahigara et al. 2013; Vidal et al. 2016; Vinzi et al. 2010; Yan and Su 2009)

1.3.1 QSAR Modeling Methods

Figure 1.2 shows the most useful modeling methods to be used in the construction of QSAR models. The strengths and weaknesses of these modeling methods are also displayed. As it is aforementioned and further discussed in the following sections, the QSAR should be built using modeling methods for qualitative or/and quantitative issues and according with the target endpoint.

1.3.1.1 Modeling Methods for Qualification

Linear Discriminant Analysis (LDA) Qualitative classification and dimensionality reduction are the uses normally given to this method. LDA looks for a hyperplane to project a set of data points. The aim is the separation of classes of an endpoint. The equation that defines the hyperplane mathematically is a linear discriminant function, i.e., $\mathrm{DS} = \sum_{i=1}^{n} b_i X_i$, where DS represents the discriminant score and b_i is the coefficient of the molecular descriptor X_i. The use of LDA to modeling QSARs for pesticides was already confirmed in toxicity predictions (Martin et al. 2017).

Knowledge-Based Expert Systems (KBESs) These methods are able to agglutinate, simulate, and use relevant knowledge. In this sense, KBESs are usually computer programs that simulate the analytical skills and experience of human experts. KBESs are being used in the development of QSAR models (Fjodorova and Novič 2014). However, only old studies are found with pesticides (Judson 1992; Russom et al. 1997). Anyway, taking into account the KBESs strengths (Fig. 1.2), the attention should be redirected to these methods.

k-Nearest Neighbor (kNN) This method classifies an unknown compound by measuring distances and based on the class of k nearest neighbor training compounds. So far, this is not a modeling method extensively used to develop pesticide-oriented QSARs. Anyway, kNN modeling method has shown good capacity for the prediction of acute contact toxicity of pesticides on honeybees (Como et al. 2017). kNN also modeled QSARs for nanomaterials using small data sets to find statistically significant relationships between biological effects and physicochemical/morphological properties (Fourches et al. 2010).

1.3.1.2 Modeling Methods for Quantification

Gaussian Processes (GPs) These methods foresee an early probability distribution for the model underlying the data. Then, the probability distribution is updated based on observed data. Therefore, it is a matter of generalizing the Gaussian probability distribution to an infinite set of functions. GPs have shown an excellent capacity to find the main descriptors to perform an accurate toxicity estimation of organic contaminants (Jin et al. 2014).

Artificial Neural Networks (ANNs) Relationships and patterns in data are identified by these modeling methods. Knowledge is collected from experience for data mining. ANNs are widely used for the study of pesticide (eco)toxicity. In this sense, Hamadache et al. (2016, 2018) have developed recently an ANN-based QSAR to predict acute oral toxicity of herbicides on rats and acute contact toxicity of pesticides on bees. Automated variants of this kind of modeling method have been used to build nano-QSARs (Winkler et al. 2014). Dispersibility of carbon nanotubes in organic solvents have also successfully modeled by ANNs (Salahinejad and Zolfonoun 2013).

Partial Least Squares (PLS) Linear relationships between descriptors and endpoints are assumed. PLS are especially appropriate when these descriptors are more numerous versus the number of samples and highly collinear. The problem of the collinear descriptors can be avoided by taking out the latent factors that cause the variations in the descriptors. The response of the endpoint should be modeled at the same time (Henseler 2010; Lodhi and Yamanishi 2010; Vinzi et al. 2010). PLS are especially though to solve quantitative issues of linear relationships. However, the need to solve qualitative problems such as classifications has also conducted to use PLS with this purpose with both classical pesticides (Freitas et al. 2016) and nanomaterials (Golbamaki et al. 2016; Bigdeli et al. 2015). Nonlinear versions of the PLS method with the algorithm kernel-based PLS have also been developed for nanomaterials in order to study roadside atmosphere (Mehdikhani et al. 2013).

Multiple Linear Regression (MLR) A mathematical equation of the type $Y = b_0 + \sum_{i=1}^{n} b_i X_i$ can be used to define this kind of modeling methods, where Y is the endpoint, b_0 is the model constant, and b_i is the coefficient of the molecular descriptor X_i. The contribution and significance level of the molecular descriptors on the studied endpoint are obtained from the weights of the respective coefficients. However, collinear descriptors can conduct to misinterpretations. Anyway, MLR is one of the most popular modeling methods because it is simple and easily interpretable. MLR has shown good results, for example, in the study of bioconcentration factors for pesticides (Jackson et al. 2009; Yuan et al. 2016). MLR has also been successfully used with nanomaterials on the solubility study of fullerenes (Pourbasheer et al. 2015a; Sikorska et al. 2016) and photocatalytic activity and zeta potentials of metal-oxide nanoparticles (Mikolajczyk et al. 2016; Wyrzykowska et al. 2016).

1.3.1.3 Modeling Methods for Qualification and Quantification

Support Vector Machines (SVMs) Despite the versatility of these modeling methods, they have shown higher performance than other methods used specifically for qualitative or quantitative purposes (Darnag et al. 2017; Yao et al. 2004; Czermiński et al. 2001). SVMs have not been so extensively used with pesticides as other modeling methods. However, it has shown excellent results for both qualitative purposes (e.g., classification of inhibitors of insect juvenile hormone (Doucet and Doucet-Panaye 2014; Doucet et al. 2013)) and quantitative purposes (e.g., prediction of half-life of some herbicides (Samghani and HosseinFatemi 2016)). SVMs have also been allowed to construct qualitative- and quantitative-based nano-QSAR models (Liu et al. 2013; Pourbasheer et al. 2015b).

Principal Component Analysis (PCA) This tool allows reducing the dimensionality of a data set, showing graphically relationships between molecular descriptors and endpoints. PCA has been used efficaciously as modeling method of both QSARs for study of, for example, soil sorption of carboxylic acid herbicides (Freitas et al. 2014), carcinogenic potential, and mammalian toxicity of thiophosphonate pesticides

(Petrescu and Ilia 2016) and nano-QSARs using small data sets (Hassanzadeh et al. 2016).

Decision Trees (DTs) These display a tree-like structure by simulating iterative branching topologies. Decision rules linked to molecular descriptors form branches at each intersection. Classes define the ending leaves of the tree. Data points are classified in these classes based on the aforementioned decision rules. DTs are machine-learning models aimed to pattern recognition and data mining. The use of DTs to build QSARs for pesticides is scarce. However, in the last years, there was a significant growth in their use. Among these works highlight the ones performed by Basant et al. (2016a, b, c) to model toxicity of pesticides in multiple species. Classification of the environmental risks linked with nanomaterials for regulatory decision-making after performing their risk assessment has been proposed using DTs (Chen et al. 2016). Maybe random forest is the most used modeling method with nanomaterials from DTs family because it shows a better generalization capacity mainly for quantitative purposes (Cassano et al. 2016; Gonzalez-Durruthy et al. 2017; Helma et al. 2017).

1.3.2 Validation of QSAR Models

Validation of QSAR models gives believability to the results obtained by them. The validation set size can affect severely the validation metrics designed for estimating the exactitude of the outcomes (Leonard and Roy 2006). This is a fairly common problem during the development of the nano-QSAR models. However, transparent and simple read-across algorithms for a pre-evaluation of nanomaterials risk are beginning to be developed successfully using a limited data set (Gajewicz 2017). There are good reviews focused on the validation metrics for qualitative- and quantitative-based QSAR models for external and internal validation (Roy et al. 2015). Chirico and Gramatica (2012) proposed that the quantitative structural relationship models with the R^2-based statistical parameter lower than the thresholds already set in earlier studies should be rejected.

Special attention must be paid to the five principles for the QSAR models validation of the OECD to accurately estimate the activity of chemicals (OECD 2007). The OECD principles were stablished with the aim of promoting QSAR tools for regulatory purposes. The experimentally modeled system is clearly identified by the first principle, i.e., defined endpoint. The descriptors of the model and the mathematical method of calculation are incorporated within the second principle, i.e., unambiguous algorithm. The nature of the modeled chemicals, established by the endpoints and descriptors, is defined by the third principle, i.e., defined domain of applicability. The well-defined domains establishment is of great importance to the correct use of QSARs. This fact has led to the development of several approaches with this aim (Cao et al. 2017; Kaneko and Funatsu 2017; Sahigara et al. 2012). A simplification of the whole set of issues discerning between external and internal validation is performed by the fourth principle, i.e., measures of goodness of fit, robustness, and predictivity. Anyway, it has to be clarified that the predictive capability of the quantitative structural relationship models can only be determined by subjecting the model to external validation by means of a set of compounds not used during the building of the model (Pavan et al. 2006; Tropsha 2010). Finally, models with mechanical associations between endpoints and descriptors are recommended by the fifth principle, i.e., mechanistic interpretation.

1.4 Quantum Chemistry (QC)

Taking into account that all quantum systems follow the Schrödinger equation, QC uses this equation to calculate properties of atomic and molecular systems successfully. However, the exponential difficulty to fully describe quantum states supports the impossibility of achieving it by classical computing. In fact, this equation can only be solved accurately for very small systems using this kind of computing. This difficulty interested Feynman to contemplate the possibility whether a quantum computer would be able to simulate quantum mechanics efficiently (Feynman 1982). Since then, works on quantum algorithms has been published until today, but large-scale, general-purpose quantum computers do not exist yet. However, as was announced by the "Nature" journal recently, the world is about to have its first quantum computers (Zeng et al. 2017). With this background, the first significant applications of quantum computers will be focused on the understanding of any system where quantum mechanics can have a protagonist (Brown et al. 2010; Buluta and Nori 2009; Georgescu et al. 2014). Until then, the current approximations in QC for calculation of molecular properties allow studying molecules of hundreds of atoms with high accuracy, using classical computers. Among these approximations, the ab initio methods result from first principles of quantum mechanics. All these methods determine the total energy of the system and the electronic wave functions but with a high computational cost. In return, any property of a system associated with its electronic structure can be estimated accurately. Semiempirical methods use considerations obtained experimentally to simplify equations, reducing the computation time greatly although usually at the expense of the accuracy.

QC has demonstrated to be an applicable tool not only to characterize the structure and relative stabilities of organic compounds isomers but also to find reaction pathways in important degradation processes from an environmental point of view, such as photolysis and hydrolysis (Alcamí et al. 2001). QC also allows to correlate toxicity and chemical reactivity based on substituent effects or/and structural changes (Wang et al. 2009). Moreover, QC reactivity descriptors used in ligand-based QSAR studies achieve a more precise approximation of the enthalpic contribution to ligand-target interactions than classical QSAR (De Benedetti and Fanelli 2014). The potential scope of this revision could be vast due to the huge amount of ab initio methods well-established. However, we have decided to focus the attention on a particular set of methods based on density functional theory (DFT), because they have demonstrated to be very trustworthy methods for compounds up to several hundred atoms, i.e., the size of standard pesticides. Moreover, they offer good results consuming a workable amount of computing time.

1.4.1 Density Functional Theory (DFT)

DFT is based on the demonstrated fact that properties and energy of the ground electronic state of a molecule are established by the electron density exclusively (Hohenberg and Kohn 1964). Therefore, the exact energy of a system is function of the density. The problem arises from the lack of knowledge about the precise functional, i.e., mathematical relation, between the total energy and the density. The number of proposed functionals in the open literature until the moment is enormous. However, a correct choice of the functional depends of the system. An appropriate choice is decisive to obtain a good description of the system. Without a doubt, the B3LYP functional is among the most commonly used ones for organic molecules (Alcamí et al. 2001). B3LYP connects the Becke's three-parameter nonlocal hybrid exchange potential (Becke 1993) with the nonlocal correlation function of Lee and collaborators (Lee et al. 1988; Stephens et al. 1994; Vosko et al. 1980).

Currently, DFT is used as a standard technique to perform the geometries optimizations and to get the final energies of diverse stationary points for a broad diversity of systems at the ground state, obtaining good agreement with experimental values. DFT has well-demonstrated a conciliation between the fast ad hoc and semiempirical approaches and the one computationally expensive ab initio to compute with exactitude key universal concepts of molecular reactivity and structure to determine molecular descriptors. In this sense, it is expected that the use of DFT calculations using the B3LYP functional could provide a precise description of the electronic ground state properties for the major part of the current pesticides (Sousa et al. 2007). Time-dependent density functional theory (TD-DFT) is an extension of DFT to treat excited states of large systems by means of a viable computing time (Casida and Huix-Rotllant 2012). Therefore, TD-DFT is especially useful in those cases where degradation of pesticides is performed by photochemical reactions. In this sense, Elroby and Aziz (2011) used TD-DFT to study the photodecomposition of an important group of pesticides as pyrethrins. This process leads to the formation of chrysanthemic acid through the ground state rather than the excited state, contrary to what might seem. TD-DFT has also allowed studying adiabatic processes and emission (phosphorescence and fluorescence) and absorption energies. Indeed, TD-DFT calculations to determine spectral features of chlorothalonil fungicide were in agreement with experimental results in both relative strength and line shape (Dhas et al. 2011). Finally, although DFT methods are very reliable, it is recommended to confirm that the chosen method and functional provide good results by comparing them with experimental data or with the more reliable ab initio methods, especially in the kickoff studies of new systems.

1.4.2 Quantum Chemical Descriptors

The most important property for describing the ground states is the electron density. Many quantum chemical descriptors are suggested based on electron density. These descriptors correlate satisfactorily with the molecular reactivity of a large number of organic compounds (Lee et al. 2015), providing a plausible understanding of their reactivity. Reactivity of chemicals is an issue of special importance to address their risk. A branch of QC associated to DFT is the named as conceptual density functional theory (CDFT) (Domingo et al. 2016). CDFT defines global reactivity descriptors for a molecule as a whole. However, they can also be expressed to refer only a part of the molecule, as an active center. The high sensitivity of the values reached by the descriptors to the number of orbitals used during calculations (denoted as basis set) and to the level of theory chosen, i.e., functional, obliges a full study in each case. Three of the most useful global descriptors of the systems defined in QC are the electronegativity (χ), hardness (η), and electrophilicity (ω) (Pearson 2005). χ represents the aptitude of an atom in an atomic or molecular system to attract bonded electrons. χ is defined as a function of ionization energy and electron affinity (Mulliken 1934). η describes the compactness degree of the electron cloud of the system under study. ω symbolizes the electrophilic power of species and is accepted as the ratio of χ to η (Parr et al. 1999). Among these descriptors, χ allowed to model acute toxicity of several chemicals to *Daphnia magna* (Reenu 2015). Moreover, during the phototoxicity study of polycyclic aromatic hydrocarbons toward *Scenedesmus vacuolatus* and *D. magna* were obtained positive correlations between η and $\log EC_{50}$ (Al-Fahemi 2012). Local electrophilicity, i.e., philicity ($\omega^{\alpha}(r)$), was suggested as a good descriptor for intra- and intermolecular reactivities, encompassing individual as well as several reactivity sites (Chattaraj et al. 2003).

On the other hand, although DFT is an excellent option to identify good descriptors for a broad range of relative small systems, the emerging use of nanopesticides could conduct to surpass the DFT potential. Molecular systems with high sizes, as those derived from metal-oxide nanoparticles (Ahmed et al. 2018), could also entail the use of other functionals such as the Perdew-Burke-Ernzerhof (PBE) functional (Perdew et al. 1996). In this sense, it was already observed the necessity of study clusters of MoS_2 with dimensions greater than 2 nm by the density-functional tight-binding (DFTB) method (Javaid et al. 2017). Other studies showed that clusters of metal-oxides nanoparticles larger than 40 atoms should be studied by semiempirical methods, e.g., Parameterized Model 6 (PM6) (Jagiello et al. 2017). However, there is no adequate global approach so far, and a comprehensive assessment is needed case-by-case in order to determine the best descriptors.

It should also be taken into account that with nanopesticides may be the case in which the current computational chemistry capacities are fully exceeded. In these circumstances, the physicochemical and (eco)toxicological concerns of nanopesticides should be considered (see (Antunović et al. 2011; Barlow et al. 2009; Kah and Hofmann 2014; Kookana et al. 2014; Peters et al. 2014; Villaverde et al. 2017) for further details). In this sense, descriptors related with characteristics such as chemical composition, concentration, and especially morphological aspects of nanopesticides as shape, size, surface area, etc. seem the reasonable option. Nevertheless, all those descriptors measured experimentally and with potential to be associated with the effects studied could be useful. The chemical composition of nanopesticides may be defined using 0D descriptors, while descriptors such as those based on images of microscopy may be valuable to describe morphological aspects (Glotzer and Solomon 2007). Other research groups have proposed complementary methodologies to describe chemical composition for both nanomaterials and chemicals, using, for example, a single descriptor of correlation weights based on either graphs of atomic orbitals or molecular graphs (Toropov et al. 2005). A quasi-simplified molecular input line entry system was also proposed to illustrate physicochemical properties, molecular structures, and experimental conditions with nanomaterials (Toropov et al. 2016; Toropova et al. 2016).

1.4.3 Approaches for (Eco)toxicological and Photochemical Studies

Prediction of chemical (eco)toxicity of pesticide DPs is of special interest during their risk assessment, as they are not available commercially, and the isolation of many of them is a problematic task. QC can be used to model (eco)toxicity of chemicals to organisms. Theoretical QC data can be correlated with experimental (eco)toxicities using QSAR models, in terms of, for example, EC_{50} of pesticides toward *S. vacuolatus* and *D. magna* (Fumagalli et al. 2013). Indeed, CDFT analysis is beginning to be implemented in some software packages to perform DFT calculations, which simplifies the QSARs development. The first step in this process should be the selection of the most valuable descriptors. The amount of quantum chemical descriptors that can be determined by DFT studies is huge, so the most valuable descriptors can be chosen by principal components analysis. Then, the most useful regression model/s can be selected after their evaluation based on a stepwise multiple linear regression method that uses the forward-selection and backward-elimination. Both molecular basis sets and level of theory should also be weighed. Finally, the QSAR model/s should be validated (Pavan et al. 2006; Tropsha 2010). QSAR models with goodness of fit measures greater than the thresholds defined by Chirico and Gramatica (2012), and low values of both mean absolute error and root mean square error should be accepted.

On the other hand, comprehensive photodegradation studies of pesticides using QC should include firstly both conformational exploration and relative stabilities of reactants and products, comparing at least some of the results with experimental or well-known data in order to confirm the suitability of the QC predictions. The next step should comprise identification of the probable intermediaries and transition states that could be formed in the course of the reaction path. It is recommended to perform these studies at the ground state, optimizing all the imaginable geometries and using a level of theory reasonable in accordance with the computational capacity available. Moreover, all harmonic vibrational frequencies must be determined by means of the level of theory used during the geometry optimizations. This is a key issue to find the stable structures and transition states and to calculate the corresponding vibrational energies. After geometry optimizations, the level of theory is improved to diminish the errors and to achieve more accurate energies. Finally, the oscillator strengths and the low-lying excited states can be determined by TD-DFT.

1.5 Conclusions and Future Perspectives

Modern pesticide regulations aim to provide consumers a high level of protection without neglecting animal health and the environment. Modern pesticide regulations worldwide such as the European Regulation (EC) No. 1107/2009 (EC 2009b) and official bodies and agencies such as JRC, EFSA, and ECHA are beginning to promote the standard theoretical chemistry methods as complementary tools within the risk assessment process of pesticides. With the current development of the computer-based chemical modeling technologies, their use is well agreed among the stakeholders for screening of compounds of concern (i.e., pesticides, metabolites, DPs, and impurities) during first stages of risk assessment and for supporting physicochemical and (eco)toxicological results obtained experimentally.

Theoretical calculations can be an important tool when metabolites, DPs, and impurities are difficult to isolate or do not exist for their experimental risk assessment. Therefore, scientists should continue working on the development of computational tools to estimate accurately the harmful effects of these compounds. Harmful effects on green algae or crustaceans are accepted as indicators of their effect on superior organisms.

The potential of QSAR models has already been demonstrated with standard chemicals/pesticides. In this sense, pesticide regulations worldwide are beginning to accept these tools as confirmatory technique of experimental results. However, the next step to fully accept QSARs as a standard technique with their own space within the pesticide risk assessment process must be focused on the development of QSAR models more robust and reliable. In this sense, databases with information regarding physicochemical and (eco)toxicological properties using increasingly standardized assays and with less experimental error should be developed. Moreover, the search for new and novel molecular descriptors related to these properties is important.

In addition, the modeling methods should also be improved making their application of broader spectrum, so that they can be used to obtain accurate results with both qualitative and quantitative issues and according with the target endpoints. Mechanical tools that allow choose the best modeling method are also welcome. Currently, the most useful modeling methods to QSAR models development are LDA, KBESs, and kNN for qualitative issues, while GPs, ANNs, PLS, and MLR are for quantitative issues. SVMs, PCA, and DTs are versatile modeling methods for both kinds of issues.

New challenges for QSAR models arise from the new agrochemical tools for crops protection such as nanopesticides. The future widespread use of QSAR models will also lie in their ability to adapt and take into account the concerns derived from these new technologies. In this sense, suitable nano-QSARs development need still collects further key information on nanomaterials/nanopesticides and their DPs, such as the physicochemical properties linked with their safety (volatility, surface charge, etc.) and degradation feasibility. Innovative nanodescriptors able to join both size-dependent and chemical properties are also necessary. Then physicochemical and (eco)toxicological endpoints should also be interconnected with these theoretical and experimental nanodescriptors using appropriate modeling methods.

There are not well-developed databases for nanomaterials yet. Efforts to solve this lack are ongoing. However, many data from research studies are obtained using diverse processes. In this sense, the construction of reliable data sets requires to obtain accurate data of nanomaterials/nanopesticides using a systematic, standard, and consistent protocol and well-defined methods. Moreover, the amount of data should be adequate and specifically for nanomaterials/nanopesticides to let splitting data into training and test sets. Following these guidelines should help achieve support and acceptation of regulatory authorities.

Although the trends in the development of pesticides are to larger molecules, the great development reached in computation allows using the QC as methodology for the study of pesticides and their DPs. DFT methods can be used to study the reactivity in the environment. Indeed, quantum descriptors that contain information related to electronic density correlate well with the molecular reactivity of a large number of compounds. This fact demonstrates the capacity of QC to obtain suitable descriptors and to leave from a good position to participate in a potential future development of improved QSAR models for pesticide risk assessment purpose. DFT methods seem the most suitable ones to calculate molecular descriptors with classical pesticides while DFTB and semiempirical methods with nanomaterials/nanopesticides. Photochemical degradation, adiabatic processes, and energies of emission and absorption can be studied by TD-DFT methods, while ecotoxicity usually correlates well with parameters obtained from CDFT.

An international agreement on how to validate and to demonstrate the suitability of any QSAR model to the target compounds during presentation of the scientific documentation for risk assessment of pesticides is also required. The five principles for the QSAR models validation of the OECD could be a great starting point.

Application of computer-based chemical modeling technologies should harmonize the criteria and decisions during the pesticide risk assessment.

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Chapter 2
Moss Bag Biomonitoring of Airborne Pollutants as an Ecosustainable Tool for Air Protection Management: Urban and Agricultural Scenario

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Abstract Urban and agricultural areas are highly anthropogenically devastated environments with diversely and densely distributed pollution sources. These usually highly populated and cultivated areas together represent a big part of the Earth's surface, and it is of crucial interest to monitor and control presumably high air pollution in these areas. Complex urban topography demands a high density of air quality monitoring stations while extensive and frequent agrochemical treatments in cultivated areas require repetitive measurements of pollution at the same site. The application of moss bags represents an easy-to-apply screening technique which has been used for biomonitoring of air pollutants. The technique has been mainly developed for application in areas where the naturally growing biomonitors are absent. It is successfully used for biomonitoring of potentially toxic elements including rare earth elements (PTEs) and persistent organic compounds, mostly polycyclic aromatic hydrocarbons (PAHs). In the last decade, we investigated crucial variables of the moss bag technique application (species-specific, time- and site-dependent pollutant enrichment) through a series of studies performed in the urban area of Belgrade and agricultural areas in Serbia. Starting from 2005, we have examined the moss bag technique for biomonitoring of PTEs at specifically polluted sites within the city such as crossroads, street canyons, tunnel and garages and, finally, overall city area. Thereafter, since 2015, we tested the technique application in conventional and organic vineyards. The interchangeable use of two moss species, *Sphagnum girgensohnii* (a species of the most recommended biomonitoring genus) and *Hypnum cupressiforme* (commonly available in Serbia), for performing the biomonitoring of PTEs was discussed in the studies. The results showed that the studied moss species could not be interchangeably used for airborne element assessment, except for Cr, Cu and Sb. In the urban area, 2-month bag exposure ensures accumulation of the elements and adequate replicability of the results even at air

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pollution background sites. Otherwise, in the agricultural area, this period does not guarantee detectable element moss load if the bag exposure does not coincide with the agrochemical application time (which is variable in different vineyards). Hence, in a vineyard ambient, moss bags should be exposed during the whole grapevine season comprising unpredictable treatments of grapevine during the vegetation season. The moss bag technique enables uniformly biomonitoring of the air pollutants over all anthropogenically devastated areas since successfully overcomes the issue of lack naturally growing mosses.

Keywords Air pollution · Toxic elements · Moss biomonitoring · Urban and agricultural areas

2.1 Air Pollution Issue

There is nothing so substantial like breathing fresh and clean air.

Nowadays air pollution represents one of crucial environmental and social issues with far-reaching consequences on an ecosystem and human health. The overcoming of this burning issue requires both the continuous assessment of the environmental impact and concomitantly upgrade of regulations and policies (EEA 2017). Despite the dramatic progress of monitoring and control of pollutants in the last several decades, air pollution still represents an issue that continues to harm the environmental and human health. Although the level of air pollution is substantially lower than in the past, there are numerous areas, such as urban, industrial and agricultural, with intensive anthropogenic activities leading to overexcess of pollutant concentrations above the permitted levels (Guerreiro et al. 2014; EPA 2018). Nevertheless, air pollutants can harm public health and welfare even at very low levels.

Air pollution issue especially threats urban and agricultural environments which represent highly anthropogenically devastated areas with diversely and densely distributed pollution sources. These highly populated and cultivated areas represent in sum a big part of the Earth's surface. More than half of the world population lives in urban dwellers with the intention that urban areas currently occupy roughly 3% of the planet surface, which will continue to expand (Potere and Schneider 2007; Seto et al. 2011). In parallel with rapidly urbanising areas, agriculture intensifies on remaining natural habitats and is likely to expand to new areas, putting pressure on land resources (Jiang et al. 2013). According to the Food and Agriculture Organisation (FAO) of the United Nations, agricultural land covers 38.4% of the world land area as of 2015 (FAOSTAT 2018). Specifically, pastures are 68.4% of all agricultural land (26.3% of global land area), arable land (row crops) is 28.4% of all agricultural land (10.9% of global land area), and crops (e.g. vineyards and orchards) are 3.1% (1.2% of global land area).

Particulate matter (PM) is currently considered to be the reliable indicator of health effects of ambient air pollution (Burnett et al. 2014; WHO 2014). Particle pollution is the term used for a mixture of solid particles and liquid droplets found in the air. It can be directly emitted from vehicles, smokestacks of power plants, construction sites, unpaved roads, fields and different industries or airborne in complex reactions of directly emitted chemicals. These particles come in many sizes and shapes and can be made up of hundreds of different organic and inorganic chemicals (pollutants). In European Union (EU) legislation, few of the first regulated pollutants were PM10 and PM2.5 (particles of 10 and 2.5 μm in diameter, respectively) and several associated toxic elements (As, Cr, Hg, Ni and Pb) (Kuklinska et al. 2015). It has been prescribed by the Convention on Long-Range Transboundary Air Pollution (CLRTAP), which was signed in 1979. Particles with diameter < 10 μm (PM10) penetrate deep into lungs causing serious respiratory and cardiovascular illness depending on the PM-associated pollutants (Kelly and Fussell 2012). In addition, As, Cr, Hg, Ni and Pb represent type I carcinogenic substances according to the International Agency for Research on Cancer (IARC), while other elements, depending on the concentrations, have toxic or carcinogenic effects, even rare earth elements (REEs) (Dołęgowska and Migaszewski 2013).

The main source of air pollution in urban areas is road transport activity (Pant and Harrison 2013). This pollution source consists of the exhaust and the non-exhaust traffic-related emission. Automobile tailpipe emits to atmosphere products of incomplete fuel combustion and lubricant volatilisation, which highly depends on technological improvements and regulations. Non-exhaust emissions can be related to wearing of vehicles' parts, such as tires, brakes, clutches, wheel bearings and engines, or abrasion of street furniture and enter into the air by resuspension due to traffic-induced turbulence (Pant and Harrison 2013). Exhaust and non-exhaust sources contribute almost equally to total traffic-related PM10 emissions. Specifically, PM10 can originate from non-exhaust vehicle emissions in the range between 16 and 55% and from total traffic emissions ranging between 11 and 21% (Grigoratos and Martini 2015). Based on the available literature, globally 25% of PM2.5 pollution in urban ambient contributed by traffic (Karagulian et al. 2015). Brake wear has been recognised as one of the most important non-exhaust pollution sources. The most important chemical constituents of brake wear are Fe, Cu, Ba and Pb, while the most commonly used key tracers of brake wear are Cu and Sb (Grigoratos and Martini 2015). Elemental markers which indicate vehicular emissions are Cu, Mn, Fe, Zn, Ba, Sn, Ni, Mo and Sb (Birmili et al. 2006).

Agricultural areas distinguish from the noncultivated areas by the excessive and frequent application of chemicals for improving crop growth. Agrochemicals significantly contribute to elevating potentially toxic element (PTE) concentrations in the agricultural soils and cultivated plants, further threatening human health through the food chain. The prolonged application of mineral fertilisers and pesticides-fungicides has resulted to Cu, Zn, Cd, Pb and As accumulation in the agricultural soil where Ni, Cr, Co and Fe concentrations are controlled by parent material influences (Komárek et al. 2010; Kelepertzis 2014). The concentrations of Ni, Cd, Zn, Pb, As and Cr correlate with the P concentrations suggesting that the rock phosphate is the major source of these elements (Nziguheba and Smolders 2008;

Jiao et al. 2012). The research interests have also been induced by widespread application of fertiliser containing REEs, especially in China (Wen et al. 2001).

Improving knowledge and understanding of air pollution and developing effective policies for its reduction remains; therefore, it is a challenge and a priority in Europe (Guerreiro et al. 2014). However, regulatory monitoring stations, which provide ambient air quality measurements, are often unevenly distributed and are mainly concentrated in the urban areas. The costs for their acquisition, installations and technical maintenance, the provision of a reliable energy supply and the inaccessibility of many sampling sites represent the main limitations to regulators and their efforts to increase the number of the monitoring stations. Therefore, the challenge is the constitution of a complementary approach to conventional strategies providing information on air pollutant concentrations over large areas and overcoming the limitations of point measurements inherent to fixed devices. Beside ground stations of monitoring networks, currently, the progress in portable monitoring device solutions and satellite telemonitoring is evident (Marć et al. 2015). However, living organisms wherever are present reflect the ecological state of their particular habitat, and it can be considered as a 'database' through bioindication or bioaccumulation of pollutants.

2.2 Biomonitoring Concept for Air Quality Assessment

> *There is no better indicator for the state of a species or a system, than that species or system itself.* (Thomas Tingey)

Pollutants ones emitted into the environment necessarily impact the organisms provoking their specific or unspecific effects to the exposure which is defined as bioindication and bioaccumulation (Markert 2007). Thus, an organism that vanishes from the natural habitat in the presence of pollution represents a *bioindicator* and can give useful information about the quality of the environment. Contrary, an organism that accumulates the ambient pollution reflecting the quantity of pollutants is known as a *biomonitor*. The good biomonitor would be a species (or its part) that internal composition linearly reflected the quantitative composition of the ambient. However, due to the complexity of environmental abiotic and biotic factors, diversity of the species and synergistic effects of pollutants, the particularly biomonitor's response cannot be easily described and predicted by mathematical formulae and schemes. Otherwise, biomonitor gives time-integrated information about the ambient pollution that complements the potential of instrumental measurements.

The scientists worldwide have investigated specific biomonitor response to particular pollutants in the ambient, which would be reproducible in time and space. The use of plants for biomonitoring purpose has an advantage over animals since they are sedentary organisms that testifying about the quality of the environment at the certain site. Investigation usually starts from the reduction of a great diversity of species to a few representative bioindicators/biomonitors and their further application in monitoring of certain pollutants.

Two substantially different approaches in biomonitoring of pollutants are defined as *passive biomonitoring* by examination of organisms naturally occurring in the ecosystem and *active biomonitoring* by using biomonitors bred in laboratories or growing at the pristine area and exposed in a standardised form in the field for a defined period of time (Markert 2007).

Biomonitoring is a suitable method for source identification, and, thus, the application of biomonitors in air quality management is appropriate. The relative ease of sampling, the absence of any need for complicated and expensive technical equipment and the accumulative and time-integrative behaviour of biomonitor give biomonitoring of air pollutants advantages for their continued practice in the future, especially in large-scale surveys.

Active biomonitoring especially offers great possibilities of application in air quality management due to the possibility to control many parameters of measurements (the exposure time and measuring site/position).

2.2.1 Mosses as Biomonitors of Air Pollution

In the evolutionary tree, mosses represent a blind branch, i.e. primitive organisms without vascular tissues which characterised vascular plants. They are cosmopolitan organisms that occur on a wide range of substrates, such as soil, rock, bark, wood and even leaf cuticles, and they are absent only from the marine ecosystem (Vanderpoorten and Goffinet 2009). Instead of root system, moss has rhizoids, which hold it adhered to the substrate. The above-ground part of moss, cauloid, collects water and nutrients directly from precipitation and dry atmospheric deposition with only negligible element uptake from the soil (Zechmeister et al. 2003). Except lacking a developed root system, these ubiquitous organisms have other morpho-physiological adaptations, such as a large surface area and high (cat)ion-exchange capacity of the cell membranes (González and Pokrovsky 2014) which make them as an appropriate surface for atmospheric deposition of pollutants. These features recommend mosses for their application in biomonitoring surveys, led by the premise that *the content of ambient air pollution could be reflected in the content of the moss tissues*.

Starting from the late 1960s (Rühling and Tyler 1973), the idea of using mosses to measure atmospheric deposition of PTEs has been studied by scientists worldwide, but mainly in Europe. A lot of studies carried out to testify different mosses, especially the carpet-forming species, as biomonitors of atmospheric deposition of inorganic and organic pollutants (Aničić Urošević et al. 2017a, and references therein). Moreover, in 1987, the international ICP Vegetation Programme (International Cooperative Programme of Air Pollution on Natural Vegetation and Crops) has been established by the United Nation Economic Commission for Europe (UNECE) that focus on the systematic use of the moss biomonitors for the assessment of airborne pollutants (heavy metals and nitrogen) and their impact on the environment (https://icpvegetation.ceh.ac.uk/). Since 1990, within the Programme, the European Heavy Metals in Mosses Survey has been conducted every 5 years using the unique protocol, with an ever-increasing number of participants of currently 36 countries (Frontasyeva et al. 2017). The use of mosses as biomonitors of PTEs was evaluated in comparison with the mean values of the element determined by European Monitoring and Evaluation Programme (EMEP) network of regulatory monitoring stations (http://www.emep.int/). The clear scientific evidence about the agreement between regulatory and biomonitoring data has been found for Cd and Pb (Aboal et al. 2010; Harmens et al. 2012), the elements with high covalent binding potential.

One of the elementary criteria for selecting a particular species for biomonitoring purposes is often its sheer abundance in the study area. Within ICP Vegetation Programme, four moss species are recommended for collection, *Pleurozium schreberi* as the most frequently sampled species in European countries (ca. 42%), followed by *Hylocomium splendens* (23.5%), *Hypnum cupressiforme* (19.6%), *Pseudoscleropodium purum* (7.7%) and other species (7.1%) (UNECE ICP Vegetation 2015; Schröder et al. 2016). Specifically, in southern and central European countries, the moss species from the *Hypnum* sp. and *Pseudoscleropodium* sp. genera are widespread and commonly used in large-scale biomonitoring studies (UNECE ICP Vegetation 2015). It should be noted that moss species from *Sphagnum* genus exhibit the highest comparative biomonitor advantages above other species due to the large surface and the highest proton and metal adsorption capacity (González and Pokrovsky 2014). However, this moss genus is not widespread and inhabits the northernmost/southernmost areas of the planet (peat bogs, conifer forests and moist tundra areas), while in the moderate climate zone, this moss can be very rarely found only in damp and shadowed habitats at high altitudes (mountains). Some moss species, such as *Hylocomium splendens*, have clear annual growth segments, while the others have not, but it is assumed that upper green part of the mosses can be associated with 2.5–3 years old (Zechmeister et al. 2003). Anyhow, terrestrial mosses are valuable tools for assessing atmospheric levels of pollutants. As a confirmation of this hypothesis, the European Committee for Standardization has recently regulated the biomonitoring of air quality using terrestrial mosses (EN 16414 2014).

2.2.2 *Active Moss Biomonitoring (***Moss Bag Biomonitoring***)*

Despite ubiquitous distribution of mosses, there are areas from which mosses are expelled/repressed, such as urban and agricultural and sometimes industrial areas. Asphalted and landscaped surfaces, which are dominant in urban areas converting them to ‘moss deserts’, except cemeteries where moss cushions may remain undisturbed during long periods and used for biomonitoring purpose (Natali et al.

2016). The areas with extensive production of cultivated plants also characterised with the absent of autochthon species, and mosses ‘lose the battle’ and vanished.

To overcome the scarcity or absence of mosses in certain environments enables active biomonitoring approach, i.e. transplanting moss from unpolluted pristine area to the polluted area of interest. The ‘moss bag technique’ is the most common type of active biomonitoring with terrestrial mosses that is reported in the literature. The technique was introduced by Goodman and Roberts (1971) and modified in the following years regarding the moss species used, pretreatments, the bag preparation and the exposure. The comprehensive review of the moss bag technique application over urban and industrial areas is given by Ares et al. (2012). In Finland, the moss bag technique is nationally standardised (SFS 5794 Finnish Standards Association 1994). At the international level, the technique is patented as ‘passive contaminant sensor device’ (EP3076171-A1; WO2016156443-A1, Patent 2016). However, for the application of the technique is still lacking the internationally standardised protocol.

Note that active approach in biomonitoring has several advantages in comparison to the passive one – lower variability of the measured values among the subsamples, better replicability of the measurements, lower initial pollutant level, the well-known exposure time, minimising the possible edaphic influence on the concentrations of certain elements, lack of phenotypic and/or genotypic adaptation and overcoming inaccessibility of many sampling sites. The lack of the technique is losing the moss vitality in the process of their relocation from the natural habitat. However, the growth of moss tissue during exposure time sometimes can ‘dilute’ the real pollutant values. Devitalisation of moss prior to its use as transplant material is recommended to avoid growth of the plant during the exposure period, especially in humid climate zone (Fernández et al. 2010).

Active moss biomonitoring has been studied mostly in urban and industrial zones and rarely in agricultural areas (Ares et al. 2012; Capozzi et al. 2016a, Milićević et al. 2017). In the last 13 years, we investigated crucial variables of the moss bag technique application (species-specific and the time- and site-dependent pollutant enrichment) through a series of the studies performed in the urban area of Belgrade and agricultural areas in Serbia. Starting from 2005, we have examined the moss bag technique for biomonitoring of PTEs including REEs (Aničić et al. 2009a, b, c), and we tested the technique application at specifically polluted sites within the city such as crossroads (Vuković et al. 2016), street canyons, tunnel (Vuković et al. 2013), garages (Vuković et al. 2014), airport (Vuković et al. 2017) and, finally, overall city area (Vuković et al. 2015a, b). Thereafter, since 2015, we tested the technique by applying it in an agricultural area, i.e. conventional and organic vineyards (Milićević et al. 2017, 2018a, b). The interchangeable use of two moss species, *Sphagnum girgensohnii* (a species of the most recommended biomonitoring genus) and *Hypnum cupressiforme* (commonly available), for biomonitoring of PTEs was examined in the studies.

For each of the studies, the moss *Sphagnum girgensohnii* Russow was collected in a pristine area of north Russia (Domkino, Dubna). The low concentrations of the majority of the studied elements in the moss recommend this site as an appropriate background area for its collecting (Aničić et al. 2009a). Another species, *Hypnum* *cupressiforme* Hedw., was collected in the protected area 'Vršačke planine' in Serbia. Both species were transplanted in the study areas by using the bags.

The bags were made from nylon net with 2 mm mesh size as flat form 10×10 cm^2, and loosely packed with the moss, and by using nylon string hang 2 to 4 m above the ground, while in the street canyon study, additional heights of bag exposure were tested.

2.3 Urban Scenario

Complex urban topography – buildings, roadway configurations and other urban features – causes high spatial variability of air pollutant concentrations, and it needs to be considered in an evaluation of urban air quality. Although scarce, regulatory measurements confirmed a complexity of air pollutant emissions and their dispersion across the urban settings (Baldauf et al. 2013). There are a lot of 'hot spots' of air pollution within cities, such as street canyons, tunnels, crossroads, bus stops, parking garages/places, roadside microenvironments, etc. However, not all the sites are accessible for installation of measurement devices, and they can be subject to vandalism. In this context, moss bag biomonitoring in urban areas provides a useful complement to monitoring stations because overcoming the limitations of measurement devices such as expensiveness, technical maintenance, electrical supply, discrete measurements, etc.

Inspired by growing public health concerns regarding elevated air pollutant exposure in urban areas and adverse human health effects, since 2005, we have performed a series of moss bag biomonitoring studies in the urban area of Belgrade (Serbia). *Selection of the moss species* is a key factor in biomonitoring studies. Furthermore, *the optimal moss bag exposure period* is one of the crucial variables in the methodology of the moss bag technique used to monitor the air quality. The 'optimal' time refers to the minimum period for achieving the significant and consistent moss element uptake that reflects the ambient element content. *The vitality of moss* during exposure strongly influences the element accumulation and/or depletion in the moss tissue, while the availability of water plays a key role in moss physiology.

Dry and Wet Moss Bag Biomonitoring vs. Bulk Deposition Our first moss bag study (Aničić et al. 2009a) was carried out at three representative urban sites in Belgrade city close to the regulatory measurements. Precisely, during 2005/2006, *S. girgensohnii* moss bags were exposed for five consecutive 3-month periods, next to the collectors for total bulk deposition (BD). In addition, to test the role of water in element moss uptake, the treatments with (DRY MB) and without irrigation (WET MB) were applied to the exposed moss bags (Fig. 2.1). Regarding the element content in the unexposed moss, significant accumulation of the examined elements in the moss was observed over the exposure periods indicating that the used moss species is an efficient biomonitor of PTEs. Significantly higher element

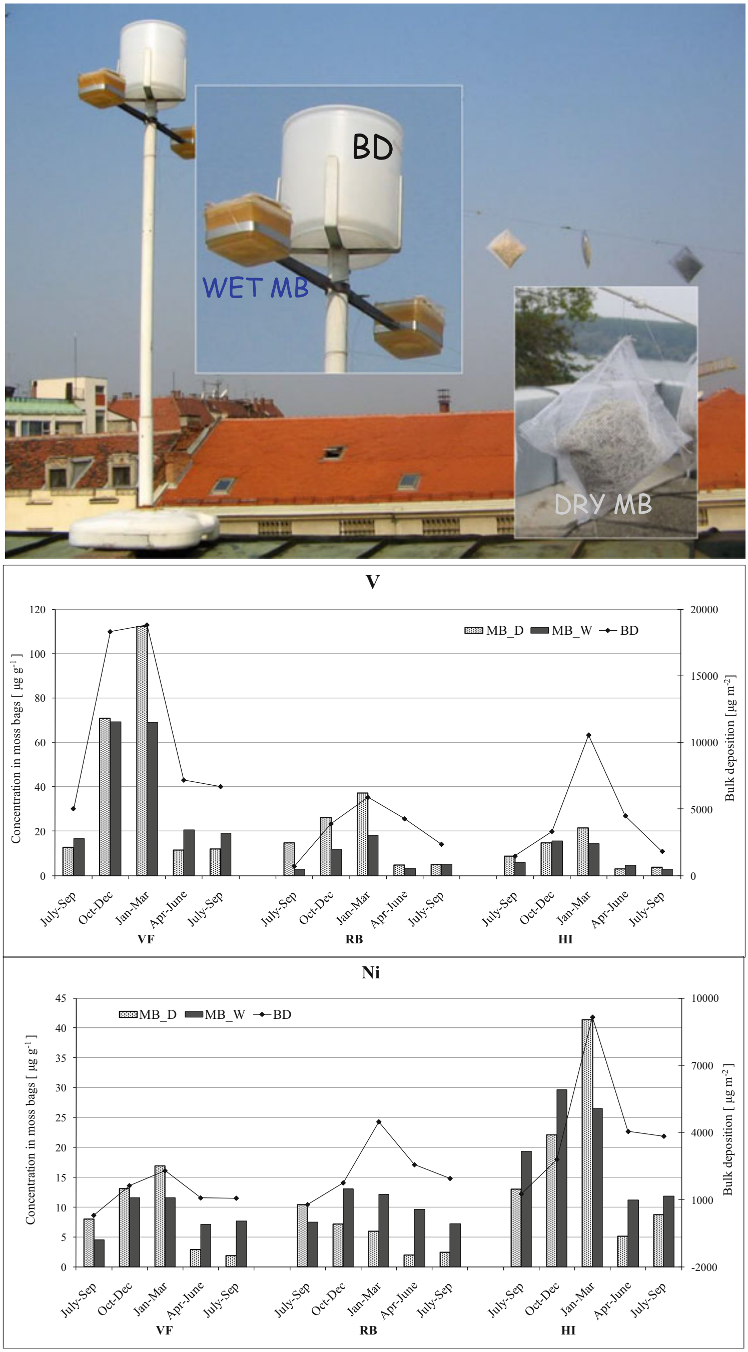

Fig. 2.1 Experimental setup: upper, dry and wet moss bags vs. bulk deposition collector; down, V and Ni concentrations (μg g^{-1}) in the dry (MB_D) and wet (MB_W) moss bags and bulk deposition collectors (BD, μg m^{-2})

concentrations were measured in the wet than in dry moss bags (Fig. 2.1). *The element concentrations in both types of monitors (moss and bulk collectors) followed the same pattern* at the corresponding sites. Significant correlations between the element concentrations in the moss and bulk deposits were found for Al, V, Cr, Fe, Cu, Zn and Pb (in DRY MB) and Al, V, Fe, Ni, Cu, Pb and As (in WET MB) (Aničić et al. 2009a, b).

The comparison of moss element accumulation in *Hypogymnia physodes* and *Dicranoweisia cirrata* transplants to bulk precipitation was investigated a long time ago by Pilegaard (1979) who found the significant correlation for Cd, Cr, Cu, Fe, Mn, Ni, Pb, V and Zn. However, recently observation suggests that most of the significant correlations between *Sphagnum denticulatum* bags and the bulk deposition involved Cd and to a lesser extent Cu and Zn (Ares et al. 2015a). The same authors, in the study, that was designed similar to ours (Aničić et al. 2009a, b), noted the lack of any correlations between the concentrations of the elements in *Pseudoscleropodium purum* bags (irrigated and devitalised) and the bulk deposition (Ares et al. 2015b).

Obviously, the moss bag biomonitoring of elements is highly species-specific, and also it depends on the bag preparation methodology. Except of harmonisation and standardisation of the moss bag biomonitoring among the interested in parties, further comparative research between the moss bag technique and the regular method for assessing the element atmospheric deposition (UNE-EN-standard 15841:2010) is needed.

Dry and Wet Moss Bag Accumulation Capacity vs. Exposure Time In 2007, in the suburb of Belgrade, we exposed *S. girgensohnii* moss bags to air pollution from 0.5 to 5 months, in consecutive 15-day periods, searching for an optimal moss bag exposure time. As it was presented in the previous studies (Aničić et al. 2009a, b), the water irrigation treatment was applied to the half of the exposed moss bags. For 49 elements measured in the moss samples, the next conclusions were highlighted (Aničić et al. 2009c):

(i) Higher element accumulation was obtained in the wet than in dry moss bags, but with similar *linear-like trend of the element enrichments from 0.5 to 5 months of exposure*; finally, we have a preference to 'dry bag concept' as simpler installation in comparison to the wet one.
(ii) Although the elements were significantly accumulated in the moss even after 0.5-month exposure, prolonged moss bag exposure is advisable at low polluted sites; e.g. *2-month exposure will assure the positive element concentration 'signal' in the moss tissue* exposed in the differently polluted microenvironments (Fig. 2.2).

In the review paper (Ares et al. 2012), after the careful evaluation of the previous studies, it is recommended that the moss bag exposure period should be between 30 and 45 days. Afterwards, the same authors conducted the extensive study in three

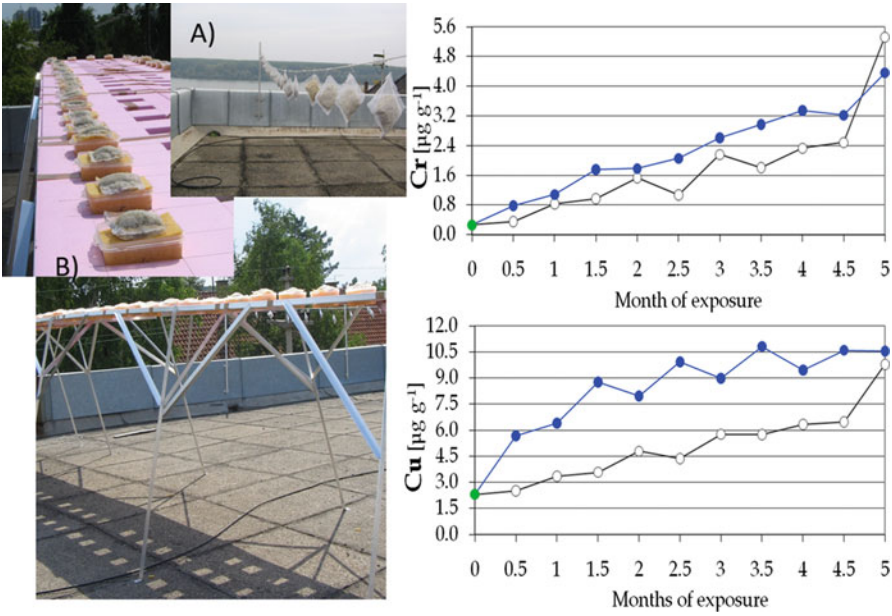

Fig. 2.2 Experimental setup: left, (**a**) dry and (**b**) wet moss bags; right, concentrations (μg g^{-1}) of Cr and Cu in the moss bags exposed from 0.5 to 5 months in steps of 15 days

European countries, and they concluded that moss bag exposure during 3 weeks was not enough to achieve a consistent element accumulation signal in all tested environments (urban, industrial, agricultural and background) (Capozzi et al. 2016b). However, our latter study regarding the urban background of air pollution carried out in the botanical garden (Belgrade) showed that the significant element enrichment was in the first 15 days of the moss exposure, while consistent 'signal' was achieved after 2 months (Aničić Urošević et al. 2017b). This finding is in agreement with the conclusions of our first study regarding time-dependent element enrichment in the moss bags (Aničić et al. 2009c).

Moss Bag Biomonitoring of Airborne Elements in Various Urban Microenvironments Based on the conclusions from the previously performed methodological studies (Aničić et al. 2009a, b, c), the moss bag biomonitoring (DRY MB) was implemented in various urban microenvironments with presumably high air pollution, such as the city tunnel, street canyons, parking garages and crossroads in the urban area, as well as the airport in the suburb of Belgrade. During 2011/2012, *S. girgensohnii* moss bags were exposed at each of the mentioned sites to test small-scale spatial of the element concentrations present in the specific ambient.

The results of the applied biomonitoring confirmed that all the studied sites characterised with high element enrichment in the exposed moss, especially the city tunnel probably due to the intensive traffic flow and semi-indoor environment (Vuković et al. 2013, 2014). *Along the city tunnel, decreasing trend of the element*

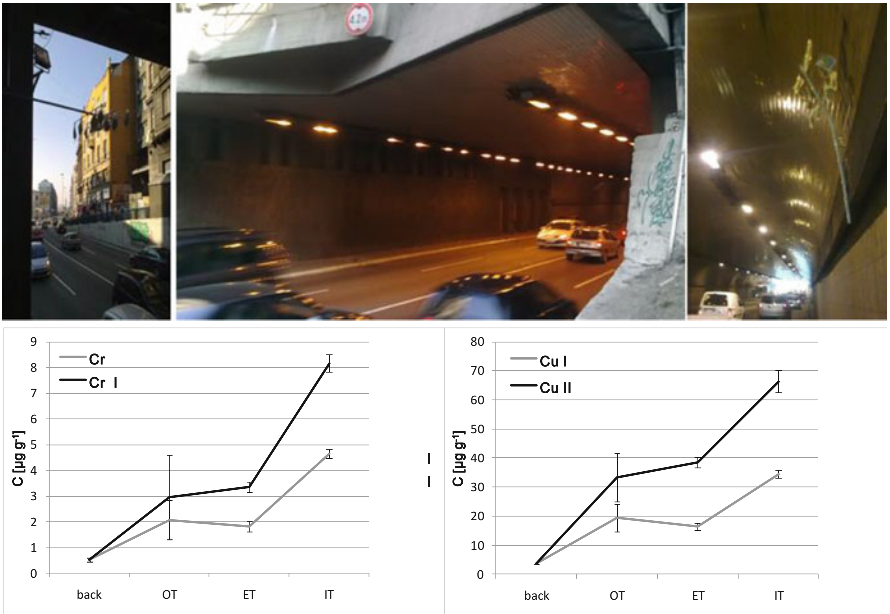

Fig. 2.3 Moss bag exposed in the city tunnel: OT, outside tunnel; ET, entrance tunnel; IT, inner tunnel (upper); the spatial trend of Cu moss concentrations along the tunnel: Cu I, after 5 weeks; Cu II, after 10 weeks; back, unexposed moss (down)

concentrations was observed in the moss bags exposed inside, at the entrance and outside of the tunnel. Further, even 5 weeks of the bag exposure led to the marked element enrichment in the moss; this continues to increase up to 10 weeks of the exposure (Fig. 2.3) (Vuković et al. 2013). According to our knowledge, this is a unique published study performed in the tunnel environment by using moss bag technique, except the conference proceedings by Ndlovu et al. (2013) regarding the moss and lichen bags exposed in the road tunnel. The authors concluded that elements associated with vehicle emissions in the tunnel were considerably accumulated in moss bags (*Leptodon smithii* and *Pterogonium gracile*) even after a short exposure time of 7 days continuing with enrichment up to 19 days (the next collection of moss bags). Road tunnels are microenvironments usually without extra space for setting the measuring devices and where easy-to-apply moss bag technique shows the clear advantages.

The term ‘street canyon’ refers to relatively narrow street with buildings lined up continuously along both sides that contribute to the creation of poor air dispersion conditions giving rise to air contamination (Vardoulakis et al. 2003). These urban microenvironments often represent a hot spot of air pollution. Hence, we decided to expose the moss bags in the five street canyons at heights of about 4, 8 and 16 m and to explore whether the ambient element content changes with height. The results showed that *moss bags can reflect small-scale changes in the element concentrations along the vertical profile in the street canyons*. The highest moss element content in

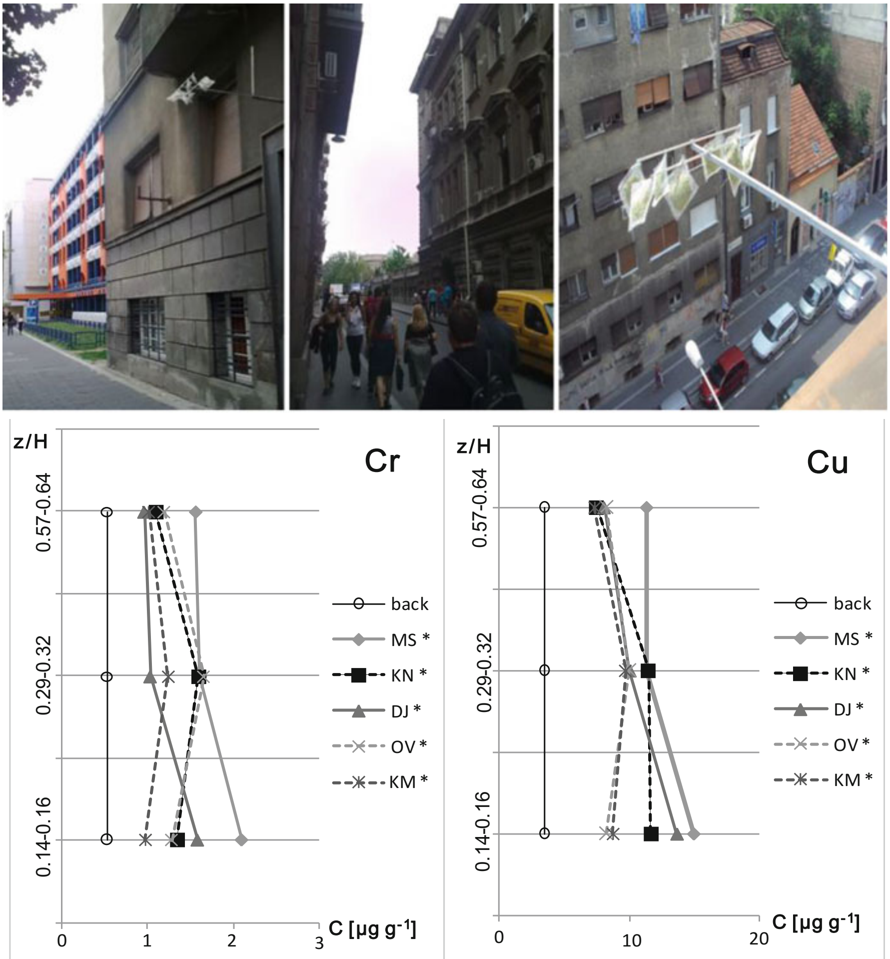

Fig. 2.4 Moss bags exposed in street canyons (MS, KN, DJ, OV, KM), back, unexposed moss; z/H, heights of about 4, 8 and 16 m above the ground divided with the height of the canyon

the several streets was found at about the second height of bag exposure while in the other streets it was at the first height (Fig. 2.4) (Vuković et al. 2013). Adamo et al. (2011) also applied the moss bag (*Hypnum cupressiforme*) biomonitoring in the street canyon of Naples, and they pointed out the significant difference in the vertical distribution of the certain elements (Al, As, Ba, Co, Fe, Pb, Ti, V and Zn), which was the highest in the moss bags exposed at 4 m in comparison to those exposed at 12 and 20 m. However, several elements (Cd, Cu and Mo) were found in the highest concentrations at the roof level of the canyon.

In reality, the regulatory monitoring of air pollutants performs at a street level only (in so-called breathing zone, 2–4 m above the road level, at which people act and breathe). However, the moss bag studies suggested that residents in certain streets may be more exposed to PTE air pollution than pedestrians emphasising the neediness for evaluation the exposure of human population in high-level apartments beside those in the breathing street zones.

Dispersion of airborne elements in street canyons is complex due to the competing influence of the street geometry and, consequently, directions of the dynamic and thermal-induced vortices and traffic intensity. Thus, the element contents in the exposed moss bags were higher in deep and regular street canyons in comparison to that of the avenue type, the latter even with a higher traffic flow (Goryainova et al. 2016).

However, regarding the investigation of the representative height of the bag exposure, Ares et al. (2014) exposed moss *Sphagnum denticulatum* at eight different heights above ground (0.5, 1, 1.5, 2, 2.5, 3, 4 and 5 m) in industrial, urban and rural areas. Since the most replicable results were obtained for Cd, Cu, Hg, Pb and Zn determined in the moss bags exposed at 2.5 and 4 m, the latter is declared as suitable. Due to practical constraints (e.g. to avoid vandalism, measurement within breathing zone), the height of about 4 m could be recommended for the bag exposure in moss biomonitoring surveys (Vuković et al. 2013; Ares et al. 2014).

Parking garages represent microenvironments where employees and attendants are potentially exposed to elevated concentrations of air pollutants due to very intensive vehicle activities in stop-and-go mode and poor natural ventilation. Additionally, wearing of brake linings and tires and dust resuspension represent the uppermost contributors to the increased PM concentrations during parking (Birmili et al. 2006). The measurement of gaseous pollutants (CO, CO_2, NO_x) in public parking garages is a routine, unlike PM and its associated toxic elements. Our moss bag study was the first one performed in semi-indoor microenvironment such as parking garages. The aim of the study was to test small-scale differences in the ambient element content within four garages by using moss bags exposed at the entrance and at the position in the interior.

In general, relative accumulation factors (RAFs) of the elements in the moss tissue were low despite the garages were assigned as air pollution hot spots, situated in the street canyons. Parking garages characterised by an absence of atmospheric deposition, low air humidity as well as poor air conditioning, which had a strong influence on the element capture by the moss bags. Thus, despite high traffic flow and slow-motion cars (stop-and-go regime), the relatively low moss element enrichment was found in the garages' interior, contrary to the toll gates (Fig. 2.5). Still, the significant difference between the moss element concentrations at the entrance in comparison to the interior indicating that *moss bag can reflect small-scale horizontal spatial variations of airborne elements in parking garages* (Vuković et al. 2014).

The networks of the regulatory air quality monitoring have been typically designed to assess regional and temporal variations of air pollution. Otherwise, for micro-scale setting, the sampling station should be placed at a distance of at least 25 m from the edge of crossroads and not on the carriageways of roads (Directive 2008/50/EC). Hence, the examination of long-term on-road exposure of pedestrians, drivers, commuters, cyclists and workers to the traffic-related toxic elements requires an alternative approach.

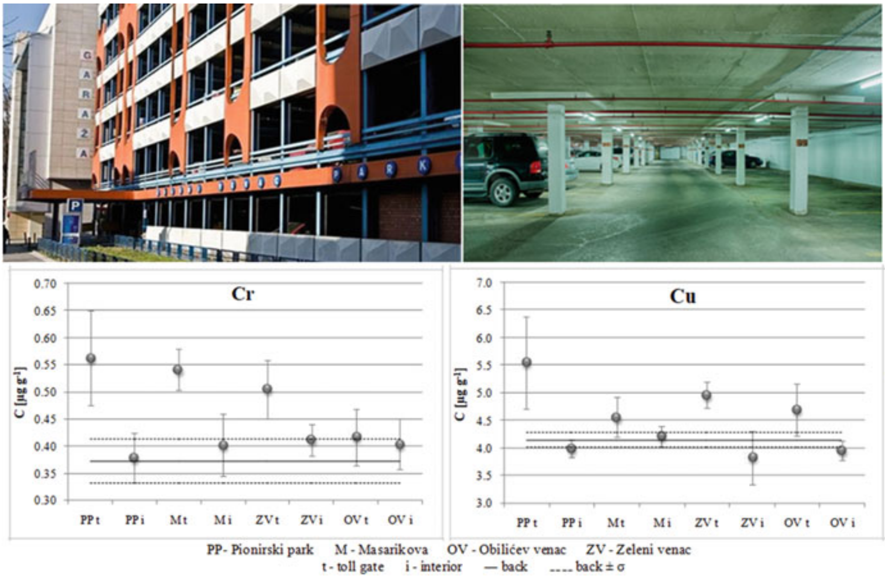

Fig. 2.5 Moss bags exposed in four parking garages (PP, M, ZV, OV): t, tool gate; i, interior; – back; --- back±σ

Following the previously defined neediness, during summer of 2014, the sensitivity of the moss bag technique was tested at the near-road side close to big crossroads, two- and one-lane streets in Belgrade. This street study confirmed the ability of the *S. girgensohnii* and *H. cupressiforme* moss bags to reflect the small-scale air pollutant distribution influenced by the substantially different traffic flows at big crossroads, two- and one-lane streets (Vuković et al. 2016). For the majority of the elements, *the moss bags identified a common pattern of decrease in the concentration from crossroads to two- and one-lane streets*. A strong correlation between Sb, Cu and Cr concentrations in the mosses with the counted traffic flows emphasised these elements as the reliable traffic tracers (Fig. 2.6). Otherwise, in the pedestrian zones, the moss bags observed the significantly lower element concentrations than in the traffic-occupied streets. In the urban study, Rivera et al. (2011) also found that the metal concentrations in *Hylocomium splendens* moss bags were strongly associated with the number of bus lines in the nearest street. These findings support the hypothesis that the traffic emissions are the substantial contributor to the urban air pollution.

In our study performed at the streets, two moss species were tested for the hypothesised phenomenon, a species from the most recommended genera, *S. girgensohnii*, and the common species for the study area, *H. cupressiforme*. Despite both mosses followed a similar pattern of the element distribution among the studied sites, linear regression analysis showed that the studied moss species could only be interchangeably used for the assessment of Cr, Cu and Sb within on-road microenvironments (Vuković et al. 2016).

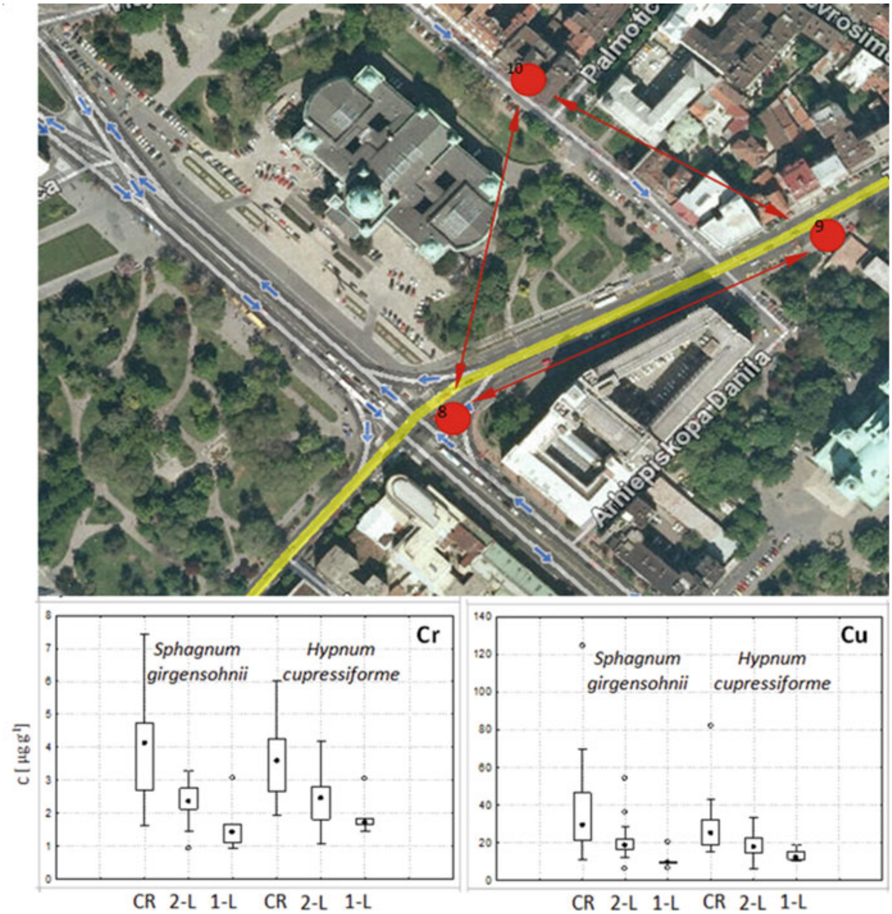

Fig. 2.6 Concentrations (μg g^{-1}) of Cr and Cu in the moss bags exposed at crossroads (CR), two-lane (2-L) and one-lane (1-L) streets

Air transportation sector is also one of the factors implying the air quality degradation. Airports are usually located close to the cities, and they are closely linked by well-developed public transport making together expanded suburbs with possibly disturbed air quality. For the United Kingdom, Yim et al. (2013) reported that the number of early deaths per year would rise from today to 2030 due to the increased aviation activities. The entire ‘airport system’ includes flight facilities and supporting infrastructures such as intermodal transportation systems for passengers and cargo moving or road traffic including private cars, taxis and buses. Thus, sources of the air pollutants at the airports comprise aircraft exhausts, then tires, brake and asphalt wear during landing and takeoff processes and emissions from the ground service equipment.

In 2013, we applied moss bag technique to assess the presence of airborne PTEs at three sites within the international airport ‘Nikola Tesla’ (Belgrade, Serbia): (i) at the runway (two positions, left and right), (ii) auxiliary runway and (iii) parking lot (Vuković et al. 2017).

Considering all studied sites at the airport, Zn, Na, Cr, V, Cu and Fe were the most enriched elements in the exposed moss bags and significantly differed between the sites. *S. girgensohnii* moss bags showed an *increase of Al, Co, Cr, Cu, Fe and V concentrations from the runway sampling sites over the auxiliary runway to the parking lot*, except Zn. The element concentrations at the airport were in the range of their concentrations measured in the suburban zones of the Belgrade city, but lower than in the industrial and urban central zones (Fig. 2.7) (Vuković et al. 2015a). This study emphasised moss bag biomonitoring as an easy operational and robust method for assessment of air quality within microenvironments with restriction in positioning referent instrumental devices, such as an airport runway.

Moss Bag Biomonitoring for the Extensive Screening of Air Pollution Across the Entire Metropolitan Area Air quality monitoring stations are mainly positioned at presumably air pollution hot spots to check if there exist overcomes of the pollutant target values, and there are rarely stations measuring the background area pollution. However, complex urban topography strongly influences the variation of air pollutants on a small-scale, even among the neighbouring streets. Doubtless, there is a need for increasing a spatial resolution of the monitoring sites. The moss bag biomonitoring was a suitable method to cover the whole area of Belgrade city in the biomonitoring surveys of the air pollution during the summer and the winter of 2013/2014.

In the extensive summer study, we exposed moss bags at 153 sampling sites in order to form a dense monitoring network, which enables the mapping and zoning of the city air pollution. Two mosses, *S. girgensohnii* and *H. cupressiforme*, were exposed in parallel to perform the species intercomparison regarding the element uptake capacity (Vuković et al. 2015a). The results of linear regression analysis showed that the studied moss species could not be interchangeably used for the airborne element assessment, except for Cu and Cr (Fig. 2.8). Although significantly higher relative element accumulation was obtained by *S. girgensohnii* bags in comparison to another species, both *mosses observed clear distinctions between high-, moderate- and low-pollution land use classes in the city*. Moreover, the mosses revealed new pollution hot spots in addition to the sites previously recognised by the regulatory monitoring. Thus, moss bag biomonitoring could be applied as a pragmatic approach for optimising the representativeness of regulatory monitoring stations.

The extensive moss bag biomonitoring of the airborne elements was successfully carried out across several European cities at 23 sites in Girona and Salt, Spain (Rivera et al. 2011); 50 sites in Santa Cruz de Tenerife, Spain (Ares et al. 2011); and even 230 sites in Warsaw, Poland (Dmuchowski and Bytnerowicz 2009). According to the final recommendation of the studies, moss bags represent a suitable

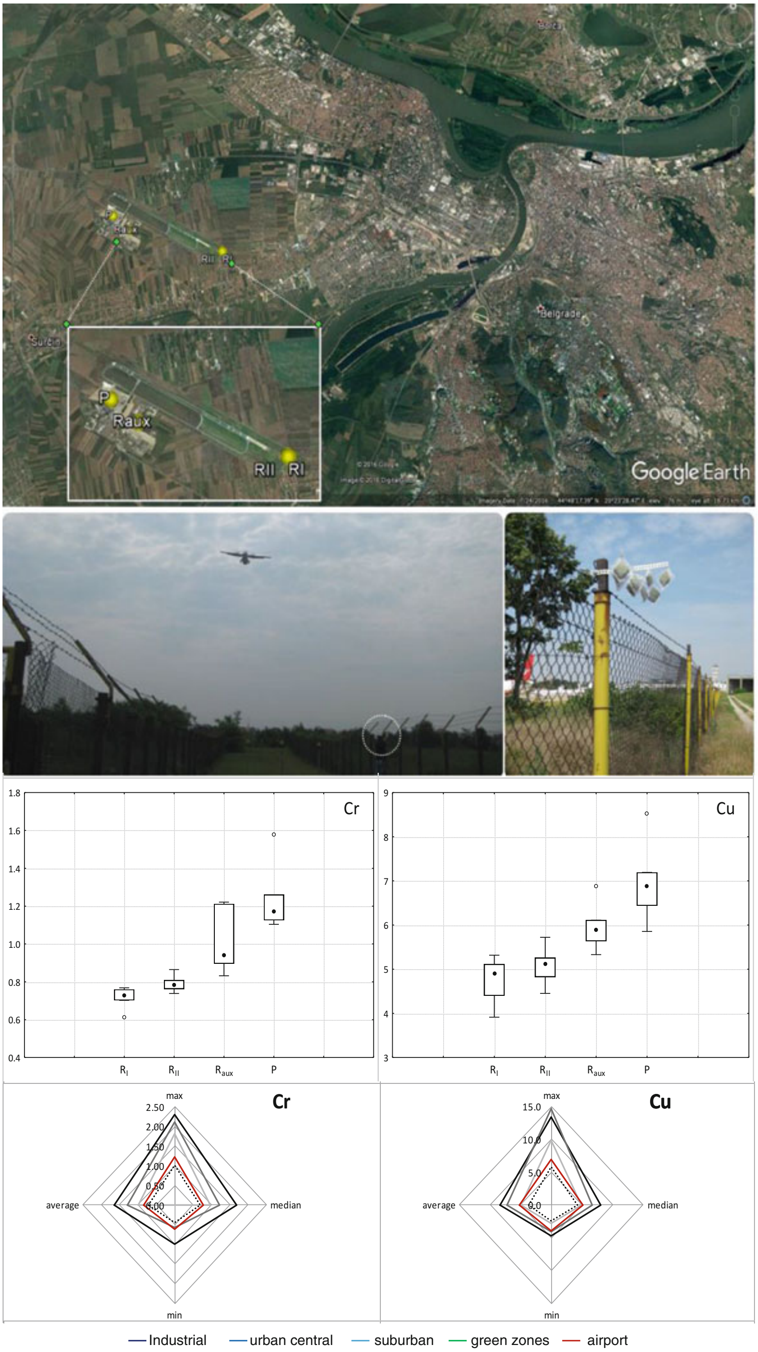

Fig. 2.7 Minimum, maximum, median and average concentrations (μg g^{-1}) of Cr and Cu in the moss bags exposed across the international airport 'Nikola Tesla' (Serbia) and within different land use classes across the Belgrade urban area: industrial, urban central, suburban and green zones

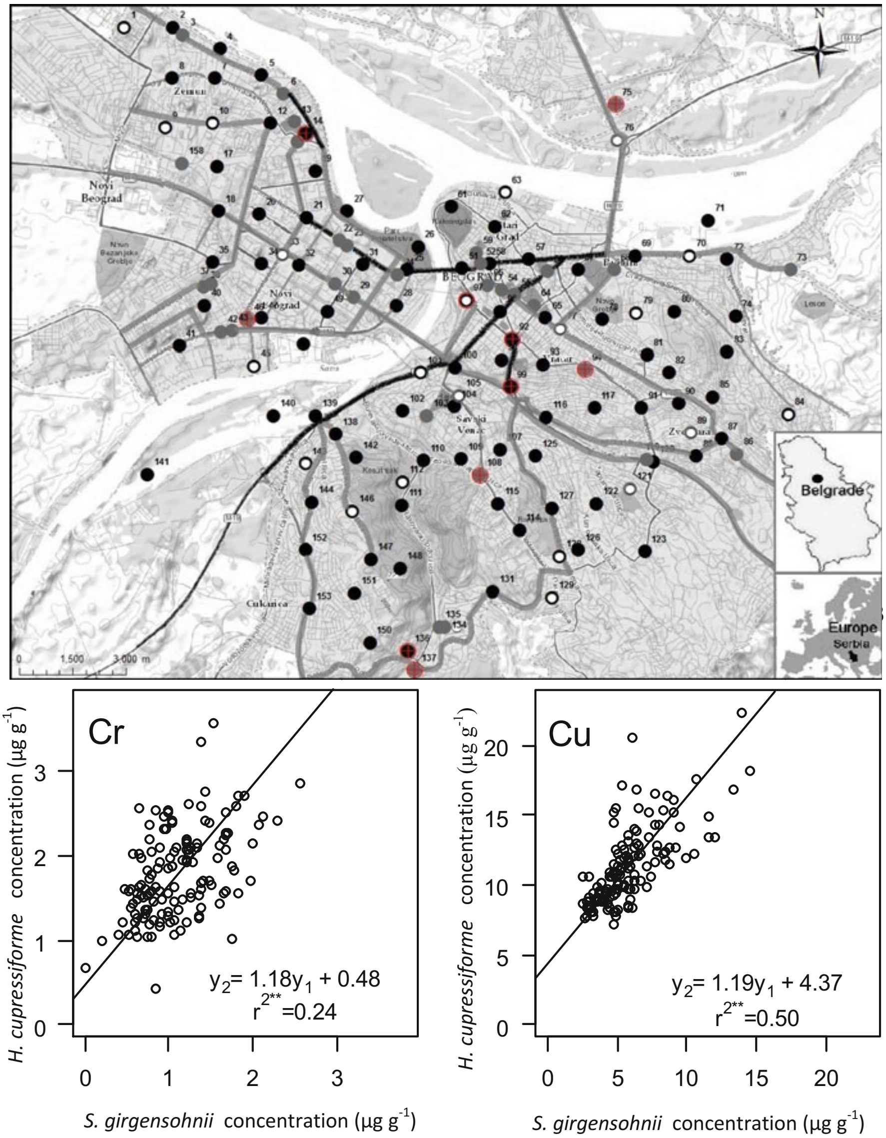

Fig. 2.8 Map of the Belgrade study area with biomonitoring sites (circles); public transportation systems I, II and III according to the traffic load and land use classes (lines); regulatory monitoring stations (red circles); down – type II regression lines for Cr and Cu concentrations (µg g^{-1}) in mosses *S. girgensohnii* and *H. cupressiforme*; the significant coefficients of determination at $p < 0.001$ level (**)

technique for an inexpensive environmental monitoring programme, which could be a complementary use to the regulatory monitoring.

In many countries with moderate to continental climates, fossil fuel and wood combustion processes are particularly intense during the winter, i.e. heating season. Namely, residential heating includes heating plants and individual heating sources which primarily use oil or coal combustion to generate heat. The combustion processes lead to the elevated release of airborne pollutants (PM and its associated elements) (Pacyna and Pacyna 2001).

Since Belgrade lies in the moderate continental zone with an average temperature of 0 °C in January, the heating plant system operates during winter (October–April) and supplies around 200,000 households in the city. In addition, 140,000 households are using individual heating sources combusting coal or oil fuel. There is no precise data on the total fossil fuel consumption of individual heating sources and, consequently, on the air pollutant emissions and dispersion.

Hence, during the winter 2013/2014, in the vicinity of the heating plant chimneys and within the residential zones with individual heating units, we exposed *S. girgensohnii* moss bags to perform PTE biomonitoring including REEs. The aim of this experiment was to estimate the influence of the residential heating system operating during the winter to the airborne element content in the city generally affected by traffic emissions. The results showed that during the heating season, the study area was polluted by the elements far more than in the preceding summer (Vuković et al. 2015b). Among the determined elements, the moss samples were especially enriched by V, Ni, Sb, Cu and Zn. The significant and very high correlation was observed between Ni and V (Fig. 2.9), which are well-known as the tracers of oil combustions (Pacyna and Pacyna 2001).

Exposure to REEs, which are also considered as emerging pollutants due to their detrimental health effects (Pagano et al. 2015), has raised questions since their utilisation is growing worldwide (EPA 2012). In our study, significantly higher concentrations of REEs were measured in the moss samples exposed at typically urban sites than in those at green city zones (Fig. 2.9) (Vuković et al. 2015b). This result indicates that the REE moss entrapment is partially affected by anthropogenic activities. It may be supposed that crustal dust is a dominant component of road dust. Thus, the moss enrichment with road dust is primarily dependent on the resuspension process induced by vehicle movements but also on traffic intensity and certainly duration of the moss bag exposure. In the previous study performed in Belgrade by Aničić et al. (2009c), there were also observed the increase of REEs in the exposed moss with the prolongation of the exposure time.

Moss Bag Biomonitoring for Measuring the Background Air Pollution Moss bag technique has been predominantly adopted for biomonitoring of PTEs across highly polluted urban and industrial zones since they represent 'moss deserts'. However, we tested the application of the technique for measuring the urban background air pollution within the botanical garden 'Jevremovac' (Belgrade) as the presumable background site within the city. The *H. cupressiforme* bags were exposed at three sites: the garden boundary, the garden inner and control-sheltered site. The results

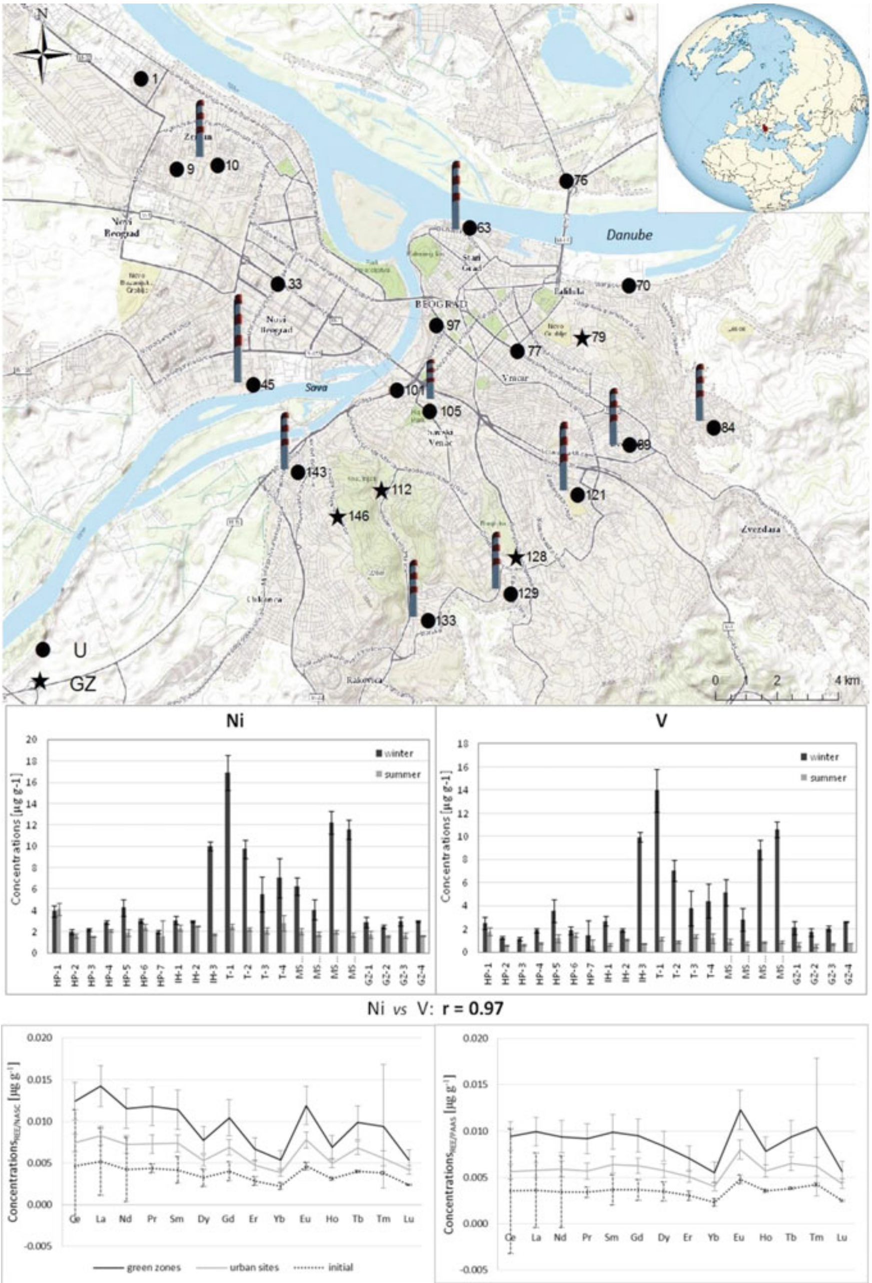

Fig. 2.9 Map of the Belgrade city area; moss bag biomonitoring sites: U, urban sites, and GZ, green zones; the heating plants are indicated by chimney symbol; concentrations (μg g^{-1}) of Ni and V in the moss exposed close to the heating plant chimneys over the city with standard deviation bars ($n = 3$) and the significant correlation coefficients (r) for winter; data for the preceding summer were taken from our previous study (Vuković et al. 2015a); median concentrations (μg g^{-1}) of the REEs normalised against NASC and PAAS shale in the moss bags exposed during the winter; the REE order on the x-axis is according to their abundances in the shale

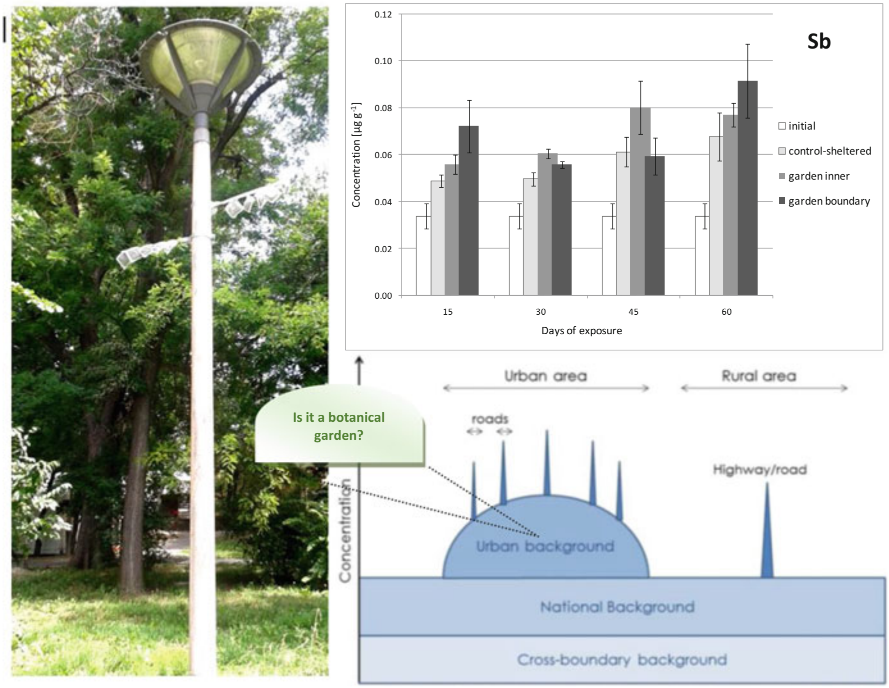

Fig. 2.10 Moss bags exposed in the botanical garden 'Jevremovac', Belgrade (left); a schematic illustration of urban background of the air pollution (down right); Sb concentrations (µg g^{-1}) in the moss *H. cupressiforme* exposed at three sites within the garden; initial – Sb concentration in the unexposed moss

showed that the average levels of moss PTEs were markedly lower within the botanical garden in comparison to those obtained at the sites in surrounding street ambient (Vuković et al. 2016), but still significantly higher than in the moss pristine habitat (Aničić et al. 2009a; Vuković et al. 2015a, b). Despite the botanical garden located in the central heavy traffic-occupied, urban area, low level of airborne elements was observed, by the moss bags. Antimony as a typical tracer of non-exhaust traffic emissions, i.e. deterioration of tire, brake, engine and vehicle component (Grigoratos and Martini 2015), was the most enriched element in the moss samples, especially at the garden boundary site, which is relatively close to the street with high traffic frequency (Fig. 2.10). Notwithstanding, the botanical garden could be recommended as a control site for the measurement of urban background pollution which might be effectively measured by the moss bag technique (Aničić Urošević et al. 2017b).

2.4 Agricultural Scenario

Treatment of soil and crops by the agrochemicals has become a common practice in agriculture aiming the improvement of the nutrient supply in soil (fertilisers) or crop protection and disease control (pesticides − herbicides and fungicide). For economic reasons, fertilisers are usually not sufficiently purified during the processes of manufacture, and they could contain impurities, such as toxic elements. Moreover, toxic elements are often the constituents of pesticides. Manganese, Zn, Co and Pb are the most common PTEs that soil receives through conventional agricultural practices. Superphosphate fertiliser contains Cd, Co, Cu and Zn as impurities, while in sulphate fertiliser, Pb and Ni were detected. Pesticides can contain Cd, while the highest levels of Fe, Mn, Zn, Pb and Ni are found in the herbicides (Gimeno-Garcia et al. 1996). Specifically in the vineyards, except widely applied Cu-fungicide treatments, the application of conventional inorganic phosphorus fertilisers may also contain some toxic elements as impurities – Cr, Cd, Cu, Zn, Ni and Pb (Thomas et al. 2012).

The soil is the final collector for contaminants released by the agricultural activities but also the pollutant emission source to the atmosphere by resuspension processes (Wuana and Okieimen 2011 and references therein). Heretofore, no special attention is paid to the areas with agricultural activities, continuously emitting significant amounts of air pollutants (Guerreiro et al. 2014). Monitoring of the air pollution in agricultural areas has rarely carried out probably due to some practical constraints, intensive agricultural activities, privately owned plots, lack of electricity, etc.

The passive approach to the moss biomonitoring of the air pollution is hardly applicable to cultivated areas where native mosses are vanished due to intensive agricultural activities. However, an alternative, active moss biomonitoring of the pollutants (PTEs) can be suitable for agricultural areas, although it has been rarely carried out thus far (Capozzi et al. 2016a, b) and never before in vineyard ambient. Regarding the application of moss bag biomonitoring in different scenarios of the air pollution, it is of importance to establish the key parameters (species selection and exposure time) determining the method applied in an agricultural land use class. In addition, the initial element concentration in unexposed moss material is the crucial premise for its the later pollutant capture during the bag exposure (Culicov and Yurukova 2006; Di Palma et al. 2016).

In 2015, we performed a comprehensive study in the conventional vineyard located in grapevine-growing area so-called Oplenac Wine Route (Serbia), for which it is expected to be the low polluted area. However, there are conventional grapevine productions in vineyards affected by the frequent agrochemical treatments of the plants. Besides soil and grapevine sampling and the element bioavailability assessment (Milićević et al. 2018a, b), the moss bag biomonitoring was applied to assess the air pollution by the PTEs in the vineyard (Milićević et al. 2017). Since there was no previous experience with the moss bag exposure in the vineyard ambient, and there was no information about the schedule of agrochemical applications in the studied vineyard, we decided to biomonitor airborne PTEs during the whole grapevine season (from April to September). Although the previous studies performed in the urban area (Aničić et al. 2009c) promote 2-month moss bag exposure as an appropriate for achieving reliable 'signal' of the element concentrations in the mosses, in the vineyard ambient, this exposure period might be insufficient. Thus, we exposed the *S. girgensohnii* and *H. cupressiforme* moss bags for 2-, 4- and 6-month periods (3 × 2 months, 1 × 4 months and 1 × 6 months) covering the whole grapevine season.

Comparing different exposure periods of the moss bags in the vineyard, the element concentrations in the mosses were gradually increasing with time. Two-month bag exposure nevertheless was sufficient to achieve a reliable 'signal' for the majority of the determined elements, especially for As, Cr, Cu, Ni, Fe and V. However, the highest load of elements was during the moss exposure at the beginning of the grapevine season suggesting about the most frequent agrochemical treatments in this period. Accordingly, if the bag exposure did not coincide with the agrochemical application time, which is variable in different vineyards, 2-month bag exposure could not guarantee the detectable moss element load. Hence, *in the vineyard ambient, moss bags should be exposed during the whole vegetation period such comprising unpredictable treatments of grapevine during the vegetation season*. Six-month bag exposure covers whole grapevine season and could be recommended for intercomparison of the air pollution among different vineyards. Moreover, principal component analysis (PCA) grouped the results of 6-month exposed mosses (*S. girgensohnii* and *H. cupressiforme*) in the same quadrant (Fig. 2.11).

The results of the study showed that the element enrichment capacity significantly differed between the studied moss species, and it was higher for *S. girgensohnii* than *H. cupressiforme*. However, both species proved to be efficient biomonitors since the elements significantly accumulated in the mosses during 2 months and the concentrations were gradually increasing with prolongation of the exposure time up to 6 months.

In parallel, with moss bag biomonitoring of the air pollution in this vineyard, the soil and the grapevine samples were analysed. According to the significant correlations between the element concentration in the mosses and in the grapevine leaves, the leaves could also indicate the air pollution by PTEs (Co and Cr) in the vineyard. Therefore, the grapevine leaves collected 1 month before harvest could be a potential indicator of ambient Co and Cr pollution in the vineyard (Milićević et al. 2018b).

Finally, vineyard represents a prevailing diffuse air pollution source of PTEs through the regular agrochemical treatments and the soil resuspension, which was confirmed by the increased Cr and Ni concentrations in both the topsoil and the moss samples.

Our further investigation was related to looking for the air pollution background in the agricultural areas and, accordingly, the second study we conducted in the organic vineyard. Contrary to the grapevine production in the conventional vineyard with frequent application of various agrochemicals, hopefully upon to the prescribed values, organic production implies a plant growth without pesticides application, with the possible use of natural fertilisers (compost and manure). Organic viticulture

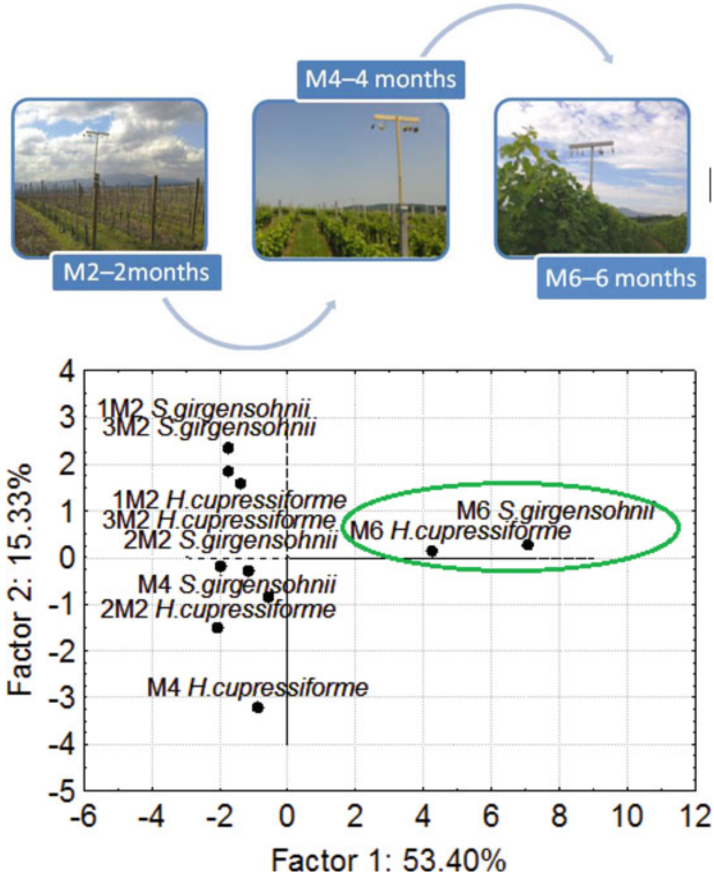

Fig. 2.11 Moss bag biomonitoring of PTEs during the grapevine season (upper); the principal component analysis of the data (down): M2, 2 months; M4, 4 months; and M6, 6 months of exposure

production started at the end of the twentieth century, in parallel with the development of contemporary analytical methods for testing the quality, environmental awareness and research on the food impact on human health (Wheeler and Crisp 2009).

In Serbia, there are only three vineyards that are organically grown, and in one of them for the first time, we conducted the moss bag biomonitoring in 2016. We carried out a study in the organic vineyard 'Grocka', located near the Danube River, Serbia, with the aim to estimate whether the soil, plant (grapevine) and air in the organic ambient less enriched by PTEs than in the conventional vineyard. The *S. girgensohnii* moss bags were exposed in five parcels in the organic vineyard for 2 and 4 months. Since there was no any agrochemicals treatment in this vineyard, it was expected that the 'signal' of element concentrations in the mosses could be low

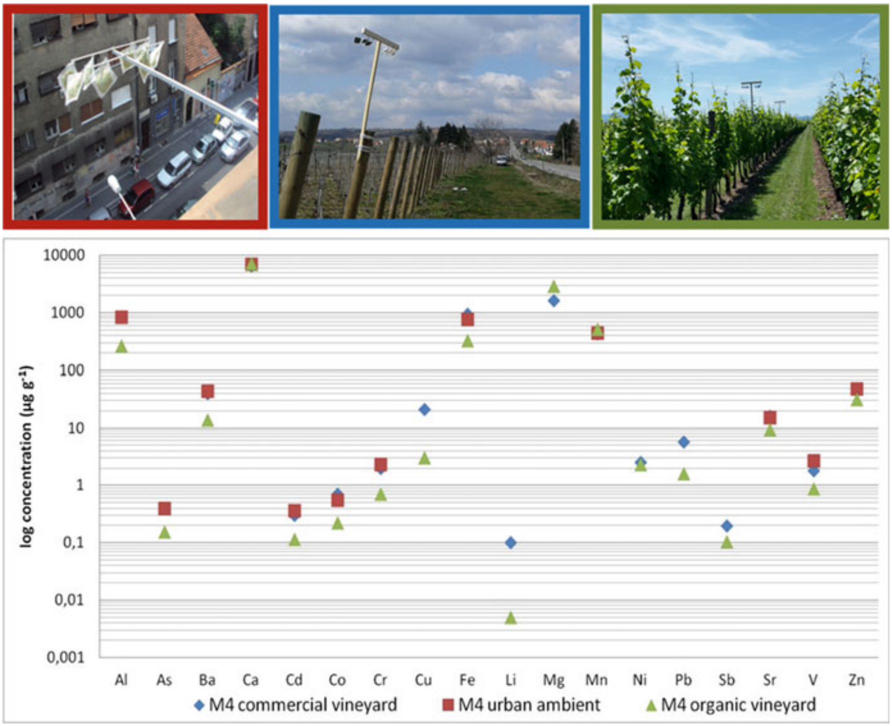

Fig. 2.12 The comparison of the median element concentrations (µg g^{-1}) in *S. girgensohnii* moss bags exposed for 4 months in organic vineyard (green), conventional vineyard (blue) and urban ambient (red)

or undetectable during 2-month bag exposure, and thus, the prolonged exposure time (4-months) of the bags were also considered.

Through the prolongation of the exposure time, the element concentrations in the mosses were increasing as in the previous study conducted in the conventional vineyard. The median values of the element concentrations in the moss bags exposed for 4-months were compared with the concentrations in the same moss species exposed for 4-months in the conventional vineyard and in the urban area of Belgrade (Fig. 2.12). *The concentrations of all measured elements in the moss samples indicate that there were lower PTE concentrations in the mosses exposed in the organic than in the conventional vineyard*. This claim has been confirmed by calculated RAF values, which were lower than in the conventional vineyard (Milićević et al. 2017) and the urban area (Vuković et al. 2015a). The calculated RAFs indicate slightly higher values for Al, B, Cr, Cu, Sb, V and Zn. Specifically, in comparison with the parcels 1, 2 and 3, the higher values (RAF: 1–4) were estimated in parcels 4 and 5 that are located near the Danube River and which are not protected by the trees and shrubs against breakthrough of air pollutants.

To conclude, the moss bag biomonitoring in the vineyards clearly stated differences in the element distribution in time, but not too conspicuous in the space probably due to the fact that vineyards represent diffuse pollution sources. Thus, the technique proved to be a simple, cost-effective and reliable tool for the air pollution assessment in the agricultural areas. Otherwise, according to the lower element concentrations accumulated in the mosses and in compilation with absent of the agrochemical treatments, the organic vineyard could be assumed as an agricultural background of the air pollution.

2.5 Conclusion

Currently the level of air pollution, especially in anthropogenically devastated urban and agricultural areas, seriously affects environmental and human health. The complexity of the spatio-temporal air pollutant transport and the dispersion over settlements and plant-growing areas highlighted a need for highly resolved pollutant measurements. However, this issue is still inadequately corroborated by the regulatory monitoring network due to the balance between costs and practical constraints.

Biomonitoring is another approach to evaluate the state of the environment through the systematic use of organisms or their parts that reflect the ambient pollution. Mosses, belonging to the cryptogams, are considered as the most appropriate biomonitors of air pollution. The active moss biomonitoring approach (the moss bag technique) proved to be a suitable alternative in so-called moss ‘deserts’, such as urban and agricultural areas. Dozens of papers regarding moss transplant application in the assessment of air pollution end with the statement that ‘moss bags can be used as an easy-to-apply screening technique in environmental monitoring programme and pragmatic complements to regulatory monitoring networks raising the spatio-temporal resolution of air pollution measurements’.

Our experience in the moss bag biomonitoring of airborne PTEs is related to its application in the urban and the agricultural ambient. We found that moss element entrapment is strongly species-specific, and, except for Cu and Cr, examined moss species *S. girgensohnii* and *H. cupressiforme* could not be interchangeably used in the same study. The mosses proved to be sensitive on spatio-temporal variation of the airborne elements even on a small scale (10 m and 15 days) if there is variability in topography or emission sources or the source strength. However, a reliable ‘signal’ of the element enrichment in the moss could be achieved after 2-month bag exposure even at the air pollution background sites. Although moss data were not directly comparable to the regulatory measurements, the significant correlations were obtained only for some of the measured element concentrations (V, Ni, Cu and Pb). Thus, biomonitoring can be used for the screening air pollution in an area searching for the pollution hot spots or for optimising the representativeness of regulatory monitoring stations.

However, at this stage, due to a scattered application of mosses in individual studies using the non-harmonised methodology, the biomonitoring results are hardly intercomparable. To integrate biomonitoring into the environmental policies, concerning the limit and target values of air pollutants, the protocol of the moss bag biomonitoring technique application should be standardised and validated on an international level. The perspective is in improving the quality, reproducibility, and therefore usability of the biomonitoring data collected from diverse research studies. Despite the later methodological review paper (Ares et al. 2012), harmonisation of the moss bag biomonitoring protocol, or in some cases a simple matter of agreement, is still required with the aim of further standardising the technique for its use as a regular environmental monitoring tool by official organisations.

Due to evident applicable advantages, moss bag biomonitoring can be used as an ecosustainable tool for air protection management not only in urban and agricultural ambient but also in remote areas and places hardly available for instrumental measurements (e.g. volcanic craters, tunnels) and in the quite exotic application as stratospheric biomarkers. This chapter moves beyond the attempt to promote biomonitoring as an effective approach for screening air quality, which should be considered for implementation into laws and regulations against air pollution.

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Chapter 3
Use of Lichens in Biological Monitoring of Air Quality

Gülşah Çobanoğlu Özyiğitoğlu

Abstract This chapter focuses on biomonitoring of air quality using lichens in the industrial, urban and suburban areas in cities and in the vicinity of pollution sources, mainly based on the studies carried out in the last decades. Also lichen diversity studies in natural areas and in polluted sites, analytical methods and statistical analyses used in these studies are discussed. In addition, the text covers complementary information on the subject, for instance, environmental and anthropogenic factors which are effective on pollution sensitivity of lichen communities, negative effects of pollution on structure of lichen, metal uptake mechanisms and comparative analysis of data relating to changes in lichen vitality parameters. In particular, it is emphasized how to utilize the lichens featuring bioindicators and biomonitors to determine air quality in terms of quantities and impacts of airborne pollutants such as sulphur dioxide, heavy metals, particulate matters and radionuclides. With respect to lichen biomonitoring, the appropriate biological methods, their advantages and disadvantages, past to present studies on this subject in the world, the assessment of the relevant literature and the reliability of the obtained results are reviewed from a broad perspective. It is envisaged that this compilation will serve as a guiding source for biologic monitoring of air quality and creation of management and conservation strategies with lichens today.

Keywords Air quality · Air pollution · Bioindicator · Biomonitor · Lichens · Heavy metals

3.1 Introduction

Despite the relatively low concentration of sulphur dioxide in recent years due to the discouraging the use of fossil fuels, pollutants in the atmosphere together with global climate change still pose a serious threat to human health. The effects of air

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pollutants on human health can be listed as the reduction of the immune function of the body, the diminution of lung function, changes in the respiratory and circulatory system and the induction and promotion of human allergic diseases, respiratory diseases and other diseases (Cen 2015). Constant and serious precautions must be taken to monitor the sources of pollution. In order to be able to reach sustainable air quality, it is necessary to first determine the level of air pollution and then find solutions to reduce pollution rates. Instantaneous or ongoing air pollution levels can be measured in several ways, directly or indirectly.

Lichens are successful examples of the coexistence of some fungi (mostly *Ascomycota*) and green algae (*Chlorophyta*) and/or blue-green algae (*Cyanobacteria*), represented with approximately 20,000 species in the world. This common life, "symbiosis", is a mutualistic association (which both partners benefit), as it is often accepted. According to Vernon Ahmadjian's opinion, the mushroom is a controlled parasitic strain on algae (Ahmadjian 1982). The terms "mycobiont" for the fungal partner and "photobiont" for the photosynthetic partner are frequently used, while the symbiotic life partners in lichens are referred to as "symbiont". This symbiotic unity forms a common "thallus" without roots and cuticles (waterproof outer cover) and is essentially the intake of minerals from the atmosphere. These properties of lichens, when combined with their extraordinary abilities to evolve over a wide geographical range and their accumulation of much more than the needs of mineral elements, have put them among the best biological indicators of air pollution (Garty 2001; Wolterbeek 2002).

A variety of chemical, physical and biological techniques have being applied to determine the level and environmental impact of pollutants deposited in the atmosphere. Studies over the past three decades have drawn considerable attention to the relationship between lichens and air pollution and their role in monitoring air pollution in terms of particulate matter (Rossbach et al. 1999; Garty 2001; Adamo et al. 2008; Freitas et al. 2011; Malaspina et al. 2014), trace elements (Wolterbeek 2002; Bargagli et al. 2002; Uğur et al. 2003; Balarama Krishna et al. 2004; Conti et al. 2012; Caggiano et al. 2015; Will-Wolf et al. 2017), radionuclides (White et al. 1986; Gaare 1987; Başkaran et al. 1991; Biazrov 1994; Pipiška et al. 2005; Ramzaev et al. 2007; Yazıcı et al. 2008; Iurian et al. 2011) and persistent organic contaminants (Augusto et al. 2013; Ratier et al. 2018).

In this chapter, lichen biomonitoring studies are discussed in terms of contributions to air quality management. Examination of studies on lichen monitoring contributes to awareness of the environmental change caused by air pollution, measures to be taken and new approaches to conservation and management of the environment.

3.2 Biological Advantages of Lichens as Bioindicators

Lichens are plantlike organisms that develop on various types of "substrates" such as tree (epiphytic), rock (epilithic) and soil (epigeic) in most ecosystems on earth. Similar to plants, thanks to its chlorophyll partner capable of photosynthesis, lichen can produce food for itself. In fact, lichens also called “lichenized fungi” are included in the kingdom of *Fungi*, not the plants (Plantae), in the classification based on the phylogeny of the fungal partner. In thallus, at least two members from three kingdoms, fungi, algae (Protista) and cyanobacteria (*Monera* or *Bacteria*), can live together at the same time. Fungal species that cannot produce their own nutrients come together with certain microscopic algae or cyanobacteria species (such as *Trebouxia*, *Trentepohlia* or *Nostoc*) that can live freely in nature but often prefer to form lichen (Nash 2008).

Lichen species also have a wide variety of morphological diversity. Thallus types with very different shapes, sizes and colours may be “fruticose” (1 m long hanging from one point on trees or standing upright) or “foliose” spreading in the form of a rosette with large and small lobes on the substrate or “crustose” which can be as small as 1 cm deep buried in the substrate or 10 cm wide on the surface.

Because of many reasons, lichens benefit as biological monitoring tools in atmospheric deposition studies. Lichens are allowed to be compared at a universal level since they have a wide geographical spread. As an additional advantage, lichens, which are perennial and slow-growing organisms, show a single morphology that does not change over time, rather than like the flowering plants seen by season. So the morphological changes in lichens themselves are the effects of time-dependent accumulation.

Lichens are “poikilohydric” organisms whose metabolic activity is limited by atmospheric humidity. The absence of stomas and cuticles in lichens in high plants means that pollutants in the air are absorbed by the entire surface of the tallus. Perhaps most important is the ability of lichens to accumulate many elements in much greater quantities than their physiological needs (Nash 2008). It is reported that lichens absorb 100 times more sulphur dioxide than vascular plants (Winner et al. 1988). When compared with flowering plants in terms of air pollution indicator role, thalline plants such as lichens and mosses are more prominent. Because, when it comes to monitoring the quality of the air, the choice of lichens living as a whole tallus (without spilling leaf or flower) for many years gives longer term and reliable results.

The high susceptibility of lichens to pollution is closely related to their biology. Long-living lichens exposed to pollutants throughout the year as living perennial organisms have to maintain the symbiotic balance. All lichen species are not sensitive to pollution at the same time. But in general they can only tolerate pollution at a certain tolerance limit. For this reason, they have gained importance in monitoring the quality of the air. Because of the variety in the lichen communities, distribution maps based on the frequency of certain species come at the beginning of this work.

The second approach is to examine the morphological and anatomical changes of lichen species in response to pollution. The third way is to examine the physiological response (membrane integrity, CO_2 gas exchange, chlorophyll, pigment destruction, N_2 fixation and enzyme activity). Some of the changes that occur in pollution-damaged lichens include morphological and anatomic symptoms, fine-structure symptoms, membrane system disorders, chlorophyll fluorescence disorder, physiological disorders and reproductive-developmental and growth rate disorders (Nash 2008). While some of these changes (morphological and physiological) can be observed in the field, some changes can be observed with transplantation studies or controlled laboratory studies.

3.3 Air Pollution Monitoring Related Terms and Definitions

The term "monitoring" can be defined as the process of gathering information at different points about system state variables in time in order to evaluate the status of the system and to be inferred about the changes over time (Yoccoz et al. 2001). While focusing on the monitoring of biological diversity, that is, "biomonitoring", the systems of interest are typically ecosystems or components of such systems (communities and populations), and relevant variables are quantities such as species richness, species diversity, biomass and population size (Upreti et al. 2015).

By combining various definitions, "air pollution" can be defined as follows: the presence of contaminants or substances (chemicals, particulate matter (PM) or biological materials) in the air that interfere with human health or welfare, and other living organisms, or cause other harmful environmental effects on ecosystems. Air pollution exists at all scales, from personal to global. Ambient air pollution scales may be further subdivided into local, urban, regional, continental and global. The spheres of influence of the air pollutants themselves range from molecular (e.g. gases and nanoparticles) to planetary (e.g. dispersion of greenhouse gases throughout the troposphere). It is stated that when the local scale shows a spatial dimension about 5 km radius on the world surface, the urban scale has a radius of about 50 km, and the regional scale has a radius of 50–500 km. The continental scales range anywhere from 500 to 1000 km but are often driven by wind, because this road is passed by the pollutant. Of course, the global scale extends worldwide. Air pollution arises from numerous sources and processes. Air pollution and other atmospheric data include information about the air pollutants, the media (layers of the atmosphere and components of the hydrosphere), the modifiers (physical, chemical and biological substances that transform and transport the agents within the media) and the receptors (human individuals, human populations and ecosystems and their components) (Vallero 2008).

The term "air pollution" is not synonymous with "air quality". "Air pollution", pollutants and "air quality" are defined by the effects of pollutants including humans, animals, inorganic substances, monuments, etc. (Garty 2001). "Air pollution" refers to atmospheric smoke, mineral-rich dust, sulphur dioxide (SO_2), nitrogen oxides (NOx), sulphur (S) and nitrogenous (N) compounds, and fluorine (F), and photooxidants (such as ozone and PAN) refers to air toxic substances.

Many terms used for organisms in environmental pollution have different meanings. "Bioindicator" or biological indicator refers to the ability of organisms to show the presence and amount of pollutants in the atmosphere in relation to the response to different levels of pollutants. Biological indicators that provide qualitative information at the level of air pollution are called "bioindicators", while biological monitors that allow quantitative data to be identified by time are defined as "biomonitors". The practice in which biomonitors are used is the "biological monitoring" or "biomonitoring" phenomenon. "Bioaccumulator" term is used for biological agents holding metals in the air. "Bioremediators (phytoremediators)" means biological remedies, so they should exhibit the properties of removing, eliminating or protecting the contaminants from the environment. Bioremediators are short-lived living organisms that accumulate high amounts of toxic substances with large biomass. Although lichens are good bioindicators and bioaccumulators, they are not considered to be air remedial and environment protective bioremediators. The reason is that it is difficult to elucidate the true source of the metals that accumulate in the large amount of lichen biomass that comes from the very slow growth (Shukla et al. 2014). The terms "biological indicator" and "biological accumulator" cannot be used interchangeably.

For the term "biomonitor", Markert et al. (1997) used a definition of "informative organisms or communities of organisms comprising certain elements and substances and/or on the quantitative effects of environmental changes or environmental quality, including morphological, histological or cellular structures, metabolic-biochemical events, behaviour, population structures and changes in these parameters".

Seaward (1995) has introduced a contemporary approach to the monitoring of some contaminants with living materials and the assessment of human technology in the biosphere. However, it does not replace the measurement of pollutants physically and chemically. Biological monitoring is recommended as a complementary or alternative method in extensive and inexperienced comprehensive research that requires extensive instrumentation. Thus, besides physical and chemical data, physiological data showing viability are also provided.

The qualities required for an organism to be a "biomonitor" are listed by Garty (2001) as follows:

1. The organism should have the ability to accumulate metal in measurable quantities.
2. The organism or its parts should be appropriate in terms of quality and distribution on the earth and sample collection is feasible.
3. The study should be reproducible with the same qualifications.
4. The expenditures required for the collection and analysis should be acceptable (Wolterbeek 2002).

3.4 The Role of Lichens in Atmospheric Pollution Assessments

General atmospheric pollutants classified by Hutchinson are as follows:

1. Primary pollutants: SO_2, NO_2 and F compounds that remain in the same chemical form in the atmosphere

2. Secondary pollutants: resulting from chemical reactions of primary pollutants during transport in the atmosphere, such as sulphuric acid (H_2SO_4) and nitric acid (HNO_3) occurring in acid rains, also (O_3) ozone and peroxyacetyl nitrate (PAN)
3. The third group of pollutants: industrial organic compounds that contain toxins in the air, agricultural pesticides, trace metals and metalloids

Usually, sulphur and nitrogen compounds are found in the form of gaseous in the atmosphere, whereas heavy metals are found attached to particulate matter (PM). Some particles come naturally from volcanoes, dust and sandstorms, forest and pasture fires, live vegetation and sea spray effects. In addition, various human activities such as power plants, industrial activities and the use of fossil fuels in motor vehicles produce significant amounts of particles. They cause an increase in cancer, heart problems, respiratory diseases and infant mortality (Garty 2001).

Lichen diversity, spatial and temporal distribution of species, is one of the most valuable biological tools for environmental evaluation particularly on the air pollution. Lichen diversity value (LDV) based on epiphytic taxa is the European method developed for environmental stress/quality indication (Svoboda 2007).

Lichens have been used as indicators around the city pollution and emission sources since their susceptibility to gas pollutants such as SO_2 (sulphur dioxide) have been noticed in the 1960s. With their ability to accumulate the elements found in low concentrations in the air, the lichens have become a frequent topic from that year until today. There are hundreds of articles on this (Henderson 2000), among which the oldest are about lichen communities interacting with pollutants in the gas state (Gilbert 1965, 1970; Hawksworth and Rose 1970; LeBlanc and De Sloover 1970; Showman 1975; Türk and Wirth 1975).

In addition to being sensitive to air pollutants, lichens are also good metal accumulators. Mineral nutrients, metals and heavy metals are found in rainfall and dust, as well as in natural and anthropological substrates (shell, soil, rock). The elements Pb, Ni, Hg, Cr, Zn, Ti and V are among important metal pollutants (Hutchinson et al. 1996). The term “heavy metal”, which is often used in biological studies, refers to elements that are toxic to living organisms when they are physically present in high amounts in the atmosphere, whether metal, transition metal or semimetal.

3.4.1 Bioindicator Role of Lichens in Air Pollution

Bioindicators are living organisms that react to environmental pollution with their life functions. Because of the biological properties, lichens, which have potency to reflect air pollution, are at the forefront of bioindicators. The features that allow lichens to be reliable indicators of atmospheric changes are listed Branquinho et al. (2015) as follows:

1. Lichen species differ in their susceptibility to atmospheric changes.

2. Lichens are slow-growing organisms, and their morphologies do not show seasonal changes.
3. Lichens have a wide distribution and can be found in almost all terrestrial biomes.

The distribution of lichen species in a region can provide estimates of atmospheric pollution, especially the level of sulphur dioxide. Since the susceptibilities of species to air pollution are different, the distribution of epiphytic lichen species in some European countries is zoned by the level of air pollution according to the winter average SO_2 values (Nimis et al. 2002). Thus, it is possible to estimate the SO_2 level in that region by looking at which lichen species are present in a region.

The first qualitative zoning scale established by Hawksworth and Rose (1970) for this purpose indicates ten regions described in England based on estimates of sulphur dioxide pollution. Region 1 is defined as the absence of epiphytic lichens when the average winter SO_2 level exceeds 170 μg m^{-3}, whereas region 10 refers to the region where the highest number of lichens is present when the SO_2 level is less than 10 $μgm^{-3}$. For example, *Lobaria pulmonaria*, *L. amplissima* and *Usnea florida* can be present below level of 30 μg m^{-3} SO_2, while *U. articulata* and *U. filipendula* only in regions with pure air. Due to the impacts of climatic and geographical conditions in the lichen distribution, different regions do not have the same lichen species. Therefore, it is not possible to apply exactly the same chart to the estimation of the air pollution level of another country. This chart is specific to that country as it is done in the UK, and similarly for new regions or countries where the natural lichen flora is designated, new lichen zoning scales can be created based on their lichen species.

3.4.2 Lichens as Biomonitors of Air Quality

Environmental assessments have been carried out on lichen populations for long-term pollution effects. For instance, over a period of 15 years, changes in lichen communities under the influence of climate and pollution have been investigated in terms of deposition of nitrogen (N) and sulphur (S) compounds in Norway by Evju and Bruteig (2013), where the largest change in species composition was found in the site with the biggest reduction in sulphur deposition. The degree to which the lichen species, physiology and morphology and symbiotic life partners are individually affected by air pollutants has been questioned (Bačkor et al. 2010; Piovar et al. 2011; Vannini et al. 2017). For instance, physiological and ultrastructural effects induced by acute exposure to ozone (O_3) were investigated in *Xanthoria parietina* by Vannini et al. (2017). They put forward that the hydration state may play a major role in determining the extent of the damage, and the presence of parietin may support the recovery.

Due to their slow growth and long life, lichens are important living things used in monitoring the environmental changes of a region depending on the air quality.

Numerous studies have been carried out using lichens (Conti and Cecchetti 2001) or mosses (Harmens et al. 2010; Behxhet et al. 2013) as biological tools.

Majority of the recent lichen biomonitoring studies is documented on the spatial distribution of elements or radionuclides in urban or suburban areas (İçel and Çobanoğlu 2009; Freitas et al. 2011; Rani et al. 2011; Doğrul Demiray et al. 2012; Conti et al. 2012; Shukla et al. 2012; Sujetoviene and Sliumpaite 2013; Malaspina et al. 2014; Paoli et al. 2015; Petrova et al. 2015; Çobanoğlu and Kurnaz 2017); in forests or natural sites (Blasco et al. 2011; Klimek et al. 2015); in vicinity of pollution resources such as factories, mills, mines or thermal power plants, etc. (Uğur et al. 2003; Boamponsem et al. 2010; Behxhet et al. 2013; Paoli et al. 2015; Protano et al. 2015; Lucadamo et al. 2016; Boonpeng et al. 2017); and in the Arctic (Singh et al. 2012). A large number of publications on biomonitoring of air quality with lichens have been screened worldwide in the literature, and selected publications from the last decade are listed in Table 3.1.

Pollutants in the atmosphere can be sourced both from nature and from human activities. Lichen surveys for biomonitoring include the following pollution parameters:

- Heavy metals and/or trace elements (many documents, see Table 3.1)
- Atmospheric nitrogen and sulphur (Van Herk et al. 2003; Evju and Bruteig 2013)
- Particulate matter (PM) (Adamo et al. 2008; Freitas et al. 2011; Malaspina et al. 2014)
- Polycyclic aromatic hydrocarbon (PAH) concentrations (Blasco et al. 2011; Shukla and Upreti 2009)
- Radionuclides (Iurian et al. 2011)
- Nanoparticle emissions (no study with lichens yet but with bryophytes (Walser et al. 2013)

Besides lichen monitoring studies, there is also a number of moss surveys in this regard (Balarama Krishna et al. 2004; Ramzaev et al. 2007; Harmens et al. 2010; Behxhet et al. 2013).

3.5 Environmental Factors Affecting Lichen Diversity

One of the most important factors that the lichens show sensitivity is “atmospheric pollution”, which is directly or indirectly due to human activities. Biotic and abiotic factors are influential in this sensitivity. In biological monitoring studies, physical environmental conditions and human-induced factors should also be considered.

Lichens are used as an important indicator for evaluations in terms of hemeroby (the impact and grade of human activities in ecosystems). Indicator species are determinants of vegetations that are damaged at various degrees. For example, while well-preserved forests contain the Xanthorion communities, the Lobarion communities are only available in forests away from hemerobic effects (Zedda 2002). In a variety of studies conducted on roadside lichens (soil, rock and tree

Table 3.1 Lichen species diversity in the biomonitoring studies in the last decade are listed chronologically

Lichen species	Growth form	Substrate	Publication	Region, Country	Method, Pollutants
Pseudevernia furfuracea	Fruticose	Epiphytic	Adamo et al. (2008)	Naples, Italy	Bag technique, multi-element analysis, PM_{10}
Hypogymnia physodes	Foliose	Epiphytic	Williamson et al. (2008)	Karabash, Russia	Transplantation technique, multi-element analysis
Phaeophyscia hispidula	Foliose	Epilithic-Epiphytic	Shukla and Upreti (2009)	Dehradun City, India	PAHs, Soxhlet apparatus
Parmelia sulcata	Foliose	Epiphytic	Boamponsem et al. (2010)	Tarkwa, Ghana	Sb, Mn, Cu, V, Al, Co, Hg, As, Cd, Th
Evernia prunastri	Fruticose	Epiphytic	Blasco et al. (2011)	The Pyrenees, Spain and France	PAHs, DSASE
Lobaria pulmonaria	Foliose	Epiphytic			
Parmelia sulcata	Foliose	Epiphytic			
Pseudevernia furfuracea	Fruticose	Epiphytic			
Ramalina farinacea	Fruticose	Epiphytic			
Usnea sp.	Fruticose	Epiphytic			
Favoparmelia caperata	Foliose	Epiphytic	Freitas et al. (2011)	Porto, Portugal	Lichen diversity value (LDV), CO, CO_2, SO_2, NO_2, O_3, PM_{10}
Parmotrema chinense	Foliose	Epiphytic			
Punctelia subrudecta	Fruticose	Epiphytic			
Cladonia fimbriata	Fruticose	Epigeic	Iurian et al. (2011)	Salzburg, Austria	^{137}Cs, gamma spectrometry
Cladonia squamosa	Foliose	Epigeic			
Pseudevernia furfuracea	Fruticose	Epiphytic			
Hypogymnia physodes	Foliose	Epiphytic			
Phaeophyscia hispidula	Foliose	Epiphytic	Rani et al. (2011)	Uttarakhand, India	Cu, Pb, Ni, Zn, Fe, Cr, Hg, Cd
Usnea barbata	Fruticose	Epiphytic	Conti et al. (2012)	Patagonia, Argentina	Multi-element analysis
Xanthoria parietina	Foliose	Epiphytic	Doğrul Demiray et al. (2012)	Kocaeli, Turkey	Multi-element analysis
Pyxine subcinerea	Foliose	Epiphytic	Shukla et al. (2012)	Uttarakhand, India	PAHs, Soxhlet apparatus

(continued)

Table 3.1 (continued)

Lichen species	Growth form	Substrate	Publication	Region, Country	Method, Pollutants
Cladonia amaurocraea	Fruticose	Epigeic	Singh et al. (2012)	Ny-Ålesund, Arctic	Multi-element analysis
Cladonia mediterranea	Fruticose	Epigeic			
Cetraria fastigiata	Fruticose	Epigeic			
Flavocetraria nivalis	Fruticose	Epigeic			
Physcia caesia	Foliose	Epigeic			
Pseudophebe pubescens	Fruticose	Epigeic			
Umbilicaria hyperborea	Foliose	Epigeic			
Xanthoria elegans	Foliose	Epigeic			
Hypogymnia physodes	Foliose	Epiphytic	Evju and Bruteig (2013)	Norway	N, S
Melanelia olivacea	Foliose	Epiphytic			Monitoring lichen species composition
Evernia prunastri	Fruticose	Epiphytic	Sujetoviene and Sliumpaite (2013)	Kaunas, Lithuania	Transplantation technique, Cd, Cu, Pb
Evernia prunastri	Fruticose	Epiphytic	Malaspina et al. (2014)	Genoa, Italy	Transplantation technique, multi-element analysis, PM_{10}
Platismatia glauca	Foliose	Epiphytic	Caggiano et al. (2015)	Agri Valley, Italy	Bag technique, multi-element analysis
Evernia prunastri	Fruticose	Epiphytic			
Ramalina fraxinea	Fruticose	Epiphytic			
Pseudevernia furfuracea	Fruticose	Epiphytic			
Hypogymnia physodes	Foliose	Epiphytic	Klimek et al. (2015)	Beskidy Mountains, Poland	Cd, cu, Ni, Pb, Zn, AAS
Evernia prunastri	Fruticose	Epiphytic	Paoli et al. (2015)	Molise, Italy	Transplantation technique, multi-element analysis
Pseudevernia furfuracea	Fruticose	Epiphytic	Petrova et al. (2015)	Plovdiv, Bulgaria	Bag technique, multi-element analysis

(continued)

Table 3.1 (continued)

Lichen species	Growth form	Substrate	Publication	Region, Country	Method, Pollutants
Pseudevernia furfuracea	Fruticose	Epiphytic	Protano et al. (2015)	Latium region, Italy	Transplantation/ bag technique, As, Cd, Ni, Pb, 12 PAHs, 17 PCDDs and PCDFs, 27 PCBs
Pseudevernia furfuracea	Fruticose	Epiphytic	Lucadamo et al. (2016)	Calabria region, Italy	Transplantation technique, multi-element analysis
Parmotrema tinctorum	Foliose	Epiphytic	Boonpeng et al. (2017)	Map Ta Phut, Thailand	Multi-element analysis
Physcia adscendens	Foliose	Epiphytic	Cobanoglu and Kumaz (2017)	Istanbul, Turkey	Multi-element analysis
Evernia mesomorpha	Fruticose	Epiphytic	Will-Wolf et al. (2017)	Wisconsin, USA	Multi-element analysis
Flavoparmelia caperata	Foliose	Epiphytic			
Physcia aipolia/ stellaris	Foliose	Epiphytic			
Parmelia sulcata	Foliose	Epiphytic			
Punctelia rudecta	Foliose	Epiphytic			
Xanthoria parietina	Foliose	Epiphytic	Ratier et al. (2018)	Provence, France	Multi-element analysis

species), it has been found that dust and traffic density in the form of wind scattered in the metal content of soil profiles and vegetation on the highway are effective. Motor vehicles emit nitrogen oxides (NOx), carbon monoxide (CO), sulphur dioxide (SO_2), hydrocarbons, volatile organic compounds, airborne particles and various metals. Lead (Pb) is a common indicator of anthropogenic (human-induced) activity in atmospheric accumulation in industrialized countries. It is possible to use lichens and mosses as a monitor of the change in lead (Pb) pollution from motor vehicles (Garty 2001).

A variety of studies have been carried out to examine the respiratory tract cancer cases in relation to the material properties of metal-containing particles in airborne dust. Airborne association of particulate matter and gaseous pollutants is closely related to human respiratory tract diseases. In a study conducted at Armadale (Central Scotland), values of lichens were shown with their supporting roles in interpreting respiratory tract infections and the highest lung cancer mortality seen in Scotland between 1963 and 1973 (Garty 2001). In a study conducted by Cislaghi and Nimis (1997), lung cancer in young male individuals in certain regions of Italy showed very highly positive correlation with lichen variability ($r = 0.95$; $P < 0.01$). In the case where the common anthropogenic pollutants SO_2, NO_3^-, dust and SO_4^{-2} are positively related ($r = 0.93$, 0.87, 0.86 and 0.85, $P < 0.01$), an association with non-anthropogenic substances (such as Cl^-, Ca^{+2}, Mg^{+2}, HCO^{-3}, K^+ and Na^+) has not been achieved. Such studies clearly demonstrate the effects of anthropological activities.

It is known that the average concentration of sulphur dioxide (SO_2), especially winter, increases with population density, especially with smoke, industrial and commercial centres and residential areas. It has been reported that lichens are more sensitive to SO_2 than to smokers (Gilbert 1970). The epiphytic crustose lichen known as "the most pollutant species" in Western and Central Europe is *Lecanora conizaeoides*, and the amount of sulphur is a limiting factor for this species since it is colonized by the level of SO_2. In a study conducted by Hauck et al. (2001) in the Harz Mountains of Germany, it has been reported that this sulphur-loving lichen species also decline in the case of falling sulphur values in tree barks, and it is also stated that competition with other pollution-tolerant epiphytic species is also an important element in the distribution of the species. Hauck et al. (2011) reported the populations of *L. conizaeoides*, one of the most common epiphytic lichens that have been adapted to very low pH (about 3) and high SO_2 values in Europe, have decreased significantly in the last 20 years. A slight increase in acidity (0.4 pH units) has been stated as the cause of this, with the decrease in sulphur dioxide values in the recent years.

Like other plants, lichens are mentioned to be sensitive to pH. Tree bark pH and susceptibility to toxic substances are the primary factors affecting epiphytic lichen composition (Van Herk 2001). Most nitrogen-loving species (nitrophytes) show low sensitivity to the toxic effects of sulphur dioxide, and their only requirement is high bark pH. The increase in bark pH has led to a large increase in nitrophytic species in Switzerland and the disappearance of acidophytic species in the last decade. It has been revealed that there is an almost linear relationship between measurements of ammonia (NH_3) concentration in air and the number of nitrophytes on *Quercus*. The abundance of nitrophytes is not related to the SO_2 concentration. Most of the acidophytes were highly sensitive in areas with concentrations of 35 μgm^{-3} or more NH_3, and all acidophytes disappeared (Van Herk et al. 2003). Accordingly, it has been argued that current methods that use species diversity to monitor or estimate SO_2 air pollution require some modifications; otherwise air quality may be incorrectly assessed in relatively good regions with high NH_3 levels.

SO_2 is harmful to lichen species at lower pH values, becoming more severe as acidity increases. However, when the pH is low, this does not always lead to the poor lichen flora, because well-developed lichen communities can be found in regions with low SO_2 (Gauslaa 1985). The calcareous substrata are more suitable for lichen colonization, such that the high pH of the substrate, such as in lime mortar and cement, can reduce the toxic effect of acidity, allowing the lichen to survive the pollution. Acid rain affects the lichens directly or indirectly by increasing the acidity of the substrate. It is also the case for epiphytes. For example, *Parmeliopsis ambigua*, which is prevalent especially in bark-free conifers, has been reported to have spread in recent years in regions with moderate pollution in the UK, possibly in response to rising bark pH. On the other hand, pollution-sensitive species such as *Lobaria pulmonaria* have largely disappeared in tree barks such as *Quercus* (Seaward 1989).

In a study intended to show a vertical change of bark pH in the *Picea abies* forest unaffected by acid rain, bark pH was found declining from ground level to upper branches and high again in the terminal branches, resulting in an unusual species composition. It has been reported that the high-bark pH-dependent Lobarion communities developed on *P. abies*. Species have their own pH requirements; it has been noted that acid rain, which is stated to have a pH value at almost industrial level, affects the distribution of lichen in situations where pH of the substrate changes (Kermit and Gauslaa 2001).

Normally the pH of the rains is 5.6, because CO_2 is balanced with carbonate and bicarbonate ions when dissolved in water. But today, the pH of the rains is 4–5 and sometimes lowers. The fog versus rain occurs normally under stationary atmospheric conditions and a much higher concentration of ions. In this case, the pH of the fog was recorded as 2–3. There are not only direct acid effects of acid rain and fog on lichens but also indirect effects which cause substrate conditions to change. For example, it has been reported that the acidity of tree bark, both in and around cities and copper mines, has increased (Nash and Gries 1991).

The distance to the source of pollution, elevation, wind direction, air temperature and moisture are the most influential factors in the degree of pollution. It is stated that the physiological activity of the lichens is dependent on the amount of water and that the conversion of sulphur into a less toxic form is regulated accordingly. Thus, lichens in polluted areas, if the humidity is high, will be adversely affected, and their drying will slow down as the process of converting pollutants to less toxic form increases (Gilbert 1970).

The "habitat" characteristics that are effective in lichen development and spread are "macrohabitat factors" (sunlight, wind, temperature, humidity, chemistry of atmospheric air) and "microhabitat factors" (substrate-type, tree, rock, man-made material, etc., soil structure and chemistry, forest canopy, concentration changes of atmospheric gases and so on). In atmospheres with fluctuating pollutant content and levels, the importance of microclimate and microhabitat conditions (such as shadow, light, humidity) is noticeably evident when lichens are able to respond to pollution and even survive (Huckaby 1993). In the regression models created for a forest ecosystem, the ecological variables such as pure or mixed stand, tree species, tree diameter and number of lichen species are stated as the most expressive environmental factors (Sevgi et al. 2016).

Altitude is one of the factors that influence the spread of lichens. It is emphasized that since the SO_2 is spreading and rising in the air, as the altitude increases from the ground, the lichens are more affected by pollution (Showman 1975). In a study of lichens on the periphery of pollution source, it was shown that the first factor affecting the degree of susceptibility of lichens to pollution was the distance to the source, and the altitude affects the lichen frequency positively (Oksanen et al. 1991). According to this, in the near vicinity of the source, the number of the taxa is low, and the values are close to each other. As the distance increases, the number of the taxa increases, and this increase becomes even faster as the altitude increases.

Studies of the dependence of metal content on lichens on topography show that chemistry (H^+, NH_4^+, Na^+, K^+, SO_4^{-2}, NO^{3-}) and associated acidity, which accumulate significantly in the high forests, are another determinant of the metal composition of lichens exposed to fog and clouds at high altitudes. In lichens, the content of caesium (^{137}Cs) increases with altitude. Lead (Pb) is highest in the middle elevations (200–400 m). Mercury (Hg) content is almost twice as high as in the high forest in the tundra below 400 m. It has been stated that the level of mercury drops as it moves away from the sea edge. Antarctica is seen as the "cleanest" area in the world due to its geographical location. Natural and artificial radioactivity is the lowest level here (Garty 2001). Furthermore, it has been reported that the presence of thick lichen-moss cover on the soil inhibits the permeation of Cs-radionuclides (^{137}Cs) into the soil (Ramzaev et al. 2007). Lichens can be suggested as biological monitors of radionuclides, which are caused by nuclear accidents and nuclear accidents, with high concentrations of radionuclides that they acquire from the atmosphere as a result of slow growth and long life.

Secondary metabolites unique to lichens provide them with the advantage of being able to survive in an ecological niche by giving them habitat adaptability. Many environmental factors (biotic and abiotic) affect the expression of PKS genes involved in the production of these metabolites (Deduke et al. 2012). Therefore, it appears that air quality is an important factor that directly affects lichen chemistry and secondary pathway of metabolite synthesis, in relation to the level of heavy metals and other pollutants in the air.

3.6 Metal Accumulation in Lichens

A major portion of the metal content of lichens has atmospheric origin (Garty 2001), but at the same time, it is documented in many studies that they have captured particles from the substratum (Bačkor and Loppi 2009). These particles can be stored for long periods unchanged by being held on the lichen surface or in the intercellular spaces. The lichens thus accumulate heavy metals in quantities exceeding their requirements and tolerate them in complexity with extracellular crystals or lichen acids. The toxicity of the metals in the retained and stored particles is determined by the chemical and physical factors such as the amount of metals, their chemical form and their solubility in water, pH and temperature. The metals in the air are taken up by dissolving or catching particles in the lichen thallus. Soluble metals tend to settle in extracellular or intracellular regions. Classical and modern histochemical methods used to determine the location of metals within the lichen thallus have been reported comparatively (Rinino et al. 2005).

There are three main mechanisms of metal accumulation (Nash 2008):

1. Capture of solid particles
2. Extracellular binding with exchange sites on the cell walls of symbionts
3. Intracellular uptake

In the third, PM adsorbed onto thallus surface and penetrates into intercellular spaces (Shahid et al. 2016). Element accumulation in lichen thallus depends on various factors, such as the nature of the element, environmental parameters, production of secondary metabolites, growth form of lichen, part of thallus and its specific morphological/anatomical properties (Garty 2001; Bačkor and Loppi 2009). For instance, in *Cladonia* species, crystals are accumulated in intensively in thallus deformations and in granular parts (Rola et al. 2016; Osyczka et al. 2018).

Metal accumulation in the lichen is a dynamic process, and it has been observed that it was taken to the thallus quickly – in a few hours – when it was immersed in metal solutions in the investigations.

In transplantation studies, lichens reacted to atmospheric heavy metal changes within a few months. The duration of many elements in the lichen tall is 2–5 years (Bačkor and Loppi 2009).

There is considerable intercellular space in the lichens, which is evidence that particles of dust, soil and metal are trapped in these spaces (Nash 2008). Information on the contents of particles displayed by SEM (scanning electron microscope) on cross-sections and surface was obtained by energy-dispersive X-ray (EDX) analysis method.

The metal content of lichens depends on the texture and its morphological structural properties. Most of the lichens requiring metal-rich surfaces belong to the genera *Acarospora*, *Aspicilia*, *Lecanora*, *Lecidea*, *Porpidia*, *Rhizocarpon* or *Tremolecia* (Bačkor and Fahselt 2004). The amount of metal varies in the same parts of different species. In foliose lichens (*Flavoparmelia baltimorensis* and *Xanthoparmelia conspersa*), the amount of metal is found more than in fruticose lichens (*Cladonia subtenuis*). Also, metal amount is greater in *Hypogymnia enteromorpha* than in *Usnea* and similarly in *Parmelia sulcata* than in *Anaptychia ciliaris*. Again it is in decreasing order in the foliose *Xanthoparmelia conspersa* and *Peltigera canina* and crustose *Lecanora subfusca*. Character of the lichen thallus surface (mucilage, cilia, hairs, holes, isidia and roughness) influences the particle retention. For example, in *Usnea* and *Alectoria*, the feature of holding more particles than *Umbilicaria* is striking (Garty 2001).

Al, Fe, Mg and Mn elements are abundant in the earth's crust. Unwashed lichen thalli have high metal content due to dust and soil. High-contrast contaminated dust samples collected with equipment placed in hotel ventilation in the city centre by Rossbach's method were compared with lichen samples affected by trace contaminants transportable to remote areas (Rossbach et al. 1999). In *Usnea* species and dust, the element concentrations are highest for Cr, Zn and Fe and lowest for Ca, Rb and Sr.

Sections taken from lichens have shown that the central parts generally contain more metals than the edge parts. Also, the average contents of Fe, Pb, Zn, Mn, Cr and Al were found higher in the inner parts of various *Parmelia* species than in the outer parts. This is related to the age of lichen. In the case of these saxicolous foliose lichens, the inner parts are older, and the edges are younger. On the other hand, the slowly growing epilithic crustose lichen *Protoparmeliopsis muralis* has accumulated more Pb in the edge regions than in the thallus centre (Garty 2001).

Lichen potential contribution of habitat on the metal content of the thallus is another issue to be considered. Substrates, metallic rocks and metal-containing soils that the lichens live on should be considered in determining the metal content of the lichen. In fact, most of the metal content of lichen is of atmospheric origin. Zn, Cu and Cd concentrations of lichen, moss and snow samples were found to be in the same order in snow samples and cryptogams under snow, but in flowering plants, Pb contents were found to be 10 times higher than in the snow sample (Garty 2001). Using the methods of EDX-microanalysis (Energy-Dispersive X-ray) and X-ray mapping, the accumulation of elements in *Lecidea lithophila* and *Rhizocarpon oederi* lichens which developed on the old copper mine residues for centuries has been compared with the amount in the substrate (Bačkor and Fahselt 2004). According to this, Al, Si, and K are found at very low concentrations in the apothecium in both species compared to the substrate, while C is higher than in substrate as expected, and O, Na and Mg are at the same level.

In the study on the rocky coastal area of Baikal Lake, aquatic species of *Verrucaria*, which cover the rocks in the depth of 1.5 m, were examined for their chemical composition. In *Verrucaria* species, the same elements (Ca > K > Fe > Al > Mg > P > S > Na > Mn > Sr > Ba) were dominant that are often found in the rocks. Compared to the element structure of the water layer near the bottom, the lichens are dense with elements slowly passing to the water: Gd > Sm > Pr > Nd > Al > La > Dy> Tb > Y > Lu > Ce > Yb > Be> Tm > Co > Nb > Mn > Zn. Compared with the compound of rock, *Verrucaria* thalli were enriched by Hg > As> P > Zn > Li > S > U > Mo > Se > Cd > Ca > Tl > Sr > Pb > Be. In relation to the rock surface, it was noted that the water lichens accumulate As> P > Zn > Li > S > U > Mo > Se > Cd > Ca > Tl > Sr > Pb > Be in the most intense order, respectively (Kulikova et al. 2011).

Many lichenologists acted to monitor the atmospheric mercury (Hg) toxic metal, which is not only collected in aquatic but also in terrestrial ecosystems. Uptake of Hg in lichens and their accumulation in particulate form have been studied in volcanic and geothermal fields and in mine areas. Lichens in urbanized and industrial areas are also effective markers for Hg in the air (Garty 2001). Study results around the thermometer factory have shown that mercury contamination can be transformed into a form retained by some chemical binding agents on its main elemental form, on lichen or moss surface, or may be diffused into lichen/moss cells (Balarama Krishna et al. 2004). It has also been proposed that lichen and moss can be used as sorbent material for the purification of mercury-methylene from inorganic aqueous solutions.

3.6.1 The Extracellular Metal Exchange

Lichens absorb the metal ions from the rainwater through the extracellular absorption, while they release the H^+ ions or weakly bound metal ions to carry out ion exchange. Regarding the biomonitoring application of metal contaminants in the air, advantages of these characteristics of lichens are utilized. Various types of organic materials such as dead biomass, bacteria, filamentous fungi, algae and higher plants contain metals bound to carboxyl, aldehyde, hydroxyl, sulphide, phosphoryl or amine groups. In metal uptake in lichens, the mycobiont is active rather than the photobiont. The chitin material, which is the polymer of acetyl-D-glucosamine in the fungal cell walls, is the main binder in this case (Garty 2001).

The biosorption of Cu and Co metal ions by infrared spectroscopy (IR) was investigated in the biomass of *Penicillium cyclopium* from free-living fungi, and the hydroxyl groups were identified as the main group binding heavy metals. Amides and carboxyls are the least bonded groups. The uptake of Cu and Co metals is realized as the result of the ion-exchange mechanism with K^+, Mg^{++} and Ca^{+2} (Tsekova et al. 2006).

Branquinho and Brown (1994) by the method they use found that when the element Pb is treated with thiol-rich chemicals, it is replaced by cations such as Cu and left to extracellular exchange areas, and they showed that this led to significant intracellular K ion loss due to membrane integrity deterioration.

It has also been shown that pH is also an effect in the metal bonding. For example, in a study by Akçin et al. (2001), dry lichen samples were mixed with different concentrations of metals and adjusted to pH 2–10 with nitric acid and ammonium hydroxide. In aqueous acid solutions, metal ions competed with H^+ ions to bind to the cell walls. It is stated that the metal bonding is performed optimum at pH 4 and reaches the maximum level.

In natural *Hypogymnia physodes* samples, the relationship between time, temperature, pH, and inhibitor (formaldehyde) was assessed by caesium (^{137}Cs) bioaccumulation in controlled laboratory conditions (Pipiška et al. 2005). In the study, it was noted that caesium intake was achieved at an optimum 20 °C and a pH range of 4.0–5.0 and was lower in the presence of metabolic inhibitors.

3.6.2 The Intracellular Metal Uptake

The content of intracellular metals in lichen thallus has been reported to be relatively stable over time, and at the same time, the binding of extracellular metals and particle capture may continue (Bačkor and Loppi 2009). Experiments made on *Ramalina* for Cu (Branquinho et al. 1999) and for *Peltigera* on Cd (Brown and Beckett 1984) have shown that the intracellular metal uptake is much slower and less in contrast to the extracellular uptake.

Intracellular metal uptake has been shown to be stimulated by light and closely related to metabolism. It has been reported that the intracellular Cd uptake in the dark decreases very rapidly. Light-induced Cd uptake represents active entry into the algal cells, but it is unclear as to which symbiont plays a role in the intake and whether requires energy in the dark. Intracellular uptake is also dependent on the species. Metals in the live and heat-killed lichen trusses also differ according to species (Garty 2001).

Interactions between lichens and heavy metals have been examined in the Cd^{2+}- and Ni^{2+}-containing solutions of cyanolichen *Peltigera rufescens* and green algal lichen *Cladonia arbuscula* subsp. *mitis* growing on old copper mine-spoil heaps in Slovakia by Bačkor et al. (2010), in terms of ultrastructural changes as well as physiological parameters such as membrane integrity, pigment composition, chlorophyll a fluorescence, photosynthesis, respiration, contents of ATP, amino acids, ergosterol, ethylene, nonprotein thiols, activity of antioxidant enzymes and expression of stress proteins. The results of the study showed that toxicity of the non-redox active metals Cd and Ni was lower than the redox-active metal Cu on these lichen species, with physiological findings containing no significant sensitivity.

3.6.3 Location of Metals in Mycobiont and Photobiont

Various studies using TEM (transmission electron microscope), SEM (scanning electron microscope) and EDX (energy-dispersive X-ray) have found that Cu and Zn are present in different parts of photobiont and mycobiont cells depending on the species. For example, dark rhizines and veins in *Peltigera* species contain high amounts of metal in metal-rich habitats. The rhizines in *Peltigera canina* are responsible for metal absorption, accumulation, displacement and regulation. The high metal content of this lichen's medulla and rhizines causes a considerable loss of potassium (K). The metal deposition capacity of the *Peltigera* species was found to be maximum level for Fe, Mn and Pb in their rhizines (mycobiont) and for Cu, Ni and Zn in the photobiont parts (Garty 2001).

X-ray microanalysis applications have shown that Fe deposition builds up in certain lichens (e.g. *Acarospora smaragdula*) an outer crust covering the upper cortex and accumulation gradually decreases from the upper cortex towards algae layer, medulla and lower cortex. When SEM combined with EDX analysis, visual and quantitative information about the locations of the elements in the thallus is provided. A study conducted in this way in *Hypogymnia physodes* showed that Fe and Al bind to the algal layer and algae-containing soredia more than medullary hyphae in the first stage (Farkas and Pátkai 1989).

Trapelia involuta, which is formed directly on secondary uranyl minerals and U-enriched iron oxide and hydroxide minerals, accumulation of U, Fe and Cu is concentrated on the apothecium exciple and epithecium. As a result of the TEM investigation, it is found that the distribution of U, Cu and Fe and that of the melanin-like pigments are strongly correlated to one another, not mineral particles or organic crystals (Kasama et al. 2003).

Piovar et al. (2011) assessed the long-term effect (14 days) of copper (Cu) on the levels of intracellular and total accumulation, growth, assimilation pigment composition, chlorophyll a fluorescence, soluble protein content and oxidative status (production of hydrogen peroxide and superoxide) in two algal species (free-living alga *Scenedesmus quadricauda* and the lichen alga *Trebouxia erici*). The presence of Cu negatively affected growth, assimilation pigments, chlorophyll a fluorescence, soluble protein content and oxidative status in both algae. However, *Scenedesmus* was much more sensitive compared to *Trebouxia*.

3.7 Methods Used in Biomonitoring with Lichens

Due to the rapid growth of the population, industry, agriculture and technology in the world, environmental pollution has inevitably come to the fore. In the settlement areas where atmospheric pollution is noticed, various methods applied locally have to be developed depending on the pollutant types (SO_2, radionuclides, heavy metals, etc.) and levels, and some of them are becoming more common nowadays. Since the emergence of the idea that measurable, long-term, cheap and reliable results can be obtained by means of biological methods, work has been increasingly carried out in the determination and monitoring of the quality of the environment. In most countries, a limited number of air pollution measurement stations in large cities and industrial areas record the concentration of particulate matter and SO_2 per day. However, it is not usually found in places with moderate pollution. Assessing the level of pollutants' effects on vegetation has been arised as an alternative approach in assessing air pollution. Estimates based on epiphytic vegetation show that lichens that grow very slowly and live for a long time may be much better indicators of quantitative levels of air pollution than quantitative chemical measurements made in a certain time period as being communities that can make more equilibrium with their environment.

In recent years, various methods were proposed for assessing environmental quality (air pollution) on the basis of lichen data. Qualitative methods can be converted into quantitative methods by quantifying the number of species in the region, the distributions and the frequency of species at the same time. Quantitative methods are generally applied by elemental analysis instruments and statistical analyses to determine the levels of pollutants (metals and radioactive substances) that accumulate in lichen thalli.

Atmospheric pollutants cause acute morphological and usually physiological damage on lichens. Chronic harms develop after prolonged or repeated exposure to pollution, which is a slowing, growth-related disorder of more species than damage to tissues. It results in the disappearance of susceptible species in population at the community level (Çobanoğlu 2015).

Lichen biomonitoring methods can be classified in different forms according to the purpose and content of the application. According to Huckaby (1993), two analytical methods can be used to quantitatively determine the response of lichens to airborne pollutants and to assess their susceptibility: (1) gradient analysis study and (2) fumigation study. In the gradient analysis study, harmful effects of contamination grades on lichens exposed to pollution, measurable environmental effects and quantities in species richness are analysed. It is usually studied around a pollution source. Species can best be examined in their own environment because not only air pollution but also climate and substrate-related properties (such as fire, grazing animals) also affect lichens. In the fumigation study, the quantifiable responses of the lichens exposed to the pollutants in a closed system under laboratory-controlled conditions are generally examined for physico-chemical events.

Various methods implemented within the scope of air quality monitoring studies using lichens up to date can be classified (Çobanoğlu 2015) mainly under the following headings:

A. Passive biomonitoring
   1. Method based on whole lichen floras (general lichen study and mapping method)
   2. Method based on bioindicator species and IAP (index of atmospheric purity) method
   3. Quantitative laboratory analysis (multi-element and radionuclide analysis)

B. Active biomonitoring
   1. Transplantation
   2. Controlled fumigation
   3. Culturing

While determining air quality, "active methods" result in controlled effects of pollutants directly on lichens under controlled conditions, whereas "passive methods" result in determining amounts accumulated in lichens or by monitoring the natural lichen floras, which are affected by pollutants (Hoodaji et al. 2012).

3.7.1 Passive Biomonitoring Methods

The first two passive methods are qualitative (indirectly quantitatively expressed) assessments based on the distribution of lichen species that constitute the general lichen flora or selected as bioindicators. The other can be based on quantitative analyses that can determine the quantities and effects of air pollutants in the lichen to be measured directly (Huckaby 1993). In principle, the first two methods for assessing contamination in a region can be applied alone or in combination with quantitative methods at the same time. However, in order to obtain more specific areas and levels of pollutant types, it is necessary to use the passive biomonitoring method which is applied to content analysis. Multi-element analysis is at the forefront of this (Çobanoğlu 2015).

For example, when the "Calibre Lichen Bioindication Method" is used together with the index of atmospheric purity (IAP) method, which is based on regression analysis, in the statistical evaluation of the frequency of lichen species selected in a region, the indication of the integrated air pollution problem can be detected early (air pollution early warning system) (Herzig et al. 1989). In Switzerland, where these two methods are applied comparatively, very common foliose lichen *Hypogymnia physodes* has been shown as the best bioindicator species for various emission components (SO_2, NO_x, O_3, heavy metals, pesticides and other organic compounds). The area is divided into five groups of lichens (lichen desert, internal strength zone, outer strength zone, transition zone and normal) parallel to five regions (critical, high, medium, low, very low air pollution) in terms of the total emission. Eventually Pb, Fe, Cu, Cr, Zn, total S and P elements decreased with decreasing pollution level and showed a negative relation with IAP. With the decrease in total air pollution, the only element that increased in lichen content was calcium (Ca) and showed a positive correlation with increasing IAP values.

1. Method based on whole lichen flora (general lichen study and mapping method). Repeated studies in the general lichen study show changes in species distribution in the same region. It is an easier method of monitoring than others, and it shows the change in the quality of the air over time in large areas.

The species distribution maps are performed by squaring. It is similar to the method of classical species mapping. Mostly corticolous (living on bark) lichens are studied, but if not available, saxicolous (living on rock) and terricolous (living on soil) species are studied. It requires an expert lichenologist to be based on all lichen flora. This method is suitable for the monitoring of air quality in a wider area, for a pollution-source environment and for ecologically variable and complex locations. “Mapping method” or “distribution map” is, according to many researchers, the best method of biomonitoring for areas with moderate-to-high air pollution (Gilbert 1970; Hawksworth and Rose 1970; Huckaby 1993; Showman 1988) and is still valid today.

Observations made independently of each other in England, Munich and Paris show that in the 1800s, the likeness disappeared in urbanized regions. The burning of coal to warm up homes and workplaces created smoke clouds over the cities, and this air pollution caused the lichens to disappear. Sernander’s classical work in Stockholm was followed up after the city influence was noticed in Europe during the 1900s (Sernander 1926). According to this, the city centre, which has almost no lichen, is called “lichen desert”. “Struggle zone” is a region in which some of the species live well. The “normal zone” is the area where species live without being affected by pollution. Such zoning studies have begun to spread around cities. The identification of species by mapping studies and quantitative techniques and the identification of air pollution communities have entered into a rapid development process. In 1930, the colourless gas “sulphur dioxide” (SO_2) was now well recognized as a phytotoxic agent. In the mid-1970s, experimental studies have shown that many lichens are SO_2 sensitive. Species such as *Lobaria pulmonaria* have disappeared in many areas. Species such as *Lecanora conizaeoides*, which are able to tolerate pollution, have been found to have spread widely (Nash and Gries 1991).

It has been argued that Hawksworth and Rose’s (1970) approach to creating general zones based on the number and quantity of species is a method that can be applied quickly considering the species richness, which does not require much information. The zone consisting of epiphytic lichen species indicates which species are distributed in SO_2 pollution at which point in the region. However, when the scale is being constructed with this method, care should be taken not to apply it in places close to other sources of pollution, such as keeping the number of examined trees as high as possible.

The richness of epiphytes in a locality suggests that the air there is clean, but the opposite may not be true (LeBlanc and De Sloover 1970). Gilbert (1970) thought that using groups instead of individual species for mapping would produce a more accurate picture. The distribution of lichen species in the region can be mapped by showing different colours (depending on pollution zones). Wirth (1988) suggests that the methods used to measure the susceptibility of lichens to air pollution should be addressed not only by monitoring changes in floristic species but also by a phytosociological approach, which will also be observed in lichen communities.

2. Method based on bioindicator species and IAP (index of atmospheric purity). Working with indicator species is the study of one or more of the known species susceptible to air pollution and other parameters by quantitative methods.

The advantages of this method are the identification of several indicator lichen species (especially fruticose and foliose) assigned to species and only the time-dependent development of these species in the field. In addition, these species will provide the most effective result in the problem of air pollution. It is a method that does not require advanced technology and complicated analyses, is inexpensive, has few staff, can be done in a short time and generally gives more reliable results. On the other hand, it should be well defined which species are sensitive indicator species in that region. For this purpose, gradient analysis studies and fumigation applications are made to select pollution-sensitive species correctly. A method based on measurements may also be applied in order to precisely and sensitively detect the change in pollution in time in the lichen communities. Thus, the species can be monitored for modification by quantitative analysis. In the quantitative analysis studies, tables are formed by giving the values according to frequency ratings. These values can then be converted to % ratios. However, some of the disadvantages of this method are that it is exhausting, the need for skilled workers for continuous and seasonal data during the year and the possibility that the results are influenced by many other factors (Huckaby 1993).

The index of atmospheric purity (IAP) established by LeBlanc and De Sloover (1970) is an ecologically based index, based on the incidence and frequency of lichen formation in the sample. The reliability of IAP studies increases the proportion of susceptible species recorded on the ground. The lower the proportion of susceptible species, the more trees should be examined in the area. However, if the total number of species in a field is low, more trees cannot be recovered by examining them. The IAP values of all fields are plotted on a draft map of the study area (Showman 1988). Values are usually grouped by IAP range. The completed IAP map, if any, can be compared to the emission points and air quality data of that zone. The IAP regions primarily reflect species richness and are very useful if the same tree types are studied within the study area (Garty 2001). Numerical values of species distribution by locality and frequency level can be obtained. Maps showing the pollution-related lichen distribution generated by such studies and index of atmospheric purity (IAP) maps are used (Herzig et al. 1989).

Each type of lichen separated by pollution levels has a bioindicator role and may naturally vary from region to region. However, it is also possible to make some generalizations. Especially because they are more sensitive, epiphytic lichens are often used as indicators. An industrial field of so-called epiphyte desert has been questioned as to whether it can be taken as an indicator (Van der Gucht and Hoffmann 1990). According to this, saxicolous species was found to be less susceptible than corticolous species, determined by distribution maps of *Lecanora dispersa* and *Xanthoria parietina* in the same areas. Zones were formed by a sequence in which saxicolous and epiphytic species coexist. As a result, distribution maps of corticolous and saxicolous lichens are very similar and thus reveal sources of pollution in the region. In another study (Showman 1975), *Flavoparmelia caperata* and *Punctelia rudecta* species were used as bioindicators, and distribution maps were presented. In different studies, the indicator lichen species also show differences.

In another study, two lichen species – *Xanthoria parietina* and *Ramalina canariensis* – compared in terms of biomonitor performance against atmospheric dioxins and furan (PCDD/Fs) toxic organic compounds yielded significantly different results. More chlorinated PCDD/Fs and metals were better captured and accumulated by *X. parietina* than *R. canariensis* (Augusto et al. 2009).

According to the survey in Italy (Nimis et al. 1990), *Flavoparmelia caperata* was reported to be the best indicator, whereas *Leprocaulon microscopicum*, *Lepraria incana* and *Haematomma ochroleucum* (probably due to waterproof crustose thalli) were the most tolerant species to air pollution, based on the relationship between sulphur dioxide (SO_2) pollution and IAP lichen diversity (frequency of the species in sample area).

Some lichen species belonging to fruticose *Usnea* and *Ramalina* and foliose species such as *Parmelia* and *Lobaria*, which have a relatively larger surface area, are the most sensitive species. In particular, sensitivity lists can be created for lichen species in some countries where the lichen flora is complete or nearly complete checklists and their distribution is determined.

3. Quantitative laboratory analysis (multi-element and radionuclide analysis). Analyses of species selected as biomonitor from lichens that have spread to a region are used to measure and monitor the accumulation of atmospheric elements in a given time interval.

Concentrations accumulated in lichen samples are considered to indicate air pollutant rates. Prior to analysis, samples are cleaned of dust and other substances, and then are passed through grinding and acid dissolution pre-treatments by being protected from contamination. Analytical measurement is then made available for devices such as atomic absorption spectrophotometer (AAS) or mass spectrometry (MS). IAEA-336 lichen (*Evernia prunastri*), developed by the International Atomic Energy Agency (IAEA), is frequently used as an international reference material in such air quality monitoring surveys with lichens (Conti and Cecchetti 2001). How to prepare the multi-element reference material used for environmental pollution studies was explained by Freitas et al. (1993). Spatial distributions of the element levels measured by multi-element analysis are shown on maps prepared with computer software such as ArcGIS, Grass GIS and Surfer using geographic information system (Doğrul Demiray et al. 2012; Bustamante et al. 2013; Paoli et al. 2015; Çobanoğlu and Kurnaz 2017).

Epiphytic macro-lichens, with generally common distributions, foliose or fruticose characters to have large broad surfaces, are among the most preferred species in biomonitoring studies. “Species specificity” is an important phenomenon in lichen biomonitoring surveys. The property of “widespread and continued growth” of the lichens was stated as the main reason for selecting the indicator taxa in environmental monitoring studies (Siddig et al. 2016).

Based on the worldwide current studies on biomonitoring with lichens (25 of the papers cited in this review) (Table 3.1), the number of how many times a lichen species used is as follows: *Pseudevernia furfuracea*, 7; *Evernia prunastri*, 5; *Hypogymnia physodes*, 4; *Parmelia sulcata*, 3; *Xanthoria parietina*, 2; *Phaeophyscia hispidula*, 2; *Favoparmelia caperata*, 1; and species of the genera *Cladonia*, 4; *Physcia*, 3; *Parmotrema*, 2; *Ramalina*, 2; and *Usnea*, 2, though it actually varies by country (Fig. 3.1). Accordingly, it is clear that epiphytic fruticose and/or foliose species as best biomonitoring agents are at majority.

Studies on radionuclides are usually made by measuring caesium and uranium concentrations with the gamma-ray spectrometer (GRS). Many studies have been conducted to evaluate the effects of the Chernobyl nuclear accident (White et al. 1986; Gaare 1987; Feige et al. 1990; Taylor et al. 1988; Başkaran et al. 1991; Biazrov 1994). From these studies, it is concluded that lichens may have important bioindicator roles that show the lasting effects of radioactive contamination.

In a radioactive monitoring study first made in Turkey (Topçuoğlu et al. 1992), measurements (caesium radionuclides, ^{134}Cs and ^{137}Cs) performed in a variety of lichen samples before and after the accident showed that radioactive contamination was large in all samples, especially at higher levels in the eastern Black Sea Region.

In a recent study in Salzburg, caesium (^{137}Cs) radionuclide were measured in *Cladonia fimbriata*, *Cladonia squamosa*, *Pseudevernia furfuracea* and *Hypogymnia physodes* lichens and some species of mosses by gamma spectrometry, and the rates were reported to be quite high even after 20 years after the accident (Iurian et al. 2011).

In an attempt to determine the level of environmental uranium in the Balkan countries, measurements were made on *Pseudevernia furfuracea*, *Evernia prunastri*, *Ramalina fastigiata* and *Cetraria islandica* lichen samples, which showed a very high concentration of *Evernia* collected from Greece but not a common contamination in the Balkans (Loppi et al. 2003).

Fig. 3.1 Cosmopolitan-spread lichen species that can survive moderate or even more air pollution, *Xanthoria parietina* and *Physcia* sp. (Photo G. Özyiğitoğlu)

3.7.2 Active Biomonitoring Methods

Active biomonitoring is the monitoring of air quality with lichens transported to a region suspected of pollution from the natural environment (with the response given by lichen) (Huckaby 1993). In some cases, active monitoring may be performed in nature or may be achieved by applying contaminated source-controlled fumigation (Hoodaji et al. 2012). It must be planned and repeated absolutely carefully.

1. Transplantation. Transplantation is taking the lichen from its natural location and transporting it to the area where air pollution will be monitored.

It is studied in a region that has already been affected by air pollution (Çobanoğlu 2015). This method is currently applied in many studies (Malaspina et al. 2014; Paoli et al. 2015; Lucadamo et al. 2016). The method of hanging transplanted specimens in locations exposed to pollution in nylon mesh bags (approximately 4 m above the ground) is referred to as “bag technique” (Adamo et al. 2008; Caggiano et al. 2015; Petrova et al. 2015).

The methodology of transplantation with *Hypogymnia physodes* around a copper mine in Russia and the distance effect to the source have been investigated (Williamson et al. 2008). Particle sources have been identified as mine-smelting and converter, flotation wastes, metallurgical slags, local road dusts and suspended particles in the air above and above the ground, and which were more effective was investigated. Accordingly, it was concluded that the mine melting furnace (Cu and

Fe is the highest) is the most effective source (<10 km) for transplants. The particulate matters, which remain longer in the atmosphere and higher in terms of Pb and Zn, have spread in a wider area as a powder from the converter. It has been determined that the mine has an area of influence of about 30 km.

Another study in which lichen *Usnea barbata* was used as a transplant showed that in the samples analysed at the end of 1 month and 1 year, of 26 elements, K, Mg and Mg were found at higher concentrations while Al, Ca, Co, Cr, Ni and Na with lesser levels. This lichen has demonstrated the ability to reflect the atmospheric level of the background in the selected field (Conti et al. 2012).

2. Controlled fumigation. The fumigation work shows the measurable response of the lichens exposed to pollutants in a closed system (with air circulation) under controlled conditions. For example, closed and controlled systems such as continuously stirred tank reactors, open-top cabinets, sectional cabinets and miniature tub cabinets are used.

The most common responses measured are selected from physiological events, for example, according to the order of sensitivity to pollution, nitrogenase activity, K + output/total, electrolyte flow, photosynthesis, respiration and pigment status, etc. (Huckaby 1993).

3. Culturing. This method is designed for the purpose of observing the effects of contamination at the controlled conditions by replicating cultured species more rapidly. However, mycobionts and photobionts isolated from lichens cannot be actively applied yet because they do not achieve the desired success in laboratory culture studies (since they do not show growth and development beyond a certain stage).

Culturing steps; first, the separate cultures of the algae and fungi partner, then the synthesis and development of the new lichen unit by bringing them together (Toma et al. 2001). Mycobiont can be derived from reproductive parts, from the spore or from the thallus propagules (Yamamoto et al. 2002). In vitro culture methods of lichen thalli and isolated symbionts (algae and fungi) can be improved according to the present scientific requirements, and it is possible to achieve better performance for different purposes.

3.8 Lichen Monitoring in Sustainable Air Quality Management

Urban air pollution with SO_2, NOx, CO, volatile organic compounds (VOCs) and particulate matter is still a serious problem in developed or developing countries. PM pollution refers to all solid and liquid particles in air which are harmful particularly due to trace metal content. In general, the main sources affecting air quality are vehicle traffic, domestic heating and industrial facilities, as well as agricultural activities.

Over the years, a great deal of forest ecosystems have been destroyed and even destroyed, despite some precautions, due to various human activities such as fires, tourism and construction. This leads to radical changes such as an increase in marginal effects in the forests, microclimate changes and loss of forest environment. The degradation of forest ecosystems affects forest biodiversity negatively after numerous reductions and extinctions. Biodiversity is an important component that governs ecosystem resistance, dynamism, balance and productivity (Shukla et al. 2014).

In order to address environmental issues and ensure sustainable development, an integrated effort should be made to identify local, regional and global resources and address a wide range of environmental issues. Sustainable development is a concept in which basic human needs are fulfilled conserving the natural environment for future generations without destroying or depriving their natural systems.

Biomonitoring is such an affordable and reliable method for monitoring ongoing environmental problems. It is now very well-known that lichens affected by atmospheric changes with time reflect the air quality. Consequently, understanding the temporal trends of biomonitoring and examination of the effects of urban pollutants on the lichen organism under stress conditions seems important and valuable.

Economically feasible, socially acceptable and environmentally sound, applicable management and monitoring methods should be developed for the determination and follow-up of air quality. In addition to periodic chemical measurements, biomonitoring studies with lichens, alone or in alternative and supportive applications, should not be neglected to monitor changes in air quality. Biological monitoring data indicate the presence and changes of pollutants in the environment. Biomonitoring species ensure data for the spatial distribution of the concentration of contaminants in areas.

3.9 Conclusions

After understanding that certain lichen species are susceptible to air pollution (SO_2) at different grades, the field of study and application of biological monitoring of air quality directly with living cells has been increasing steadily. “Natural living creatures for environmental quality monitoring” is a more naturalistic approach to the environment. Various methods have been developed to biologically measure by means of bioindicators such as lichen. Although it is not a complete standard for the application of these biological methods, it has been seen that, when the right selection is made, it can be used as an alternative to air pollution measuring stations, which are usually limited to large cities and industrial areas. Atmospheric concentrations of various pollutants (trace elements, heavy metals, radionuclides and organics), not only sulphur dioxide, can be determined by analysis on biomonitor lichens, so that periodic follow-up of air quality from the biologic route is possible.

Some of the important conclusions that can be drawn from the studies on the monitoring of the air quality with lichens mentioned here are as follows:

1. The biostructural properties of lichens are significantly effective at the rate for retaining elements from the atmosphere.
2. Selection and application of the most suitable biomonitoring method(s) to the working region are very important in reaching the accurate results.
3. While the likelihoods of selected lichens for analysis in one area are expected to reflect exactly the concentrations of atmospheric contaminants, the effects of the various microhabitat, substrate or climatic factors affected by the scratch and the instantaneous anthropological factors are ignored. In this respect, the average element rates obtained from a large number of samples may yield more reliable results. Factors affecting the susceptibility of lichens in the outcome evaluation of these studies should also be considered as a whole.
4. Qualitative observations are also necessary because it may be difficult to keep the variables in the areas where the quantitative analysis samples are collected. For example, identification of lichen species diversity in an area and tracking of changes in lichen flora for many years will provide supportive data in determining the level of pollution.
5. Careful study of the regulatory mechanisms in lichens for bioavailability, accumulation, toxicity and heavy metal detoxification is necessary.

The use of genotoxicity tests can improve the more efficient use of lichens as biomonitor when monitoring air pollutants. In-species genetic diversity analyses will clarify the responses of species to different environmental and experimental conditions and at the same time contribute to a better understanding of the variability of tallus metal content in a single species (Bačkor and Loppi 2009).

Physio-biological events such as respiration, photosynthesis and nitrogen fixation occur in the metal centre depending on various oxidative metalloproteins or metalloenzymes, for example, iron in cytochromes and haemoglobin, copper in amine oxidase and superoxide dismutase, manganese in photosystem II, molybdenum in nitrogenase, cobalt in vitamin B12 coenzyme and nickel in bacterial dehydrogenases. The oxidation state also governs the toxicity of the elements. On the other hand, it is known that metals are excreted by sweat, saliva and tear secretions through urinary tract, bile pancreatic and small intestinal evacuation routes. For most metals, the best defined one is the urine path, and there is little information about the others. The concentrations of most metals in blood (all blood, plasma, serum) and in urea reflect the exposure. Depending on the location within the body or the half-life, the elimination can be determined by these parameters; for example, some heavy metals such as Pb and Cd may remain in some tissues for years (Nieboer et al. 1999).

The decrease in the number of species of a live group suffering from air pollution in vegetation will certainly affect other living groups as well. If one of the circles in the food chain is affected by pollution, it ultimately reaches people by affecting others those connected to it (e.g. animals that feed on or feed from it and then other animals that feed on it). Thus, pollution will directly harm human beings both directly and through impairment of natural balance. In this respect, the methods developed by the approach of qualitative and quantitative determination of the level of pollution effects on vegetation can be used as an early warning system against pollution.

In Western Europe, an increase in epiphytic lichens was observed in response to global warming, whereas a decrease in terricolous ones was recorded. Rising numbers of *Trentepohlia* algae and southern-spread lichen species have been reported to be increased at a faster rate in the areas affected by pollution than the forests (Aptroot and Van Herk 2007). Changes in the lichen flora in 22 years (1989–1995) in Switzerland have been investigated in a study by Van Herk et al. (2002): during the years when the temperature increases became more evident, NH_3 increased compared to the decrease of SO_2. It has been concluded that subtropical species show a great increase (83%), while arctic-alpine/boreal species show a decrease of about 50%. Monitoring the long-term changes in the lichen flora will provide valuable evidence that not only will the air quality of the region be followed, but also the response of the nature against global warming, when the methods in which climatic data are combined in the following years.

Biological monitoring has a strategic precaution in nature-environment-human relationships. The use of biological monitors as supportive or alternative to expensive and instantaneous measurements will provide significant contributions to addressing the challenges posed by viable health, especially in urban and industrial space planning and the adverse effects of rapidly developing technology.

This is a comprehensive review of the role of lichens in biomonitoring environmental quality in the last 45 years ranging from the first studies that began in the 1970s to the present day, and it is a reference source for future work in this regard.

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Chapter 4
Organochlorine Pesticides (OCPs) in Atmospheric Particulate Matter: Sources and Effects

Sushil Kumar Bharti, Shyamal Chandra Barman, and Narendra Kumar

Abstract In the recent past, a significant amount of pesticides has been used in the field of agriculture to increase the crop yield worldwide. Among pesticides, different types of pesticides have been used in agriculture; among them organochlorine pesticides (OCPs) contribute a significant proportion. Application of OCPs in the agricultural field facilities increased production, but due to the lipid-soluble nature, pesticides enter the food chain and become available to human beings. Being very economical and effective against pests, earlier OCPs were effectively used worldwide to combat plague, malaria and typhus. However, after the Second World War, scientific community noticed the adverse impact of these pesticides on the human health. At the Stockholm Convention, the use of 12 persistent organic pollutants (POPs) was completely banned for agriculture. Despite the ban on POPs, their residual levels are still being detected in various environmental matrices due to environmental persistence and long-distance transport of these chemicals. The concentration of atmospheric OCPs is determined in different steps, viz., extraction, cleaning, analysis, and quantification. Quantification studies have revealed that the highest concentration of OCPs is still detected in developing countries including India and China besides several developed countries. Severe exposure to OCPs can lead to cancers and can also affect the pulmonary and nervous system to aggravate Alzheimer's and Parkinson's diseases. For sustainable development, the use of synthetic chemical pesticides should be reduced, and the use biopesticides should be recommended for increased production.

Keywords Organochlorine pesticides · Particulate matter · Polyurethane foam · Soxhlet extraction

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4.1 Introduction

The pesticide is a general term used for insecticides, fungicides, herbicides, rodenticides, molluscicides, nematicides, and plant growth promoters (Aktar et al. 2009). Due to their massive use for intensive food production along with preservation in both developed and developing countries, pesticides are among the most widely used anthropogenic chemicals contributing to the global contamination of the environment (Baraud et al. 2003; Yusà et al. 2015; Espallardo et al. 2012). These organochlorine pesticides (OCPs) are polychlorinated compounds with a high chemical stability and are classified as persistent organic pollutants (POPs) due to their chronic toxicity, persistence, and bioaccumulation (Syed et al. 2013; Barakat et al. 2013; Ben Hassine et al. 2012; Zhou et al. 2008; Jones and Voogt 1999). OCPs have been widely used in the last century to protect crops and increase the agriculture production to achieve food security for the world's growing population (Wang et al. 2008; Ozkara et al. 2016; Kumar et al. 2018).

Although OCPs increase agricultural production, but being lipid soluble they bioaccumulate through the food chain and become a risk for human being (Afful et al. 2010). Because of the toxic nature, OCPs have been banned in several countries since 1970, but still they are detected in water, sediments, and ambient air which indicate its recalcitrant nature (Fox et al. 2001; Albaiges et al. 1987; Iwata et al. 1994; Hogarh et al. 2014). Dermal exposure, ingestion, and inhalation are the three main routes for OCP exposure in humans, while ingestion is considered to be a main route for chronic exposure to OCPs (Morgan et al. 2005). But in recent years, numerous studies reported that inhalation is the major route for chronic exposure of OCPs in rural and urban area of developing and developed countries (Nascimento et al. 2017; Lopez et al. 2017; Degrendele et al. 2016; Socorro et al. 2016; Coscolla et al. 2014; Chakraborty et al. 2010; Srimurali et al. 2015; Devi et al. 2011).

4.2 Historical Overview of Organochlorine Pesticides

During the Second World War, significant amount of OCPs was used for controlling the plague and malaria and certain disease in crops. These OCPs (aldrin, dichlorodiphenyltrichloroethane (DDT), dieldrin, β-benzene hexachloride (BHC), 2, 4-dichlorophenoxyacetic acid (2, 4-D), chlordane, and endrin) were inexpensive and very effective against pest (Jabbar and Mallick 1994; Delaplane 2000). In 1939, the Swiss chemist Paul Hermann Muller discovered the insecticidal action of DDT after having been used significantly in agriculture against pests and has also been used by civilians and soldiers to control malaria, plague, and typhus. After 1945, several studies confirmed that OCPs undergo a slow decomposition in the presence of insolation (photolysis) and humidity and become persistent in the atmosphere for several days, while in the polar atmosphere, they become persistent for several years (Huang et al. 2006). In 1962, American scientist Rachel Carson highlighted the toxic effects of DDT and other pesticides in her famous book *Silent Spring* that DDT and other pesticides are effective against target and nontarget organisms after their application in the agricultural field (Jabbar and Mallick 1994; Delaplane 2000; Kumar et al. 2018).

In 1972, endosulfan, dieldrin, and lindane were restricted to be used in agriculture and for other purposes (Mahmood et al. 2015). However, on May 21, 2001, 179 countries agreed to sign the international treaty recognized as the Stockholm Convention, which anticipated the ban of 12 POPs, including DDT. With the agreement of an initial of 128 parties and 151 signatories, Stockholm convention came into force on May 17, 2004 (Mahmood et al. 2015; Shahawi et al. 2010). Among these 12 POPs, 10 POPs were among the category of intentionally produced chemicals that are classified as organochlorine pesticides, viz., aldrin, endrin, chlordane, DDT, dieldrin, heptachlor, mirex, toxaphene, HCB, and PCB (Harner et al. 2006; Kelce et al. 1995). But recently several studies confirmed that despite ban on OCPs, they are still present in traces as a historical residue in atmosphere due to long-range transport (Nascimento et al. 2017; Lopez et al. 2017; Degrendele et al. 2016; Socorro et al. 2016; Coscolla et al. 2014; Chakraborty et al. 2010; Srimurali et al. 2015; Devi et al. 2011; Bozlaker et al. 2009; Baek et al. 2013).

4.3 Worldwide Consumption Pattern of Organochlorine Pesticide

According to the report of the US Environmental Protection Agency, 5 billion pounds of pesticides including herbicides, insecticides, and fungicides were used in different sectors in the United States (Merrington et al. 2002). Among these, more than 1.2 billion pounds of pesticides were used in the United States, representing more than 20% of total world use (Kiely et al. 2004). Approximately 888 million pounds of pesticides are used in different sectors in the United States. Of the 888 million, 76% of pesticides were used in the agricultural sector, followed by 12.5% in industry, commerce, and the government sector, and the remaining 11.5% was used in the household gardens (Lah 2011). Another 2600 million pounds of chlorinated pesticides (OCPs) were used as disinfectants and 800 million pounds for the preservation of wood worldwide (Gao et al. 2012). In Asia, China became the second largest consumer of pesticides after the United States, and during 1960–1970, China manufactured enormous amount of organochlorine, organophosphate, and carbamate pesticides (Rajinder et al. 2009). Since 1983, China has banned the application of HCH, DDT, and other organochlorine pesticides. Whereas, application of organophosphorus, parathion methyl, parathion, methamidophos, and phosphamidon pesticides have been banned for export and import in China since 2007 (Zhang et al. 2011).

In Asian countries, India is the second largest consumer of pesticides and ranks 12th worldwide. The production of organochlorine pesticides, viz., gamma-hexachlorocyclohexane (γ-HCH), was started from 1952 in Calcutta. Noticeably, γ-HCH is famous as gammaxene in India, which has been used as an insecticide and also to control of lice and scabies (Mathur 1999). During 1958–1998, the production of technical-grade pesticide has been increased from 5000 metric ton to 102,240 in India (Aktar et al. 2009). In India, 76% of the pesticide is used as an insecticide, and the rest of the pesticide is used as an herbicide and fungicide in the production of cotton crops, followed by paddy and wheat (Mathur 1999). According to the report of FAO (2010), 210 metric tons of pesticides were used as herbicides, insecticides, fungicides, and herbicides in different sectors of Germany. Among 210 metric tons, 60% were used as herbicides and 35% as fungicides and bactericides, and the remaining 5% was used as an insecticide in Germany. France is known to be the largest consumer of pesticides after Germany, where 576 metric tons of pesticides were used in different sectors. Out of 576 metric tons, 58% of the total pesticides were used as fungicides and bactericides and 38% as herbicides, and the remaining 4% was used as an insecticides. Apart from Germany and Spain, the consumption pattern of pesticide is entirely different in Japan, where approximately 511 metric tons of pesticides is used of which 44% of total pesticides is used as fungicides and bactericides, while 38% is used as insecticides, and the remaining 18% is used as herbicides (Zhang et al. 2011)

4.4 Commonly Used Organochlorine Pesticides and Their Structures

To ensure food safety, a large amount of pesticides have been used in agriculture in the recent past. Among these pesticides, much of the organochlorine pesticide has been used for different purposes in developing countries. Some of the common organochlorine pesticides found in ambient air and their structure have been shown in Fig. 4.1.

4.5 Sources of Organochlorine Pesticides in Ambient Environment

Generally 15–40% of OCPs is dispersed into atmosphere during spray drift process, and their fate is influenced by partition between the particulate and gaseous phases (Yates et al. 2015; Sanusi et al. 1999; Sauret et al. 2008). However, approximately 90% of the applied OCPs were lost due to volatilization during application to plants and soil (Bedos et al. 2002; Espallardo et al. 2012; Sarigiannis et al. 2013). A schematic diagram of distribution and source of OCPs is illustrated in Fig. 4.2.

Characteristic of OCPs such as semi-volatility, high stability, and hydrophobicity favors the long-range transport and widespread distribution of OCPs in ambient air (Wania and Mackay 1995). Being semi-volatile in nature, OCPs are often adsorbed to the surface of particulate matter and transported over long distances even in remote areas, generating secondary products that could be even more hazardous than originally emitted OCPs (Socorro et al. 2016; Coscolla et al. 2014). OCPs can also enter into atmosphere through waste incineration, chlorinated product synthesis, and agriculture soil suspension (Chakraborty et al. 2013).

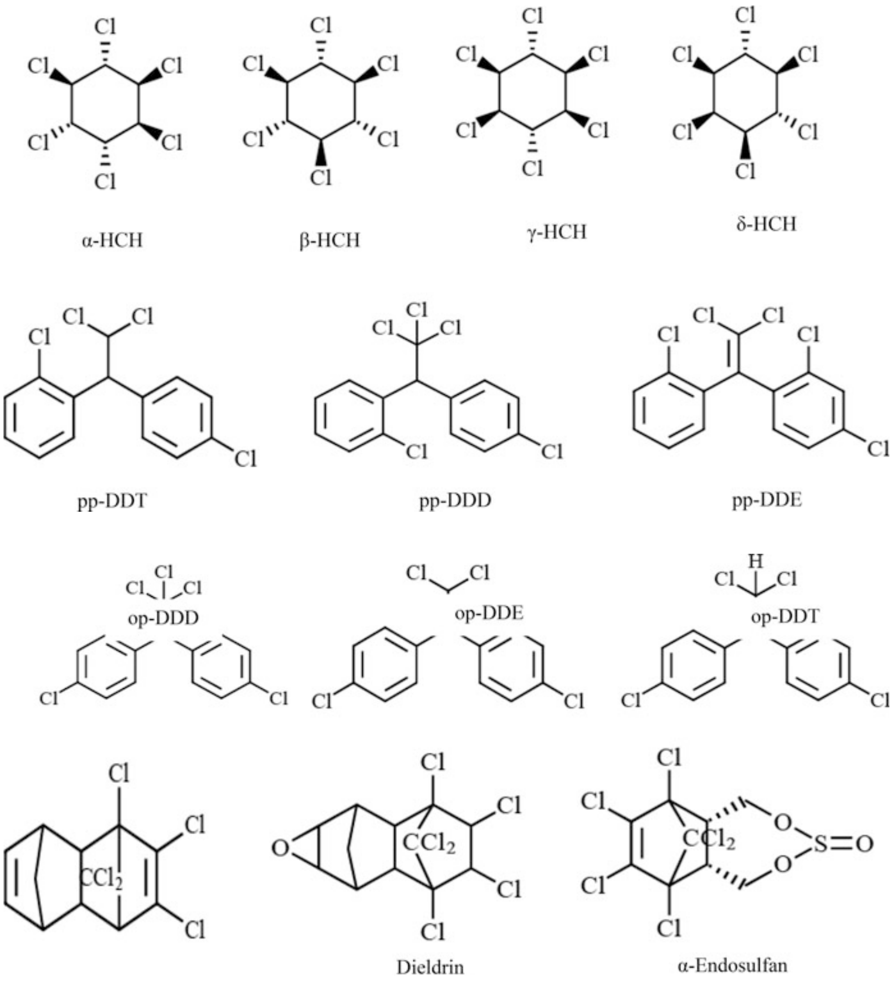
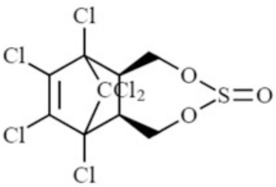
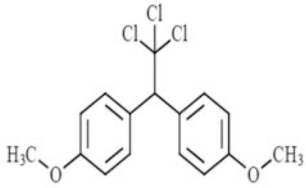


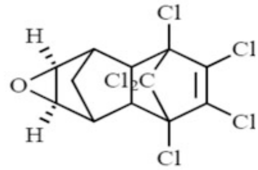
Fig. 4.1 Chemical structure and stereochemistry of commonly used OCPs



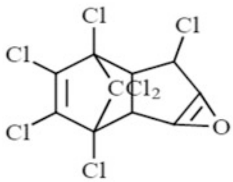
β-Endosulfan



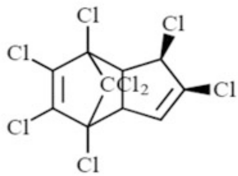
Methoxychlor



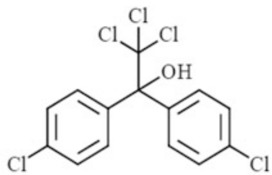
Endrin



Heptachlor



Chlordane



Dicofol

Fig. 4.1 (continued)

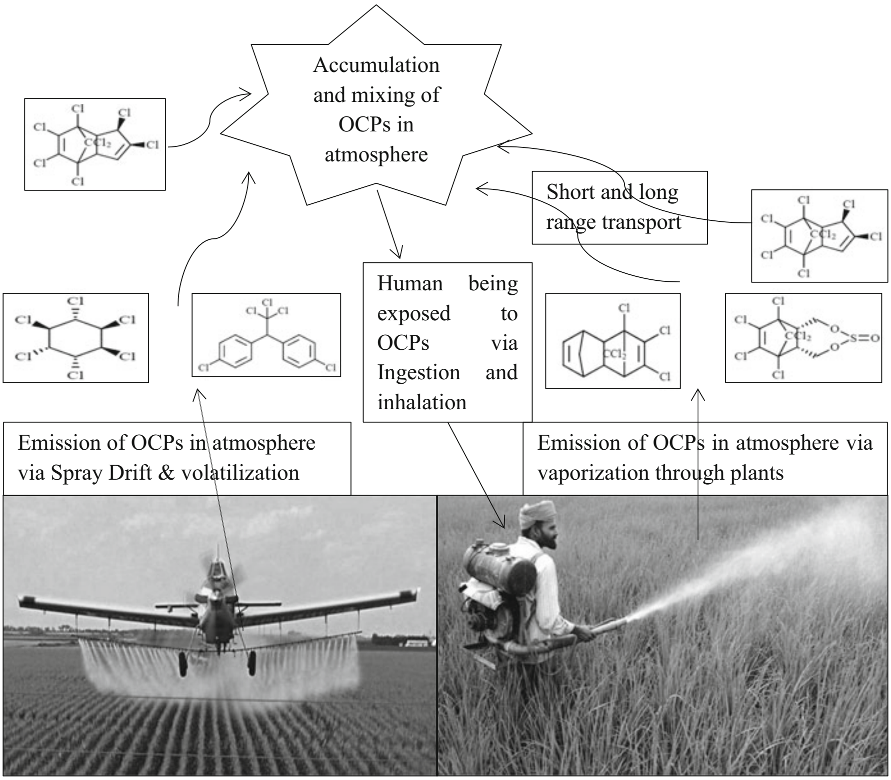


Fig. 4.2 Distribution and sources of commonly used organochlorine pesticides into atmosphere

4.6 Sampling of Atmospheric OCPs Associated with Particulate Matter (PM_{10} and $PM_{2.5}$)

There are two types of sampling procedures for estimating atmospheric OCPs: by collecting particulate matter using a high-volume sampler, and at the same time, the gaseous phase of OCPs may also be monitored using the XAD, an absorbent resin placed on the filters sandwiched between polyurethane foam. The particulate matter was collected on two types of filters, viz., glass and quartz fiber filter papers, with a diameter ranging from 25 to 90 mm and 110 to 150 mm, respectively. Monitoring of PM_{10} and $PM_{2.5}$ can be carried out using high-volume sampler and fine dust sampler at a flow rate of 1.1–1.3 and 13.7 m^3/min, respectively (Bharti et al. 2017). Prior to exposition, glass or quartz fiber filter paper should be heated for 24 h at 300 °C to eliminate organics, and after elimination of organics, weight of blank filter paper should be taken to microbalance. Further, for more accurate results, it is equilibrated in desiccators containing silica gel for 24 h and weighed using a pre-calibrated electronic balance before and after sampling. In addition, a blank filter paper should also be taken to and from the field, and the same gravimetric analysis should be performed for chances of any contamination.

4.7 Extraction of Atmospheric OCPs Associated with Particulate Matter (PM_{10} and $PM_{2.5}$) and Gaseous form of OCPs Using Polyurethane Foam (PUF)

The analytical procedure to estimate the OCPs concentration associated with atmospheric particulate involves the following steps: extraction, cleaning, analysis, and quantification. In general, extraction is considered as the most crucial step, as the objective of the extraction is to isolate most of the OCPs from the sorbent or particulate matter or polyurethane foam using organic solvent. Organic solvent such as acetone, dichloromethane (DCM), or mixture of hexane and DCM should be used in Soxhlet to extract particulate and gaseous phase of atmospheric OCPs. Soxhlet extraction is a strenuous and slow process, which takes approximately 8–24 h for the complete extraction of atmospheric OCPs. Generally, 150–200 ml of solvent is consumed during the extraction, but the recovery of the sample (60–70%) is usually very low in this process, which can be confirmed by spiking the standard OCP on filter paper and PUF disk. In addition, a prolonged heating period (8–24 h) can transform thermally labile analytes during extraction; to avoid the transformation, some alternative techniques, viz., accelerated solvent extraction (ASE), Soxtec extraction, agitation-assisted extraction, ultrasonic extraction, and microwave-assisted extraction (MAE), are frequently applied (Sanusi et al. 1999; Qiu et al. 2004; Seiber et al. 1990; Briand et al. 2002; Coscolla et al. 2009). A detailed comparative statement of the extraction technique and extraction procedure has been discussed in Table 4.1 and Fig. 4.3, respectively.

Table 4.1 Comparison of different extraction techniques to estimate atmospheric OCP

Extraction technique	Solvents used for extraction	Quantity of solvent	Time consumed	Types of samples	Sampling recovery	References
Soxhlet	n-Hexane, mixture of n-hexane and DCM	150–400 mL	4–48	Particulate and gaseous phase	Lower	Sanusi et al. (1999)
Soxtec	n-Hexane, mixture of n-hexane and DCM	50–100 mL	1–4	Particulate and gaseous phase	Lower	Qiu et al. (2004)
Agitation assisted	n-Hexane, mixture of n-hexane and DCM	100–300 mL	1–3	Gaseous phase	Poor	Seiber et al. (1990)
Ultrasonic	n-Hexane, mixture of n-hexane and DCM	100–300 mL	30 min–1 h	Gaseous phase	Poor	Briand et al. (2002)
Microwave assisted	n-Hexane, mixture of n-hexane and DCM	40–100 mL	20–40 min	Particulate Phase	Good	Coscolla et al. (2009)

4.8 Levels of Atmospheric OCPs

The highest concentration (pgm^{-3}) of OCPs has been reported in Tamil Nadu, India (BDL-41400). Among the 13 atmospheric OCPs, concentrations of γ-HCH, heptachlor, and mirex were found to be dominant in ambient air (Srimurali et al. 2015), while the second highest levels of OCPs have been reported in Northern China, and its concentration ranged from 140 to 34,730 pgm^{-3}. Among 20 congeners of OCPs, concentrations of ∑HCH, ∑DDT, ∑chlordane, and ∑endosulfan were found to be dominant in ambient air of Northern China (Ding et al. 2015). According to Chakraborty et al. (2010), the concentration of atmospheric OCPs ranged from 120 to 17,000 pgm^{-3} in 7 metropolitan cities of India; the concentration of ΣHCH was found to be the highest followed by ΣDDT, Σchlordane, and Σendosulfan. Results of studies conducted worldwide on the distribution and atmospheric levels of OCP are illustrated in Table 4.2.

4.9 Risk Associated with Atmospheric OCPs

Fine particles with an aerodynamic diameter less than 2.5 μm ($PM_{2.5}$) are considered hazardous to human health due to their long-term residence in atmosphere and ability to penetrate deep into the lungs on prolong exposure (Lelieveld

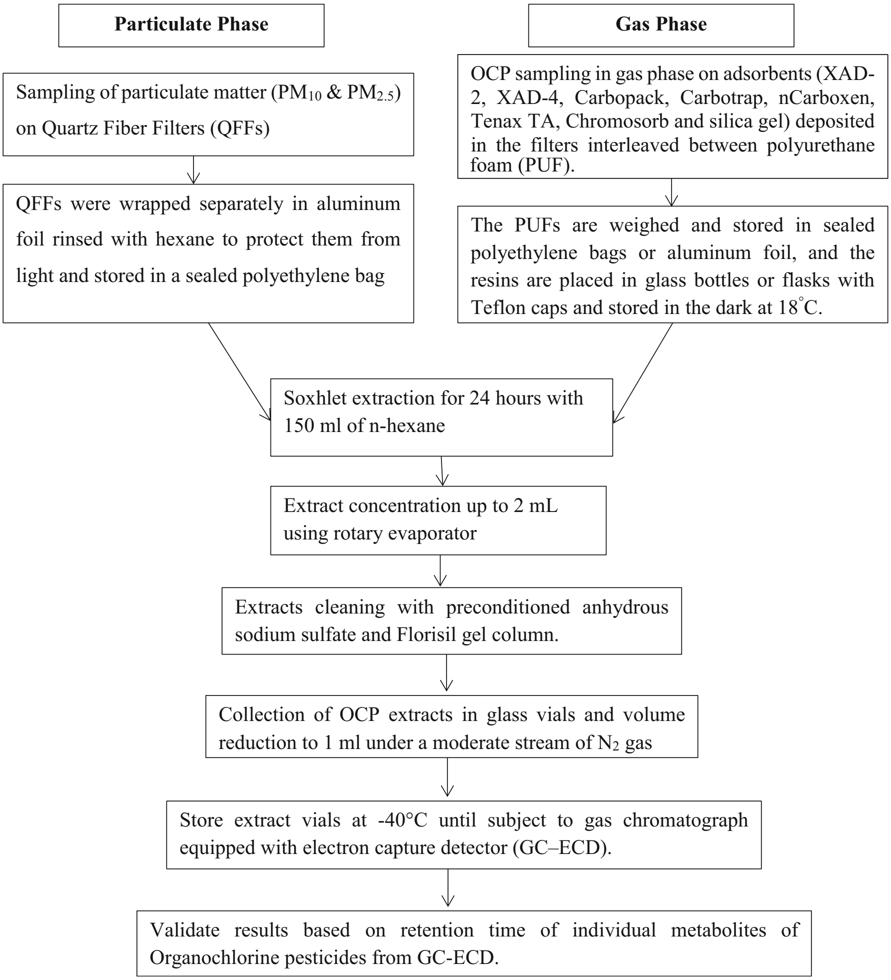


Fig. 4.3 Procedure for extraction of OCPs present in the gaseous and particulate phase

et al. 2015; Pope and Dockery 2006). In favorable meteorological conditions, OCPs or hazardous substances adsorbed on fine particles are transported to a remote location due to long residence time of fine particles (Bossi et al. 2016; Zhang et al. 2016a, b; Socorro et al. 2016). It has been estimated that 1–2.5 million tons of organochlorine pesticides are used annually in agriculture worldwide, and their 15–20% are emitted directly into the atmosphere through dispersion, volatilization, and evaporation (Fenner et al. 2013; Zhang et al. 2016a, b). Among OCPs, the adverse effects of insecticides are more severe than herbicides and fungicides (Zhang et al. 2016a, b). The direct inhalation of insecticides is directly related to the incidence of cancer. However, it can also alter the central nervous and endocrine system that leads to Alzheimer's and Parkinson's diseases (Yan et al. 2016;

Table 4.2 Global status of organochlorine pesticide associated with particulate matter

S. No.	Location	Conc. (pgm^{-3})	Duration	References
1	Hazlerigg, England	22–500	1998–99	Lee et al. (2000)
2	Zagreb, Croatia	0.4–42.2	2000–01	Dvorscak et al. (2015)
3	Taihu Lake, China	36–767	2001–02	Qiu et al. (2004)
4	Hong Kong, China	103–1440	2003–04	Li et al. (2007)
5	Guangzhou, China	93–2258	2005–06	Li et al. (2007)
6	Beijing, China	32–9434	2005–06	Wang et al. (2008)
7	Yangtze, China	460–2720	2005–06	Tang et al. (2008)
8	Beijing, China	27–1400	2005–09	Zhang et al. (2011)
9	New Delhi, India	120–17,000	2006–07	Chakraborty et al. (2010)
10	Lancaster, UK	19–352	2006–07	Cabrerizo et al. (2011)
11	Bursa, Turkey	519–1030	2008–09	Cindoruk et al. (2008)
12	Valencia, Spain	8–30,000	2008–14	Lopez et al. (2017)
13	Tamil Nadu, India	ND-41,400	2009–10	Srimurali et al. (2015)
14	Jinan, China	92–481	2009–10	Xu et al. (2010)
15	Todos os Santos Bay (TBS), Brazil	20–315	2010–11	Nascimento et al. (2017)
16	Punjab, Pakistan	55–99	2010–11	Syed et al. (2013)
17	Lake Chaohu, China	2–173	2010–11	He et al. (2015)
18	Kosetice Observatory (Czech Republic)	ND-344	2012–13	Degrendele et al. (2016)
19	Valencia, Spain	4–383	2012–13	Coscolla et al. (2014)
20	Northern China	140–34,730	2014–15	Ding et al. (2015)

Parron et al. 2013; Kamel F 2013). Risk assessment based on daily inhalation exposition (DIE) revealed that infants and people suffering from lungs and heart disease are highly susceptible to atmospheric OCPs (Bharti et al. 2017; Marks et al. 2010; London et al. 2012).

4.10 Control Measures of Atmospheric OCPs

Since the last two decades, there has been great pressure on the agriculture sector to ensure food security throughout the world. In order to ensure food security, 70% of the total pesticides are being used in this sector and contribute significantly to atmospheric OCPs by different ways due to their semi-volatile nature. However, direct inhalation and dietary exposure of OCPs in any form are considered to be hazardous to human health. Therefore, it is a concern of the scientific community to explore the distribution pattern of atmospheric OCPs worldwide. To reduce the levels of atmospheric OCPs, the application of hazardous synthetic pesticides should be discouraged, and the use of biopesticides should be encouraged. Additionally, a comprehensive integrated pest management (IPM) may be used to prevent the growth of pests that become resistant to the pesticide, and the protection of beneficial insects should also be ensured.

4.11 Conclusion

In order to estimate the severity of atmospheric OCPs on human health, concentration of pesticides is monitored in both developing and developed nations. It is crucial to monitor the levels of atmospheric OCPs emitted during spray drift and volatilization from plants to soil. The techniques used for the extraction of OCP are labor-intensive, have low recovery and requires of large volume of solvent for the complete extraction and recovery of the sample is very low; therefore the use of recent eco-friendly and cost-effective extraction techniques such as agitation-assisted, ultrasound-assisted, and microwave-assisted extraction should be recommended.

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Chapter 5
Vehicle-Generated Heavy Metal Pollution in an Urban Environment and Its Distribution into Various Environmental Components

Vidhu Gupta

Abstract Pollution caused by vehicles and its rapidly growing number is a serious concern all over the world. Vehicular pollution is primarily known for emitting various kinds of organic and inorganic gaseous pollutants in to the atmosphere, but recent studies show that vehicles are one of the chief sources of creating heavy metal pollution in an urban environment via processes like exhaust of diesel and petrol, corrosion of metallic parts, engine wear, tyre and brake pad wear and road surface degradation due to vehicular movement. Studies show that apart from fuel burning, tyre and brake wear particles lead the contribution of heavy metals into an urban environment. Due to easy availability and low cost, two wheelers dominate the road traffic and become a major source of air pollution in most of the developing countries. Heavy metals emitted in ambient air ultimately get deposited on other environmental component like hydrosphere and lithosphere which ultimately affect flora and fauna living in it. Some heavy metals are able to create toxicity at low level of exposure, and metals like nickel, cadmium and chromium are able to produce carcinogenicity in humans. Meteorological and geographical conditions of an area play a major role in distribution and deposition of heavy metals. There is an urgent need to make an effective environmental management plan for urban areas which include promotion of new technologies, adaption of biofuels, green belt development and public participation.

Keywords Vehicular pollution · Heavy metal · Tyre and brake pad · Meteorological · Management plan

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5.1 Introduction

Problem of environmental pollution is increasing day by day in both developed and developing countries due to urbanization and industrialization. The trend of migration of people from villages to towns and cities has been seen all over the world as cities are concentrated centres of production, consumption and waste disposal. The proportion of the world's population living in urban areas, which was less than 5% in 1800, increased to 47% in 2000 and is expected to reach 65% by the year 2030 (United Nations 2006). Urbanization of an area includes good infrastructure, presence of various other amenities and well-connected routes of transportation. Roads are important infrastructure of an urban area that contributes a major part in stimulating social and economic development of a country. The USA boasts the world's largest road network, followed by China and India, the world's two most populous countries. Because of their versatility, flexibility and low initial cost, motorized road vehicles overwhelmingly dominate the markets for passenger and freight transport throughout the world. Calculating the total number of motor vehicles on the planet is an inexact science, but the number is growing rapidly. The automotive trade journal *Ward's AutoWorld* had estimated that the total crossed 1 billion vehicles sometime during 2010. The vehicles include passenger cars; light-, medium-, and heavy-duty trucks; and buses but not off-road or heavy construction vehicles. Just 40 years ago, in 1970, the world total was only a quarter of a billion vehicles, a number that took 85 years to achieve. The 1970 total doubled in just 16 years to 500,000,000 by 1986. It took 24 more years to double again to the current 1 billion. By some projections, the world could house as many as 2.5 billion vehicles by 2050.The estimated total number of vehicles in India is more than 200 million up to the year 2016.

Although road transportation speeds up the development of a nation, on the other side, it is inserting large amount of toxic pollutants into the environment. It is reported that vehicles are responsible for more than 40% of the total air pollution and this percentage increases up to 70–80% for megacities in developing nations (Bharti et al. 2017). Vehicles mainly emit two kinds of pollutants: (1) gaseous pollutants and (2) particulate pollutants. Gaseous pollutants basically come out via fuel exhaust and further categorized into inorganic and organic gas pollutants. Oxides of sulphur (SO_2, SO_3, etc.), oxides of nitrogen (NO_2, NO, N_2O, etc.), oxides of carbon (CO_2, CO, etc.), ammonia and ozone are well-known inorganic gaseous pollutants, whereas aliphatic and aromatic hydrocarbons like benzene, benzo(a) pyrene, aldehydes, ketones, etc. come under organic gaseous pollutants. Particulate matter which is emitting out from vehicles in solid and liquid form is a mixture of various inorganic and organic pollutants, but heavy metals are of particular concern. Tearing, wearing of tyre and brake pad, corrosion of metallic parts and paints and fuel emission are mainly responsible for particulate matter pollution which carry various kinds of heavy metals in its chemical composition. Heavy metals are found ubiquitous in nature and generated via both natural and anthropogenic sources; second they show a tendency to accumulate various environmental components and are able to magnify their concentration as we move upwards in trophic level. Heavy metals are defined as metallic elements that have a relatively high density compared to water. With the assumption that heaviness and toxicity are interrelated, some heavy metals are able to induce toxicity at low level of exposure.

The primary source of heavy metals in the environment is lithosphere. Heavy metals occur naturally in the earth's crust and may be released into the soil and atmosphere via process of weathering and volcanic eruption, respectively, which are two main natural sources of heavy metals in the environment. Although natural sources contribute significant amount of heavy metals, anthropogenic activities are mainly responsible for heavy metal contamination in an urban environment. In an urban environment, heavy metals derived mainly from vehicular and industrial emissions. Industrial sources include ore extraction and mining industries, coal-based thermal power plants, pesticide industries, textile industry, oil and petroleum refinery, battery industry, etc., whereas vehicles generate heavy metals via two main ways, i.e. exhaust and non-exhaust ways. After coming out from different vehicular sources, heavy metals remain suspended in atmosphere and ultimately get deposited into surrounding environment via dry and wet deposition. Deposition and distribution in turn depends on many factors and meteorological conditions. Heavy metals show tendency to accumulate in plants and animals and ultimately create toxicity in human beings. There were various clinical studies that have been done for toxicity analysis of various heavy metals. The aim of this review paper is to summarize the sources of vehicular-generated heavy metals and its distribution over other environmental component.

5.2 Sources of Vehicular-Generated Heavy Metals in Urban Areas

Urban environment may receive heavy metal loads from different sources but one of the most important being vehicle emissions (Table 5.1). Vehicles generate heavy metals into the atmosphere mainly via exhaust and non-exhaust vehicular emissions. Exhaust category mainly includes petrol and diesel emission, and non-exhaust category includes wearing and tearing of various vehicular components like tyre and brake pad wear, engine wear and corrosion of metallic parts and paints which basically create particulate matter pollution. Apart from exhaust and non-exhaust category, road surface degradation and road paint corrosion also contribute heavy metals into the atmosphere (Lindgren 1996; Legret et al. 2005). The US EPA highlights 21 toxic substances that can mainly be assigned to road traffic. Some heavy metals such as Pb, Cu, Sb, Cd, Ni or Zn are among them. Main vehicular sources which emit heavy metals are as follows.

Table 5.1 Concentration of heavy metal in the world soil

Metal (μg g-1)	Soil	
	typical	Range
Ni	40	10–1000
Pb	10	2–2000
Cr	100	5–3000
Cu	20	2–100
Cd	0.06	0.01–0.07
Zn	50	10–300
Mg	–	–
Mn	850	100–4000
Fe	38,000	7000–550,000

Source: Bowen 1979

5.2.1 Fuel Exhaust

Diesel and gasoline are two main fossil fuels which are used to power most of the road vehicles because petroleum fuels carry much more energy than other substances. These two fossil fuels are basically made from hydrocarbons, but various potentially toxic heavy metals are present in crude oil. Presence of heavy metals in petroleum product depends on two main factors: first the geological location in which crude oil is being formed where metals found in rocks are absorbed into the crude oil; second heavy metals in crude oil are the introduction of drilling mud fluids into the oil well during crude oil extraction (NNPC/PTI 1987; Stanisley 2002). The heavy metals in the crude oil distribute themselves into the petroleum fractions and invariably act as contaminants.

When fuel burn carbon and hydrogen combine with oxygen to make carbon dioxide gas and water, the energy that held the molecules together is released as heat. Along with various gaseous emissions, metals are emitted to the ambient air via exhaust pipe or catalytic converter. Arsenic, cadmium, chromium, copper, mercury, nickel, lead, selenium and zinc are the main heavy metals emitted from the burning of diesel and gasoline fuel. The gasoline used as fuel in automobiles may contain metalloids and metallic elements such as Pb, Cu, Zn, Ni, Fe, As, Cd, Hg, Se and Ti (Fig. 5.1). These elements are derived from the raw product but can also be introduced as additives during production or contaminants during storage (Ozaki et al. 2004).

5.2.2 Brake Pad Wear and Tyre Wear

Brakes and tyres are used to stop and accelerate vehicles, respectively. Wearing and tearing of tyres and brake pad take place due to friction between road surface and vehicular component, during braking and acceleration process. The tyres are basically made from rubber which are fitted around a metallic frame, and brake pads are

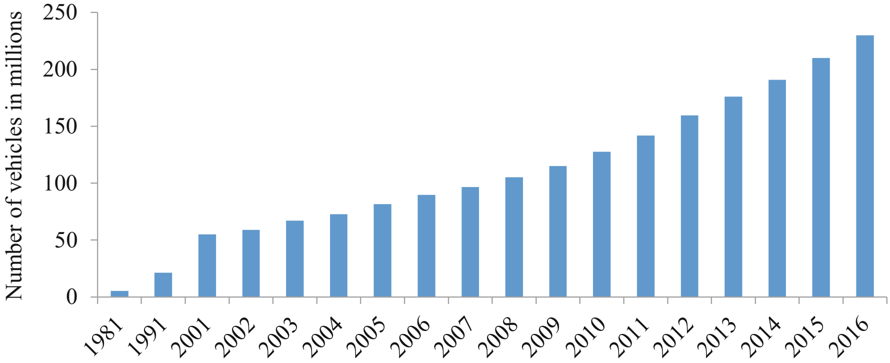

Fig. 5.1 Total number of vehicles across India from 1981 to 2016

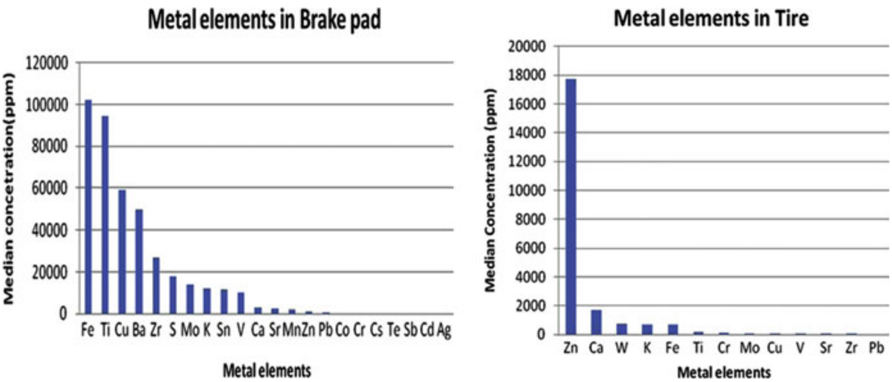

Fig. 5.2 Metal concentration (ppm) in brake pads and tyres analysed by XRF in 2008. (Source: Apeagyei et al. 2011)

combination of non-metallic, semimetallic to fully metallic materials (Figs. 5.2 and 5.3). Detailed analyses of tyre wear dust have been conducted by various researchers which show that heavy metals like Fe, Zn, Cd, Cr, Cu, Co, Hg, Mo, Ni and Pb were associated with dust from tyre wear in significant amount (Fukuzaki et al. 1986; Fauser et al. 1999; Adachia and Tainoshob 2004; Schauer et al. 2006; Hjortenkrans et al. 2007). Zn was the most abundant heavy metal from tyre wear, and its high concentrations resulted from the use of ZnO and ZnS to the tyre during vulcanization (Smolders and Degryse 2002; Ozaki et al. 2004). Another source of heavy metals from vehicles is wear particles from brake pad linings. During braking, brakes are exposed to extensive heat from friction, which results in the emission of particles. The worn particles of tyre and brake pad dispersed directly into the environment. It has been investigated that brake pads are a major source of metal emission such as Fe, Ti, Cu, Ba, Zr, Sb, Mo, K, Sn, V, Ca, Sr, Mn, Zn, Pb and Co, and tyre wear is an important source for Zn, Ca, W, K, Fe, Ti, Cr, Cu, etc. (Apeagyei et al. 2011).

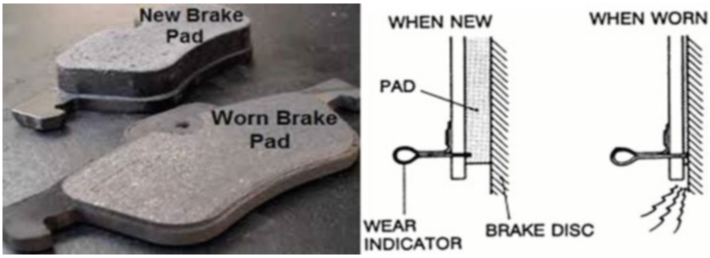

Fig. 5.3 Image of new and worn brake pad

Adachia and Tainoshob (2004) and Hjortenkrans et al. (2007) have reported that brake dust mainly contained Fe, Cu, Sb, Ba, Al, Si, S, Ti, Zn, Ni, Cr and Pb and a small amount of Cd. The extent of wearing and tearing of tyre and brake pad depends on the characteristics of tyres, types of vehicles, condition of road surface, vehicle operation mode, road design, etc.

5.2.3 Engine Oil and Engine Wear

Engine, or motor, oil is designed to lubricate the inner components of internal combustion engines, as well as to protect them against corrosion and keep them cool while in use. It's made from two main elements: base stock and additives. The base stock commonly makes up 95% of the solution and is either made from petroleum, synthetic chemicals or a mixture of the two. The base stock is responsible for lubricating an engine's moving parts and removing built-up heat. The additives, meanwhile, account for roughly 5% of the oil, and it is these chemicals that are responsible for finely controlling oil viscosity and lubricity, as well as protecting engine parts against wear. For example, zinc dialkyldithiophosphate (ZDDP) is a frequently used additive for preventing wear, while magnesium sulphonates help the oil to break down impurities and engine sludge. Table 5.2 shows the common sources of heavy metals used in gasoline or diesel engine oil.

5.2.4 Road Abrasion

Road abrasion takes place due to the friction which generates between tyres and road surface of vehicles due to continuous movement and braking process. Due to continuous abrasion, road surface particles loosen out and ultimately came out into the environment. Asphalts are significant sources of Ni and As in road dust (Ozaki et al. 2004). It has been reported that the concentrations of Ni and Zn in road bitumen were higher than in raw bitumen (Gadd and Kennedy 2000). It should be noted that more tyre abrasion occurs when a vehicle drives on a concrete motorway compared

Table 5.2 Common sources of the elements in a gasoline or diesel engine oil

Aluminium	Pistons, bearings, cases (heads and blocks)
Chromium	Rings, a trace element in steel
Iron	Cylinders, rotating shafts, the valve train and any steel part sharing the oil
Copper	Brass or bronze parts, copper bushing, bearings, oil coolers, also an additive in some gasoline engine oils
Lead	Bearings
Tin	Bearings, bronze parts, piston coatings
Molybdenum	Antiwear additive, coating on some new rings (washes off as break in occurs)
Nickel	Trace element in steel
Manganese	Trace element, additive in gasoline
Silver	Trace element
Titanium	Trace element
Potassium	Antifreeze inhibitor, additive in some oil types
Boron	Detergent/dispersant additive, antifreeze inhibitors
Silicon	Airborne dirt, sealers, gaskets, antifreeze inhibitors
Sodium	Antifreeze inhibitors, additive in some gasoline engine oils
Calcium	Detergent/dispersant additive
Magnesium	Detergent/dispersant additive
Phosphorus	Antiwear additive
Zinc	Antiwear additive
Barium	Detergent/dispersant additive

with an asphalt surface so fuel consumption becomes higher on concrete surface (Duong and Lee 2011). Bitumen and mineral filler materials in asphalt road surfaces contain different heavy metal species, including Cu, Zn, Cd and Pb (Winther and Slento 2010). Road abrasion is influenced by various factors: vehicle speed, climate, moistness of the road and type of asphalt and share of heavy-duty vehicles (Johansson and Burman 2006).

5.3 Deposition and Distribution of Heavy Metals in Various Environmental Components

The pathways of heavy metal transportation into the soil and water environment are dry and wet deposition processes and runoff water. Deposition takes place on any surface where particulate matter gets a chance to settle down. It settles down may be on exposed soil surface, water surface, plants or any physical material. Before deposition heavy metal-laden particles travel long distances due to particle size of the pollutant, wind direction and wind velocity (Reinirkens 1996; Barbosa and Hvitved-Jacobsen 1999). The relationship between the metal content of urban soils and distance from the roads has been widely investigated, and many studies have shown that metal concentrations decrease exponentially with the distance from roads. It is well documented that soil pollution by heavy metals is generally concentrated in the first few metres to tens of metres on either side of the road pavement and then sharply decreases with distance from the road (Motto et al. 1970; Harrison et al. 1985; Turer et al. 2001; Blok 2005; Li 2005). The degree of contamination of pollutants in an environment depends on factors such as site-specific pollution sources (i.e. industrial activities), the topography and the architectural design of the location (i.e. narrow roads, high density of high buildings, open spaces) and the presence and density of the surrounding vegetation (Chronopoulos et al. 1997). The following are the main factors which affect the heavy metal distribution in an urban environment:

1. Climatic and geographical factors
2. Road-related factors
3. Vehicle-related factor
4. Traffic-related factors

5.3.1 Climatic and Geographical Factors

Metrological conditions like wind velocity, wind direction, frequency and intensity of rainfall profiles, duration of fog conditions and morphology of the soil and vegetation cover have known to play their part in the dispersion of contaminants (Piron-Frenet et al. 1994; Melaku et al. 2008). Wind patterns strongly influences the spatial dispersal of heavy metal. Contamination usually declines within 20 m, and the pattern of decline is influenced by prevailing wind patterns (Haqus and Hameed 1986). In addition to point sources that spread metals within a restricted area, deposition of redistributed metals in soil and dust and long-range atmospheric transport of metals have led to increased soil metal concentrations in many urban areas today, including areas located away from major roads and industrial activities (Paterson et al. 1996; Ljung et al. 2006). Indeed, long-range atmospheric transport of metals has been recorded for the Eastern Mediterranean basin regions, derived from as far as the Northern Africa, Central and Western Europe and the Sahara Desert (Chester et al. 1996; Koulousaris et al. 2009). Rain washes out the atmospheric pollutants so that ultimately concentration of heavy metals also decreases in soil and atmosphere. Speed of rain and runoff water displaces the pollutants away from the highways. Rainwater also helps in leaching heavy metals in deeper soil. Winter and foggy condition concentrates vehicular emission near the sources, and dispersal of heavy metals is minimal. Transport rate and travel distance of metals increase substantially when they reach aquatic environments. In the terrestrial environment, metals can be localized in the soil, either close to the surface or deep below the surface, if pollution levels in the past exceeded those in the present.

Geographical condition of a region also contributes towards the dispersal of pollutants. In hilly areas dispersal is not very frequent due to mountain restrictions, but in desert-like condition, dispersal of pollutants increases. If there is vegetation cover along the highways and roads, then the dispersal and mobility of heavy metals are also restricted. The centre and inner side of city experiences ‘canyon’ effect of buildings, which has a direct influence on dilution and dispersion pathways of the heavy metals released from motor vehicles (Namdeo et al. 1999). Particles tend to fall out within the urban roadway ‘canyon’ resulting in higher heavy metal levels than found alongside motorways, where higher traffic densities are observed.

5.3.2 Road-Related Factors

Roadway factors affecting the pollution levels are carriage way width, lateral clearance, medians, shoulder width, smoothness and surface material of road, etc. As the road width increases, the manoeuvrability to movement of the vehicles will be increased, which results in the reduction of pollutants. Dividers reduce the obstruction caused by the opposing vehicles, which results in the reduction of number of accelerations and decelerations so that the fuel consumption will be minimized, thus reducing the emission levels of pollutants (Harrison et al. 1985; Wigington et al. 1986; Munch 1993). The road having more twist and turns and tunnels (mainly in hilly terrain) enhances the load of pollutants than the roads found in plain areas. The difference in tyre and road wear materials will be mainly associated with the difference in the road surface materials such as asphalt and concrete (Duong and Lee 2011). More tyre abrasion occurs when vehicles drive on a concrete highway than on an asphalt highway because the concrete surface is rougher than the asphalt surface. Also, the increased energy consumption of vehicles driving on a rough concrete highway versus an even asphalt highway could result in increased heavy metal concentrations in the road dust from the concrete highway.

5.3.3 Vehicle Factor

The age of the vehicle, its condition and servicing frequency, type of engine (2-stroke, 4-stroke), speed of vehicle and vehicle miles travelled come under the vehicle factor category. The older vehicles will emit more pollutants than a newer one, if they are not maintained properly. Vehicles with 4-stroke engine would produce lesser emissions than 2-stroke engine. Similarly, vehicles with catalytic converter will emit less pollutant. Most of the by-products of automobiles comprise of different fraction particles. These fractions include the ultrafine particles which are formed in the engines and tailpipes, fine particles produced mainly by chemical reactions and coarse particles which are formed mechanically by the abrasion of road materials, tyres and brake linings (Olukanni and Adebiyi 2012). Though the use of unleaded gasoline has caused a subsequent reduction in fuel emissions of Pb, it may still occur in exhaust gas and come from worn metal alloys in the engine (Snowdon and Birch 2004). The highly elevated concentrations of the heavy metals in road dust from the highways probably result from the influence of the high emissions from increased engine emissions and tyre and road abrasion by high-speed vehicles (Duong and Lee 2011).

5.3.4 Traffic Factor

Traffic factors such as traffic volume, traffic congestion, average speed of the flow, etc. come under this category. When the traffic volume is more, the greater vehicular load will lead to greater emissions of heavy metals from vehicles. The contamination of heavy metals especially Pb, Cd and Cu in roadside soil is related to the traffic density on the roads (Olajire and Ayodele 1997; Kartal 1992). The levels of nickel, cadmium, copper and zinc were also reported to correlate with traffic density (Fergusson et al. 1980; Thornton 1988; Narin et al. 1997; Narin and Soylak 1999). Traffic composition also contributes significantly to the pollution levels because emission rate varies for different types of vehicle. Hence, the same amount of traffic volume with different vehicular compositions produces different amounts of pollutants. Speed limits also affect the amount of pollution because faster drive consequently increases fuel burning. Therefore, introducing lower speed limits on motorways is expected to cut both fuel consumption and pollutant emissions. Therefore, one of the major reasons behind the high heavy metal levels within inner cities is the ‘stop-start’ pattern that is often observed. Changes in traffic flow patterns and congestion in specific inner city areas (roundabouts, traffic lights and junctions) result in the possible release of many heavy metals, both from combustion particles and the wear and tear of the vehicular component especially tyres, brake linings, etc. (Charlesworth et al. 2003; Ewen et al. 2009).

5.4 Impacts of Vehicular-Generated Heavy Metals on Urban Environment

Heavy metals emitted from various vehicular processes primarily get into the atmosphere, thus creating particulate air pollution like particles which are less than 10 micron metre and particles less than 2.5 micron metre and ultrafine particles less than 0.1 micron metre. These heavy metal-laden particulate matters react with other chemicals and form secondary air pollutants like smog. These particulate matters also influence the local weather and in winter season reduce the visibility. Contaminated street dust can potentially affect an urban air environment via resuspension in air. Road dust resuspension has proven to be one of the most important sources for airborne particulate trace metals in urban areas (Pereira et al. 2007). Dust-borne heavy metals accumulate in topsoil due to atmospheric deposition by sedimentation, impaction and interception and ultimately disturb the nutrient dynamics (Li et al. 2007; Lu et al. 2009). In general, influences between air and soil pollution are mutual. Just as the atmosphere can transfer a large amount of heavy metals into urban soils through precipitation (Ritter and Rinefierd 1983; Patel et al. 2001), soil dust can also contribute to the concentration of heavy metals in the air (Chen et al. 1997).

Excessive accumulation of heavy metals in soil may lead to elevated heavy metal uptake by crops, which in turn can affect food quality and safety (Muchuweti et al. 2006). On the soil, these pollutants can be transported to the aerial parts of vegetation (Wiseman et al. 2013). Some heavy metals are considered persistent bioaccumulative toxins and may be bioavailable in ecosystems (Basta et al. 2005). In the case where plants and animals are raised for human consumption, high levels of metal accumulation may pose health hazards to humans.

Sediment and dust transported and stored in the urban environment have the potential to provide considerable loadings of heavy metals to receiving water and waterbodies, particularly with changing environmental conditions (Morrison et al. 1990). There are only few measurements of pollution patterns in combination with leaching characteristics of highly polluted roadside soils (Li 2005; Hjortenkrans et al. 2008; Saeedi et al. 2012).

Due to the non-biodegradability and long half-lives that make heavy metals more persistent in the environment, their accumulation in the urban soil has a harmful effect on environmental quality including the biota and human beings in the long term (Zhuang et al. 2009). Heavy metals adhering to or absorbed by dust particles can enter the human body though through three main pathways (Ferreira-Baptista and De Miguel 2005; Shi et al. 2011):

- Ingestion of dust particles
- Inhalation of dust particles
- Dermal contact with dust particles

Pb, Cr, Zn, Cd and other toxic metals will continue to accumulate in urban environment due to their non-biodegradability and long residence time; thus they are known as ‘chemical time bombs’. In particular, more concern needs to be shown for children than adults because of their frequent hand-to-mouth activities, higher absorption rate from the digestion system and haemoglobin sensitivity to toxic metals (Meza-Figueroa et al. 2007; Zheng et al. 2010). Children daily ingest, on average, 50–200 mg of soil via hand-to-mouth behaviour (Calabrese et al. 1999; Oomen et al. 2003). Children and the elderly, whose immune systems are either underdeveloped or age compromised as well as the inadvertent ingestion of significant quantities of dust through hand-to-mouth pathways, are more vulnerable to toxicity (Rasmussen et al. 2001). Pollutants attached to surface dusts can be transferred to the surrounding aquatic environment with runoff and can cause a serious threat to the water environment and human health (Jartun et al. 2008; Zhao et al. 2011).

There are many published studies that have documented the adverse effects of lead in children and the adult population. In children, these studies have shown an association between blood level poisoning and diminished intelligence, lower intelligence quotient (IQ), delayed or impaired neurobehavioral development, decreased hearing acuity, speech and language handicaps, growth retardation, poor attention span and anti-social and diligent behaviours (Amodio-Cocchieri et al. 1996; Kaul et al. 1999; Litvak et al. 1998).

Cadmium, chromium and nickel compounds are classified as human carcinogens by several regulatory agencies. The International Agency for Research on Cancer and the US National Toxicology Program have concluded that there is adequate evidence that cadmium is a human carcinogen. Epidemiological investigations have reported respiratory cancers in workers occupationally exposed to Cr (VI)-containing compounds.

5.5 Conclusion

Vehicular emission is of the main source of heavy metal pollution in any urban environment. Heavy metals come out from vehicles via exhaust and non-exhaust sources. Heavy metals primarily get introduced in atmosphere and ultimately get deposited in various environmental components mainly via dry and wet deposition methods. The distribution and dispersion of heavy metals chiefly depends upon wind velocity, rain events and intensity of rain, humidity, topography and vegetation cover of an area, etc. In biological system heavy metals get accumulated via bioaccumulation and biomagnification processes. Contamination of air, water and soil system ultimately affects the human health and especially young children especially below 5 years of age. There is an urgent need for comprehensive epidemiological studies to show how heavy metals are affecting human's different functional systems and use this information in order to provide policy tools for air quality. It is also important to quantify the geogenic and anthropogenic contribution of heavy metals because there is still insufficient information about the differentiation between anthropogenic and geogenic dust particles.

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Chapter 6
Antioxidative Response of Water Macrophytes to Changes in the Living Environment During Vegetation Season: An Experimental Study

Tanja Maksimović, Dino Hasanagić, and Biljana Kukavica

Abstract The study investigated the changes in the antioxidative metabolism of the aquatic macrophytes (*Phragmites communis* Trin., *Utricularia vulgaris* L. and *Salvinia natans* (L.) All.) in the area of the Bardača ponds in order to determine the response of plants to different conditions in the living environment during one growing period (May–October). The studies included physicochemical analysis of water and determination of the activity of peroxidase, polyphenol oxidase, ascorbate peroxidase and catalase in the leaves of *Phragmites communis* Trin., *Utricularia vulgaris* L. and *Salvinia natans* (L.) All. The obtained results showed increased activity of peroxidase, catalase and polyphenol oxidase and decreased activity of ascorbate peroxidase with senescence in all three plant species. Changes in enzyme activity during the season did not show the same trend and varied significantly in relation to the investigated species. Also, it is important to emphasize that the investigations of antioxidative metabolism of selected plant species are among the first to be made in natural conditions and showed that the aquatic macrophytes represent good bioindicators of the aquatic habitat.

Keywords Antioxidative metabolism · *Phragmites communis* · *Utricularia vulgaris* · *Salvinia natans*

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6.1 Introduction

During the evolution, the aquatic macrophytes have adapted to life in the water environment, based on the fundamental changes in their vegetative organs, and in conformity with the specific gas, thermal and light regime of the water environment. The water environment provides some advantages over the air but also poses many difficulties related to oxygen deprivation (anaerobic conditions), weakened light and lack of mineral elements, as well as with the flow of water masses (Lukina and Smirnova 1988; Prasad et al. 2006; Rai 2009; Bornette and Puijalon 2011; Dar et al. 2014). With regard to this, water plants have developed various structural adaptations which are of crucial importance for their survival in the aquatic environment: the presence of aerenchyma, the development of threadlike or strip leaves, epistomatic leaves or complete absence of stomata, heterophilia and reduction of the root system as they uptake nutrients from the water with their entire surface (Lukina and Smirnova 1988; Stevanović and Janković 2001; Prasad et al. 2006).

As one of the leading primary producers, water macrophytes play a key role in biogeochemical cycling, providing food to all consumers in trophic chains (Prasad et al. 2006; Dar et al. 2014). They directly affect the hydrology and dynamics of freshwater ecosystem sediments on water flow (change or decrease in speed) and capture of particles or resuspension (Bornette and Puijalon 2011). Macrophytes are considered important components of an aquatic ecosystem not only as a food source for aquatic invertebrates but also because they act as efficient bioaccumulators and heavy metal bioindicators (Prasad et al. 2006; Rai 2009; Kumar et al. 2017, 2018). The water macrophytes can be successfully applied in the phytosanitation of water basins, whereby the physicochemical and biological characteristics of water are improved (Prasad et al. 2006). They also protect the coastline from erosion, stabilize it and, as sediments improve the appearance of the coastal part of the water basins (Krischik et al. 1997; Prasad et al. 2006), have antithermic and allelopathic effect (Szczepanska and Szczepanski 1973; Prasad et al. 2006). Because of all these key functions, aquatic plants are important indicators of the ecological status of aquatic ecosystems, so it is of great importance to preserve such communities in freshwaters (Bornette and Puijalon 2011; Dar et al. 2014). Given the very complex conditions of habitat, aquatic macrophytes need to develop mechanisms at the metabolic level that would allow them to survive under conditions of exposure to different types of stress (Bornette and Puijalon 2011).

As a result of the influence of different abiotic and biotic factors in aquatic ecosystems, oxidative stress occurs which represents an increased level of reactive oxygen species (ROS: superoxide anion radical ($O_2^{\cdot-}$), hydrogen peroxide (H_2O_2), hydroxyl radical ($^{\cdot}OH$), etc.). Oxidative stress leads to disturbance of the redox homeostasis in the cell, whereby the balance is shifted to oxidation processes. Such conditions in the cell lead to the oxidation of biologically important macromolecules, proteins, lipids and DNA, and impairment of their structure and function, which can even lead to cell death (Gill and Tuteja 2010; Karuppanapandian et al. 2011). Plant cells have developed a highly efficient antioxidative protection system composed of enzymatic and non-enzymatic components that control the ROS level in the cell and prevent macromolecule damage (Ellawala et al. 2011; Zaman and Asaeda 2013; Chalanika and Asaeda 2017). Enzymatic antioxidative metabolism consists of superoxide dismutase (SOD), catalase (CAT), peroxidase (POX), ascorbate peroxidase (APX) and ascorbate-glutathione cycle enzymes. The most important non-enzymatic components of plant cell antioxidative metabolism are ascorbate (ASC), glutathione (GSH) and phenolic compounds (PhOH) (Gill and Tuteja 2010; Karuppanapandian et al. 2011).

Class III Plant Peroxidases (POX; EC 1.11.1.7) are glycoproteins with heme prosthetic group involved in various metabolic processes. POX play a very important role in the growth and differentiation process, auxin catabolism, protein cross-linking in cell wall, oxidation of phenol in the cell wall lignification process, suberin synthesis in the process of senescence and antioxidative protection (Sánchez et al. 1995; Kukavica et al. 2007; Almagro et al. 2009; Dorantes and Zúñiga 2012; Veljović-Jovanović et al. 2018).

Catalase (CAT; EC 1.11.6) is a tetrameric heme enzyme that catalyses the degradation of H_2O_2 into H_2O and O_2 and is necessary for ROS detoxification during stress conditions (Gill and Tuteja 2010). Significant increase in CAT activity was observed in plants exposed to increased intensity of light, while other stress factors such as drought and heavy metals reduce its activity (Scandalios et al. 1997; Karuppanapandian, et al. 2011). Increased activity of CAT, SOD and POX was recorded by Hanfeng et al. (2010) with *Ceratophyllum demersum* grown in hydroponic conditions in which eutrophic conditions were imitated.

Ascorbate Peroxidase (APX, EC 1.11.1.11) belongs to Class I plant peroxidases and catalyses the ascorbate oxidation by hydrogen peroxide. It shows higher affinity for hydrogen peroxide than catalase indicating that these two enzymes belong to two different classes and that APX is involved in fine modulation of the hydrogen peroxide concentration, while the catalase is included in the elimination of increased H_2O_2 production during stress (Mittler 2002; Mittler and Poulos 2005).

Polyphenol oxidases (PPO, E.C. 1.10.3.2) are oxidoreductases that catalyse the oxidation of phenolic substrates by reacting directly with oxygen without cofactor. Polyphenol oxidases participate in the regulation of auxin levels in plant tissues. With senescence their activity increases (Kar and Mishra 1976; Durán and Esposito 2000; Dorantes and Zúñiga 2012; Ionită 2013). Constabel and Barbehenn (2008) reported that PPO plays a key role in biosynthesis of plant pigments and lignin and in defence reactions of plants to pathogens. The polyphenol oxidase activity also depends on the chemical environment such as oxygen level, phenols content and pH.

There is little information on the antioxidative response of macrophytes in natural conditions of habitat. Most of the studies dealt with monitoring the influence of temperature, different light regimes as well as competitive relationships that occur (Herb and Stefan 2006; Spencer and Rejmánek 2010; Bornette and Puijalon 2011; Dar et al. 2014).

Therefore, the research aim in this study was to monitor the changes in the antioxidative metabolism of aquatic macrophytes in the Bardača wetland area to determine the response of plants to different conditions of abiotic stress during the vegetation period (May–October). Three plant species were used for research: *Phragmites communis* Trin. as an emergent species, *Utricularia vulgaris* L. as submerged (unrooted) and *Salvinia natans* (L.) All. as floating (unrooted). The research included physicochemical water analysis and monitoring of enzymatic activity changes of peroxidases, polyphenol oxidases, ascorbate peroxidases and catalases as well as phenols content.

6.2 Study Area

Bardača is a complex of lakes positioned in the northern part of Bosnia and Herzegovina, (45° 6′ 6″ N, 17° 26′ 26″ E), located between the right bank of the Sava River and the left bank of the Vrbas River (Fig. 6.1). The geographical location of the Bardača area is at the centre of the moderate belt at about 100 m above sea level, at the foot of Mount Motajica. The lakes in this area were artificially created and are used primarily for the production of warm water fish species. On the World

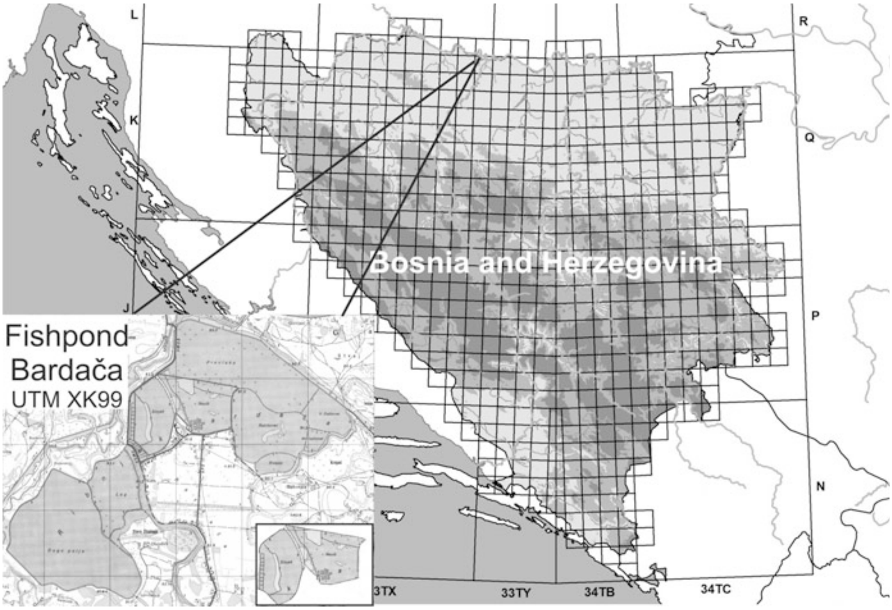

Fig. 6.1 MGRS (Military Grid Reference System) network with squares of 10 × 10 km and numerated squares 100 × 100 km in B&H. Map of Bardača fishpond (a detail from topographic map 1:25000, Nova Gradiška (Razboj-Ljevčanski) 4–4, Vojnogeografski institut, 1977 (eng. *Military Geographic Institute*))

Wetlands Day, 2 February 2007, under the Ramsar Convention, Bardača was selected for the list of the wetlands of international significance, which confirmed its international importance as an “Important Bird Area”. The macrophytes prevailing in this wetland are extremely important for migratory birds and aquatic fauna in general. The investigations were conducted at the following localities: *Necik* is located in the centre of the pond complex, with an area of 40 ha, with an average depth of 110 cm, while *Sinjak* encompasses the northernmost edge of the pond, with an area of 40 ha and average depth of 180 cm (Đurić et al. 2004).

6.3 Experimental Procedure

6.3.1 Physicochemical Water Analysis

The water and air temperature were determined by a mercury thermometer in the morning hours. Water transparency was determined by a Secchi disc. The oxygen concentration was determined using the Hach HQ30 flexi oximeter, and the pH metre Eutech Cyberscan PC 10 was used for pH value and electric conductivity and turbidimeter Eutech TN-100 to determine turbidity. Samples were always taken at the same profile points, and the measurements were done in a layer of water 30–50 cm below the surface. The samples were then transported on ice at a temperature of +4 °C, and within 24 h, their analysis was performed.

6.3.2 Preparation o0f the Plant Material for the Measurement of Enzyme Activities

To measure activities of POX, PPO, CAT and APX, fresh plant material was washed with distilled water, dried with paper towels, packed in aluminium bags, labelled and then placed in a container with liquid nitrogen. To determine the enzymatic activities, the plant material was first grounded to a powder in the liquid nitrogen. For the POX activity, the powdered plant material was extracted in 100 mM Na-phosphate buffer (pH 6.4) containing 1 mM PMSF (phenylmethanesulfonyl fluoride) and 0.1% TWEEN. The ratio of plant tissue/extraction buffer (w:v) used was different depending on the plant species (1 g: 4 mL for *Phragmites communis*; 1 g: 3 mL for *Utricularia vulgaris*; 1 g: 2 mL for *Salvinia natans*). To determine the polyphenol oxidase activity, 0.2 g of fresh plant material was extracted with 2 mL of buffer (100 mM Na-phosphate buffer (pH 6.4)). To determine CAT activity, plant material (1 g) was extracted in 4 mL buffer containing 50 mM Na-phosphate buffer pH 7 (4 mL), 0.2% TWEEN and 1 mM PMSF. To determine APX, plant material (0.5 g) was extracted in 4 mL buffer containing 50 mM Na-phosphate buffer (pH 7), 1 mM ascorbate, 1 mM EDTA and 1 mM PMSF. After homogenization with the buffer, the homogenates were centrifuged at 3000 rpm for 15 min, and the resulting supernatants were used for analyses of POX, PPO, CAT and APX activity.

6.3.3 Determination of POX Activity

Reaction mixture according to Teisseire and Guy (2000) with little modification was used for POX activity measuring. Total peroxidase activity in the soluble protein fraction was determined spectrophotometrically (Shimadzu UV-160, Kyoto, Japan), monitoring the absorbance increase at 430 nm for 3 min. The reaction mixture contained 100 mM Na-phosphate buffer pH -6.4, 17 mM pyrogallol and different sample volumes depending on plant species. Reaction was started by adding 4 mM H_2O_2. Activity of solPOX was expressed as the amount of purpurogallin, resulting product of POX reaction in $\mu mol \cdot mg_{prot}{}^{-1} \cdot min^{-1}$ using $\varepsilon = 12\ mM^{-1}\ cm^{-1}$ for purpurogallin.

6.3.4 Determination of PPO activity

PPO activity was determined spectrophotometrically measuring the absorbance increase at 420 nm (A_{420}, $\varepsilon = 12\ mM^{-1}\ cm^{-1}$) for 10 min. Reaction mixture contained 100 mM Na- phosphate buffer (pH 6.4), 6.67 mM pyrogallol and 100 µl of sample. PPO activity was expressed in $\mu mol \cdot mg_{prot}{}^{-1} \cdot min^{-1}$.

6.3.5 Determination of CAT Activity

CAT activity was measured according to modified method of Aebi (1984) spectrophotometrically measuring the absorbance decrease at 240 nm with hydrogen peroxide ($\varepsilon_{290} = 0.04\ mM^{-1}\ cm^{-1}$) as substrate. Reaction mixture contained 50 mM Na-phosphate buffer, pH 7, different sample volumes depending on plant species and 100 mM H_2O_2. CAT activity was expressed in $\mu mol \cdot mg_{prot}{}^{-1} \cdot min^{-1}$.

6.3.6 Determination of APX Activity

APX activity was determined according to Nacano and Asada (1981) by measuring absorbance decrease at 290 nm for 3 min with ascorbate as substrate ($\varepsilon_{290} = 2.8\ mM^{-1}\ cm^{-1}$). Reaction mixture contained 50 mM Na-phosphate buffer, pH 7, 500 mM EDTA, 0.5 mM ascorbate and different sample volumes depending on plant species. APX activity was expressed in $\mu mol \cdot mg_{prot}{}^{-1} \cdot min^{-1}$.

6.3.7 Determination of Total Phenols Content

To determine the total phenols, the leaves were extracted in 5 mL of 80% ethanol, after which the homogenate was centrifuged for 15 min at 3000 rpm and the resulting supernatant was used for further analysis. Total phenols content in extracts was determined spectrophotometrically (UV-VIS Shimadzu UV-160, Kyoto, Japan) by method of Singleton and Rossi (1965) with gallic acid (GA) used as standard. Total phenols content was expressed as equivalent gallic acid expressed on fresh weight of plant tissue (μg g^{-1} EGA FW).

6.3.8 Statistics Analysis of Study Work

All data were statistically processed in SPSS programme (Statistical Package for the Social Sciences). The analyses were conducted in three independent replicates, and the analysed parameters were processed by the analysis of variance analysis (ANOVA) of factorial assay, descriptive statistics and comparison of the obtained data. For comparison of results and testing of intergroup differences from ANOVA within the post hoc tests, LSD test was used for significance level $p < 0.05$. Values were expressed as the mean values ± standard error (SE).

6.4 Experimental Results

6.4.1 Physicochemical Water Analysis

In the experimental period, the water temperature values at the locality Necik in accordance with air temperature varied from 15.5 °C in October to 29.6 °C as recorded in July (Table 6.1). pH value oscillated from 7.62 in May to 8.28 in September, and in average the water was slightly alkaline. Electrical conductivity ranged from a minimum of 330 μS cm^{-1} in June to maximum 570 μS cm^{-1} in October, indicating a moderate load of water by dissolved ions.

In May, water was relatively rich in oxygen, and the highest decrease from 8.14 mg L^{-1} (May) to 3.36 mg L^{-1} was recorded in July and August. Also, in July and August, water due to intense oxidation of organic matter contained very little dissolved oxygen corresponding to saturation of only 44.4%. The highest turbidity was measured in September (95.3 NTU) when the lowest transparency (only 16 cm) was measured as well (Table 6.1).

Unlike the locality Necik pond, Sinjak pond had a slightly higher water temperature during the research period with the highest value measured in July (29.8 °C) and the lowest during October (15.6 °C). The Sinjak pond had a slightly lower pH of water during the research period, so the water was slightly alkaline (8.04). Electric conductivity ranged from a minimum of 291 and 325 μS cm^{-1} during the summer

Table 6.1 Physicochemical parameters of water in the studied localities (Necik and Sinjak)

Parameters	May	June	July	August	September	October
Locality Necik						
Air temperature (°C)	16.8	24.8	27.5	25.1	27.4	17.5
Water temperature (°C)	17.3	25.40	29.60	26.00	25.7	16.30
pH	7.62	7.70	7.68	7.64	8.28	8.00
Electrical conductivity (μS cm^{-1})	373	330	530	525	368	570
Turbidity (NTU)	10.07	64.00	58.20	60.5	95.30	42.30
Dissolved oxygen (mg L^{-1})	8.14	4.98	3.36	3.80	6.99	7.86
Saturation (%)	85.1	61.6	44.50	48.20	77.40	83.90
Transparency (cm)	56	30	25	23	16	18
Locality Sinjak						
Air temperature (°C)	15.2	25.4	27	27.5	28.1	17.3
Water temperature (°C)	17.6	26.60	29.80	28.1	26.70	15.6
pH	7.97	8.56	8.19	8.14	7.74	7.68
Electrical conductivity (μS) cm	522	407	339	325	291	326
Turbidity (NTU)	19.98	25.60	40.00	52.00	52.60	38.00
Dissolved oxygen (mg/L)	8.05	11.11	9.83	9.89	10.74	9.69
Saturation (%)	84.1	1433	131.6	130.0	136.1	99.7
Transparency (cm)	52	62	30	36	29	40

period to maximum during the spring (522 μS cm^{-1}). Oxygen content (Table 6.1) was higher at the beginning of the vegetation period (May–June), which is the result of intensive phytoplankton and macrophytic vegetation production, while the lower values were determined at the end of the vegetation period (August–September). Significantly lower transparency (29 cm) and increased water turbidity (52.6 NTU) at Sinjak pond were determined during August (Table 6.1).

6.4.2 *Activity of Soluble Peroxidases in Aquatic Macrophytes*

POX activity significantly varied depending on the plant species, locality and sampling period, as well as on different stress conditions that are result of sampling periodicity and other environment influences. Based on the results shown in Fig. 6.2, it can be seen that POX activity in the leaf of *Phragmites communis* at the locality Necik was the highest in May (29.96 μmol·mg_{prot}^{-1}·min^{-1}) and the lowest in July (13.78 μmol·mg_{prot}^{-1}·min^{-1}). Comparing the locality, POX activity was the highest at Sinjak and then at Necik (Fig. 6.2a, b), especially during the summer period. In relation to plant species, the highest POX activity was in the leaves of *Phragmites communis*, whereas significantly lower was recorded in *Utricularia vulgaris* and *Salvinia natans*. In *Salvinia natans* leaves at the locality Necik, POX activity was significantly lower compared to other investigated species (Fig. 6.2a).

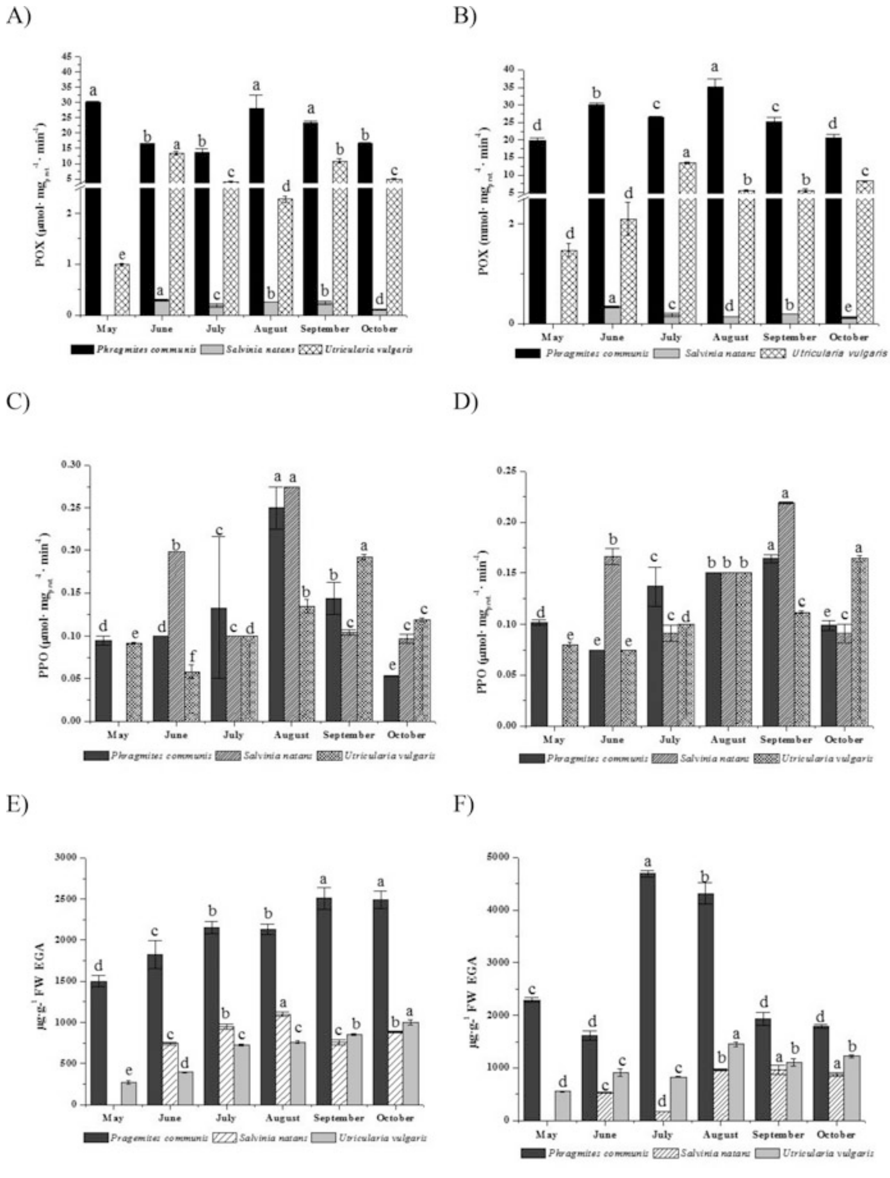

Fig. 6.2 The change in the activities of POX (**a**, **b**) and PPO (**c**, **d**) expressed in unit μmol · mg_{prot}^{-1} · min^{-1} and total phenols content in unit μg · g^{-1} FW in *Phragmites communis*, *Salvinia natans* and *Utricularia vulgaris* leaves at investigated localities: Necik (**a**, **c**, **e**) and Sinjak (**b**, **d**, **f**). The values are expressed as mean ± SE ($n = 3$). The different letters in each column show a statistically significant difference in the species for importance level $p < 0.05$

On Necik pond maximum POX activity in *Salvinia natans* was measured during June (0.29 μmol·mg_{prot}^{-1}·min^{-1}), while significantly lower was during October (0.113 μmol·mg_{prot}^{-1}·min^{-1}). POX activity in the tissue of *Utricularia vulgaris* at the locality Necik significantly changed during the investigated period. Maximum POX activity was measured in June (13.4 μmol·mg_{prot}^{-1}·min^{-1}) and September (10.86 μmol·mg_{prot}^{-1}·min^{-1}), while the minimum was recorded for May (0.99 μmol·mg_{prot}^{-1}·min^{-1}). On Sinjak pond POX activity in *Salvinia natans* and *Utricularia vulgaris* during the research period was negligibly lower compared to locality Necik (Fig. 6.2a, b).

6.4.3 Activity of Polyphenol Oxidases in Aquatic Macrophytes

In the leaf of *Phragmites communis*, PPO activities varied ranging from 0.053 to 0.25 μmol·mg_{prot}^{-1}·min^{-1}. The maximum of PPO activity was recorded in the period from July to September, while the beginning and the end of growing season were characterized by lower PPO activity. The same seasonal trend in PPO activity was noted at locality Sinjak, whereby it was higher on average (Fig. 6.2c, d).

Contrary to *Phragmites communis*, PPO activity in *Salvinia natans* tissue (Fig. 6.2c) was slightly lower. The higher PPO activity was observed at the locality Necik in relation to Sinjak (Fig. 6.2c, d). In the tissue of *Utricularia vulgaris*, PPO activity was significantly lower compared to other investigated species and varied in range from 0.058 to 0.192 μmol·mg_{prot}^{-1}·min^{-1}. PPO activity in the tissue of *Utricularia vulgaris* was significantly lower at the beginning of the vegetation period (May–July), and then a significant increase occurs compared to the beginning of the season in the period August–October.

6.4.4 Total Phenols Content

Figure 6.2e, f shows total phenols content in the leaf of *Phragmites communis.* Seasonal variations in phenols content as well as changes in locality were observed. At the pond Necik, content of total phenols ranged from 1500 to 2580 μg g^{-1} FW, with clear statistical differences noted during the research period, except in July and August. Total phenols content was the lowest in the period May–June, while the highest values were measured during September and October. The highest total phenols content in *Phragmites communis* leaves was measured during July and August at the locality Sinjak, which was on average by 50–54% higher in comparison to the same period at the locality Necik. However, at the end of vegetation period (September–October), by 25% lower total phenols content was measured in comparison to the same period at the locality Necik.

At locality Necik in *Salvinia natans* leaves during the research period, 1.3 times higher content of total phenols was determined in comparison to Sinjak. The highest total phenols content in *Salvinia natans* leaves was measured during July (945 μg g^{-1} FW) and August (1100 μg g^{-1}) and the lowest in June (743.33 μg g^{-1} FW) and September (756.66 μg g^{-1} FW). Total phenols content at locality Sinjak was the highest in August (968.33 μg g^{-1} FW), while the lowest content was measured in June (528.33 μg g^{-1} FW), which was also recorded for locality Necik.

Total phenols content in the *Utricularia vulgaris* tissue at locality Necik (Fig. 6.2e) significantly varied during the research period, whereby the measured values ranged from 268.33 to 1001 μg g^{-1} FW. At the locality Necik during the research period in the tissue of *Utricularia vulgaris*, lower total phenols content was obtained, on average by 34% compared to the same locality Sinjak. At the end of the vegetation period (August–October), the highest total phenols concentrations were measured in the tissue of *Utricularia vulgaris*. In relation to species, total phenols content on average was the highest in *Phragmites communis* followed by *Utricularia vulgaris* and then *Salvinia natans* (Fig. 6.2e, f).

6.4.5 Catalase Activity in Aquatic Macrophytes

Catalase activity in the leaves of *Phragmites communis* depended on sampling period, so the lowest activity was measured in May (61.33 $\mu mol \cdot mg_{prot}^{-1} \cdot min^{-1}$) and the highest in July and September (1713 $\mu mol \cdot mg_{prot}^{-1} \cdot min^{-1}$) at locality Necik. Catalase activity in *P. communis* leaves at the locality Necik during the research period was by 40% lower in comparison to the pond Sinjak. So, the highest CAT activity in the *P. communis* leaves at the locality Sinjak was measured in July (1708 $\mu mol \cdot mg_{prot}^{-1} \cdot min^{-1}$) and September (3955 $\mu mol \cdot mg_{prot}^{-1} \cdot min^{-1}$) and the lowest in June (121 $\mu mol \cdot mg_{prot}^{-1} \cdot min^{-1}$) and May (144 $\mu mol \cdot mg_{prot}^{-1} \cdot min^{-1}$) (Fig. 6.3a).

Figure 6.3a shows the CAT activity in the leaves of *Salvinia natans*, where it can be noted that the lowest activity was measured in July (20.33 $\mu mol \cdot mg_{prot}^{-1} \cdot min^{-1}$) and the highest in August (55.66 $\mu mol \cdot mg_{prot}^{-1} \cdot min^{-1}$) and September (86.40 $\mu mol \cdot mg_{prot}^{-1} \cdot min^{-1}$), while significant decline was recorded with senescence (October) at Necik locality. At locality Sinjak CAT activity was slightly lower in comparison to the locality Necik. In the tissue of *Utricularia vulgaris*, CAT activity was lower in comparison to other investigated species at both investigated localities. In relation to the research period, CAT activity in the tissue of *Utricularia vulgaris* significantly varied, so that the lowest was recorded at the beginning of the vegetation period (May–June), maximum during September, and significant decline of activity was determined during October. Catalase activity in the tissue of investigated macrophyte species was higher on average at the locality Necik in comparison to Sinjak (Fig. 6.3a, b).

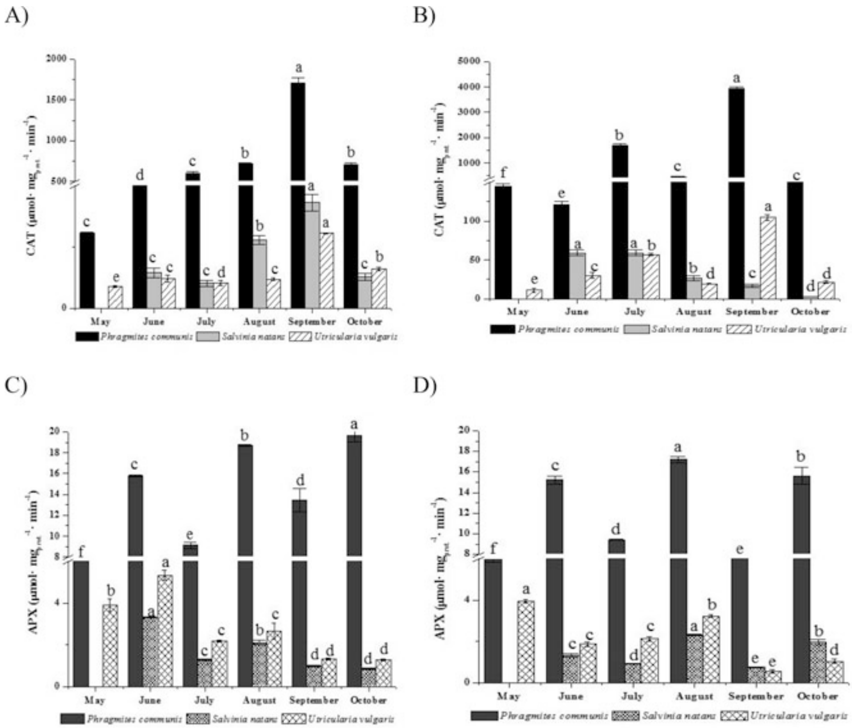

Fig. 6.3 Change in activities of CAT (**a**, **b**) and APX (**c**, **d**) expressed in unit $\mu mol \cdot mg_{prot}{}^{-1} \cdot min^{-1}$ in *Phragmites communis*, *Salvinia natans* and *Utricularia vulgaris* leaves at investigated localities (Necik-**a**, **c** and Sinjak-**b**, **d**). The values were expressed as mean ± SE ($n = 3$). The different letters in each column show a statistically significant difference for the species for importance level $p < 0.05$

6.4.6 Activity of Ascorbate Peroxidase (APX) in Aquatic Macrophytes

From the results presented in Fig. 6.3c, d, it can be seen that activity of the ascorbate peroxidase (APX) in *Phragmites communis* varied during the vegetation period and depending on the locality. APX activity varied in range from 6 to 19.65 $\mu mol \cdot mg_{prot}{}^{-1} \cdot min^{-1}$, whereby the lowest activity was determined during May and July and the highest during August and October on both investigated localities. Higher APX activity, on average, was determined in the leaves of *Phragmites communis* taken from the locality Necik in comparison to Sinjak.

Ascorbate peroxidase activity in *Salvinia natans* tissue was highest in June (3.31 $\mu mol \cdot mg_{prot}{}^{-1} \cdot min^{-1}$), followed by a slight drop during July, while for the end of the vegetation period (September–October), significantly lower activity was measured (Fig. 6.3c). The activity of the APX during the investigated period was on average 87% lower compared to activity in *Phragmites communis* and by 43%

compared to *Utricularia vulgaris*. The APX activity at the locality Sinjak (Fig. 6.3d) during the vegetation period was on average 15% lower compared to the locality Necik, with similar seasonal trend.

In the tissue of *Utricularia vulgaris* (Fig. 6.3c), the highest APX activity at the locality Necik was measured at the beginning of season, during May and June (5.34 $\mu mol \cdot mg_{prot}{}^{-1} \cdot min^{-1}$), with significant decline recorded in September (1.31 $\mu mol \cdot mg_{prot}{}^{-1} \cdot min^{-1}$) and October (1.29 $\mu mol \cdot mg_{prot}{}^{-1} \cdot min^{-1}$). The activity of APX during the investigated period in all three investigated macrophytic species was higher on the locality Necik compared to Sinjak.

6.5 Discussion

Aquatic ecosystems in recent times decreasingly retain their natural characteristics and increasingly become burdened by various types of waste substances (Marchand et al. 2010). As a consequence the disturbances of the biological balance, the mass development of phytoplankton, the light regime disorders and changes in water chemism take place, which all together directly affect the tempo and the intensity of fish growth as well as the entire aquatic ecosystem (Bornette and Puijalon 2011). Aquatic macrophytes adjust to high light intensity conditions by modifying their morphological properties and metabolism (Gong et al. 2011). Consequently, plants growing in such habitats show significant differences in the anatomic characteristics and carbon metabolism (Gong et al. 2011). Elevated temperature, over optimal level, induces irreversible damage to plants changing plant growth and development (Chalanika and Aseda 2017). High water temperature can mostly affect the submerged macrophytes, whereby the intensity of temperature change determines the severity of the consequences (Smolders et al. 2006; Bornette and Puijalon 2011; Ellawala et al. 2011; Zaman and Asaeda 2013; Dar et al. 2014).

Our results indicate that high temperatures measured during the summer period probably caused the increase of POX, PPO and APX activity as a reaction to heat stress (Figs. 6.2 and 6.3). Chalanika and Aseda (2017) have shown on several aquatic plants that temperature increase (30–35 °C) was followed by a rise of H_2O_2 level and CAT and APX activities in comparison to control. Changes in temperature, as one of the most important physical characteristics of water, play an important role, because it also affects other parameters, causing the minimum of oxygen content in summer at the locality Necik (Table 6.1). High saturation of oxygen during the entire vegetation period was found for the locality Sinjak. The autumn minimum in the oxygen content (Table 6.1) is probably the result of intensive processes of degradation of the produced biomass and the consequence of a targeted water release, in order to be able to perform the autumn fishing.

Finally, it can be stated that the water of the Bardača wetland is characterized by a favourable oxygen regime, medium mineralization, mild alkalinity, increased turbidity, decreased transparency at the end of the season and elevated temperature up to 30 °C in the summer period.

6.5.1 Peroxidase Activities

Plant peroxidases are involved in a large number of metabolic processes (Sánchez et al. 1995; Kukavica et al. 2007; Almagro et al. 2009; Dorantes and Zúñiga 2012; Kumar et al. 2016) and along with catalase are very important enzymatic antioxidants that participate in eliminating and releasing cells from excess peroxide produced in normal metabolic processes and stress conditions (Veljović-Jovanović et al. 2018). Changes in peroxidase activity occur as response to different types of abiotic and biotic stress: exposure to pathogens and chemical agents (heavy metals, herbicides), increased intensity of light and mechanical injuries (Sprechner et al. 1993; Cipollini 1997; Xiang et al. 2012). Different types of stress have a different effect on POX activity, but plant species has also a great influence, whereby the activity may vary depending on the stress factor as well as its duration (Dorantes and Zúñiga 2012; Alfadul and Al-Fredan 2013), which was demonstrated in our paper as well. Some researches (Dorantes and Zúñiga 2012; Alfadul and Al-Fredan 2013) confirmed that younger leaves had lower POX activity, and in the more mature, especially during the reproductive phase, activity increased (July–August–September), so POX can be considered as maturation indicator, i.e. the lignification was followed by an increase in peroxidase activity. According to our research, it can be said that the POX activity varied significantly during the season, but these differences were more pronounced in relation to the species (Fig. 6.2). It is likely that high temperature (July–August) and increased illumination, pronounced eutrophication, activated antioxidative enzymes and their combined functions contributed to the elimination of H_2O_2 generated during stress and mitigated the oxidative damage caused by heat and light stress. Our results indicate that POX activity is probably associated with hydrogen peroxide accumulation especially in high-temperature conditions and intensive illumination, which was particularly pronounced during the summer period (August) when the highest POX activities were registered. Based on the data from the literature (Antonielli et al. 2002), we can assume that *Phragmites communis* in the conditions of increased temperature and intensity of light shifts from C_4 to C_3 metabolism, and as a result thereof, the defence mechanisms are activated that induce increased activity of the antioxidative metabolism enzyme (Figs. 6.2 and 6.3).

Based on the obtained results, we can say that POX activities in *Salvinia natans* during the investigation period were significantly lower in the older compared to the younger leaves. It is known that peroxidases also participate in the auxin catabolism, responsible for plant growth (Apel and Hirt 2004; Passardi et al. 2005). Increased POX activity in *Salvinia natans* at the beginning of the season can be considered as one of the ways of this enzyme's participation in managing plant growth processes. Changes in peroxidase activity during the season are likely to result from various environmental influences as well as morpho-anatomic characteristics of the same species (Lizieri et al. 2012). Given the fact that it is a floating plant that is constantly exposed to various stress impacts (light, high temperatures, flows, air pollutants, pathogens, herbicides), each of these factors can directly or indirectly, depending on the length of exposure, impact the change in activity of the investigate enzymes. Peroxidase activity in the tissue of *Utricularia vulgaris* significantly varied during the season, which is probably a consequence of the development phase but also of the effects of various stress factors. It is believed that various mechanical stimuli may induce changes in POX activity, as shown in the paper of Cipollini (1997). Given the fact that submerged plants are constantly exposed to flow of water masses (Stevanović and Janković 2001), it can be assumed that very often their injuring happens and that they are exposed to pathogen attack (Minibayeva et al. 2015). With the appearance of damage on plants, there is induction of activities of peroxidases that participate in lignin construction and in mechanical strengthening of cell wall around the injury (Almagro et al. 2009). We also observed an increase in peroxidase activity along with the high content of phenols in older leaves, indicating possible correlation between lignification of cell walls during maturation and POX activities (Fig. 6.2) (Cevahir et al. 2004: Myriam et al. 2009).

In addition to the role in lignification and suberization, peroxidases play an important role in eliminating apoplastic and intracellular H_2O_2. Furthermore, most of the soluble phenols and peroxidases within the cell wall are placed in vacuoles (Takahama 2004). Also the vacuole has transporters for ascorbate and hydrogen peroxide. Apoplastic and vacuolar POX in POX/phenol/ascorbate system remove excess peroxide under conditions of disturbed cellular redox homeostasis (Takahama 2004; Haque et al. 2014; Lee et al. 2007; Minibayeva et al. 2015; Veljović-Jovanović et al. 2018).

Results obtained in this paper have shown that the highest peroxidase activity was observed in *Phragmites communis* followed by *Utricularia vulgaris* and *Salvinia natans.*

6.5.2 Polyphenol Oxidase Activities

Polyphenol oxidases catalyse the oxidation of aromatic (especially phenols) and inorganic substrates while simultaneously reducing oxygen concentration in water and have an important application in reducing toxicity in wastewater (Dorantes and Zúñiga 2012). The role of PPO in the response of plants to different types of abiotic stress was demonstrated (Sofo et al. 2005; Lee et al. 2007; Haque et al. 2014).

Increased PPO activity under drought conditions is associated with its role in protein preservation and ROS removal (Veljović-Jovanović et al. 2008). It is assumed that polyphenol oxidases participate in the regulation of auxin levels in plant tissues (Dorantes and Zúñiga 2012). With senescence their activity increases. Activity of polyphenol oxidases also depends on the chemical environment such as the level of oxygen, phenols and pH (Constabel and Barbehenn 2008). In our study, the activity of PPO in all three investigated macrophytic species was high during August and September, while the significantly lower activity was measured in May and June (Fig. 6.2). Ionită (2013) in his research states that changes in PPO activity depend on temperature. The same author also states that the PPO activity depends on the plant species and that the PPO activity increases with increase of temperature to a certain limit and then decreases due to protein denaturation (already at 40 °C). A significant increase in PPO activity during the summer period can be associated with the measured higher temperatures in that period (expressed arid period). Such seasonal activity can also be associated with phenols synthesis as well as with the senescence process (Kar and Mishra 1976). In their research, Kar and Mishra (1976), in the leaves of *Oryza sativa*, determined an increase in activity of peroxidase and polyphenol oxidase and reduction of catalase activity with senescence, which was consistent with the results obtained in our paper. Given that they are predominantly localized in chloroplasts and their phenolic substrates are accumulated in vacuoles, they are directly involved in pseudo-cyclic electron transport processes (Mehler reaction) (Vaugh and Duke 1984; Constabel and Barbehenn 2008). Hence, increased PPO activities at the end of the vegetation period (September) can be interpreted as the consequence of the senescence process, intensive phenols synthesis and intensified oxidation processes (Thipyapong et al. 2004). Also, in the paper of Thipyapong et al. (2007), authors assumed that the products generated in reactions catalysed with PPO induce cell death and help redistribute nutrients to younger tissues. Our results have shown that PPO activity in the tissue of *Salvinia natans* was increased compared to *Phragmites communis* and *Utricularia vulgaris* (Fig. 6.2). The reason for that may be in different influences of abiotic factors. Likewise, polyphenol oxidases are considered to be defensive proteins in plants, and their increased activity during the research period can be the plant response to pathogenic and mechanical damage (wind, lawnmowers) (Vaugh and Duke 1984; Constabel and Barbehenn 2008).

6.5.3 Total Phenols Content

Given that the aqueous environment is a complex medium, aquatic macrophytes have developed different strategies and adaptations to stress factors, one of which is the production of bioactive secondary metabolites, i.e. phenolic compounds (Dorantes and Zúñiga 2012). Phenols biosynthesis and accumulation are controlled endogenously during growth (Strack 1997) or regulated by exogenous factors such as light, temperature, heavy metals and other stress factors (Dixon and Paiva 1995). It has been proven that phenolic compounds form an integral part of the cell wall structure, mainly as polymers (lignin) (Michalak 2005; Balcerek et al. 2009), and since lignification is more pronounced with senescence, it is probably one of the reasons for increased phenols biosynthesis at the end of the season. According to some researches total phenols content ranged from 0.1 to 8.2 mg g^{-1} FW (Johnson et al. 2008; Balcerek et al. 2009). The authors pointed out that plants with higher total phenols content have better potential for higher antioxidative activity, which can be related to our results.

Increase of phenols content with senescence indicates that these compounds can be associated with the lignification process, i.e. cross-linking of phenol components (ferulic and coumaric acid) in the cell wall (Maksimović-Dragišić et al. 2008). At both investigated sites, the maximum values of phenols content were determined at the end of the vegetation period, whereby it is noted that the higher values of total phenols were measured at locality Sinjak for *Phragmites communis* and *Utricularia vulgaris*, while for *Salvinia natans*, higher content was determined on basin Necik (Fig. 6.2). Wastewaters originating from agriculture, settlements and industry are characterized by higher phenols content (Meikap and Rot 1997), so the increased phenols concentrations at the locality Sinjak are likely the result of the wastewater inflow from surrounding agricultural land and settlements.

Total phenols content in *Salvinia natans* (Fig. 6.2) varied from 173 to 1100 μg g^{-1} FW, whereby maximum values on both localities were measured during the period August–September. In this period, maximum activities of PPO and POX were also recorded, and their activity is known to increase with increase of phenol concentrations and enhanced oxidative processes (Thipyapong et al. 2004). In the leaves of *Oryza sativa*, Kar and Mishra (1976) also determined the increase of phenols content during senescence, which was in accordance with the results obtained in this paper. Since it has been found that phenols primarily accumulate in vacuoles (Lattanzio et al. 2012), the increase in the phenols content with senescence is the result of proteolytic processes due to which the release of phenolic acids and phenols from the vacuoles occur (Kar and Mishra 1976), which can be linked with the results obtained in our paper. According to the research results of Đurđević (2000), the total phenols concentration for *Salvinia natans* was 17.5 mg/g, which was significantly lower compared to determined values in this paper.

Seasonal variations in total phenols content in *Utricularia vulgaris* were identical as with *Phragmites communis* and *Salvinia natans*, i.e. the lowest at the beginning, and the highest values were recorded at the end of the vegetation period September–October (Fig. 6.2). The highest phenols content at the end of the vegetation period could be explained by the processes of senescence, growth slowing, inhibition of auxin synthesis and increased synthesis of phenols (Lattanzio et al. 2012).

Phenolic compounds due to their structure can directly remove the reactive oxygen species and are synthesized in the response of plants to different types of biotic and abiotic stress (Takahama 2004; Thipyapong et al. 2004; Michalak 2005; Balcerek et al. 2009). Additionally, phenols are POX substrates, and increased POX activity, phenols substrate consumption and lignification can occur with senescence (Veljović-Jovanović et al. 2018).

In aquatic ecosystems, primarily of the lake and pond type, allelopathic relations between submerged and floating macrophytes as well as submerged plants and phytoplankton are very pronounced due to their competitive light and C source relations (Leu et al. 2002), which is probably expressed also in investigated species in this paper. So, *Myriophyllum spicatum* with strong allelopathic potential attributed to the content of polyphenolic compounds (up to 10%) can inhibit growth of *Potamogeton lucens* and *Ceratophyllum demersum* (Hilt and Gross 2008). Research by Leu et al. (2002) indicate that the presence of polyphenols and allelopathic active secondary metabolites, with *Myriophyllum spicatum*, inhibits PS II activity and decreases the photosynthesis intensity of cyanobacteria and spinach. It is possible that allelopathic relationships between submerged and floating plants have disturbed their physiological and biochemical mechanisms in this paper as well.

6.5.4 Catalase

Changes in catalase activity are different depending on plant species, stress type and stress intensity (Fig. 6.3). It is important to note that CAT is extremely sensitive to stress conditions (such as increased light, salinity, drought and heavy metals) which reduce the level of protein exchange and thereby reduce CAT activity (Karuppanapandian et al. 2011). Reduction of CAT activity can limit plant tolerance to stress from the outside environment.

Increased CAT activity in all investigated macrophytic species was recorded during September, while in relation to species, the highest was determined in cane. Kar and Mishra (1976) stated a decrease of CAT activity and increase of POX and PPO activities in the leaves of *Oryza sativa* with senescence. In our paper, the CAT activity in *Phragmites communis* leaves was at maximum during September, with a drastic drop of 94% recorded in October. Catalase plays an important role in removal of H_2O_2 produced in photorespiration especially under conditions when the plant is exposed to some abiotic stress such as drought (Sofo et al. 2015). On the other hand with senescence, by shutting down the basic function of peroxisome (photorespiration), CAT disappears, becoming a target of protease activity in peroxisomes (Sandalio et al. 2009). In stress conditions, the catalase tetrameric molecules are degraded to monomeric, acting as peroxidase, and the reduction of activity may be due to high consumption and inactivation of the enzyme itself (Agraval and Mishra 2009).

The results obtained in this paper for CAT activity changes may also be related to changes in water levels during the study period. Xiang et al. (2012) determined the increase of CAT and POX activity in *Phragmites communis* with drop in water levels, indicating that enzymes were involved in plant response to droughts and water stress. The lowest catalase activity was measured in the tissue of *Salvinia natans*, which was directly exposed to increased intensity of light and temperature. It is known that CAT is extremely sensitive to increased light and has a faster exchange, similar to D1 protein exchange in PSII (Karuppanapandian et al. 2011). This may be the result of light absorption by heme group or may be due to inactivation with H_2O_2. However, the stress conditions that decrease the level of protein exchange, such as salinity, drought and heavy metals, reduce the CAT activity (Karuppanapandian et al. 2011). Reduction of CAT activity can limit plant tolerance to stress from the outside environment.

Based on obtained results, it was determined that younger leaves of *Utricularia vulgaris* had lower CAT activity compared to older ones. Jana and Choundri (1980) came to similar results in submerged plants *Vallisneria spiralis* and *Hydrilla verticillata*. Decrease of CAT activity (October) in *Utricularia vulgaris* can be taken as an important indicator of senescence. Increase of CAT, SOD and POX activity was recorded by Hanfeng et al. (2010) in *Ceratophyllum demersum* grown in hydroponic conditions in which eutrophic conditions are imitated. The authors assume that *Ceratophyllum demersum* is adapted morphologically and anatomically in eutrophication-induced stress conditions, so with the duration of stress, the decrease of antioxidative defence enzyme activity has been recorded. Hanfeng et al. (2010) found that at the time of increasing trophic levels, there is an increased formation of aerenchyma forming the cavity, indicating the possible response of submerged plants to eutrophication stress. Therefore, we can assume that one of the reasons for the changes in the activity of antioxidative enzymes (CAT and POX) in our paper during August–September may be the intensification of the eutrophication process.

Increased CAT activity in all investigated species was recorded during September, and during this period, low APX activity was recorded. When one component of the antioxidative system becomes limiting, some other component will compensate and increase activity. Increased CAT activity, therefore, may be the compensation of the relatively low APX activity due to the increased H_2O_2 level.

6.5.5 Ascorbate Peroxidase

APX has a higher affinity for H_2O_2 than CAT and POX and may play a more important role in controlling ROS levels under stress conditions (Veljović-Jovanović 1998; Gill and Tuteja 2010). Increased APX expression in plants is shown in conditions of various types of stress such as pathogen attack, mechanical damage, UVB radiation, anoxia, increased salt concentration, excess energy, low or too high temperature, heavy metals, lack of mineral salts and herbicides (Rizhsky et al. 2002; Dabrowska et al. 2007).

The results obtained in this paper show that APX activity in *Phragmites communis* significantly varied during the season and in relation to the place of sampling (Fig. 6.3). The maximum activity on both investigated sites was registered during August and October and minimal during May (Fig. 6.3). Song et al. (2012) stated the increase of SOD, CAT and APX activity level in different ecotypes of *Phragmites communis* under high temperature-induced stress conditions (30–50 °C). During August air temperature at the investigated locality was 37.7 °C, and the water temperature ranged from 26 to 28 °C (Table 6.1), so it can be assumed that the high temperature activated antioxidative enzymes and their combined functions contributed to removal of increased H_2O_2 concentrations. In that period, the *Phragmites communis* also reacted to the drop in water levels, by targeted drainage for fishing in basins at the end of the vegetation period (October). Also, APX activity during the season in *Salvinia natans* was by 87% lower compared to *Phragmites communis* and by 38–43% lower compared to *Utricularia vulgaris*. Higher APX activity in *Salvinia natans* and *Utricularia vulgaris* (Fig. 6.3) during June and August in comparison to significantly lower APX activity during September and October is probably the consequence of changes in the content of ascorbates as substrate (Dabrowska et al.

2007; Caverzan et al. 2012; Anjum et al. 2016). Previous studies have shown that increased APX activity is associated with endogenous growth and transition from vegetative to reproductive state. During these changes it has been found that the ascorbate content increases and the indoleacetic acid content decreases and that this tendency is maintained during differentiation (Caverzan et al. 2012), which may be one of the reasons for changes in APX activity during the season in *Salvinia natans* and *Utricularia vulgaris* leaves. Also, the redox state of the cell changes with senescence, and there is more oxidized than reduced ascorbate (Dabrowska et al. 2007; Caverzan et al. 2012; Anjum et al. 2016), so it is possible that with senescence there is smaller APX activity in *Salvinia natans* and *Utricularia vulgaris.*

6.6 Conclusion

Our study showed that POX and APX activities in the investigated macrophytes declined in the following order: *Salvinia natans* > *Utricularia vulgaris* > *Phragmites communis.* For PPO and CAT activities, the order of activities was somewhat different: >*Phragmites communis* > *Salvinia natans* > *Utricularia vulgaris.* All tested parameters were the most expressed in the leaves of emersed species *Phragmites communis* in comparison with another two examined species during all months. The obtained results on different activation trends of POX, CAT, PPO and APX during the season, between emerged, submerged and floating plants and on different localities, indicate different response mechanisms to stress in investigated plant species. Also our results indicate that water quality is a key determinant of their persistence and survival. Plants that have the ability to remove and/or control the ROS level may be useful in the future to overcome the stress conditions coming from the environment.

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Chapter 7
Application of Grace Satellite Data for Assessment of Groundwater Resources in Central Ganga Alluvial Plain, Northern India

Anjali Singh and Ashwani Raju

Abstract Gravity Recovery and Climate Experiment (GRACE) is very unique to observe changes in distribution of land water storage from plant canopy to the aquifer. GRACE data gives idea about the regional changes in stored water. The groundwater withdrawal from aquifers in the entire state of Uttar Pradesh with an emphasis on the Lucknow district was studied with the help of the GRACE data and simulated soil moisture (SM) from Global Land Data Assimilation System (GLDAS). The time-series analysis of Lucknow district indicates declining trend of groundwater with mean depletion rate of 1.46 ± 0.74 cm/year. The rest of the parameters like soil moisture, rainfall, and terrestrial water storage do not show continuously declining trend. This indicates groundwater extraction at a faster rate than its recharge. To visualize the seasonal changes in groundwater storage of Uttar Pradesh from 2003 to 2012; pre-monsoon, monsoon, and post-monsoon maps were generated, to represent the overall decreasing trend. The average volumetric groundwater storage loss for the Lucknow district was found to be 0.37 km^3. A positive correlation was found between GRACE-derived results and observed water-level data of CGWB (Central Ground Water Board). It is evident from the results that remote sensing is an effective tool to interpolate observed regional groundwater data of wells and to improve estimations of groundwater storage.

Keywords Groundwater · GLDAS · GRACE · Satellite data · Uttar Pradesh

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7.1 Introduction

India is the largest groundwater consumer country with an estimated annual extraction exceeding 230 km^3 from a total of 396 km^3 utilizable dynamic fresh groundwater resources (Chinnasamy et al. 2013). Increasing urbanization sets immense pressure on the groundwater resources to supply the demands of increasing users (Kumar et al. 2018). Due to progressive growth rate of infrastructure and economic development of country, the per capita water availability in India has declined from 5176 m^3 in 1951 to 1703 m^3 in 2005 (Central Water Commission 2005).Water, climate, geology, and certain hydrological conditions are the potential parameters that control the replenishment of groundwater resources. New urban expansions, agricultural and severe industrial activities, and global and regional climate changes have stressed the hydrological cycle. Due to overexploitation, groundwater resources are getting depleted day by day. In Northern India, overexploitation of groundwater has triggered continuously lowering water table (Tiwari et al. 2009).

Currently many government organizations are monitoring groundwater resources across India. Their instrumentation errors, maintenance, project costs, and spatial and temporal gaps point fingers to low-frequency and unreliable data. Satellite-based observational techniques allow direct monitoring of regional variations in stored water leading to more precise estimation of groundwater resources (Rodell et al. 2009). Present approach studies temporal datasets of Gravity Recovery and Climate Experiment (GRACE)/Global Land Data Assimilation System (GLDAS) to estimate the fluctuations in terrestrial water storage and soil moisture for estimation of change in mass groundwater storage due to groundwater withdrawal from aquifers in the entire state of Uttar Pradesh.

7.2 Primary and Secondary Data Used for Estimation of Groundwater Storage Change

The data used in present study was collected from the GRACE satellite mission launched on 17 March 2002 as a joint collaboration of NASA and the German Space Agency and from GLDAS. GRACE is the first satellite remote sensing mission directly applicable for regional groundwater mapping (Rodell et al. 2006). GRACE mission provides data of approximate changes in terrestrial water storage on the basis of Earth's global gravity field.

CSR (University of Texas Center for Space Research), GFZ (Geo-Forschungs Zentrum Potsdam), and JPL (Jet Propulsion Laboratory) release processed monthly results of GRACE data. This data can be accessed online (http://gracetellus.jpl.nasa.gov/data/) (Landerer and Swenson 2012). Processed monthly results of GLDAS, released by NASA Goddard Space Flight Center, were downloaded for the present study from Mirador (http://disc.sci.gsfc.nasa.gov/hydrology/data-holdings). The details of various primary and secondary datasets used are presented in Table 7.1.

Table 7.1 Description of sources of primary and secondary datasets

Dataset	Units	Spatial resolution	Observation period	Source
Terrestrial water storage				
JPL RL05L and data product	EWT (cm)	1°	Jan 2003–Dec 2012	GRACE-Tellus
Soil moisture				
GLDAS-2.0 NOAH model	Kg/m^2 (mm)	1°	Jan 2003–Dec 2012	GIOVANNI-GLDAS
Precipitation				
GLDAS-1 CLM model	Centimeters	1°	Jan 2003–Dec 2012	GIOVANNI-GLDAS
In situ well data				
Water-level data	Meters	Point data	May, Nov (2005–2011)	CGWB

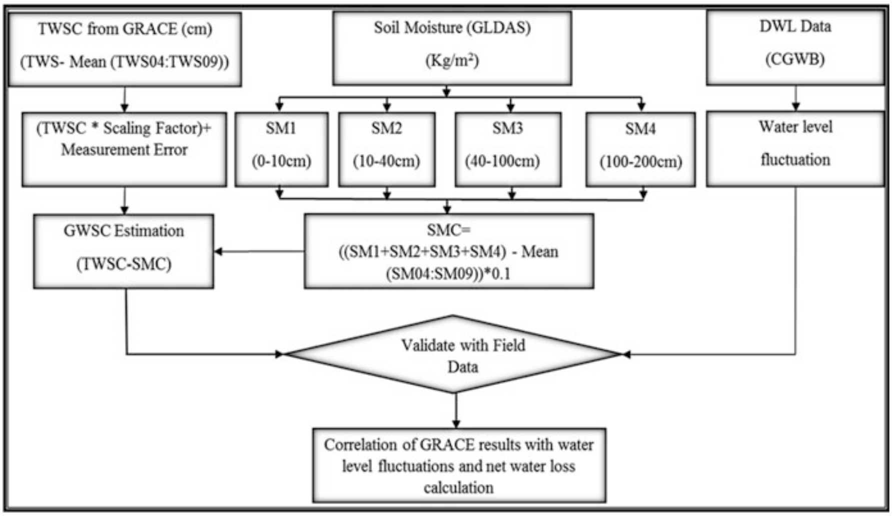

Fig. 7.1 Flowchart showing methodology for estimation of change in groundwater storage

7.2.1 Methodology for Estimation of Change in Groundwater Storage

The methodology proposed for estimation of change in groundwater storage is presented in Fig. 7.1. From 2003 to 2012, the trend of groundwater depletion in Uttar Pradesh was studied at regional scale using monthly grid terrestrial water storage data (from JPL RL05 product of GRACE mission) and soil moisture data and precipitation data (from GLDAS). To estimate the change in groundwater storage, all datasets of same resolution were used (Chinnasamy et al. 2013). The pre-monsoon, the monsoon, and the post-monsoon maps were prepared, and the results were plotted and compared. The results have also been validated using groundwater-level data of Central Ground Water Board (2009).

7.2.2 Terrestrial Water Storage Derived from GRACE

From 2003 to 2012, monthly solutions for terrestrial water storage (TWS) and soil moisture (SM) data for the entire state of Uttar Pradesh were accessed from GRACE and GLDAS databases. A destripping filter was applied to GRACE data by the CSR to minimize the north–south stripping errors (Wahr et al. 1998). A Gaussian filter was also applied to the GRACE and GLDAS data to spatially smoothen the data (Swenson and Wahr 2006). By subtracting the time mean TWS from January 2004 to December 2009, the GRACE data were further normalized as per methods described in website http://grace.jpl.nasa.gov.

7.2.3 Soil Moisture Derived from GLDAS

By using Global Land Data Assimilation System datasets, surface soil moisture was estimated for each layer (0–10, 10–40, 40–100, and 100–200 cm). To obtain the total soil moisture data, all four layers were summed up. Two potential sources of mass variability that were neglected in the present study included surface water, plant biomass, and snow water equivalent. The latter has not been important as study area has no snow cover (Chinnasamy et al. 2013). GLDAS gathers grids of total soil moisture every 3 h. The collected grids were averaged, and a time-averaged grid from January 2004 to December 2009 was subtracted from all the individual grids to normalize the data.

7.2.4 Estimation of Change in Groundwater Storage

By using GRACE-derived terrestrial water storage and GLDAS-derived soil moisture (GRACE and GLDAS data of similar spatial and temporal resolution), equivalent water thickness or groundwater storage was calculated as per Eq. 7.1. (Rodell et al. 2009)

$$\mathbf{GWS{=}TWS - SM} \tag{7.1}$$

where TWS is terrestrial water storage, SM is soil moisture, and GWS is groundwater storage.

Subsequently, the calculated pre-monsoon (March–May), monsoon (June–September), and post-monsoon (October–November) changes in groundwater storage from 2003 to 2012 were interpolated in Arc GIS using Kernel smoothening interpolation and masked for the entire state of Uttar Pradesh. Pre-monsoon, monsoon, and post-monsoon changes in groundwater storage maps were generated to visualize the status of groundwater storage trend. The time-series analysis representing the trend of terrestrial water storage anomaly, soil moisture anomaly, rainfall anomaly, and groundwater storage anomaly has also been done from 2003 to 2012 for the study area.

7.3 GRACE/GLDAS Data Interpretation

Figures 7.2a and 7.2b indicates the seasonal (pre-monsoon, monsoon, and post-monsoon) normalized equivalent groundwater thickness, as per Eq. (7.1) after removing soil moisture and surface water components, over the entire state of Uttar Pradesh. Variations in map color represent changes in water mass in terms of total net groundwater storage. Time-series analysis was done for study area (Lucknow district) only. Time-series analysis (Fig. 7.3) of GRACE/GLDAS data demonstrated that rainfall, total water storage, and soil moisture did not show much variations, while groundwater storage trend shows a declining trend from 2003 to 2012. This suggests that the area was either using the groundwater immensely for the irrigation or the decline was due to urban development. Thus, anthropogenic activities could be the main reason for the groundwater depletion in study area. The mean groundwater depletion rate of the study area was -1.46 ± 0.74 cm/year. The average volumetric groundwater storage loss was also calculated for the study area which was 0.37 km^3.

The validation of the GRACE/GLDAS-derived results was done only for the study area (Lucknow) using water-level data of Central Ground Water Board 2009. Figures 7.4a and 7.4b reveals that the GRACE/GLDAS-derived groundwater storage fluctuation estimations closely follow the trend observed in the groundwater monitoring wells. The comparison between GRACE/GLDAS data and observed well data indicated a favorable positive trend. A subsequent regression analysis between GRACE/GLDAS-derived groundwater storage fluctuation and observed groundwater-level fluctuation yielded a coefficient of determination (r^2) value of 0.89 for pre-monsoon and 0.77 for post-monsoon season.

7.4 Conclusion

The assessment of groundwater quantity was done using GRACE/GLDAS data. For this purpose, terrestrial water storage (GRACE) and soil moisture data (GLDAS) were used. To visualize the seasonal changes in groundwater storage of Uttar

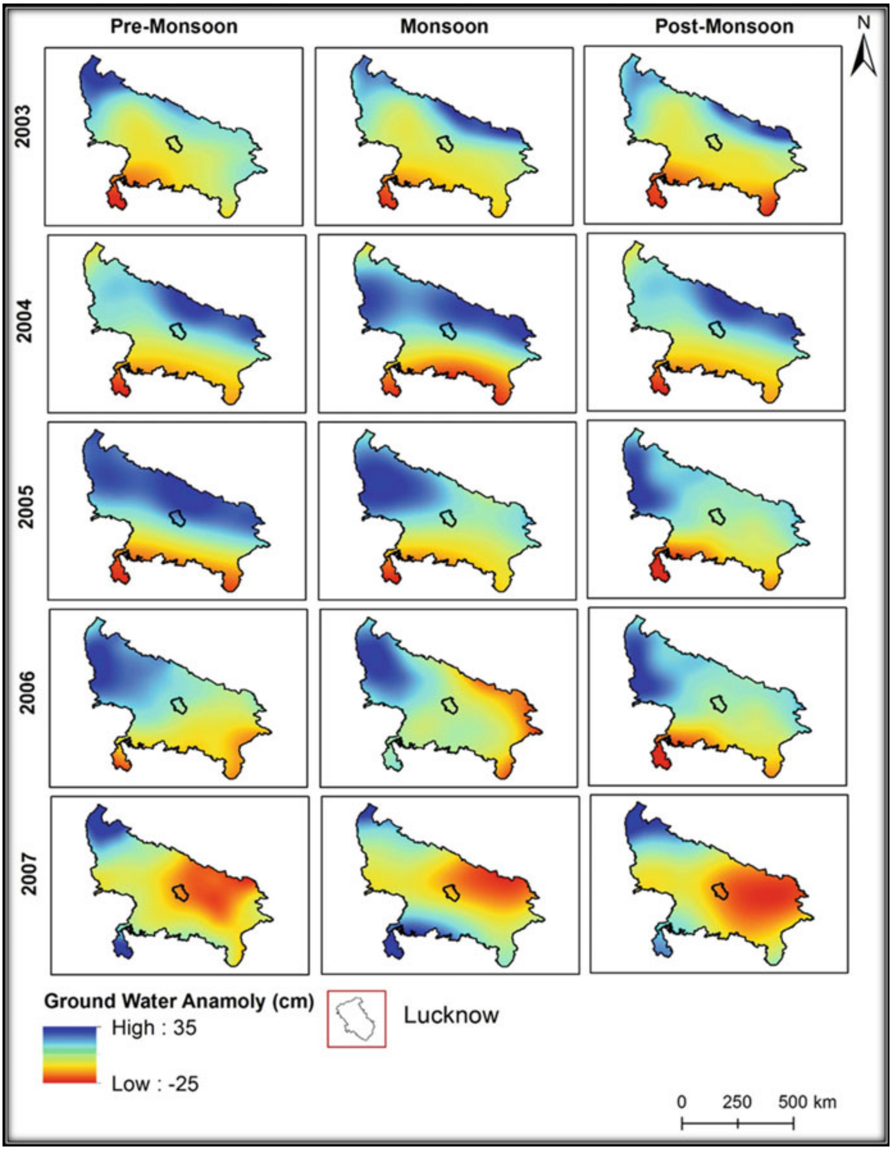

Fig. 7.2a Yearly GRACE/GLDAS gravity solution for total groundwater storage from 2003 to 2007 in Uttar Pradesh, India

Pradesh from 2003 to 2012, pre-monsoon, monsoon, and post-monsoon maps were generated which represented the overall decreasing trend from 2003 to 2012. Time-series analysis of Lucknow district indicated declining trend of groundwater, while other parameters like soil moisture, rainfall, and terrestrial water storage were not showing continuously declining trend with respect to groundwater. This indicated

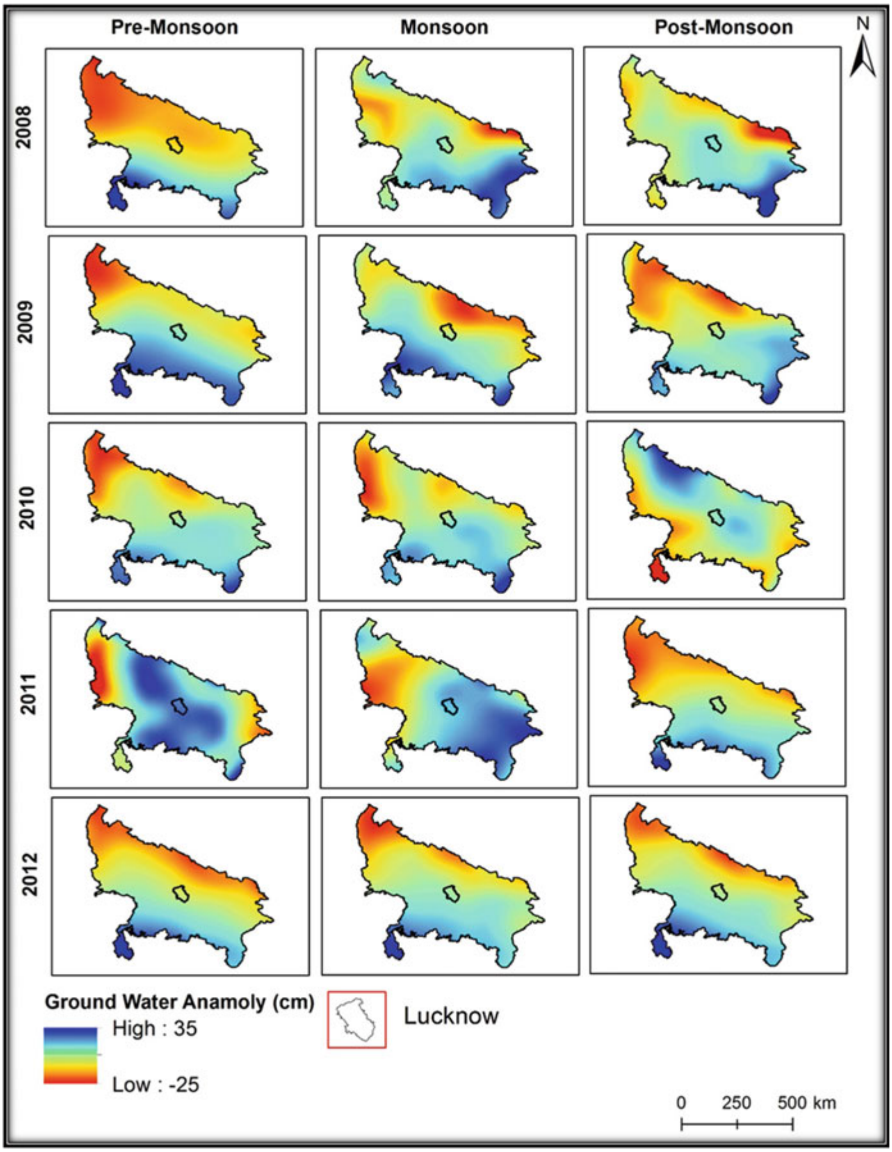

Fig. 7.2b Yearly GRACE/GLDAS gravity solution for total groundwater storage from 2008 to 2012 in Uttar Pradesh, India

that groundwater extraction was faster than recharge. The mean groundwater depletion rate was -1.46 ± 0.74 cm/year. The average volumetric groundwater storage loss was also calculated for the Lucknow district which was 0.37 km^3.GRACE-derived groundwater fluctuation was validated with groundwater fluctuation estimated from the water-level data of Central Ground Water Board for Lucknow area

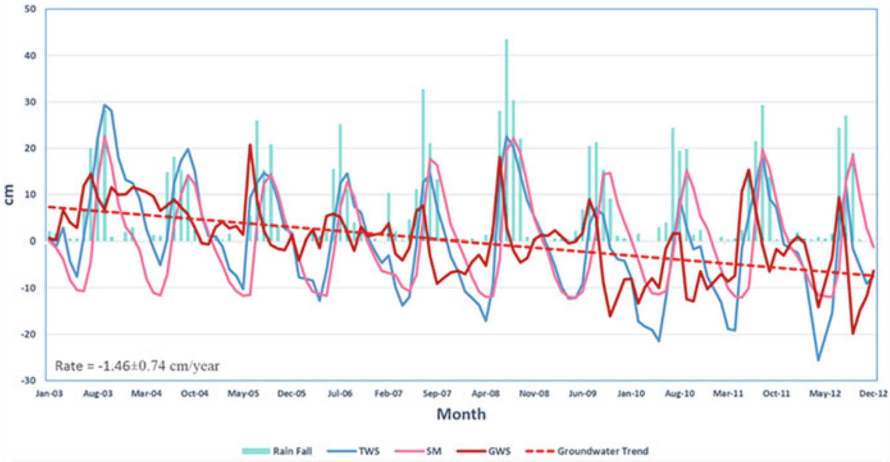

Fig. 7.3 Time series of water storage anomalies in study area from 2003 to 2012

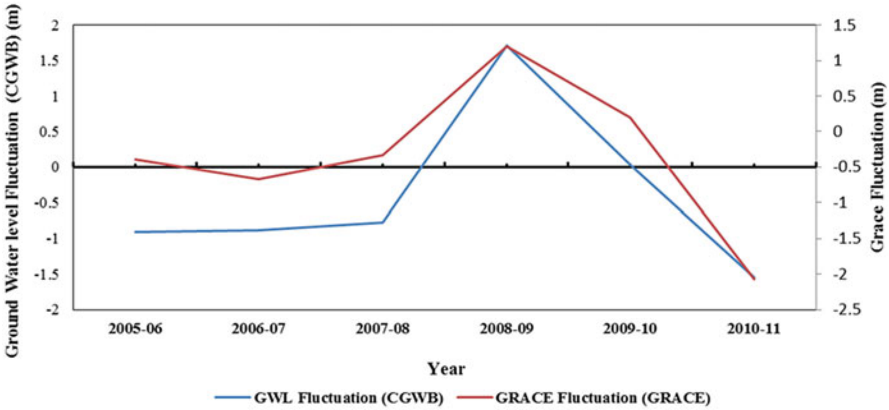

Fig. 7.4a Comparison between pre-monsoon groundwater fluctuation derived from GRACE/ GLDAS and observed groundwater-level fluctuation at Lucknow district in Uttar Pradesh from 2005 to 2011

only for pre-monsoon and post-monsoon seasons. The results were favorably validated. A positive correlation was found between GRACE-derived results and observed water-level data of Central Ground Water Board.

GRACE-derived results showed that remote sensing is an effective tool to interpolate the observed regional groundwater well data and helps to improve the estimations of groundwater storage. The present study shows that GRACE/GLDAS data are a relatively cost-effective and high-frequency tool for regional-scale estimation of groundwater depletion rate. The results could be productive for policymakers and land use planners to consider precautionary measure for water users on long-term basis.

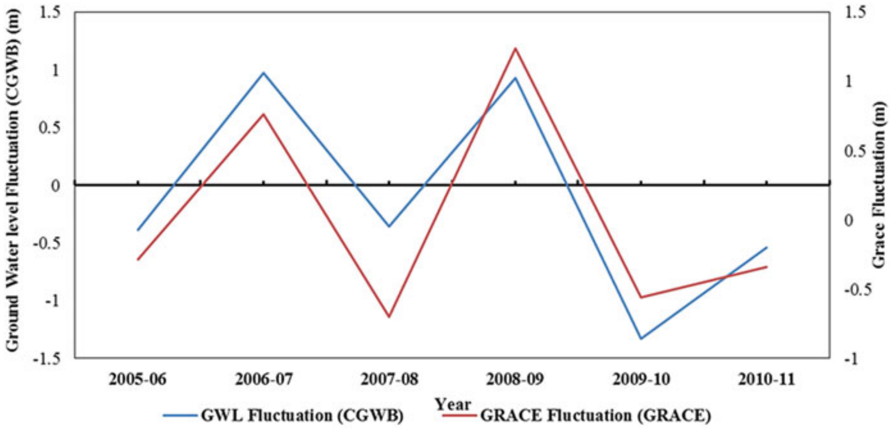

Fig. 7.4b Comparison between post-monsoon groundwater fluctuation derived from GRACE/GLDAS and observed groundwater-level fluctuation at Lucknow district in Uttar Pradesh from 2005 to 2011

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Chapter 8
Restoring Environmental Flows for Managing River Ecosystems: Global Scenario with Special Reference to India

Venkatesh Dutta, Urvashi Sharma, and Ravindra Kumar

Abstract Most of the major river basins throughout the world are under stress due to cumulative impact of droughts, over-allocation of water resources and water quality deterioration. Various previous and ongoing water resource development projects have caused both short-term and long-term ecological degradation resulting in interrupted fluxes of water, sediment and nutrition and declining river health across all the river basins. It is evident that most of the key manipulations of flow regimes are associated with in-channel large dams that are designed to store water during the wet season and deliver it downstream or off-stream as and when required. A lot of scientific studies are in progress to understand the fragile river ecosystem and to mitigate the adverse ecological impacts. A broad general agreement has emerged from all these scientific discussions, to protect fresh water biodiversity as well as maintain the ecosystem services by maintaining natural flow variability or keeping flow regimes similar to natural flows. The best ecological outcomes in a river basin result from conditions when environmental water passes through rivers and associated wetlands in ways that they mimic natural conditions. With this shift in thinking, a broader 'riverine ecosystem' perspective on assessment of instream environment came up, which gradually switched to more inclusive terms such as 'environmental water allocation' and 'environmental flows'. Various studies undertaken to measure and implement environmental flows indicate that key to improving rivers' health is maintaining more natural and variable flows including good water quality. This paper focuses on three things: firstly, the effects of hydrological alterations on Indian river ecosystems as well as from other countries; secondly, the science and management of environmental flows to sustain the river ecosystems; and thirdly, the need of strong legislature in developing nation's water framework directives. This study also indicates that there is considerable opportunity for improving the data gathering techniques and the overall methodology for the environmental flow assessment.

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Keywords Water allocation · Environmental flows · Catchment planning · River basin management

8.1 Introduction

Studies have shown that there is substantial and widespread effect of anthropogenic factors on river ecosystem (Dynesius and Nilsson 1994; Kingsford 2000). These changes range from effect on geomorphology and hydrology of the river system (Brandt 2000; Wohl 2018) to loss in ecological services and degradation of biodiversity (Richter et al. 2003; Poff et al. 2010). Altered flow regimes also lead to loss of biodiversity due to fragmentation and destruction of habitats of fishes, other freshwater fauna (Armitage et al. 1987), benthic biota (Ward 1976), riparian vegetation (Nilsson 1996) and crocodiles (Dudgeon 2000a). Before the 1980s, the river management systems were mainly 'site-specific engineering controls' focused on individual species conservation in a fragmented way without linking physical habitat and ecology. However, during the early 1990s, researchers started focusing on the water requirements for the river, associated habitats and the environment. The continuous progress in the literature of e-flows by joint efforts of scientists, NGOs, water managers and related policymakers resulted in the consolidation, expansion and globalization of the assessment process. They have defined biological integrity as 'the capability of supporting and maintaining balance, integrated, adaptive community of organisms having a species composition, diversity and functional organizations comparable to that of nature habitat of the region' (Angermeier and Karr 1994). Thus the concept of environmentally acceptable flow regime came into river management planning (Poff and Ward 1989; Stanford et al. 1996). Studies have been done to understand the relationship of hydrological variability with the river ecosystem integrity (Dutta et al. 2018; Meißner et al. 2018; Ngor et al. 2018). With all this work, the concept of e-flow evolved, to mitigate the considerable human modifications of hydrological regimes and ecosystem degradation such as those from building of dams and diverging structures on rivers, reallocation on water to urban communities and riverfront development. The objective for e-flow assessment (EFA) is basically to modify the existing flows to restore the natural or nominal flow regimes. Present e-flow assessment methodologies have become like an umbrella panel covering different methods and models aiming to re-establish floodplain ecosystems and improve habitat conditions.

8.2 Environmental Flows: A Paradigm Shift

Rivers, streams and wetlands need assured amounts of water with appreciable quality to support healthy aquatic ecosystems. The normal riverine flow is changed due to construction of dams, water abstractions as well as addition of water to the river from different sources such as outflow from sewage treatment plants, all these cumulatively alter the natural flow of the river. E-flows are designed to mimic the natural condition of rivers. During Brisbane declaration in 2007, e-flows were defined as 'the quality, quantity, and timing of water flows required to sustain freshwater, estuarine ecosystem and the human livelihoods' well-being that depend on the ecosystem' (Acreman and Ferguson 2010). Others have also defined e-flows as per their understanding and requirements of water flow: the World Bank defined environmental flows as 'the quality, quantity, and timing of water flows required to maintain the components, functions, processes, and resilience of aquatic ecosystems which provide goods and services to people' (Brisbane Declaration 2007). IUCN has defined e-flows as 'the water regime provided within a river, wetland or coastal zone to maintain ecosystems and their benefits where there are competing water uses and where flows are regulated' (https://www.iucn.org/theme/water/our-work/environmental-flows). The Conservation Gateway has defined e-flows as 'the quantity and timing of water flows required to maintain the components, functions, processes and resilience of aquatic ecosystems and the goods and services they provide to people' (https://www.conservationgateway.org/ConservationPractices/Freshwater/EnvironmentalFlows/Pages/environmental-flows.aspx). International Rivers organization has defined it as 'quantity, timing, and quality of water flows below a dam, with the goal of sustaining freshwater and estuarine ecosystems and the human livelihoods that depend on them' (https://www.internationalrivers.org/environmental-flows). There are two broad ways to compensate the changes in e-flows: first is by monitoring the releases of water below dams and second is by protecting the flow in unregulated rivers. The variability of flows is another very important component in maintaining the functionality and resilience of the river ecosystems (Arthington et al. 2018). The river streams naturally experience periods of very low or no flow, or they could be flooding every year or bring occasional large floods that spread out onto floodplains (Richard and Hirji 2003).

Flow is the master variable in maintaining the river stream and protecting river features such as aquatic animals, riparian vegetation, river sand, estuaries, aquifers and groundwater, aesthetic value, recreation and cultural features, ecosystem services as well as overall functioning of environment (Table 8.1). Zeiringer et al. (2018) describe river flow as the essential process determining the 'size, shape, structure, and dynamics of riverine ecosystems'. Forbes (1895) in the USA and Antipa (1928) in Hungary and Romania, respectively, had sampled large rivers, associated floodplains and backwater to recognize this relationship. Welcome (1979) and Wohl et al. (2015) emphasized that floodplains integrity of large rivers is maintained by hydrological dynamics (flood pulses) and river floodplains connectivity. Particular flow patterns determine the shape of the stream channel, stream habitats and biotic components. Low flows are important in maintaining the flora and fauna which require low-flow velocity and water. Small floods stimulate fish spawning, flush away pollutants, clean up riverbed and sort river stones, thus giving a new habitat for seed germination and migration of fishes. Large floods are important for maintaining the river channel; they clean up cobbles and boulders on the riverbed; transport silt; deposit silt, eggs and seeds; and recharge soil moisture

Table 8.1 Value of river features along with example of e-flow requirement

Feature	Explanation of value	Example of e-flow requirement
Aquatic animals	Freshwater fishes are a valuable source of protein for associated population. Other important fauna include angling fish, rare water birds or small aquatic life that are the base of the higher food chain	Flows to maintain physical habitat, suitable water quality, migration of fish, small floods for spawning or egg laying
Riparian vegetation	Stabilizes river banks, provides food and firewood for riparian population and habitat for animals and prevents the nutrient and sediment losses from human activities in the river catchment	Flows to maintain soil moisture levels in river banks; nutrient deposition and seed distribution
River sand	Used as construction material	River flows transport sand and separate the finer particles from it
Estuaries	Act as spawning and nursery areas for marine fishes	Flows to maintain salt/freshwater balance requirements and ocean connection to estuary
Aquifers and groundwater	Acts as the source of water in lean period of flow as well as maintain the perennial nature of rivers	Flows to recharge the aquifers
Floodplains	Support fishery and flood-recession agriculture business for the riparian population	Floods to inundate the floodplain once in a year, and major floods should occur after every few years
Aesthetics	The sound of water running over rocks, the smells and sights of a river with trees, birds and fish	Sufficient flow is required to maximize natural aesthetic features
Recreational and cultural features	Water games such as river rafting, cliff jumping, etc. are promoted in clean water with rapids. Clean pools for holy rituals, ceremonies or bathing, natural beauty is appreciated by anglers, birdwatchers, photographers and aquatic animals	Adequate flows for sediment, algae flushing and also to maintain water quality
Ecosystem services	The aquatic ecosystems need to be maintained well so they can regulate associated essential ecosystem processes such as water purification, flood attenuation and controlling	Flows that maintain biodiversity and ecosystem functioning
Overall environmental protection	Minimize the anthropogenic impacts thus natural systems can be conserved for future generations	Some or all of the above types of flows

Source: Adapted from *Richard, D. & Hirji, R., (eds), Environmental Flows: Concepts and Methods. Water Resources and Environment Technical Note C1, World Bank, Washington, D.C., 2003*

level around river banks. Large floods also clean the connection between estuaries and sea, inundate back water and promote growth of new species in the floodplains. These variable flows are also important for creating geological barriers for speciation. Thus any alteration in the flow pattern can lead to depletion in water quality, establishment of invasive species and loss of biodiversity.

8.3 The Trends of E-Flow Assessment Methodologies

The foundation of environmental flow assessment (EFA) methodologies was laid down way back during the 1940s in the USA, but the real progress started in the 1970s (Tharme 2003). There are insufficient documents available to describe the route of establishment of EFA methodologies in other parts of the world, i.e. outside the USA. In countries like Australia, Japan, New Zealand, England, Brazil, Czech Republic, South Africa and Portugal, the EFA processes became popular during the 1980s, yet a large part of the world was unaware of the EFA processes and their importance in water development processes during this period (Poff and Matthews 2013). In the developing nations of the world, the process gained significant popularity during the 2000s, and several studies were undertaken in India, Nepal, China, Sri Lanka and Iran.

More than 220 EFA methodologies have been developed in 44 countries worldwide (Shokoohi and Hong 2011). Scientific community is still in process of improving the existing methods and developing new, more reliable methods including Stalnaker and Arnette (1976), Wesche and Rechard (1980), Morhardt and Altouney (1986), Loar et al. (1986), Kinhill Engineers (1988), Arthington and Pusey (1993), Growns and Kotlash (1994), Karim et al. (1995), Tharme (1996, 2000, 2003), Jowett (1997), Dunbar et al. (1998), Arthington and Zalucki (1998a, b), Arthington (1998a, b), Mahoney et al. (1998), King et al. (1999), King et al. (2003), Black et al. (2005), Poff et al. (2010), Sanderson et al. (2011), Cluer and Thorne (2014) and Martin et al. (2015).

On the basis of time and resource requirement, Tharme (2003) has divided EFA into five major categories as follows (Table 8.2):

1. Hydrological methodologies
2. Hydraulic rating
3. Habitat simulation methodologies
4. Holistic methodologies
5. Combined methodologies

Western Europe and the USA were the pioneer countries in e-flow assessment of their rivers for achieving goals of sustainable water resource management (WCD 2000; Tharme 2003; Acreman and Dunber 2004). Europe and North America share the highest percentage of hydrological methodologies, i.e. 38% and 26%, respectively (Tharme 2003); these methodologies are limited in their regional approach as they were applicable for a small region. Mainly focused on one species or single purpose by maintaining the minimum flow required to fulfill the purpose. North America leads in the application of hydraulic rating methodologies with 76% of all studies reported followed by Europe and Australia. Australia was first (Arthington

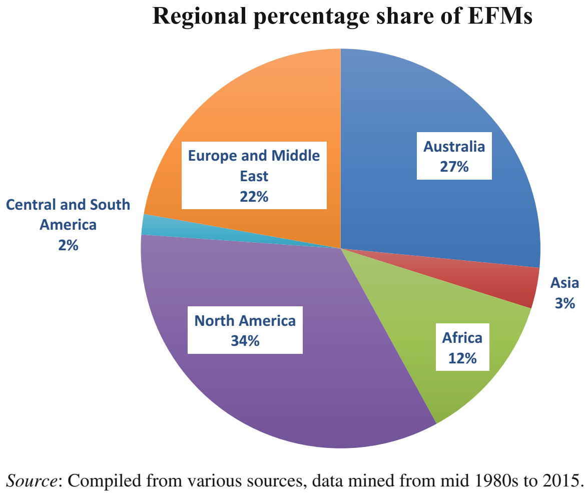
Table 8.2 General requirements and limitations of each type of e-flow assessment methodology

Assessment type	Requirements	Time	Costs	Confidence required	Limitations
Hydrological models	Hydrology	1 Day	Low	Low	The ecologically important extreme flow conditions and timing of flow are not incorporated
Hydraulic rating	Hydrology/ hydraulics	1 Week	Intermediate	Low	Detailed hydro-logical and hydraulic study were not included
Habitat simulation	Hydrology/ hydraulics/ ecology	Months	High	Fairly high	River channel is assumed to be sta-ble, and character-ization of the habitat is limited in terms of depth and velocity
Holistic	Hydrology/ hydraulics/ecol-ogy/geomor-phology/social/ water quality	Months/ years	High	High	Hard to implicate, long procedures as well as informa-tion gaps in every fundamental aspect of aquatic biology of large plain areas. Also the lack of linkage between the social and livelihoods processes in e-flow assessment and framework
Combined methodologies	Hydrology/ hydraulics/ecol-ogy/geomor-phology/social/ water quality/ expert opinions	Months/ years	High	High	Lack of data to develop the base-line conditions for the streams

Source: Authors' own elaboration

et al. 1992; Thoms et al. 2000) followed by South Africa (King and Tharme 1994) to focus on multiple ecological targets important for sustaining the ecosystem not just the economically valued species. North America is the leader in habitat simulation methodologies followed by Africa and Latin America. Australia is the leader in holistic EFMs, followed by Africa. In New Zealand (Biggs 1990) and Australia (Hughes 1987), the concept of ecological consideration for e-flow assessment developed parallel. However, absence of such methodologies in North America emphasizes on the limitation in approach of methodologies to the region where

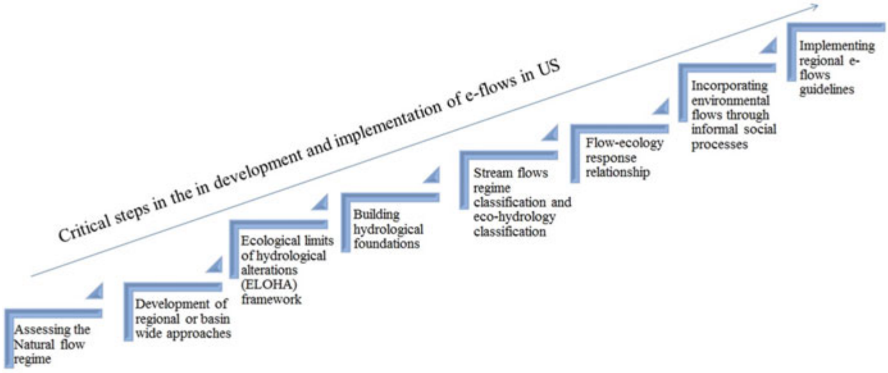
Fig. 8.1 Showing a cumulative percentage of all methods applied in different parts of the world. (*Source*: Compiled from various sources, data mined from the mid-1980s to 2015)



they originated. Combined EFMs and other approaches have the highest reported studies from Europe, i.e. 39% and 57%, respectively; however, these two types of methodologies had little or no exposure in South and Central America. Almost all types of methodology have been applied in Australia and Europe, whereas only hydrological and habitat simulation methodologies were prominently used in rest of the world. Throughout the world there are more than 220 EFA methodologies; a cumulative assessment is one to understand the percentage share of different regions on the basis of the applications of EFA methodologies (Fig. 8.1). It is apparent from the review that Australia is leading in EFM methodology development and implication. Most of the new methodologies in use are developed in mainly Australia, Europe and North America. However, the Asian countries and other developing nations of the world are using the hydrological and hydraulic methodologies of EFA and constantly working to improve the available methodologies to suit their specific requirements.

If we see the critical steps in the development of the e-flow assessment methodologies in different regions of the world, we can easily demarcate disparity between paths chosen regionally to get the desired results. In the USA the e-flow assessment started with the stream flow-based approaches back in 1997 (Richter et al. 1997); the critical steps in the expansion and implementation of e-flow assessment are shown in Fig. 8.2.

If we see the evolution of e-flow assessment methodologies in South Africa, the already existing methodologies and hydrological, hydraulic rating and habitat-rating methods were not providing the desired levels of significance for e-flow assessment. The scientists were looking forward to incorporate four bases in their analysis, i.e. biophysical, social, scenario building and economic analysis component. The major challenges that emerged during the framing of the methodology which needed equal attention in the due course of time were perennial rivers and ephemeral rivers, wetlands and estuaries, and groundwater needs to be given equal weightage in the



Source: Authors' own elaboration

Fig. 8.2 Critical steps in expansion and implementation of e-flow assessment in the USA. (*Source*: Authors' own elaboration)

study. Water quality and water resource development methods also fall in the same linage. The philosophy behind the development of holistic methodologies was as follows:

- Active management of river ecosystem which is not in pristine condition.
- Management of all major biotic and abiotic components of the ecosystem.
- The temporal and spatial variability along with full spectrum of flows should be managed.

Thus the development of holistic approaches like BBM and DRIFT was done. Holistic approaches need a large group of field experts, as shown in Table 8.3.

8.4 The Effect of Hydrological Alteration on River Ecosystem

Construction of dam on any free-flowing river changes the downstream ecological processes and further sets in motion a complex chain of reactions that completely transmutes the floodplain vegetation dynamics (Wieringa and Morton 1996; Pandit and Grumbine 2012). Very few studies have been done in India to study the effect of hydrological alterations and river regulation on terrestrial and downstream riparian ecosystems (Dudgeon 2000b, Grumbine and Pandit 2013); thus their effects remain largely unknown. A recent study by Pandit and Gumbine (2012) in relation to 292 dams proposed by Government of India in Himalayan region (GOI 2008) had pointed towards their widespread adverse impacts on terrestrial biodiversity, riparian population and future land use patterns from the proposed dams. They reported high percentage (90%) of dams which were proposed in highly diverse subtropical and temperate zones in the Indian Himalaya (Pandit et al. 2007). If such proposal gets

Table 8.3 Requirement of field experts in e-flow assessment

Field expert(s)	Responsibility
Hydrologist	To describe the river flow how it was and how it has got changed as well as how it is changing
Geohydrologist	To predict the location and height of water table and changes in subsurface flow
Hydraulic modeller	To study the surface flows and simulate hydraulic conditions
Sedimentologist and fluvial geomorphologist	To study and predict the channel response to the changed hydraulic conditions such as in-filling or flushing of pools, changes in mobility, loss or gain of flood terrace deposits, sedimentation or scouring of riffles and size-sorting of different-sized bed particles and the accumulation or loss of muddy deposits within the active channel
Water quality specialist	To predict the change in concentrations of nutrients and dissolved solids and their effects on chemical and thermal regime of the river
Vegetation specialist	To describe the expected biotic responses of any change in river channel and flow by predicting how each vegetation zone might change location, width or some other characteristic, as well as the response of individual plant species
Fish ecologist	To predict the changes in fish communities such as any shifts in abundances and condition of the fishes and community composition
Plankton, amphibian, reptile, water bird, semiaquatic species specialist	To predict and report any change in these communities due to change in biotic or abiotic factors

Source: Adapted from King and Brown (2006)

approved, it will lead to submergence of large area resulting in elimination of some sensitive species. The high density of dams and associated construction activities could also result in continental-scale effects favouring cosmopolitan, non-native species (Poff et al. 2007). This sudden species loss and invasion of non-native species will be favoured by forest loss and fragmentation (Terborgh 1974; Terborgh et al. 2001; Grumbine and Pandit 2013; Pandit 2013). Most of the dams proposed in this project were on fifth- to seventh-order river channel which when evaluated comes to an average of 1 dam/32 Km which is 1.5 times higher than the USA (Poff et al. 2007).

Kumara et al. (2010) studied Bhadra River at Lakkavalli, Shimoga District, Karnataka, India, to evaluate the impacts of not releasing environmental flows downstream to the Bhadra Dam. Results showed a gradual shrinkage of the river in its riverbed to the downstream leading to massive loss of aquatic habitat, riparian vegetation and water quality. The altered flow regimes affected birds, reptiles, riverine vegetation and various aquatic life forms, and the downstream riparian communities were compelled to change their occupations or migrate to new places in search of livelihoods.

Mehta (2001) studied the problems of water scarcity in Kutch, Western India. He emphasized on the extra basin water transfer for mitigating the water scarcity in semiarid and arid areas. He also favoured the legitimization of Sardar Sarovar Dam to meet the water problems of the area arising due to dwindling rainfall and increasing droughts. However, literature suggests that extensive canal networks have intensified the desertification as well as have a high environmental and social cost (McCully 1996). Verma et al. (2009) reported interstate water trades are not solving the problem of water scarcity; rather they have exacerbated the problem. Mehta (2001) also worked to bring local and scientific perspective together to understand the ecological dynamics and peoples' interactions with the environment. Similar work was also reported by Dahlberg and Blaikie (1999); they attempted to bring the local and scientific perspective closer to understand the ecological dynamics and anthropogenic interactions with their environment.

8.5 The Science and Management of E-Flows to Sustain River Ecosystems

Over the past two decades, the disputes among the societies due to drought, water shortage, water transfer and rising irrigation demands have brought the issues of water resources into strident focus. Water resource management is the most important, challenging and elusive issue, where people are advocating in developing a science-based e-flow approach to sustainably manage the water resources without disturbing the integrity of its aquatic resources. The first management strategies applied was in Australia, by the Murray-Darling Basin Ministerial Council (MDBMC) on Murray-Darling Basin by capping all the diversions (effective in June 1997). However the holistic basin-wide approach to define and reserve e-flows was missing (MDBMC 2000). A holistic approach, Downstream Response to Imposed Flow Transformation (DRIFT) methodology, was used in Lesotho Highlands Water Project (LHWP) in South Africa for environmental flow assessment. This hydropower project was an outcome of a treaty between South Africa and Lesotho in 1986. To maintain the EFR, construction was improved from their regular design to maintain the variability of flow downstream. Also the environmental flow release (EFR) policy was drafted to recommend and increase the existing limits of variable flow release from Mohale Dam, Matsoku Weir Dam and Katse Dam, i.e. 0.6m^3/s which was previously 0.05 m^3/s, 2.12 m^3/s from 0.5 m^3/s and 0.3 m^3/s from 1.01 m^3/s, respectively, to be released as seasonal releases and small floods (WB 2003).

India being a developing country is at a crucial stage where a lot of water infrastructure is aging. The state and central government is prioritizing various water resource management strategies and seeking sustainable solutions to reduce both consumption and loss. This current scenario is same as it was in North America and Western Europe during mid-twentieth century. Large river basins all around the world are under stress due to proposed and under-process dams that are required to meet water demand from irrigated agriculture, industrialization, and domestic users.

Southeast Asia has more than 80 dams under construction (Ziv et al. 2012), Himalayas in India has over 300 dams (Grumbine and Pandit 2013), and Andes have more than 150 (Finer and Jenkins 2012) dams which are resulting in drought conditions in the lower basin areas of the rivers (Poff and Matthews 2013). Periodic and often serious droughts make the situation worse. In developing countries, limited attention has been paid on environmental water demand. After independence, India witnessed rapid development in the form of urbanization, intensification of agriculture and industrialization which affected the rivers in multiple ways. Despite the fact that most of the Indian rivers are highly regulated or in the process of being regulated, limited or no efforts were put in assessing the EFR of Indian rivers. After the first National Workshop on Environmental Flows held at New Delhi in March 2005, a significant interest in concept of e-flows among national agencies and research institutions was brought to focus and subsequent work on estimating e-flows on various rivers. The major problems prevailing in developing countries in EFA were highlighted as failure of not incorporating and interpreting existing knowledge of aquatic ecosystem components (e.g. fish) in quantifying the e-flow requirements. There are few studies for e-flow assessment done in India which are summarized in Table 8.4.

8.6 The Need of Strong Legislature in Water Framework for E-Flows

A strong legislature throughout the world based on regional- as well as on country-level analysis using hydrological classification methods collectively with ecological calibration was suggested by Arthington et al. (2006) to provide global e-flow guidelines. The conflicts on shared water resources can be resolved by formulating well-structured and scientifically based flow management guidelines which also takes the unique physiographic and ecological areas into consideration. Australia had their first ever e-flow guidelines in 1999 which were replaced by environmental flow guidelines in 2006; very recently Australia has further amended its environmental flow guidelines in 2013. They have incorporated the importance of variable flows in there guidelines. The European Union does not have a formal term for environmental flows in their Water Framework Directive (WFD), but they have a mention of 'maintaining appropriate hydrological regimes to maintain good ecological status (GES)' (Thoms et al. 2000). In the UK, environmental standards have been set up for water resource management, first by defining the water abstraction limits and secondly by defining the ecologically suitable flow releases from reservoirs (Acreman and Ferguson 2010). Due to lack of strong legislature globally for the e-flows, the implementation of rational flows remains a major issue.

In 1987, the first National Water Policy was constituted in India for planning, development and management of water resource. This National Water Policy was later amended in 2002 and 2012. During late eighties, there was an urgent need to address the problems arising due to water impoundment and construction of dams like protecting the surrounding environment, rehabilitating the affected peoples,

Table 8.4 Studies done on different Indian rivers, methodology used and major recommendations

S. No	Location	Methodology used	Recommended e-flows			Recommendations	References
1	Cauvery River	Hydrological index methods, lookup tables, EMC-FDC approach, Tennant and modified Tennant method	Name of the site	Maintenance flow (cumec day)		Maintain the minimum flow in the river to maintain the river ecosystem	Durbude (2014)
			Belus	5.32			
			Hadige	20.79		In Indian context lookup table may not be appropriate	
			Akkihebbal	12.24			
			Kollega	91.22			
2	Upper Ganga Basin	Building Block Methodology	Name of the site	Maintenance flows as % of MAR	Drought year flows as % of MAR	Site specific e-flows	WWF-India (2012)
						Can be applied to other rivers	
			Kaudiyala	72%	44%		
			Kachla	45%	18%		
			Bithoor	47%	14%		
3	Mahanadi River	The Tennant method and Range of Variability Analysis (RVA) uses Indicators of Hydrologic Alterations (IHA)	Tenant method: minimum (low) flow should be higher than that of 7-day minimum predicted by the RVA analysis			Low flow: defined as 10% of the total flow (Montana method), whereas for the 7-day minimum flow (RVA analysis), low flow is less than 10% of the total annual flow	Bhattacharjee and Jha (2014)
			For excellent habitat: MAF for the months of October–March (4.93–161.91 cumec) and for April–September (62–1186.5 cumec) for the years 1978–2010			As per the results Tennant method isn't applicable for this basin	
4	Brahmani and Baitarani River	Flow Duration Curve approach	FDC were computed for 1-day, 7-day and 30-day mean; the results suggested the 7Q10 FDC was recommended for drought years/low-flow periods and 7Q100 FDC			The 7Q10 of FDC yearly mean is beneficial in: (i) Maintaining the water quality from discharge of wastewater or waste load allocations	Jha et al. (2008)

			was found appropriate for normal precipitation years		(ii) Protecting the habitat in drought conditions (iii) Chronic criteria for aquatic life and local extinction flow	
					7Q100 is not a common practice	
5	Sone River (Maikalsut)	Global Environmental Flow Calculator (GEFC), desktop software by the International Water Management Institute (IWMI) based on Flow Duration Curve (FDC) approach	Name of the Site	flows as % of MAR	As per the analysis: 18.9% of MAR is required to restore the stretch from Critically Modified (F) to Moderately Modified Class (C). And to Slightly Modified Class (B), 34.2% of MAR will be required	Jha et al. (2014)
			Indrapuri Barrage	5.16% and 2–5% wetted perimeter		
6	Kumbh mela (At Sangam) in Allahaba	Building Block Methodology	Kumbh mela	Water depth: 1.2 m for the entire duration and a stage of 73.53 ± 0.11 m		WWF-India, (2013)
				Flow: 225 cumecs (7950 cusecs) surface width: 175 m		
				Special Snan Days: depth of 1.5 m, a stage of 73.83 ± 0.11 m		
				Flow: 310 cumecs (10,950 cusecs)		
7	Bhadra River	Tenant method (Tenant law (TMC) analysis)	8855 TMC	Poor flow at 10%	Downstream to the Bhadra reservoir	Babu and Kumara (2009)
			26,565 TMC	Moderate flow at 30%	10 times the flow was above the excellent flow conditions	
			53,129 TMC	Excellent flow	12 times the flow was meeting the poor conditions	
					10 times the flow was above the moderate flow conditions	

Source: compiled from various sources

livestock, public health consequences and ensuring dam safety. However the effect of water storage behind dams, diversion and river basin encroachment were not given much attention. During 2002 and 2012, India's National Water Policy incorporated few improvements in the water resource planning and watershed management strategies as emphasis on hydrological perspectives for management, and catchment area treatment, soil conservation, increase in forest cover, preservation of forest and checking of dam constructions were included in the policy (NWP 2002; 2012). However the ecological water demands were kept on fourth in setting water allocation priority, and there was no mention of e-flow requirements.

If we see the state water policy in India, out of 29 states and 7 union territories, only 14 states have their own state water policies to manage the state water resources. Among all the state policies, only a few have a detailed mention of water allocation for maintaining aquatic life, wetlands and water body restoration, watershed area management and environmental water allocation strategies with respect to the ecological demand of that geological area such as Assam. Goa State Water Policy pays special focus on the ecological sustainability of Western Ghats. Most of the state water policies pay least attention on all these issues. In National Water Policy as well as in state's water policies, the ecological and environmental water requirements have not been incorporated. This is the main drawback in water management system, as human being is kept at the centre of all the planning and management works ignoring the dynamic linkages between ecology and quality of physical habitats.

Another problem is of on-ground implementation of the environment impact assessment laws. In 1994, National Environmental Impact Assessment (EIA) laws were enacted in India with specific requirements to address threatened and endangered species, protected areas and other biodiversity concerns. Even with robust environmental impact policies, their implementation remains uncertain (Grumbine and Pandit 2013). In India very less attention is paid on ecological evaluation of large-scale development projects (Bandyopadhyay and Gyawali 1994; Agrawal 2010). Lack of scientific studies and poor implementation of EIA processes is another big challenge (Pandit and Gumbine 2012), and as per the literature survey, no projects have been rejected because of loss of biological diversity, except in rare cases involving threatened areas and flagship species such as the tiger (*Panthera tigris*) (Singh 2006).

8.7 Discussion

Rivers throughout the world are under great stress due to hydrological alterations. The expertise of assessing eco-hydromorphological parameters are highly fragmented restricting synthesis of ideas and methods. The rocketing energy and water resource demands are putting the rivers and their associated ecosystems at risk. Thus there is an urgent research and data need to assess the future flow trends due to climatic uncertainties, assessment of links between ecology and physical habitat and

Table 8.5 Showing the e-flow assessment methodologies evolution trend in the past 35 years

Timeframe	Approach	Specific methodology types	Shortcomings
First generation (1980–1995)	Desktop, rapid assessment, static, based on primarily ecologically relevant hydrological indices or analysis of hydrological time series data	Hydrologic methods, hydraulic rating methods	Used to justify low-flow allocations
			Prescriptive and assessments often done in isolation
			'Get a number' syndrome for a single flow regime
			E-flow will not maintain a pristine river condition
Second generation (1995–2010)	Comprehensive habitat assessment, using primarily methods or habitat modelling	Habitat rating methods, instream flow incremental methodology (IFIM), expert panel assessment, DRIFT	May not be able to advice ecologically relevant flow restoration
			Importance and interface between changes in river's physical attributes and how the aquatic biota will be affected is not fully explored
Third generation (2010–2015)	Integration of habitat and ecosystem benefits with human well-being, structured and dynamic with ecological values in a changing climate scenario, synthesis of several EFA techniques	Ecological Limits of Hydrologic Alteration (ELOHA, Poff et al. 2010); Stream Evolution Model (Cluer and Thorne 2014)	Full tolerance of the flow-ecosystem relationships is still not possible
			Adaptive management of flow regimes with respect to changing climate/social preferences being worked out

how anthropogenic water demands are increasing along with developing holistic management plan for the water systems, along with a feedback system to evaluate the system whether or not these adaptations are attaining the desirable and economically acceptable ecological endpoints in the society (Poff and Matthews 2013). The e-flow assessment methodologies developed in the different parts of the world till date have few fundamental assumptions such as stationary climate and dynamic ecological equilibrium (Milly et al. 2008; Brown 2010; Betancourt 2012). These assumptions had been a barrier in getting the real on-ground picture of the river ecological systems, resulting in the spread of non-native species. There is a trend of development of EFA methodologies which can be seen throughout the world (Table 8.5). We have tried to divide the whole evolution of EFA methodologies during the past three decades into three generations.

The first-generation EFA methods are essentially desktop methods which may or may not be ecologically relevant. They ignore the interface between the flow regime and the aquatic species and communities. Hydraulic rating methods (HRM) were based on channel-discharge relationships and considered wetted perimeter to calculate e-flows. The breakpoints in habitat-discharge response curve were identified to relate how habitat quality degrades with reduction in discharge. They also failed to link channel morphology to habitat supporting aquatic biota. The Building Block Methodology provides an excellent approach to linking river objectives to flow requirements (King and Louw 1998). BBM was applied to assess the e-flow requirements of Ganga River by WWF-India.

The second-generation EFA methods were mostly based on habitat-rating approaches – the most common method is the instream flow incremental methodology (IFIM). IFIM was developed in the USA; it is rarely used in full, but the Physical Habitat Simulation (PHABSIM) model is used. It considers relative contributions to habitat quality and diversity through different channel forms (King and Tharme 1994), which was also later advanced by Williams (2010). Stream Evolution Model developed by Cluer and Thorne (2014) recognized that river streams might be naturally multithreaded prior to disturbance and represented stream evolution as a recurring cyclic process, not a linear phenomenon. The model recognized channel form as an outcome of evolutionary cycle within the streams that advance through the common sequence. In some cases, some streams completely skip some evolutionary stages and recovers to a previous stage or even repeat few stages of the evolutionary cycle.

In India only a few studies have been done on e-flow assessment, that too with no evidence of on-ground implication of flow requirements. Also there are no strong legislations to make e-flow assessment a mandatory exercise for all river basins of India as well as to make sufficient provisions for flow augmentation on ground. The studies done so far show that most of the researchers are still using hydrological methodologies for e-flow assessment (Durbude 2014; Bhattacharjee and Jha 2014; Jha et al. 2008; Babu and Kumara 2009) and only two studies have reported holistic approach (BBM) (WWF 2012, 2013). There is a whole room for us to learn new holistic approaches and apply them for developing river basin management plans. Also we should be very focused on adaptive management and for improvisation of our e-flow assessment knowledge and skills, as we are still lacking in having the experts in the field of fluvial morphology and flow-ecology relationships. The unavailability of on-site, timely and reliable data for the e-flow assessment processes is another big obstacle in achieving the goals. If it is available for few sites, there is fragmented responsibility and power distribution among the governing bodies like CGWB, CWC, CPCB, MoEF, etc. which create problem in gathering the data and decision-making processes for river basin management. In the context of Indian rivers, the e-flow assessment processes should be flexible enough that a 'one-size-fits-all template' should not be applied. The variation of the climatic, geographic and river ecosystem should be taken into consideration while choosing the e-flow assessment methodologies.

8.8 Conclusion

Adequate river flows with their flushing high-flows and low-flows shape and organize the physical habitat complexity and associated biotic communities. About 70% of the world's rivers are estimated to be fragmented, exploited or regulated by hydrologic alteration, with about 50% of the primary watersheds modified by flood defence embankments, impoundments and the presence of at least one large dam. It is evident fom the literature that there is a large amount of information, knowledge and experience behind the e-flows assessment, national and international environmental polices and acts rarely take e-flows for on the ground implementation. Globally there is enough room for improvement of e-flows methods and the dissemination of the knowledge and tools. Even though the number of countries that have applied the e-flows estimation techniques in basin management planning has increased significantly, the actual implementation of estimated and prescribed environmental water releases is still limited. Developed nations should extend their support to the developing nations in choosing the best suited methodology for water resource management. Global experts on e-flows estimation can readily access or share information and knowledge, ranging from terminology, models, case studies, software or related scientific literature. In India, the e-flow assessment had just started in the last decade; thus there is a lot of scope for refining the models used and the overall understanding of river systems and flow-ecology reltionships. Developing nations also need and have to work urgently on the capacity development at all levels. The training programs for officials as well as for the field experts should be organized in collaboration with experts from other countries. The focus of developing nations should be to learn from others mistakes and not repeat them in future. Further research is recommended to critically understand the connections between physical habitat and flow regulations, dynamics of biotic community and riverine ecosystems to flow restoration by integrated assessments through the main contributory disciplines of ecology, geomorphology, hydrology, civil engineering and environmental sciences.

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Chapter 9
Water Security Issues in Punjab State, Northwest India

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Abstract Water security has become an issue of concern for the Punjab state in northwest India due to depletion of water levels on account of over-exploitation of groundwater, deterioration of groundwater quality due to both geogenic and anthropogenic sources and waterlogging and salinization in southwest parts. All these problems would effect and decrease the future water supplies because 90% of the drinking water supply in the state is based on groundwater. In the present chapter, major problems in relation to water security are discussed along with the management tools such as rainwater harvesting, water conservation, and recycling and reuse of waste water, besides the use of reverse osmosis technology for removal of uranium and arsenic from groundwater to enhance the water security.

Keywords Groundwater · Depletion · Water security · Rainwater harvesting

9.1 Introduction

Punjab state in the northwest India is known for its contribution to agriculture and green revolution for providing food security to the country. It was possible only because of crucial role played by assured irrigation through groundwater and use of good quality seeds and fertilizers. Besides enhancing the agriculture production, groundwater has also played a key role in providing 90% of drinking water supply in the major parts of the state. In the southwest parts, drinking water supply is provided after treatment of canal water as groundwater of the area has salinity and alkalinity hazards (Singh et al. 2015a; Kumar et al. 2018).

Water security can be explained in simplified words as the capacity of a population to safeguard sustainable access to adequate quantities of acceptable quality water for sustainable livelihood, human well-being and economic development, for

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ensuring protection against water-borne pollution and water-related disasters. The above explanation clearly identifies two major attributes, i.e. adequate quantity and acceptable quality of water for security and sustenance. The objective of present chapter is to examine and discuss these aspects for the Punjab state in northwest India along with the management and technological tools to enhance the water security.

9.2 General Features and Water Resources

Punjab state is located in the northwestern parts of India (Fig. 9.1) and covers 50,362 Km^2. It forms the vast tract of Indo-Gangetic alluvium of Quaternary age. Majority of the state is covered by alluvium except in the northeast parts where rocks of Siwalik system are exposed. Agriculture covers more than 80% of the area of the state. The state has highest cropping intensity of 189% in the country. Agriculture consumes more than 85% of the water resources of the state. More than 97% of the cultivated area in the state is under irrigation. Groundwater is the major source of irrigation and drinking water supply and is tapped by shallow and deep tube wells. Canal irrigation is prevalent in about 25% of the area, while tube well irrigation with its share of about 75% dominates because of its assured irrigation character. A such number of tube-wells have increased from 1.92 lakhs to 14.05 lakhs during the period 1970–2015.

The annual rainfall in the Punjab state varies from about 300 to 1100 mm with an average of 680 mm.

The total availability of water in the Punjab* is as under:

Total surface water available at outlet	:	1.45 M ha
Ground water availability (from rainfall and seepage of canals	:	1.68 M ha
Total availability	:	3.13 M ha
Total demand for agriculture	:	4.76 M ha
Water deficit	:	**1.63 M ha**

*(*Source*: Irrigation Department, Punjab)

In view of the above water deficit scenario, water security has become an issue of concern as the economic development through agriculture and sustainable livelihood in rural areas is endangered. Further, drinking water supplies shall also be reduced in the future on account of environmental problems of groundwater such as depletion of water levels, waterlogging, salinity and deterioration of chemical quality of surface and groundwater. These aspects are discussed in details under the head water security issues.

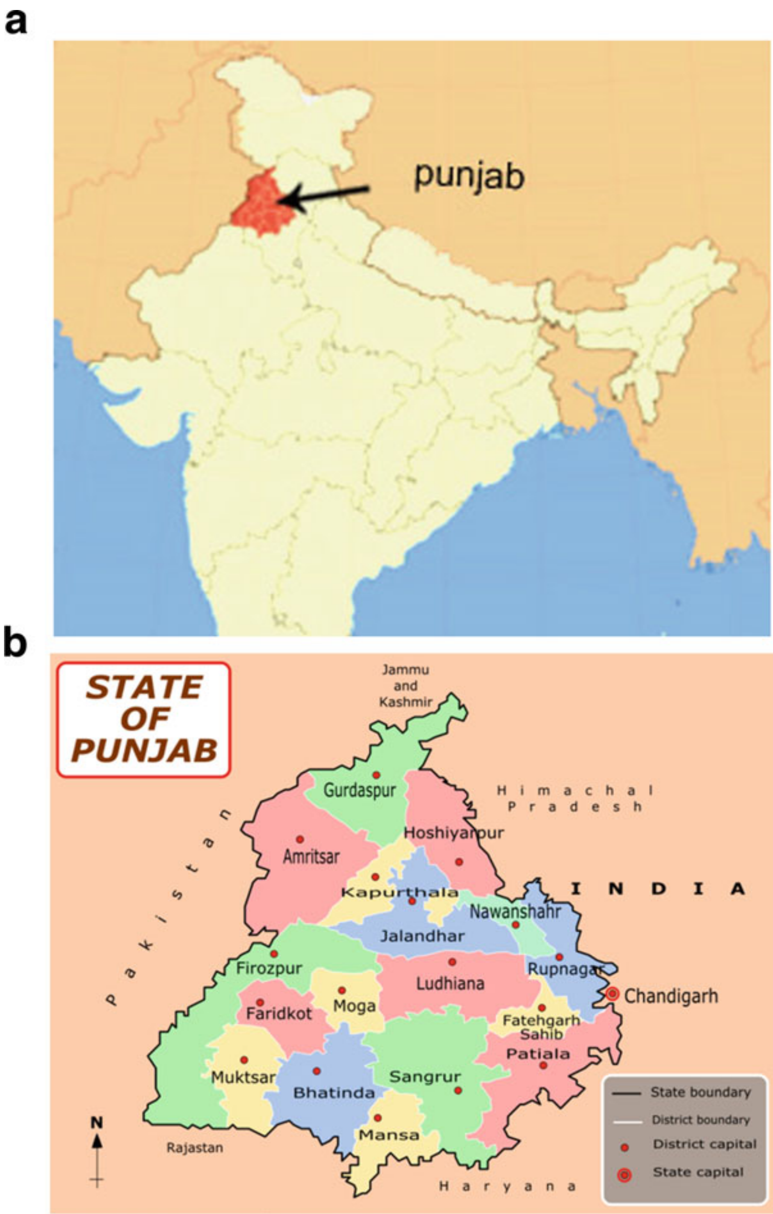

Fig. 9.1 (**a**) Location of Punjab state in India; (**b**) detailed map of Punjab state with district boundaries

9.3 Water Security Issues

9.3.1 Depletion of Water Levels

Depletion of water levels in the sweet water zone of Punjab state is one of the major issues of concern. Due to large-scale increase in a number of shallow tube wells from 1,92,000 in year 1970 to more than 14,00,000 in the year 2014 in Punjab state and predominance of rice-wheat cropping pattern, water levels have been declining fast since the last two decades (Singh et al. 2015b, c). Due to the impact of over-exploitation of groundwater in majority of areas, the depth of water levels now ranges from 10 to 20 m, and in critically over-exploited areas, it ranges between 20 and 40 m below the ground level. In order to assess the impact of groundwater overdevelopment, water levels are being monitored by the CGWB, and the state government groundwater organizations in 414 wells spread throughout the state. The results of the water level data indicate that 317 wells out of 414 show declining trend for the last 24-year period, i.e. June 1984 to June 2008 (C.G.W.B 2012). Water level data of the period 2004–2014 indicates that 68% of the state area has decline in water levels (Bhogal 2015). Majority of the areas showing significantly declining water level trend are located in districts Amritsar, Barnala, Fatehgarh Sahib, Faridkot, Tarn Taran, Ludhiana, Moga, Nawanshahr, Patiala and Sangrur. Apart from these districts, Kapurthala, Mansa and Mohali districts also show declining water level trend (Bhogal 2015). According to CGWB (2012), the maximum fall of 23.17 m in water levels at the rate of 96.54 cm/year has been observed in Moga block of Moga district followed by 22.60 m in Sherpur block of Sangrur district where water levels have been falling at the rate of 94 cm/year. Minimum fall has been observed in the Malout block of Muktsar district. Decline in water levels in Moga district has also affected chemical quality of groundwater.

According to Water Resources Directorate, Punjab and CGWB-GOI (2012), out of 138 blocks in Punjab, 110 blocks (75%) are overexploited (exploitation more than 100% of annual recharge), 3 blocks (4%) are critical (exploitation 90–100% of annual recharge), 2 blocks (3%) are semi-critical (exploitation 70–90%) and 23 blocks (18%) are safe where exploitation is less than 70% of annual recharge. The safe blocks are confined to Kandi area at the base of Siwaliks and in saline areas in SW parts, where groundwater cannot be exploited due to unfavourable lithology or chemical quality constraints. The number of over-exploited blocks has almost doubled from 53 in the year 1984 to 110 in the year 2014 (Bhogal 2015).

Depletion of water levels poses a serious threat for sustainable water supply and water security as the available water supply would get reduced with the depletion of water levels. In addition, the quality of groundwater also deteriorates with declining water levels as has been found in Moga district. Thus, both quantity and quality of water, two most important attributes of water security, shall be reduced in the future. To address the issue, water conservation, rainwater harvesting and artificial recharge to groundwater need to be adopted as strategies. Further, an attempt should be made to decrease the area in paddy. Suitable changes in policies by adopting legal framework (Alagh 2013) should be made. Modifications of subsoil water act (2009) need to be done by further postponing sowing of paddy crop by at least 4–5 days from the current date, i.e., 10th of June after taking the advice of P.A.U., Ludhiana. As a policy, subsidy should be provided to farmers as an incentive for switching to drip and sprinkler irrigation systems.

9.3.2 Waterlogging and Salinization

Water levels in southwestern parts of Punjab in saline zones have been rising in nearly 20% of the area. Further, the maximum rise 17.95 m was observed from the year 1984 to year 2001 in Lambi block of Muktsar district. Waterlogged areas (depth to water within 2 m) were earlier confined to southwest districts, i.e. Muktsar, Mansa, Faridkot and Ferozepur. Water level data for the period 2004–2014 shows that 7% of the waterlogged area is confined to Fazilka and Muktsar districts which show rising water level trend (Bhogal 2015). However, at present in year 2014, critical waterlogged areas (about 14,000 ha) exist in Muktsar district (Singh et al. 2015a).

Rising water levels and salinization also poses a serious threat to water security, safe drinking water supply and sanitation schemes. To address the issue, a holistic approach needs to be adopted for lining of canals, providing surface and subsurface drainage and conjunctive use of surface and groundwater (Singh et al. 2015a).

9.4 Deterioration of Groundwater and Surface Water Quality

Deterioration of groundwater quality largely due to geogenic (natural) causes is a major issue of concern for water security and human health being faced by the state of Punjab on account of the presence of toxic elements like uranium, arsenic and fluoride in groundwater especially in deeper aquifers (more than 100 m depth and up to 350 m depth) from where drinking water supply is provided (Sharma 2015). These problems are briefly discussed below:

9.4.1 Uranium Hazard

Malwa region of Punjab state has been in news for having uranium in groundwater beyond the permissible limits of the WHO and AERB since the year 2009. High levels of uranium and heavy metals found in the hair samples of 80% of 149 neurologically disabled children under treatment in Baba Farid Center for Special Children, Faridkot, led the Department of Water Supply and Sanitation,

Table 9.1 Showing district-wise number of villages having uranium problem in groundwater

Sr. No.	District	Number of villages affected with uranium beyond 60 ppb (permissible limit) in groundwater
1.	Amritsar	0
2.	Barnala	95
3.	Bathinda	29
4.	Faridkot	3
5.	Fatehgarh Sahib	5
6.	Fazilka	52
7.	Ferozepur	128
8.	Gurdaspur	0
9.	Hoshiarpur	0
10.	Jalandhar	0
11.	Kapurthala	1
12.	Ludhiana	22
13.	Mansa	2
14.	Moga	111
15.	Pathankot	0
16.	Patiala	3
17.	Roopnagar	0
18.	Sangrur	44
19.	SAS Nagar	0
20.	SBS Nagar	0
21.	Tarn Taran	18
	Total	**513**

Source: Sharma (2015)

Punjab, to collect samples from all the groundwater-based schemes in the state and have them analysed by BARC to have detailed data on the problem. Singh (2010) prepared a detailed status paper on the presence of uranium in groundwater. He highlighted the global, national and state scenario along with the possible causes and remedies. The results of uranium analysis of groundwater samples of all the water supply schemes in Punjab tapping deeper aquifer system (100–350 m) reveal that a total of 357 water supply schemes covering 513 villages have been found to be affected with uranium with concentration more than 60 ppb which is AERB limit for drinking water use (Sharma 2015). The maximum concentration of uranium found is about 366 ppb in Kotha Alia Lukmanapura Village of the District Fazilka (Sharma 2015). The number of villages in various districts of Punjab having uranium problem is shown in Table 9.1.

The results of isotopes in groundwater samples by BARC indicate that the uranium present in groundwater of Punjab is natural uranium. The mass percentage of 235U and 234U and 238U in natural uranium are 0.72%, 0.005% and 99.27%, respectively (Sharma 2015). Uranium is known to be nephrotoxic and affects the kidneys and human health in many ways (Singh 2010, 2014; Singh et al. 2010, 2013).

The presence of uranium in groundwater could be because of natural (geogenic) or man's activities such as contamination caused by fly ash disposal from thermal plants or by the use of phosphatic fertilizers (Singh 2010; Singh et al. 2010). In Punjab state, mobilization of uranium from sediments into groundwater under favourable geochemical environment appears to be the cause (Singh et al. 2015d). However, detailed studies on this aspect need to be carried out as a policy to understand the problem and to alleviate the problem in new areas. To address the issue, RO treatment plants are being installed in various problematic areas by the Department of Water Supply and Sanitation, Punjab (Sharma 2015).

9.4.2 Arsenic Hazard

Arsenic hazard in the groundwater of Punjab state was unheard especially in deeper water supply wells (Singh et al. 2015e). Earlier Hundal et al. 2007 reported large-scale contamination by arsenic in the entire Punjab state, but later Singh et al. 2015c ruled out this and reported sporadic occurrence arsenic in southwest Punjab. They also found that such arsenic contamination is controlled by geomorphology, mineralogical and geochemical environment. They recommended that areas close to rivers (flood plain zones) need to be tested for arsenic. Recent data generated by Department of Water Supply and Sanitation, Punjab (Sharma 2015) indicates the prevalence of problem on large scale especially in riverain tracts of Amritsar and Gurdaspur districts. 114, 42 and 21 habitations in Amritsar, Gurdaspur and Tarn Taran districts, respectively, have been found to contain more than 0.05 mg/l of arsenic levels which was earlier prescribed a permissible limit for drinking water use. However, if the recent WHO limit of 0.01 mg/l is followed, 1585 villages would fall under the unsafe category due to high arsenic concentration in drinking water. The data validates the work of Singh et al. 2014a and 2015e. District-wise data on presence of arsenic in groundwater of Punjab as per data generated by Department of Water Supply and Sanitation, Punjab (Sharma 2015) is shown in Table 9.2. In view of the above, it is clear that arsenic also poses a serious threat to sustained drinking supply especially in districts of Amritsar, Tarn Taran and river rain tracts of Ferozepur and Ropar districts. Arsenic in drinking water causes several health problems especially related to the skin and liver and various types of cancers (Singh et al. 2014a).

To provide safe drinking water supply, the Department of Water Supply and Sanitation has prepared a project for the installing 1585 AMRIT water purification units under the World Bank Project using newer technology (Sharma 2015) and to enhance the water security.

Table 9.2 Showing number of failed habitations due to arsenic problem in groundwater

Sr. No.	District	Number of samples tested		Number of failed habitations due to arsenic beyond permissible limit of 0.05 mg/I in groundwater
		Phase I	Phase II	
1.	Amritsar	486	512	114
2.	Fazilka	90	124	1
3.	Firozpur	586	440	1
4.	Gurdaspur	511	394	42
5.	Roopnagar	308	323	7
6.	Tarn Taran	328	310	21
	Total	**2309**	**2103**	**186**

Source: Sharma (2015)

9.4.3 Fluoride Hazard

Fluoride hazard is increasing in the groundwater of Punjab especially in the southwest parts of the state. This is primarily caused by geogenic sources when fluoride gets leached out from the sediments to the groundwater under favourable geochemical environment (Singh et al. 2014b). A number of villages in various districts suffering from fluoride hazard in Punjab as per data generated by Department of Water Supply and Sanitation, Punjab are shown in Table 9.3. Fluoride poses various health problems like bone and joint problem and dental and skeletal fluorosis (Singh and Kishore 2009, Singh 2014; Singh et al. 2014b).

To address the issue, water treatment plants are being installed by the Water Supply and Sanitation Department in problematic areas (Sharma 2015).

9.4.4 Pollution of Canals and Surface Water Bodies

Canal-based water supply is in practice in southwest districts of Punjab as the groundwater is not fit for drinking water. Recent data shows that, at places, the canal water is also contaminated on account of untreated waste water and other solids being discharged into them. This poses again a serious threat to safe water supply through canal network.

In addition numbers of wetlands (Harike, Ropar and Kanjali) are also facing water quality problems. From Harike, a number of canals originate which are a source of drinking water supply in southwest parts of Punjab state. To address the issue, pollution control laws need to be enforced strictly.

Table 9.3 Showing district-wise number of villages affected by fluoride in groundwater

Sr. No.	District	Number of villages affected with fluoride beyond permissible limit in groundwater
1.	Amritsar	3
2.	Barnala	4
3.	Bathinda	2
4.	Faridkot	0
5.	Fatehgarh Sahib	30
6.	Fazilka	25
7.	Ferozepur	1
8.	Gurdaspur	4
9.	Hoshiarpur	2
10.	Jalandhar	1
11.	Kapurthala	1
12.	Ludhiana	1
13.	Mansa	8
14.	Moga	2
15.	Pathankot	0
16.	Patiala	159
17.	Roopnagar	0
18.	Sangrur	23
19.	SAS Nagar	11
20.	SBS Nagar	0
21.	Tarn Taran	4
	Total	**281**

Source: Sharma (2015)

9.5 Management Tools and Conclusions

In order to address the problem of depletion of water levels, rainwater harvesting and artificial recharge; water conservation measures in agriculture, industrial and domestic sector; adoption of modern irrigation system such as sprinkler and drip irrigation; reducing crop area under paddy cultivation; and adoption of legal framework of water (Alagh 2013) are suggested. To alleviate the waterlogging and salinization, construction of surface and subsurface drains, pisciculture in saline water, adoption of cotton against paddy crop and conjunctive use of surface and groundwater should help in controlling waterlogging and salinization (Singh et al. 2015e) to address the water quality issues; installation of RO plants and adoption of techniques to reduce alkalinity of soil and water will go a long way to enhance the water security in the area.

Systematic long-term studies aiming to understand the mechanism of mobilization of geogenic contaminants like fluoride, arsenic and uranium have not been carried out except the work of few workers (Jacks et al. 2005; Singh et al. 2014a, b, 2017). Such studies are of immense importance as preventive steps such as control of pH and bicarbonate concentration in soil and water can help especially in spreading of fluoride hazard (Jacks et al. 2005). Zoltan (2013) has also shown the control of bicarbonate concentration on uranium in groundwater drawn from majority of aquifers in the USA. Similar results have been obtained in Punjab (Singh et al. 2018). These studies should be made, the results of which would help in enhancing the water security in the area.

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Chapter 10
Industrial Wastewater Footprinting: A Need for Water Security in Indian Context

Shamshad Ahmad, Pradeep K. Majhi, Richa Kothari, and Rajeev Pratap Singh

Abstract The continued population expansion with limited resources on the planet earth deteriorated the quality of the environment. To manage the water resources at regional, national and global level, the input-output models of water footprinting (WFP) in relation to the water use and consumed are taken as an objective for this chapter. Types of WFP, assessment for industrial wastewater footprinting (IWFP), associated risks with WFP and water security for sustainable growth and economy with social impacts are critically reviewed and assessed here in this chapter. Furthermore, water polices in an Indian context are also delineated to impact its role in sustainable green water footprinting (GrWFP).

Keywords Freshwater · Water footprint · Environmental impact · Sustainability

10.1 Introduction

Freshwater resources have depleted over the last 5–6 decades from all over the world due to the snowballing of population and urbanization, which amplifies the demand of agriculture for food items with an increase in shifting of consumption patterns (De-Fraiture and Wichelns 2010). Today the scarcity of freshwater due to an exponential growth of pollution is a serious issue. In the near future, there will be

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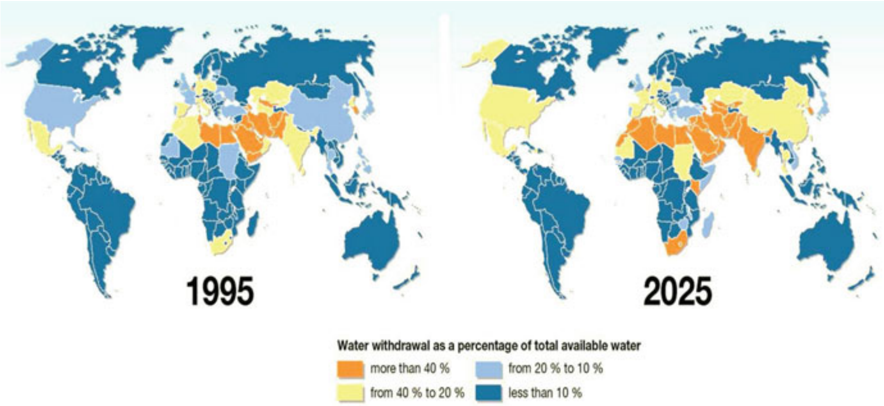

Fig. 10.1 Contemporary data for withdrawal of water (1995–2025). (http://2014.igem.org)

a substantial increase in the demand of freshwater which alters the quality. Several researchers have predicted that in the coming future, we will be a lot more dependent on water resources than at present (Fig. 10.1), and this dependency will craft grave problems like food security as well as environmental sustainability (Islam et al. 2016). A contemporary study guesstimates that universally the withdrawal of water will increase from 4.5×10^6 million m^3/year today to 6.9×10^6 million m^3/year by 2025 (Ertug and Hoekstra 2014; McKinsey 2009).

The key reasons for depletion of future water resources are exponential growth of population design, man-made domino effect which affects the economic growth, changes in production pattern of agriculture and industrial growth with trade patterns which competete over water. Incresed demand for industrial, agricultural and domestic purposes in different sectors of society will respond to increasing water scarcity and water pollution. Every segment of the society will react to the problem of water pollution and its scarcity because of the increasing demands of the food coming from industries, agriculture and other domestic sources (Fig. 10.2).

The world population is approximately 7 billion and is growing at a rate of around 1.11% per year (http://www.worldometers.info/world-population). In the past, world population growth grew deliberately, but in recent centuries, it has jumped radically, and the consumption of global water rate doubles in every 20–30 years. In fact the demand of water withdrawal has increased three times from 50 years because of the growth of population (http://www.unesco.org/water/wwap/wwdr/wwdr3/pdf/18_WWDR3_ch_7.pdf). This speedy rate of growth has caused a decline in the global availability potential of water from 12,900 m^3 in 1970 to 9000 m^3 in 1990 to about 7000 m^3 per capita per year in 2010 (http://www.unep.org/dewa/vitalwater/article186.html).

Administrative mismanagement and institutional ineffectiveness, pettiness at central, state and municipal levels, exponentially increasing population that will reach an estimated about ~1.7 billion by 2050, rapidly mushrooming

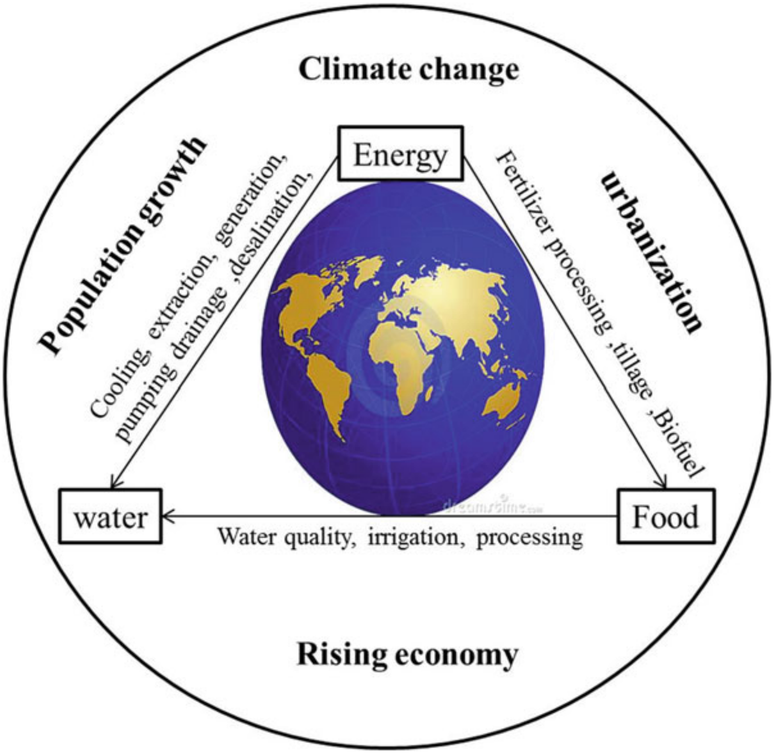

Fig. 10.2 Factors affecting the water scarcity at global level

(http://thirdworldcentre.org/ communication-media/can-india-feed-1-7-billion-people-by-2050). India supports approximately 16% of population, ~50% of land and ~25% of water resources of the world. India also has ~20% of the world's livestock population; more than 50% of these are cattle population, forming the backbone of agriculture in India (Gangwar 2013). All the water resources whether surface or ground confined near populated centres are contaminated with hazardous and organic pollutants given out by industrial and domestic processing. In the future decades, water demand is expected to grow by ~20%, fuelled primarily by the industrial requirements which are projected to double (The Food and Agriculture Organization of the United Nations 2011).

Based on the requirement of water for various purposes in the present century, water-stressed situation has developed. The range of per capita water availability is 1000–1700 m^3 per year as shown in Table 10.1. This would be considered as a water-scarce condition when the water accessibility reduces to 1000 m^3 per year. As it is evident from the table below, when the total population was only 361 million, the water availability per capita in 1951 was 5177 m^3 per year. When the population marked an increase to 1027 million in 2001, water availability per capita dropped

Table 10.1 Per capita water requirement with population growth during 1951–2050 (Ministry of Water Resource Government of India 2009)

Year	Population (million)	Water availability (m^3/year) of water per capita
1951	361	5177
1955	395	4732
1991	846	2209
2001	1027	1816
2011	1210	1545
2025	1394	1341
2050	1640	1140

considerably to 1820 m^3 per year as shown in Table 10.1 (Ministry of Water Resource Government of India 2009).

According to Bhat (2014), the availability of water per capita from 2025 and 2050 will decrease by 36–60%, respectively. The main solution to solve today's most urgent water problems is to grow the demand of global freshwater resources. In formulation of national water plans, administrative authority is conventionally engaged in national perception matching for water supplies to fulfil national demand of water. Without interrogating the total amount of water demand, the administrative authorities have surveyed to placate the use of water. All countries of the world trade water-intensive commodities (WIC), but only limited countries unambiguously prefer to protect water resources through import of water-intensive commodity products to make use of relative water abundance to produce WIC for export. Above everything, the governments don't have any estimate of the water sustainability for national consumption. Without considering the problems like water depletion or pollution in the countries that are producing imported products, there are many countries that have considerably given their WFP. While evaluating the environmental policy or national food security, the national government should have sufficient knowledge of the dependency of the country on its water resources.

10.2 Water Footprinting (WFP)

Huge amount of water is utilized by the industries in processing and product development. These processes have urged the need to improve the water and wastewater management and techniques accounting for future use by using water footprinting. The water footprint (WFP) is basically an indicator of direct and indirect water use, which is quantified in terms of volume of water consumed, vaporized or polluted. It includes the consumptive use of virtual water content (VWC) in terms of green, blue and grey water (Kothari et al. 2018). The water consumption could be measured in terms of the amount of water volumes consumed (evaporated) and/or polluted per unit of time in an area. A WFP can be calculated for

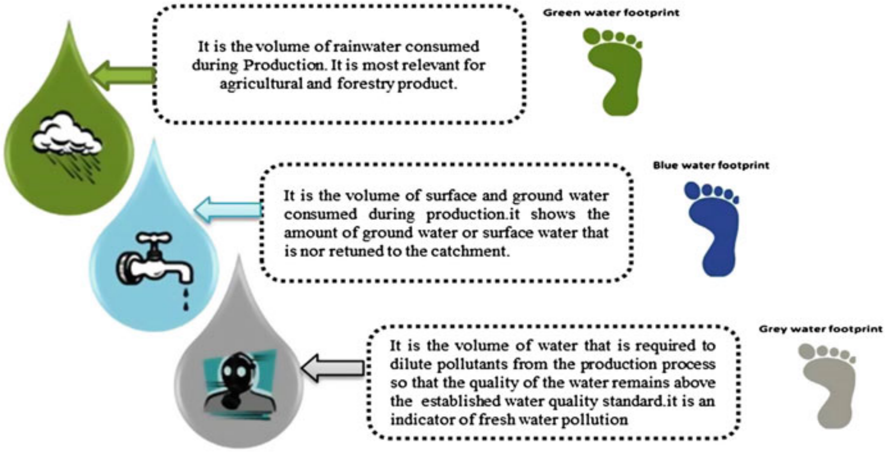

Fig. 10.3 Type of water footprinting

any distinct group of producer (economic sector, community sector, etc.) and consumer (e.g. individual, city, state, nation, etc.) This demarcates the water use as well as water pollution along with its geographical location. The idea of VWC given by Steduto et al. (2017) to manage the water scarcity in region is very diligently related to the idea of WFP. The WFP is designed for three different types of water: green water footprints (GWFP), grey water footprint (GrWFP) and blue water footprint (BWFP) which is shown in Fig. 10.3.

10.2.1 Blue Water Footprinting (BWFP)

Blue water resources (surface water like river, lake and groundwater) are expended as a result of the manufacture of the goods and amenities. The BWFP consumption touches four cases such as evaporation, incorporation of water in product, water not reimbursed to the same catchment region and water not reimbursed in the same period in which it was withdrawn.

10.2.2 Green Water Footprinting (GWFP)

GWFP means the utilization of 'green' water resources (rainwater/precipitation stored in the soil as moisture). GWFP designate the precipitation of water on land which does not flow or recharge the groundwater deposited in the soil. These waters evaporate when the crop grows.

10.2.3 Grey Water Footprinting (GrWFP)

GrWFP is the amount of freshwater required to dissolute the load of pollutants to such an extent on grounds of the prevailing standards of water quality (Hoekstra et al. 2011).

To recognize the confined impacts, WFP could be compared with the availability of resource, quality of water and quality and watershed of individual constraints. Without referencing to the location, the calculation of water footprinting which the water is impacted and consumed is considerably of less significance. WFP accounts give spatially and temporally obvious information about the ways in which water is adopted by several human activities for environmental, social and economic benefits.

10.3 Industrial Water Footprinting (IWFP) Assessment

Based on the freshwater assumption or influence, the WFP should be regarded as a volumetric sign to improve policy engagements and conflict in international, national and regional virtual water flow and trade (Yifan et al. 2014; Berger et al. 2014). This technique will also benefit to better manage the agriculture water field for allocation of volumetric indicator. Nonetheless, the agricultural sector produces less wastewater than several industries. The influence of industrial process play vital role for properly assessing the WFP and water jeopardy. Teething troubles are augmented when WFP endeavours to show the consumption of water and pollution in industries simultaneously. However, some faults are existing in these WFP when applied in industries illustrated in Fig. 10.4.

In routine fabrication of different products in industries, withdrawal of water is regarded as a major indicator in industries; this application concept is the same as the

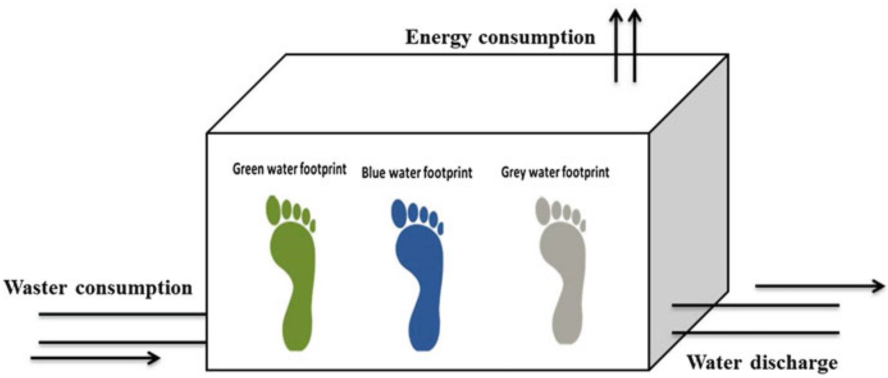

Fig. 10.4 Demands of WFP assessment for any type of industry. (Yifan et al. 2014)

Fig. 10.5 Industrial route of water cradle to grave for making beer. (Water Footprinting 2009)

BWFP (utilization of surface and groundwater). Calculation of WFP of a product based on the people consumption pattern. Zhao et al. (2015) developed WFP for consumption of cotton crop for garment production, import and export and disposal pattern of waste. Several organizations developed an approximation of the WFP for singular item, including beer (Fig. 10.5). The WFP of beer formation starts with the crop cultivation and follows the processes through to the recycling of bottles.

Assessment of IWFP is a four-step procedure which comprises (a) settling the goals for assessment of scope; (b) calculating the GWFP, BWFP and GrWFP; (c) assessing equitability efficiency and sustainability of WFP; and (d) tactical formulation of response. To make the corporate policies for water, which could be used by the companies and industries, IWFP assessment offers a fundamental methodology (Arjen et al. 2011).

Determination of the IWFP by different practices on daily time measure to understand which processes are responsible for maximum consumption of water and its pollution at the industrial activity. This directed to deep empathetic water-related difficulties which emphasized premeditated prospects for improvement of water-related difficulties. Tata group of industries in India (power, chemical and motor) required water for industrial activity from the surface water, mostly rivers and tributaries and stream, internal reservoirs groundwater resources define the BWFP, GWFP and GrWFP given in Fig. 10.6 (Water Footprint Assessment 2013). But the company/industries do not reassure for utilization of groundwater resource, but gradually participating data on water from larger number of surface water resource sites each year mention in the sustainability report.

Human water footprint (HWFP) with the earth sustainably support is predominant in WFP sustainability assessment. However, when we divide this problem, we will make out that there are several other sorts of problems that can create many intricacies in the above-stated problem. WFP sustainability has various magnitudes (environmental, social and economic); effects can be articulated at different levels (primary and secondary impacts) (Hoekstra 2015).

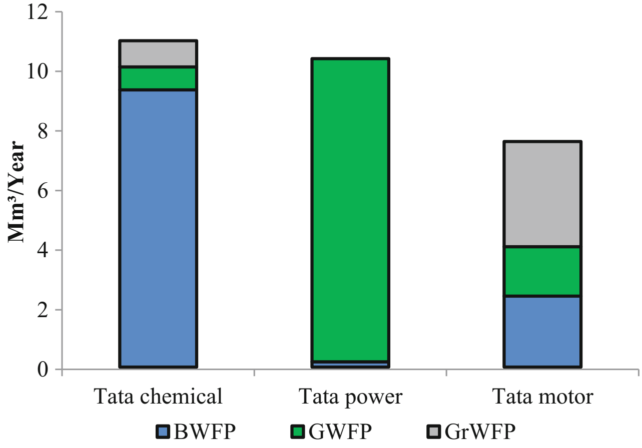

Fig. 10.6 Utilization of BWFP, GWFP and GrWFP in Tata group of industries. (Water Footprint Assessment 2013)

The IWFP sustainability of a product, producer and consumer partially or completely rests on the geographic context, temperature variation, moisture content, etc. because in this context, numerous WFP components (BWFP, GWFP and GrWFP) of a product are located. Rarely the BWFP, GWFP and GrWFP of particular product process, producer and consumer produce the water dearth problems and wastewater pollution. These problems are the collective indicator of all the activities related to water problem in the geographic area. The total WFP comprises of many minor WFP which are linked to the processes of product related to producer and consumer in a given geographical extent (Ertug and Hoekstra 2012). When the BWFP, GWFP and GrWFP of a product process contribute to the unsustainable situation, say by the producer or consumer, it can be stated that the WFP is unsustainable within that particular geographical extent.

In recent days, the unsustainable utilization of water resources creates huge challenges with the generation periods of water-consuming products. Human movements enlarge and pollute a ton of water at the sources. Globally, the major portion of water level is being used in rural creations, though there are moreover momentous water volumes consumed and contaminated in the mechanical and residential parts. A variety of industries have footprints to the environment, and those should be studied such as paper industry, dairy industry, textile industry, pulp industry, etc. to get the water status in recent days of world.

10.4 Reducing the WFP

Complete water recycling can reduce the blue and grey WFP to zero; no evaporation losses or polluted effluents are seen in closed system. The water taken from the water bodies could be returned back in them through capturing the evaporated water from the factories and cooling system. When water is incorporated into a product, the BWFP cannot be reduced to zero which is an exception. The GrWFP of thermal pollution cannot be reduced to zero, but here too the heat can be recollected from the effluents and used for some other purposes Avoiding or reducing the use of pesticides and fertilizers, using better tools and techniques and selecting an appropriate time for the application in the agricultural fields can reduce the GrWFP to a great extent. Production of GWFP and (ton/m^3). In agriculture can lower GWFP and BWFP (m^3/ton) to a great extent. Increasing water productivity is more important when water is in shortage than land as compared to giving focus on maximizing agricultural land productivity when land is scarce and water is in excess. In agriculture, the blue water should be used wisely so that yield per cubic metre increases with minimum amount of water used for irrigation. There are several strategies for reducing the BWFP, GWFP and GrWFP as given in Table 10.2.

Table 10.3 gives a brief description of the IWFP curtailment objectives per WFP element per sector. The BWFP and GrWFP are invalidated in the industrial sector. To quantitatively reduce water footprint, agricultural sector requires much research. Using organic farming can reduce GrWFP to zero, but it will take considerable time and great efforts to shift from conventional farming to organic farming. Over a time span, global blue water footprint could be reduced to half by encouraging blue water productivities by following such techniques in agricultural sector such as drip irrigation and sprinklers that make use of less amount of water.

10.4.1 Conflict and Fear in Water Security

Water is life, and life is water; its security is not only necessary for ecosystem but also for the whole earth. It is not only limited to local area, but it is the major problem with international perspectives. Water scarcity and stress both are collectively related to water availability; as water demand of an area increases, it stresses on supply and water availability. Globally, the unstable utilization of water creates a variety of environmental problems, for which a number of major factors are responsible such as using a large number of machines and timberland-based crude materials in factories and utilizing less-quality gristly rough machinery parts and very ordinary modernism/technology in industries. Day by day the utilization of water is increasing economically, and thus, it is really tough to safeguard water resources. In previous research on water footprint of various industries give ideas of the utilization of water, reuse and production of wastewater, etc. and more noticeable perspectives. There are major issues regarding water problem, and several steps/methods are being utilized for the security of water in various advance possible ways. In general, it is observed that the water demand gradually increases, but at the same time, available water remains the same; in that case water stress generally occurs as shown in Fig. 10.7.

Table 10.2 Options for reducing water footprint (Arjen and Mesfin 2012)

IWFP reduction goals – processes
Standardizing products or sites. Formulate targets to get best practices throughout the business
Minimizing water footprint: minimizing blue water footprint by reducing, reusing and recycling the water
Reduction of BWFP in hotspots. Blue water footprint should be minimized in areas where there is scarcity of water both surface and groundwater
Minimization of GrWFP: refuse or reduce chemical use; water should be treated before disposal
Reduction of GrWFP in hotspots for focusing the above procedures in areas where normal
quality of water standard is violated
IWFP reduction goals – supply chain
Approval for reduction goals with providers
Transferal to other suppliers
Develop supplementary or fully regulate the supply chain. Modification in the business module to incorporate for better control over the supply chain
Water footprint reduction targets – end use
Water use should be reduced to maximum possible extent by making use of water-extensive processes and technologies
Harmful chemicals should be avoided to cause less water pollution
WFP offsetting measures
Environmental compensation: the company's water catchment should be properly managed, and water should be used in a sustainable manner
Social compensation. Equitable use of water resources in the company's catchment area should be promoted
Economic compensation. The downstream users should be given compensation by the company which is using water of the upstream catchment
Product and business transparency
Complying with the standard definitions and methods accepted globally for accounting and assessing WFP
Water accounting should be promoted over the supply chain so that one could get an exact account of the water footprint of the products
IWFP report: efforts made for sustainable use of water and the targets achieved should be enlisted in annual report
Declaration of water footprint of product through reporting or internet
Labelling the information related to the product
Water certification scheme should be made and everyone should comply with it
Engagement
Consumer communication and community participation with the organizations
Coordination with governments to develop various guidelines and laws for minimizing water footprint
New and improved agricultural practices should be followed to increase the productivity of land (yield, ton/ha). In this way the green water footprint (m^3/ton) could be reduced
Covering the soil with mulch can reduce WFP

Table 10.3 Possible water footprint reduction targets per sector and water footprint component (Water footprinting 2009)

WFP	Agriculture	Industry
GWFP	Increase in GWFP productivity (ton/m^3) in both rain-fed and irrigated agriculture	Not relevant
BWFP	New, improved and advanced agricultural techniques such as sprinklers would decrease blue water footprint by an estimated 50%	Zero BWFP: evaporation losses reduced
GrWFP	Minimization of the chemicals in fields. Switching on to organic farming from conventional farming can bring grey water footprint to zero	Refusing and recycling of chemical products. Collecting heat from effluents. Treatment of the effluents

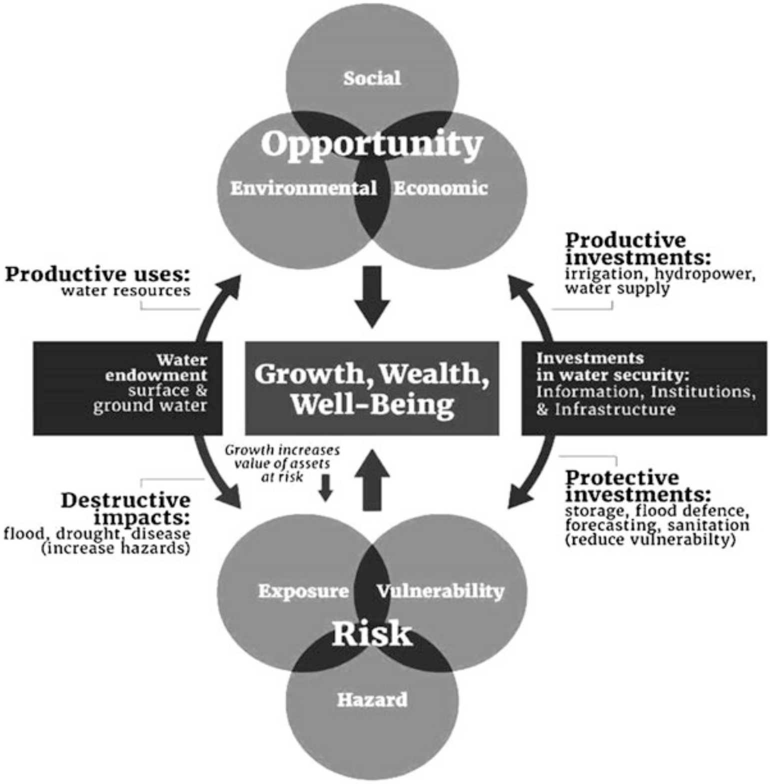

Fig. 10.7 Water security and sustainable growth: a conceptual framework. (https://www.slideshare.net/fmacleod123/securing-water-sustaining-growth.pdf)

10.4.2 The Water Security: Global Status

Water security is one of the principal issues nowadays, and its economic impacts show up through a variety of mechanisms for businesses, people, households and communities. A number of key features are responsible for it and are being discussed:

- To fulfil the basic needs, i.e. sanitation, hygiene and protection of well-being and health accessing of safe and sufficient drinking water at a very reasonable cost (United Nations General Assembly 2010).
- To keep up the capability of ecosystem as well as maintain/develop the performance of ecosystem services.
- Safeguard of recreational values, human rights, culture and livelihoods.
- Magnification of socio-economic status by supplying water.
- The transboundary water management approaches to be included in a two-way state within countries.
- Pollution, drought and floods are major issues created by water; to accept these challenges, fight against these hazards (UNU-INWEH 2013).

10.4.3 Challenges of Water Security

- About 1.2 billion people are suffering from lack of safe drinking water, and annually two million suffers diarrhoea.
- 2.4 billion people are unable to use their basic water sanitation, and annually ten million struggle with hepatitis.
- 1.8 billion people go through very unusual source of drinking water, which is infected with faeces, that puts them into a number of health hazards like polio, typhoid, cholera, dysentery, etc. It is estimated that poor sanitation, unsafe water and lack of hygiene lead about 842,000 deaths per year (WHO-UNICEF 2014).
- Presently more than 663 million people are in front of the lacking of water resources as well as improved drinking water unavailability (WHO-UNICEF 2015).
- As per estimation out of the world's population, 50% is on cities, and up to a recent data, it is anticipated being 70%. So most of the focus should be on cities. In both developed and developing countries, there is lacking of resources and sufficient infrastructure for sustainable water management (World Urbanization Prospects 2014).
- It is observed in many developing countries that to get water, women usually walk an average of 6 km daily.
- Globally more than half of hospital bed people are being seen with water-related diseases.

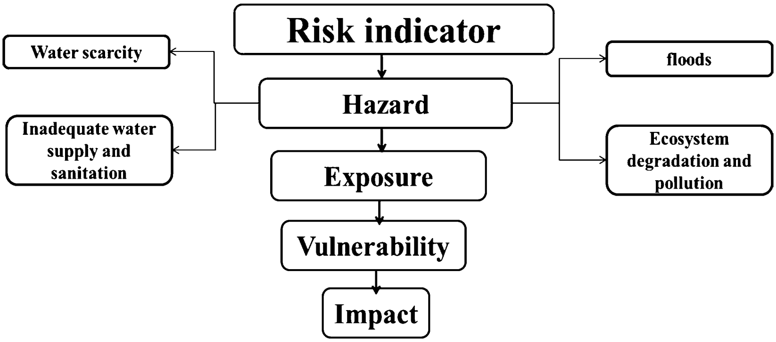

Fig. 10.8 Risk indicator in water security

10.4.4 Water Security: Risk Indicators

The factors that are mostly accountable for the insecurity of the resources of water are risk-based indicators. Risk is always dynamic and it has uncertain probability of damaging outcomes. It is a context-dependent, not a noticeable quantity, and depends on the attitudes and perceptions of various stakeholders. So, any observed risk must be complex that incorporates elements of danger, exposure and susceptibility that is given in Fig. 10.8. The security of water lies within diverse interactions of natural phenomena and human society. These kinds of interactions show various opportunities and also risks (Hall and Borgomeo 2013). Therefore, for developing a group of indicators for water security, the logic of risks can be applied, i.e. based upon four types of risks: (i) water scarcity, (ii) floods, (iii) inadequate resource of water and sanitation and (iv) ecosystem pollution and degradation.

10.4.5 Technological Advancement and Practices in Security of Water

Several technolgies exist for water security, but those are very old/unsystematic for recent days. Therefore, there is a need of refined, improved and developed technologies focusing on bigger challenges towards research/new finding/developments. The modern technologies should have greater emphasis/consciousness on ecosystem balance and sustainable development as shown in Fig. 10.9.

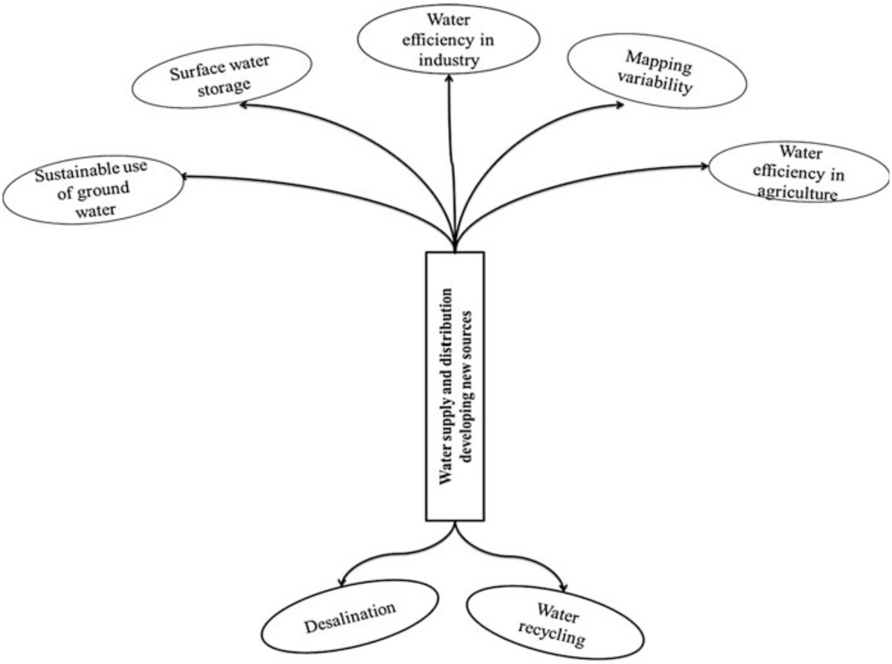

Fig. 10.9 New and better technologies, techniques and practices

10.5 Water Policy

A water policy is the need of the hour which identifies the challenges arising out of the excessive use and exploitation of water resources and to minimize the adverse effect of BWFP, GWFP and GrWFP. Water policy safeguarding the treasurable water resources are used to eradicate poverty and achieve economic growth for human development (National Water Policy 2012). In developing nations effective policies, decision-making skills and sustainable water resource management, there is a need of a number of new/advanced tools which would have the capability for development towards sustainable environmental growth, i.e. to gather knowledge about earth's water statistics and also to have knowledge over well water management system (Flanagan et al. 2016). The water policy overlay provides the most telling and clear benefits for obtaining clear understanding of the risks and opportunities for use of water. Four strategic policy issues were identified which are (a) water allocation and resource protection, (b) water use efficiency, (c) water use licensing and enforcement and (d) economic instruments and pricing.

Water policy is centralized towards the water quality by preventing the water bodies from pollution. Prevention policy includes polluter's pay principle as well as improvement in existing strategies by employing new techniques and innovation. Intervention of innovation would be helpful in elimination of pollution from various water resources like surface and groundwater which would aid for the improvement of the quality of water and to augment the recycle and reuse of water (Kathpalia and Kapoor 2002). Due to substantial amount of pressure on freshwater resources, ensuring freshwater availability is of prime importance to sustain life forms. Effective policy implementation as well as policy-related network in national and international policy is required to promote the sustainable water use. These efforts involve collecting database on micro watershed level; uniform standards for coding, classification and processing; management of freshwater demand and its conservation; and integrated planning for maximizing water usability (Water footprinting 2009). In order to achieve the desired objectives, policy should be framed with effective action plan within a time-bound manner.

10.6 Conclusion

Wastewater discharge during industrial processing directly/indirectly influences the surrounding environment. The use of wastewater footprinting methodologies developed by various governmental and non-governmental communities in collaboration with research institutions, large companies from different sectors, consultants and international institution is an informative way to improve challenges at national/regional level for water management during agricultural and industrial processing. Hence, studies which focus on the environmental impact caused by the industrial processes are the best way to assess the water footprints and water risks for the need of water security. Furthermore, policy issues with implementing strategies are also the important part for sustainable water security at national and international level.

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Chapter 11
Fluoride Contamination and Health Effects: An Indian Scenario

Ganesh Chandra Kisku and Pokhraj Sahu

Abstract Uncontaminated water is the prime requirement of drinking water and lifeline of living organisms. Although some of the minerals are essential for growth and healthy development, excessive buildup of these minerals, viz. fluoride, can pose a great health risk to flora and fauna. Fluoride is a vital element for developments and strengthens of teeth and bones, but its elevated levels are associated with many incurable negative health effects reported on human and animals in all over India. The dental caries causes due to very low concentration of fluoride < 0.5 mg/L in drinking water and excessive fluoride (> 1.5 mg/L) also causes to dental fluorosis, skeletal fluorosis and neurotoxin effect, muscles degeneration, gastrointestinal system, reproductive system, etc. The effects of fluoride illness are more prevalent in children than adults. Therefore preliminary knowledge becomes necessary for everyone to know about the fluoride concentration in the drinking water, daily diets and other environmental matrix to avoid chronic fluoride diseases. The foremost sources of fluoride in groundwater are geogenic in origin, but the secondary sources are industrial activity like phosphate fertilizers, coal-based power plant and ceramic and glass industry. The higher concentrations of fluoride have been reported in Rajasthan (0.2–69.0 mg/L), Haryana (0.17–48 mg/L), Delhi (0.4–32 mg/L), Gujarat (1.58–31 mg/L) and Assam (0.2–23 mg/L). This chapter covers the fluoride-related issues and discusses the magnitude of problems those occurring in India and possible preventive measures and preventive programmes initiated by the Government of India.

Keywords Fluoride · Groundwater · Dental and skeletal fluorosis · Environmental matrix · Hydrogeochemistry

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11.1 Introduction

Water resource has played a critical and very important role throughout the history in the growth and development of human civilization. In modern times, water resources have key role in the economic growth of all contemporary societies. Therefore, water resource assessment and sustainability consideration is of utmost importance in developing countries such as India, where water is commonly has economic and social significance (Kumar 2005; Kumar et al. 2018). The inaccessibility of uncontaminated drinking water and scarcity is the major problem in the world including India, where groundwater is main sources for drinking purpose (Mumtaz et al. 2015). It contains dissolved ions (As, Hg, U, F, NO_3^- SO_4^{2-} and heavy metals) beyond the permissible limit which is harmful and creates lots of waterborne disease. WHO have reported worldwide 748 million people are exposed to contaminated groundwater resources crisis for drinking purpose in 2012, 200 million human population in 27 nations all over the world facing critical issue of fluoride contamination while 66.64 million people in India (Mumtaz et al. 2015).

Merriam-Webster's Collegiate Dictionary (2003) defines that "Fluorosis is an abnormal condition (as mottling of the teeth) caused by fluorine or its compounds" (Dharmshaktu 2013). Fluorine is an element of the halogen groups and is among the highly reactive elements. The fluorine does not found free form in nature because of its strongly electronegative nature. Naturally it is found in the rocks, coal and clay soil. It is essential and chiefly abounded in earth crust. Fluorosis is an incurable disease mediated by the intake of F^--rich water by humans and animals. Fluoride (F) within the body form highly insoluble and stable compound calcium appetite and react with calcium phosphate hydroxide. The absorbed fluoride deposited in bones and teeth which can results in major problems in the normal functioning of bones and teeth.

$$Ca_{10}(PO_4)_6(OH)_2 + 2F^- \rightarrow Ca_{10}(PO_4)_6F_2 + 2OH^-$$

One lakh fifty thousand villages are affected by dental fluorosis in India mostly from state of Bihar, Andhra Pradesh, Rajasthan, Gujarat, Madhya Pradesh, Uttar Pradesh, Tamil Nadu and Punjab (Pillai and Stanley 2002). Rajasthan is one of the fluoride zones identified as it is in arid region and has acute water crisis. The state is unique as all the 32 districts were found to have highly contaminated groundwater with elevated level of fluoride. Vikash et al. (2009) and Jacks et al. (2005) both wrote in their research article that 10% villages of Rajasthan have excessive fluoride in water supply for domestic purpose. The chief source of fluoride was taken by humans through drinking water, particularly in fluoride-contaminated region. The release of fluoride in groundwater largely depends on geochemical process, where fluoride-containing minerals such as biotites, basalt, fluorite, shale, topaz, syenite, etc. are present. High fluoride-containing groundwater has low level of calcium due to poor solubility of CaF_2 in water. Dissolution of fluoride is dependent on pH, sodium bicarbonate, evapotranspiration, residence time of groundwater, soil types, etc. The UNICEF (1999) mentioned in its report that 20 states of India have high level of fluoride in groundwater and 65 million peoples (included six million children) were affected by fluorosis.

11.1.1 Chemobiokinetics of Fluoride

Fluoride present in water is a simple covalent bonding with cations (Na, K). Fluoride is absorbed by the gastrointestinal tract and passes through the placenta, but some amount can be also excreted as sweat and lacteal secretion and saliva. The excretion of ingested fluoride via renal system in 3 years children were found more than 4–6 h is 50% of total absorbed fluoride, but children over 3 years to adults excreted about 90%. The total absorbed fluoride in the body, just about 90%, set down in teeth and bones. Absorption capacity of soluble fluoride (inorganic) compound is high as compared to other compounds of fluoride, and biological fluoride have several years half-life. Excessive concentration of inorganic fluoride has more harmful effects than organic fluoride. Fluoride is mainly excreted with urine and other faeces (Rani 2006).

11.2 Occurrence

Fluoride is member of halogen groups and the 13th most abounded elements in earth's crust. 611 mg/kg and 285 μg/gm of fluoride were found in continental crust and soil, while various rocks such as basalt, granites, limestone, sandstone and shale contain 360, 810, 220, 180 and 800 μg/gm, respectively. Endemic fluorosis is prevalent in India since 1937 (Shortt et al., 1937). The important fluoride-bearing minerals are fluorite (CaF_2) which is less soluble in water, and it occurs in igneous and sedimentary rocks. The fluoride rich minerals such as apatite, amphiboles, hornblende and micas are replacing to OH^- and Cl^- ions of groundwater by releasing F^-. The occurrence of fluoride is not limited to only rocks but also present in soil and accumulated by plants (CGWB 2014). Beryllium, ferric ions, boron and aluminium form sturdy complexes with fluoride, while solubility of fluoride in natural water increases with binding with silica (CGWB 2014).

11.2.1 Hydro-geochemistry of Fluoride

Chemistry of groundwater principally depends on chemical composition of aquifer matrix. The quality of groundwater is generally controlled by natural processes such as aquifer matrix, weathering of rocks, dissolution of minerals, evaporation of groundwater and exchange of ions between water and rock. The rainwater is acidic in nature due to dissolution of atmospheric CO_2 and percolates downward through the soil with leached out secondary salt from soil such as sodium bicarbonate, sodium sulphate and sodium chloride.

Phosphate fertilizer is additive sources of fluoride-bearing compounds in agricultural land. Simultaneously, anion exchange reaction occurs with cations of soil (clay minerals):

$$CaX_2 + 2Na^{+}_{(aq)} \leftrightarrow 2NaX + Ca^{2+}_{(aq)} \tag{11.1}$$

Here, X is clay minerals.

The hydrogen ion concentration increases during dissolution of CO_2 and $CaCO_3$ (Saxena and Shakeel 2003; Subbarao and John 2003; Handa 1975):

$$CO_2 + H_2 \rightarrow H_2CO_3 \tag{11.2}$$

$$H_2CO_3H^+ \rightarrow +HCO_3^- \tag{11.3}$$

Bicarbonate dissociates as in hydrogen and carbonate ions (Arveti et al. 2011):

$$HCO_3^- \rightarrow H^+ + CO_3^{2-} \tag{11.4}$$

$$CaCO_3 + H^* + 2F^- \rightarrow CaF_2 + HCO_3^- \tag{11.5}$$

$$CaF_2 \rightarrow Ca^{2+} + 2F^- \tag{11.6}$$

In the presence of alkaline water, fluoride is highly mobilized, and CaF_2 settles down as calcium carbonate:

$$CaF_2 + 2HCO_3^- \rightarrow CaCO_3 + 2F^- + H_2O + CO_2 \tag{11.7}$$

In the presence of excessive sodium bicarbonates in groundwater, the dissolution activity of fluoride is high and can be expressed as (Ayoob and Gupta 2006):

$$CaF_2 + 2NaHCO_3^- \rightarrow CaCO_3 + 2Na^+ + 2F^- + H_2O + CO_2 \tag{11.8}$$

Solubility product of fluorite is low:

$$Ksp^{19} = (F^-)^2\left(Ca^{2+}\right) = 4.0^* 10^{-11} \tag{11.9}$$

11.2.2 Global Scenario

The distribution of elevated fluoride in groundwater depends upon the geology of different parts of the world; mostly in midlatitude areas, it has total deposit of 85 million tons in earth crust (Sahu et al. 2018 and Teotia and Teotia 1994). High fluoride-containing groundwater occurs in enormous parts of Africa, China, the Middle East and southern Asia (India and Sri Lanka). WHO reported that major fluoride belts extended from Eritrea through Malawi, Syria to Turkey, Afghanistan, India and China. Other similar fluoride belt is also found in America, Kenya, Iraq, Japan and Iran (Sahu et al. 2018).

Symptom of fluorosis is observed in population of a particular area having fluoride concentration in groundwater between 1.5 and 10 mg/L. 1.5 mg/L fluoride in drinking water has been recommended by WHO (2011), though it is not adopted in all over the country because it depends on volume of drinking water taken, climate and diet (Dharmshaktu 2013). The magnitude and sternness of fluoride has vary with references to environmental sitting of geography and approximately 200 million people in 29 countries around the world faces the endemic problems of fluoride in intake water or drinking water. The highest concentration of F^- in the groundwater has been observed in Kenya (1640 mg/L in Elementaita and 2800 mg/l in Nakuru Lake) followed by 177 mg/L in Ethiopia and 69.7 mg/L in India (Nair and Manji 1982; Haimanot et al. 1987; Kloos and Teklee-Haimanot 1993; WHO 2006; Dharmshaktu 2013). Bioaccumulation of fluoride found in fruit and vegetables is 0.1–0.4 mg/kg contributing normal exposure. But elevated levels are investigated in rice and barley (2–8 mg/kg), protein of fish (370 mg/kg), pulses (about 13 mg/kg), fish (2–5 mg/kg), radish (63 mg/kg), etc. (Bhattacharya et al. 2017; Mumtaz et al. 2015; Murray 1986) (Table 11.1).

11.2.3 Indian Scenario

India is the second extremely populated country in the world, but according to area, it counts under the seventh biggest country. It is predicted that by 2020, water consumption rate will increase by 20–40% and population will reach up to 1550 million. According to the Planning Commission 1996 and 2002, India has only 4% water resources, but population contributes 16 percent in the world. Ayoob and Gupta (2006) mentioned in his research article that fluoride in drinking water was first noticed in Nellore district of Andhra Pradesh (India) in 1937 (Dharmshaktu 2013). Before the 1930s, only in four states symptoms of fluorosis were observed, while it is increasing in 13, 15, 17, 18 and 19 states of India during the years 1986, 1992, 2002, 2013 and now, respectively.

Table 11.1 Range of fluoride in groundwater and affected district in different states of India

India	Range of fluoride (mg/l)	Number of affected district
Andhra Pradesh	0.11–20.0	20
Assam	0.2–23.0	5
Bihar	0.6–8.0	9
Chhattisgarh	0.3–5.0	12
Delhi	0.4–32.0	6
Gujarat	1.58–31.0	18
Haryana	0.17–48.0	14
Jammu and Kashmir	0.05–4.21	3
Jharkhand	0.19–4.5	6
Karnataka	0.2–18.0	21
Madhya Pradesh	0.08–4.2	19
Maharashtra	0.11–10.2	8
Orissa	0.6–5.7	11
Punjab	0.44–6.0	12
Rajasthan	0.2–69.0	31
Tamil Nadu	1.5–5.3	16
Uttarakhand	0.1–2.5	1
Uttar Pradesh	0.12–16	11
West Bengal	1.5–13.0	10

Source: Susheela (1999), Meenakshi and Maheshwari (2006), State of Environment Report (2009), CGWB (2014) and Mumtaz et al. (2015)

Susheela (2003) mentioned that Rajasthan, Gujarat and Andhra Pradesh are the extreme endemic areas that are affected by chronic fluorosis. The concentration of fluoride in groundwater was measured beyond 10 mg/L in 9 states out of 19 states in India, which are Andhra Pradesh, Rajasthan, Madhya Pradesh, Haryana and Maharashtra, Assam, Delhi, Gujarat, Karnataka and West Bengal (Dharmshaktu 2013), while Sahu et al. (2018) found more than 10 mg/L fluoride in groundwater of Raebareli district of Uttar Pradesh. The concentration below 10 mg/L and more than 5 mg/L was found in Bihar, Chhattisgarh, Odessa, Punjab and Tamil Nadu. Susheela (2002) has mentioned that 66 million population in 250 districts of India were at risk of endemic fluorosis, while 25 million population has been affected by problem of dental fluorosis, mainly in population below 18 years of age.

According to Teotia and Teotia (1994), deposition of fluoride in Indian earth's crust was 12 million tons. The report released from Ministry of Environment and Forest and Climate Change (Government of India) during 2009, it has been estimated that fluorosis is prevalent in 19 states of India, where around 65 million populations were affected, out of which 6 million children was reported. It is, therefore, a matter of high concern from the point of view of public health and welfare. The Ministry of health and family welfare (Government of India) had released funds during 2008-2009 in 11th Five Year Plan under NPPCF (National

Programme for Prevention and Control of Fluorosis) in 100 districts out of 230 endemic fluorosis districts in India (Dharmshaktu 2013).

11.3 Causes/Sources of Fluoride Contamination

Without environmental considerations, reckless dumping of mining and agricultural wastes and excessive use of fertilizers and agrochemicals are adding to the present fluoride crisis. Overexploitation of groundwater can cause hyperaccumulation of contaminants in the soil (Subramanian 2000; Singh et al. 2000; CPCB 2008). Fluoride present in various environmental media such as water, soil, air, flora and fauna is a contribution of both anthropogenic and natural activities. Natural presence of fluoride in the environmental matrix is because of weathering and dissolution of fluoride-containing minerals such as cryolite, fluorspar, fluorapatite, marine aerosol, volcanic ash, etc. (Dharmashaktu 2013; ASTDR 1993). The anthropogenic activities release fluoride into environmental matrix such as waste water, solid waste and stack gases releases from chemical manufacturing and processing industries of calcium fluoride, phosphate fertilizers, sodium fluoride, hydrogen fluoride, fluorosilicic acid and sodium hexafluorosilicate. Others possible manmade sources like burning of coal, application of pesticide, fluoridation of drinking water and irrigation of fluoride-containing water contributing to fluoride into environmental matrix (Dharmashaktu 2013).

11.3.1 Exposure/Potency of Fluoride in the Environment

11.3.1.1 Surface Water

In surface waters, level of fluoride is dependent upon source of volcanic emission, geographic distribution and discharge of industrial effluents (WHO 2004). According to ASTDR (1993), the concentration of fluoride in surface water is usually between 0.01 and 0.3 ppm. Fluoride concentration in sea water is 1.2–1.5 ppm higher than as compared to fresh water or surface water.

11.3.1.2 Air

Aluminium smelter plants, still mills, tiles and bricks manufacturers, phosphate processors and coal power plants are major contributors of fluoride contamination in the environment. Formation of aerosol, hydrolysis, vaporization and dry and wet deposition influence the destiny of atmospheric inorganic fluoride (Environment Canada 1994). The gaseous fluoride (hexaethane, carbon tetrafluoride, silicon tetrafluoride and hydrogen fluoride) are adsorbed on the particulate matters which are not easily hydrolysed and remain suspended in the atmosphere (US NAS 1971); this process is observed near coal-based thermal power plants and other emission sources (Sidhu 1979). Fluoride-containing airborne particles are depending upon meteorological condition, chemical reactivity, emission strength and particle size (WHO 2002).

11.3.1.3 Soil

According to ASTDR 1993, 60–6000 kilo tonnes of hydrogen fluoride is emitted via passive eruption of volcanic sources, which contributes approximately 10% to the stratosphere. Retention of fluoride in soil depends on types of soil, pH and organic contents. Water-soluble fluoride is biologically important for animal and plant. According to Davison (1983), 20–1000 μg/g is estimated in uncontaminated area while several thousands in contaminated soil.

11.3.2 Major Sources of Fluoride Ingestion by Human

Air, water, soil, drugs, food and cosmetics are various sources of fluoride ingestion by humans, but water and dietary intake are chief sources.

11.3.2.1 Water

Only drinking water contributes more than 60% of total intake of fluoride. Inorganic fluoride is the most available form, but higher concentration can cause highly toxic effect on human health. The natural fluoride content in groundwater is influenced by lithology, depth of aquifer and physical and chemical characteristics of the aquifer.

11.3.2.2 Air

The significant concentration of fluoride in and around the industrial area where workers and near inhabitant exposed to inhalation of fluoride. The fluoride pollution causing industries are aluminum smelter, glass, coal-based operated thermal power plants, fertilizers and ceramic industries.

Table 11.2 Global and Indian standard for fluoride in drinking water

Types of standards	Description guideline	Guideline value (mg/L)	References
Indian standards	Allowable limit	1	
	Permissible limit in the absence of other sources	1.5	BIS (IS-10500-2012)
WHO guidelines	Guideline value	1.5	WHO (2006)
US EPA	Desired limit	0.7	
	Permissible limit	1.2	
	Maximum contaminant level	4	NRC (2006)
Canadian guidelines	Maximum acceptable (MAC)	1.5	Ministry of Health Government of Canada (2010)
South Korea	Maximum permissible limit	1.5	ECOREA (2013)
Japan	Standard value	0.8	MHLW (2010)
Singapore	Maximum prescribed quantity	0.7	NEA of Singapore (2008)
Malaysia	Permissible limit	1.5	ESD (2004)
Ireland	Permissible limit	1.5	NEIA (2018)
UK	Permissible limit	1.5	DWI (2009)
Switzerland	Permissible limit	1.5	Bucheli et al. (2010)
Australia	Maximum impurity concentration	1.5	NRMMC (2011)
New Zealand	Maximum acceptable value	1.5	MH (2008)

11.3.2.3 Food

According to Jagtap et al. (2012), food items contained fewer amounts of fluoride in uncontaminated area, but huge amounts of fluoride have been reported in dietary product of contaminated area. Concentration depends upon fluoride contents in irrigated water and growing media such as soil. The enormous contents of fluoride are found in Indian tea leaf (39.8–68.59 mg/L) that contributes chief intake of fluoride after drinking water. Similarly fluoride concentrations found in various dietary items range between 3.27 and 14.03 mg/L (wheat), 5.6 mg/L (legumes and pulses), 1.28 and 2.29 mg/L (cabbage), 4.0 mg/L(lady figure) and 2.8 mg/L(potato).

11.3.2.4 Drugs and Cosmetics

Inorganic fluoride is applied for the prevention of tooth decay through drinking water and tablets or other drugs as a fluoride supplements. The niflumic acid is anti-inflamattory agent applied to cure of rheumatoid arthritis. Sodium fluoride used in mouthwash for preventing of oral cavity. The high concentration of fluoride also

Table 11.3 Effect of fluoride on plants and laboratory animal in India

Test animals/ plants	Fluoride in diet/dose	Effect of fluoride on test animals	References
(a) Developmental, reproductive and genotoxicity effect in test animals			
		Effect on reproductive and developmental system	
Female mice (*Mus musculus*)	10 mg/kg	Reduced protein contents in muscles, small intestine and liver with significant accumulation of glycogen in liver	Chinoy et al. (1994)
Mice (*Mus musculus*)	5 mg/kg	Damaged works of protective enzymes and damaged manufacturing of glutathione with reduced calcium under ovaries	Chinoy and Patel (1998)
(b) Effect of fluoride on human systems			
		Effect on reproductive system	
Indian pregnant women	0.12–0.42 μg/ml	Passive transfer of fluoride passing through mother to foetus (25 women)	Malhotra et al. (1993)
Indian men	1.5–14.5 mg/L	Symptoms of skeletal fluorosis and reduced testosterone serum (30 men)	Susheela and Jethanadani (1996)
		Effect on hepatic and renal system	
Indian men and women	3.5–4.9 mg/L	Kidney stone because of malnutrition in 18, 706 people	Singh et al. (2001)
		Effect on human bone	
Indian children	1.5–25 mg/L	Deformities and metabolic bone disease due to chronic ingestion of high fluoride and low dietary calcium (ninety percent in 45725 child)	Teotia et al. (1998)
(c) Effect on aquatic plants			
Macrophyte (*Hydrilla verticillata*)	20 mg/L	Reduced protein content and chlorophyll after 7 days	Sinha et al. (2000)

used in toothpastes, the concentration of fluoride varies from ~1000 to 4000 mg/L depending on the brand of the toothpaste.

11.3.2.5 Other Anthropogenic Activities

The source of anthropogenic activities includes discharge of municipal waste water and the effluents from ceramic industry, bricks manufacturing and chemical industries into water body like rivers results in accumulation of fluoride in plants and aquatic animals (Tables 11.2 and 11.3) (Jagtap et al. 2012).

11.4 Health Effect on Human

Fluoride intake has both advantageous and harmful effects; if the concentration is less than 0.5 mg/L, then its deficiency causes dental caries and weakness of bones, while their excessive intake (>1.50 mg/L) may cause fluorosis.

11.4.1 Dental Caries

Dental caries is the scientific term for tooth decay or cavities. Dental caries is demineralization of teeth due to bacterial decomposition. *Lactobacilli* and *Streptococcus mutans* bacteria attached onto the dental plaque and consume the organic matter and produce propionic, lactic and acetic acid that incise the enamel, thus forming cavity (Ayoob and Gupta 2006 and CDCP 1999).

11.4.2 Dental Fluorosis

Excessive intakes of fluoride can cause deformation of teeth during developmental stage or mottling of enamel called “dental fluorosis”. The fluoride deposits into ameloblasts (primary cell for formation of tooth enamel) and spreads out over the enamel with changing the colour from white to radish brown resulting enamel decay and loss of luster.

Dean has been measuring for quantifying the sternness of dental fluorosis in 1934. The classification of dental fluorosis based on nutritional status is given below:

- Class 0 – Normal teeth
- Class 1 – Very mild fluorosis (25% area of tooth surface covered by opaque white)
- Class 2– Mild fluorosis (50% area of tooth surface covered by opaque white)
- Class 3 – Moderate fluorosis (tooth surface affected by red brown dark)
- Class 4 – Severe fluorosis (widespread around whole tooth by brown stains) (Ayoob and Gupta 2006)

Dr. McKay first noticed symptoms of the fluorosis (mottled enamel) in the tooth enamel and began his research on association of fluoride and drinking water (McKay 1925; McKay 1928). Fluorosis was initially noticed in cattle of Nellore District (Andhra Pradesh), India, before the 1930s and foremost published in Indian Medical Gazette by Shortt et al. 1937. The dental health survey was conducted in nine states of India during 1987–1992, and dental fluorosis were observed 5–20% and 2–30% in children (6–14 years) and adult (Susheela 2003). The health survey was carried out on school children of 18 districts in Gujarat where children’s pretentious by dental fluorosis was found between 2.60% to 33%. The percent of dental fluorosis affected districts of Gujarat were observed 17.75% in Ahmadabad, 11.43% in Gandhinagar, 24.90% in Mehsana, 17.78% in Banaskantha, 14.50% in Sabarkantha, 16.87% in Baroda, 12.16% in Kheda, 8.4% in Panchmahal, 14.9% in Bharuch, 7.9% in Surat, 2.6% in Vasad, 33.0% in Junagarh, 16.6% in Amreli, 22.0% in Surendranagar, 15.5% in Jamnagar, 14.1% in Bhavnagar, 14.7% in Rajkot and 20.25% in Kutch (Susheela 2003). The dental fluorosis was found 77.1% in 17–22 years old population of Rajasthan, where the fluoride level was found 2.6 ppm in drinking water (Choubisa SL 2001)

11.4.3 Skeletal Effects of Fluoride

Bone illness or changes in bone structure and calcification of ligaments are symptoms of skeletal fluorosis, and it is caused by excessive intake or accumulation of fluoride through drinking water and diet of prevalent fluoride zone (Krishnamachari, 1986). The chronic ingestion of excessive fluoride deposited in the joint of the knee, shoulder bones, neck and pelvic creates difficulty in movements and walking. According to the reports of the WHO 1970 and 2002, accumulation of fluoride in bone depends on sex, bone types and age. Fluoride accumulation capacity of cancellous bone is high as compared to cortical bones. Ninety-nine percent of total fluoride deposits in teeth and bone of human and remaining deposits in blood and vascularised soft tissue (Husdan et al. 1976; Kaminsky et al. 1990; WHO 2002). The skeletal fluorosis was developed and 43 percent people affected in Anantapur district of Andhra Pradesh, where the fluoride level was ranged from 1.2 to 2.1 mg/L (Reddy and Prasad 2003). Long-time exposure to high level of fluoride (more than 5 mg/L) in drinking water can cause *crippling skeletal fluorosis*, and it is marked by:

- Kyphosis: unusually enlarged convexity in the bend of thoracic spine
- Flexion deformity: flexion contracture or bend of the knee
- Scoliosis: sideway curvature of the spine or vertebral column
- Paraplegia: paralysis or de-activation of muscles function in the lower body
- Quadriplegia: paralysis or permanent loss of the torso and four limbs (Ayoob and Gupta 2006)

11.5 Amelioration Techniques

11.5.1 Adsorption

The fluoride-contaminated water passes through a packed column with fluoride adsorption media like coated silica gel, activated coconut shell, activated alumina, calcite, natural clay soil, red mud, activated saw dust, bone charcoal, activated carbon, ground shell, fly ash, serpentine, magnesia, coffee husk and rice husk which are used for removal of fluoride. This method is easily prepared and suitable for household and community purposes.

11.5.1.1 Activated Alumina

Activated alumina is an attractive adsorbent with high fluoride removal capacity as compared to another adsorbent media due to highly porous aluminium oxide that exhibit more surface area. The cationic networks spread out over the crystal of alumina provide positive charge which are attracted to anionic species. Hardness and fluoride concentration of water both affect the removal efficiency of activated alumina. The process is pH specific, hydroxide and silicate act as competitor in more than pH 7, while alumina dissolves at pH below 5 (Bishop and Sansoucy 1978). In Rajasthan, India, a microfilter bucket (5 kg alumina pin down) was provided to the people in fluoride-affected area by Sarit Sanshtan Udaypur with the help of the UNICEF.

Merit

- ~90% fluoride removal efficiency.
- This process is cost-effective.

Demerit

- The processes need pretreatment.
- Specific removal efficiency at pH 5–6.
- Alumina bed fouls in high TDS.
- Regeneration is required after 5 months.

11.5.1.2 Activated Carbon

Removal of fluoride by activated carbon was used, and it was investigated in 1934 (Mckee and Johnston 1999). Activated carbon give good removal capacity under pH 3. So, the process needs to maintain pH.

11.5.1.3 Brick Pieces Column

The bricks are utilized as adsorbent of fluoride for removal of fluoride because they contain AlO_2. The brick particles is activated through burning or heating process then the activated brick particle is packed into adsorption colum. The fluoride contaminated water passing through the adsorption colum filled with activated brick particle which adsorb fluoride from raw water.

11.5.2 Ion-Exchange Resin

Many synthetic chemicals (polyanion, Amberlite IRA 400, and XE-75) were used as a cation or anions transferable resins mostly in hydroxide and chloride forms. Ammonium functional groups with chloride were used as ion-exchange resins. It is a strong-base resin for ion exchange between chloride and fluoride. The resin is cleaned after using by backwashing of supersaturated salt of sodium chloride (Meenakshi, and Maheshwari 2006).

$$\text{Resin} - NR_3 + Cl^- + F^- \rightarrow \text{Resin} - NR_3 + F^- + Cl^-$$

Several materials such as calcium, alumina, magnesium, activated carbon, sulphonated carbon and lime were used for fluoride removal as ion-exchange resin removed from 5 mg/L to 1.5 mg/L (Mohan Rao and Bhaskaran 1988).
Merit

- Fluoride removal capacity up to 90–95%

Demerit

- pH low and elevated level of chloride in treated water.
- Elevated level of alkalinity; sulphate and carbonate reduced the removal efficiency.
- Disposal of resin is a major problem.

11.5.3 Coagulation-Precipitation

Coagulation-precipitation is a process for the removal of soluble fluoride in the form of insoluble salt by adding of chemicals called coagulant aids. In this technique polyaluminium (chloride and hydroxy sulphate), brushite and aluminium salt are commonly required raw materials.

In India, the Department of Chemistry, IIT Jodhpur, developed gravity-based water filtration systems followed by precipitation method through natural materials such as neem, Ayurvedic waste, sesame, seed power of gaur, etc. (Choudhary et al. 2014).

11.5.3.1 Nalgonda Technique

This is the most famous technique used for amelioration of F^- from groundwater in India. This technique was primarily started in Nalgonda village of Andhra Pradesh. The lime and alum, both are added with rapid mixing of water in a tank, for better flocculation and sedimentation of contaminants. The bleaching powder is added for the disinfection of filtered water. The operation may be conducted on both large and small scale, and it started in various countries, i.e. Tanzania, Kenya and Senegal (NEERI 1978). NEERI Nagpur also developed hand pump attached technique under Rajiv Gandhi National Drinking Water Mission. Lime and alum (hydrate aluminium salts) are the most commonly used coagulants, and lime precipitate to fluoride can cause rising of pH up to 11–12. According to Potgeiter (1990), when alum was added in water, it formed aluminium hydroxide due to reaction with alkalinity and settled down after reaction with fluoride as a form of insoluble calcium fluoride.

Merit

- Nalgonda technique is the most effective technique for fluoride removal (NEERI, 1978).
- Technique worked well in the range between 1.5 and 20 mg/L.
- TDS and hardness should be below TDS 1500 and 600 mg/L.

Demerit

- Aluminium dissolved in treated water can cause problem.
- Maintenance required 3000 rupees for 10,000 L capacity of plant per day.
- Larger amount of sludge became a problem for drying and disposal.
- It is not an automatic process; it required manpower.

According to Rao and Mamatha 2004, Nalgonda technique is modified by Indian Institute of Science, Bangalore, by using sodium bisulphate, lime and magnesium oxide. Fluoride was removed in the form of magnesium fluoride salt.

$$MgO + H_2O \rightarrow Mg(OH)_2$$

$$Mg(OH)_2 + 2NaF \rightarrow MgF_2 + 2NaOH$$

Magnesium oxide rises pH up to 10 to 11 in treated water, and it is sharply reduced between 6.5 and 8 by dissolving in sodium bisulphate (0.15–0.2 g/L). When the concentration of HCO_3^- is higher than 200 mg/L, then it creates problem in the working of sodium bisulphate. The problem is solved by adding 0.3 mg and 0.8 mg of lime and magnesium oxide (MgO).

11.5.4 Membrane Techniques/Physical Methods

Reverse osmosis (RO) and nanofiltration both remove fluoride by their membrane. Nanofilter allows only microscopic size and removes all dissolved solid having larger size by low pressure. The reverse osmosis removes dissolved ions by semipermeable membrane and its works on opposite of osmosis process. The high pressure applies on a semipermeable membrane which not allow to larger particles passing from it. Most of the researcher found 90% removal capacity of fluoride. The main factor that affects the process is characteristic of raw water, recovery, selection of membrane, water rejection and size of plants. Babra et al. (1997) found in a study that efficiency of RO plants decreases with boosting of plants capacity. Meenakshi et al. (2004) found the following merits and demerits:

Merit

- This technique is extremely successful for fluoride removal and also reduces dissolved solids, pesticides, microorganisms, inorganic and organic pollutants, etc.
- Little maintenance and quick process.
- Without limitation of pH and temperature does not affect removal efficiency.

Demerit

- pH of treated water have low level.
- It rejects all essential mineral.
- It rejects high volume of reject water.

11.6 Preventive Measures

The following measures should be adapted for prevention and control of excessive intake of fluoride:

11.6.1 Awareness

To aware the inhabitant is a first step for prevention of negative health impact of fluoride contamination, spreading awareness about safe limit of fluoride in drinking water and their incurable effect on health through poster, interpersonal communication or group discussion in school and villages, wall painting, newspaper or news channel, etc.

11.6.2 Rainwater Harvesting and Surface Water Resource: Alternative Water Source

The water harvesting technology is a better way to supply less fluoride-containing drinking water to inhabitants. Generally groundwater has high fluoride content as compared to surface water which may be used after conventional treatment of surface water.

11.6.3 Changing the Dietary Habits

Amelioration technique shall not remove the fluoride level under safe limit; then the following prevention can be adopted through dietary habit of inhabitants:

Calcium Take calcium-rich diet in fluorosis area such as sesame seeds, curd, jiggery, green leafy vegetables, drumstick, etc. High intake of calcium reduced the absorption efficiency of fluoride.

Vitamin C It was reported that vitamins C and E protect against oxidative stress and damage of endometrial in rats in fluoride intoxication (Guney et al. 2007). Some edible items have high vitamin C contents such as orange, sprouted pulses, lemon, coriander and tomato while vitamin E in nuts, green vegetables, dried beans, white grain pulses or cereals, etc.

Antioxidants Items such as ginger, papaya, green leafy vegetables, carrot, garlic, pumpkin, etc. show antagonistic effect; thus they play prophylactic function to avoid fluorosis (Kumar et al. 2014).

Toothpaste In fluorite belt area, 4–6-year-old children can use toothpaste having low fluoride concentration for dentifrices (Villena 2000). Some dental specialist suggested to use toothpastes having low concentration of fluoride (500–550 ppm) as compared to standard concentration (1.0–1.1 ppm) of fluoride (Negri and Cury, 2002; Stookey et al. 2004).

11.7 Fluorosis Management in India

In 2008, for controlling of the troubling of fluorosis, the Planning Commission of India starts the NPPCF programme in 11th 5-year plan during 2007–2012. This programme has been handled by various NGOs and governmental bodies such as MDWS (Ministry of Drinking Water and Sanitation), RGNDWM (Rajiv Gandhi National Drinking Water Mission), MHFW (Ministry of Health and Family Welfare) and the UNICEF (United Nation International Children's Emergency Fund). Baseline data was collected by the DDWS (Department of Drinking Water Supply), Central Government, in 196 districts in 19 states of India and fund released to 100 districts in four phase, according to collected baseline data (Dharmshaktu 2013).

All districts were provided rapid management, community diagnosis, capacity building, medical and laboratory manpower, surgery, education and communication materials, etc. Nellore, Jamnagar, Nagpur, Nayagarh, Ujjain districts of India were provided fund under NPPCF programme in Ist Phase during 2008–2009, and another 15 districts were provided fund during 2009–2010 in IInd Phase. Third and fourth Phase provided fund to 40–40 districts during 2010–2011 (Dharmshaktu 2013; MHFW 2017).

11.8 Conclusion

Gradually, fluoride and fluorosis illness becomes a prevalent disease because of environmental fluoride present in the rocky surface of the underground aquifer. The underground fluoride ion becomes subsurface when groundwater is exploited for various uses. Once it contaminates land, the whole environment and flora and fauna get affected due to accumulation of fluoride. The magnitude of adverse effects of fluoride could be brought down through proper management of environmental pollution and changing the food habits. The government should give enough emphasis in time to control the fluoride-related illness before it becomes epidemic. Since there is no specific antidote for this illness, prevention is better than cure.

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Chapter 12
Role of Industries in Water Scarcity and Its Adverse Effects on Environment and Human Health

Pankaj Chowdhary, Ram Naresh Bharagava, Sandhya Mishra, and Nawaz Khan

Abstract Overpopulation day by day promotes industrial revolution, and manufacturing processes have become more efficient and productive, science has become much more advanced, and our life has changed a great deal. For water pollution and scarcity, many sources are responsible such as industrial wastewater, domestic sewage, storm water runoff, septic tanks water and agricultural practices. Out of which, industries play a key role and also release various toxic chemicals, organic and inorganic matters or sludge, radioactive sludge, sulphur, asbestos, poisonous solvents, polychlorinated biphenyl, lead, mercury, nitrates, phosphates, acids, alkalies, dyes, pesticides, benzene, chlorobenzene, carbon tetrachloride, toluene and volatile organic chemicals. These wastes when discharged into the water ecosystem without adequate treatment become very unhealthy for any type of human and other use. The industrial wastewater is responsible for many diseases such as anaemia, low blood platelets, headaches, risk for cancer, many skin diseases, etc. To prevent such type of issues, effective treatment technology, adequate treatment, water reuse, desalination, infrastructure repair and maintenance, water conservation and also strict pollution control law and legislation and their proper implementation do play an important role.

Keywords Water pollution · Industry · Organic · Inorganic

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12.1 Introduction

On the earth water is a key component for all living system. All terrestrial and aquatic living including plants and animals must need water for survival. Apart from drinking it to survive, people have many other uses of water. The water covers ~70% of earth surface in which only 3% water is used as freshwater. According to UNICEF and WHO, more than around 1.1 billion people lack access to clean, freshwater supplies, and approx. 2.6 billion people around the world are unable to use adequate sanitation (Moe and Rheingans 2006). In the geographical area, water scarcity is due to the inequity between the demand and supply for water sources. An inadequate or limited freshwater supply is one of the serious problems facing the world's poorest countries, but the populations of these countries are not the only populations to endure the burden of water scarcity (McDonald et al. 2011; Dar and Khan 2011). Millions of people across the world are unable to use clean water for their daily need due to scarcity of water. Increased population growth and its associated effects continuously raise the demand of safe water for health, hygiene, agriculture and development.

Various types of natural as well as anthropogenic practices like industrial processes play an important role in the contamination of water bodies and cause clean water scarcity. Worldwide several industries such as distilleries, pulp and paper, tanneries, textile and electroplating are responsible for clean water scarcity and also release various toxic pollutants (Chowdhary et al. 2017a, b, 2018a, b; Kumar et al. 2018) (Table 12.1). The good quality of freshwater is extremely important for the

Table 12.1 Various industries and their pollutants

Sr. No.	Name of the industry	Different pollutants emanating from industries	References
1.	Distillery Industry	Melanoidin, polysaccharides, reduced sugar, proteins, waxes, etc. Inorganic pollutants like N, K, Ca, SO4, PO4, etc.	Chowdhary et al. (2017a, b)
2.	Tannery industry	Chromium and other heavy metals	Kotas and Stasicka (2000)
3.	Pulp and paper Industry	Smoke, organic waste	Zainith et al. (2019)
4.	Textile Industry	Toxic materials, inhibitor compounds, active substances, chlorine compounds, etc.	Sandhya and Swaminathan (2006)
5.	Electroplating Industry		
6.	Food industry	Alkalies, phenols chromates, organic wastes	
7.	Iron and steel industry	Smoke, gases, coal dust, fly ash, fluorine	
8.	Nuclear industry	Radioactive wastes	
9.	Oil Refineries	Smoke, toxic gases, organic waste	

consumption of drinking, bathing, irrigation, etc. But, using a large amount of freshwater in industries for various purposes is one of the major sources of water pollution as well as water scarcity, because these industrial discharge into the aquatic and terrestrial region. These wastewater have high value of biological oxygen demand (BOD), chemical oxygen demand (COD), total solid (TS) sulphate, phosphate, phenolics, heavy metals and other toxic pollutants (Chowdhary et al. 2017a, b, 2018a, b; Zainith et al. 2016, 2018, 2019; Bharagava and Chandra 2010). The presence of such toxic pollutants from industrial contaminant within the wastewater makes it highly toxic and hazardous for the environment. Wastewater is directly discharged into rivers, ponds and other water bodies, affects human as well as other living beings by polluting water and causes water scarcity, hence reducing the yield of crops by effecting plant growth (Bharagava and Chandra 2011). The wastewater is also toxic for aquatic flora and fauna (Ho et al. 2012; Vasanthavigar and Prasanna 2011).

Various industrial practices and day-by-day increasing demands are creating pressure on environment and natural resources (Ahuti 2015). The inadequately treated sewage and industrial wastewater when discharged into aquatic bodies, used for agriculture for irrigation, causes pollution of groundwater with minerals and salts present in lower soil profile. In many countries water bodies are also contaminated with fluorides, nitrites and many types of toxic metalloids (Owa 2013). It is a well known fact that water scarcity will affect the food production, various environmental factors and biodiversity (Yadav et al. 2007). Water needs to be a global political issue not only in order to feed the projected 9 billion people that will inhibit the earth by 2050. With lower agriculture water than present, it should address the significant growth challenge of doing so in a secure, sustainable way without comprising water resources that are necessary for ecosystem services and purposes (Sivakumar 2011). Inadequate treatment of wastewater and use of huge amount of freshwater is undoubtedly a big global public health concern and challenge for our sustainable development.

12.2 An Overview on Global Water Crisis

Freshwater is a very important aspect of life being including humans, animals and plants and also for environments. Really it can differentiate between life and death and between bounty and poverty (Sivakumar 2011). Water security characterized a combined component delivering humanity with drinking water, food and fish, hygiene and sanitation, industrial resources, transportation and energy, and these all things are dependent upon maintaining environmental/ecosystem health and yield (UNEP 2009). Water is critical for the United Nations Millennium Development Goals whose aims are set to expire in 2015; it is well known that the world lags far behind on the cleaning target, which is estimated to be missed by over 1 billion people. On the earth total freshwater reserves are about 35 million km^3. This is only about 2.5% of the total stock of water on the Earth (1.4 billion km^3), while the remaining 97.5% is in the form of salt water in the oceans (96.5%) and saline groundwater (1%). The freshwater is available in a wide variety of forms and locations. A large fraction (68.7% or 24 million km^3) is locked up in glaciers and permanent snow cover in the Antarctic and Arctic regions, or in deep groundwater, inaccessible to humans. Freshwater lakes and rivers, which are the main sources for human water consumption, contain on average about 90,000 km^3 of water, or just 0.26% of total global freshwater resources (Sivakumar 2011).

US population and economy with the growth of demand of water and energy grows. The electricity generation and production of transportation fuels directly depends on the number and type of power plants. In addition, cooling technologies, air and CO_2 emission capture and sequestration requirements, quantity and type of alternative fuels used and estimates suggest that water consumption in the energy sector could grow by a factor of 3 to 4 by 2035, increasing from about 4.3 billion gallons of water per day (BGD) (17 billion litres per day) in 1995, to about 12–15 BGD (47–60 billion litres per day) by 2035 (NETL 2008). This would make the energy sector the largest nonagricultural water consumption sector in the USA. These global trends of water scarcity are the result of local and regional water crises due to high usage in industrial processing. Increasingly, community, industry and agricultural practices are seen to be in competition with nature for finite water supplies. Central Asia's Aral Sea has greatly shrunken, which is one of the best recognized examples of water crisis and competition (UNEP 2010).

12.3 Industries as Source of Water Pollution

Worldwide a large number of industries are responsible for water scarcity such as distilleries, tanneries, textiles, electroplating, pulp and paper making, photographic, automobiles, oil refineries, fertilizers, pesticides, paints and printing, and domestic sewage is an emerging threat for polluting water bodies and misuses of water

Fig. 12.1 Various industries responsible for water scarcity

resources (Fig. 12.1). The wastewater discharged from such industries is directly released into water bodies without inadequate treatment, resulting in an abundant source of genotoxic pollutants in water, including many kind of mutagenic and carcinogenic organic components.

12.3.1 Distillery Industries

Among all the industries, distillery industry is one key contributor for soil and water contamination (Satyawali and Balkrishnan 2008). In India, the number of distilleries has gone up to 319 with annual production of 3.25×10^9 L of alcohol and 40.4×10^{10} L of wastewater (Uppal 2004). This wastewater contains melanoidins and other colouring compounds due to which it appears dark brown in colour. In the production of 1 L alcohol, molasses-based distillery releases about 15 L of spent wash (Beltran et al. 2001). DWW is toxic for both aquatic and terrestrial ecosystem, in aquatic region it destroys the flora and fauna, whereas in terrestrial region it reduces the soil fertility by depleting the dissolved oxygen and reducing the manganese availability and other mineral contents, respectively (Kumar et al. 1997; Pal and Yadav 2012). Presence of a number of organic compounds, such as polysaccharides, reduced sugars, lignin, proteins, melanoidin, waxes and inorganic substances such as N, K, PO_4^-, Ca and SO_4^-, is also very high in DWW (Chowdhary et al. 2018a, b).

12.3.2 Tannery Industries

The tannery wastewater is most dangerous for the environment and all living beings. During the processing of leather, huge amount of water and chemicals are used, about 90% of contaminated discharged water (Chowdhary et al. 2017b; Dargo and Ayalew 2014; Chowdhury et al. 2013). In this wastewater various types of pollutants such as organic and inorganic compounds, sodium chlorides, sulphate, toxic metalloids and decaying suspended matter tanning materials, which are biologically degradable, are present (Akan et al. 2007; Yadav et al. 2016). The tannery wastewater destroys the normal life of the receiving water bodies and land surface (Cooman et al. 2003). The wastewaters/sludges emerging out of the leather industries are consistently loaded with chromium salts causing the biggest problem of chromium heavy metal contamination (Mishra and Bharagava 2016).

12.3.3 Pulp and Paper Industries

Paper industry plays a key role in world's economy. The pollutants generated from paper industry are divided into four categories such as air, water, solid and noise pollution (Zainith et al. 2019). Major pollutants like sulphur compounds and nitrogen oxides are released to the air, while chlorinated and organic compounds, nutrients and heavy metals are released into the wastewater. During the paper production, consumption and washing processes have many adverse environmental social impacts. The overall process of this industry is consuming huge amount of freshwater and energy (Pokhrel and Viraraghavan 2004). On the basis of production, water consumption changes, and it can get as high as 60 m^3/ton paper produced in spite of the most modern and best available technologies (Thompson et al. 2001). The main problems of the pulp paper wastewater are high concentration of organic content (20–110 kg COD/air-dried ton paper), dark brown coloration, adsorbable organic halide (AOX), toxic pollutants, etc. Furthermore many compounds present in industrial wastewater are not easily degraded and can bioaccumulate in aquatic ecosystem. Due to high concentration and chemical diversity of organic pollutants in paper industry wastewater, the number of adverse effects on aquatic population in watercourses has been observed (Kumar et al. 2014).

12.3.4 Textile Industries

The textile production industry is one of the oldest, technologically complex and significant contributors to many national economies. This industry provides a living to farmers, cotton boll pluckers and workers involved in ginning, spinning, weaving, dyeing, designing, tailoring and packing (Ahuti 2015). But these textile industries generate an excessive amount of wastewater which contains extremely high organic concentration and high colour intensity that can inflict the declining of environmental aesthetic value, interfere aquatic ecosystem and affect human healthiness (Mani and Bharagava 2016; Mani et al. 2018). The textile industry consumes more than 8000 chemicals in various processes of dyeing and printing. Approx.30–50 litters per kg of water is used to produce fine-printed cloths. The World Bank estimates that 17–20% of industrial water pollution comes from textile dyeing and finishing treatment given to fabric. Various toxic and harmful chemicals have been identified in water solely from textile dyeing, most of which are very difficult to remove or degrade or cannot be removed (HSRC 2005). This represents an appalling environmental problem for the clothing and textile manufacturers (Mani and Bharagava 2016). Textile wastewater is a cause of significant amount of environmental degradation and human illnesses (Mani and Bharagava 2016). About 40% of globally used colourants contain organically bound chlorine, which is a known carcinogen. Organic materials present in textile wastewater are of great concern, because of their high toxicity and reactivity with many disinfectants. Such toxic chemicals, which mixed with air, cause allergic reactions which are harmful for children even before birth by inhalation or absorption (Khan and Malik 2013).

12.4 Other Anthropogenic Activities Which Play a Role in Water Abatement

The contamination of water resources by industrial and faecal pollutants causes significant risks to human and animal health since several pathogens are often associated with faeces and other organic pollutants (Reischer et al. 2008; Bharagava et al. 2009). However, several toxic and carcinogenic pollutants such as heavy metals, and also organic matter, are loaded with microorganism, which can contaminate water and enter into the food chain, posing serious concern to public health (Yadav et al. 2016).

There are large numbers of known water emissions sources of municipal, industrial and agro-industrial wastewater that enter into freshwater streams which are consumed by human beings causing waterborne diseases. However, there are many washing detergents, which cause several types of water pollution that comes from residential areas in the form of household detergent and agriculture runoff in the form of herbicides and insecticides and from certain industries (Vinod et al. 2012).

12.5 Pollutants Generated from Various Industrial Process

There are various types of toxic chemical pollutants found in industrial effluent, which can be commonly classified into three classes like heavy metals, organic matter and fouling substances (oil). The pollutants, when discharged into waterways, vary by industry, which runs the scale from manufacturing to mining energy/power generation. So far, there are many guidelines in many countries for the treatment of wastewater and its release into water resources; unfortunately these guidelines or standards may not be evaluated or implemented (Bharagava et al. 2018). However, water sources that receive industrial wastewaters may become contaminated and present health risks when used for drinking water or irrigation. The major pollutants in industrial wastewater and domestic sewage include heavy metals (Hg, Cd, Cr, Pb, Zn, etc.), non-heavy metals (As, CN, F, S, Se, etc.), organic (alkanes, substituted benzenes, PAHs, phthalate acid esters, phenolics, dyes, volatile carbon, etc.), inorganic compound (chlorides, sulphides, nitrogenous compounds and solids) and microorganisms (enteric pathogenic bacterium, virus, parasites, etc.) (Mishra and Bharagava 2016; Yadav et al. 2017) (Table 12.2).

Table 12.2 Industrial pollutants and its harmful effects on human health

Pollutants	Pathway into water	Impacts on humans health
Arsenic	Natural occurrence in groundwater	Cancer of the bladder, lung and skin, birth defects, skin lesions, gangrene, respiratory ailments
Fluoride	Natural occurrence in groundwater	Dental and skeletal fluorosis, gastro-intestinal disorders, infertility
	Artificial introduction to groundwater through mining	Kidney impairment
Nitrate	Artificial introduction to surface water through use of fertilizers and industrial wastewater, Nitrate based fertilizers applied excessively leaches into groundwater	Methemoglobinemia in infants, oral and gastrointestinal cancers
		Vascular dementia, absorption and secretive functional disorders of the intestine, neural tube defects
Persistent organic pollutants (POPs)	Surface runoff contaminated with herbicide and pesticides	Acute poisoning causes skin and eye irritation, respiratory problems, systematic poisoning and death
	Herbicide and pesticide leaching into groundwater	Continuous exposure causes nervous disorders, anaemia, sterility, mental deterioration, birth defects, premature birth, neonatal death and cancer
Heavy metals	Natural occurrence	Multiple health impacts including but not limited to organ damage and failure, impairments in human development, genetic disorders, cancer
	Discharged as wastewater from manufacturing, mining and thermal power plans	

12.5.1 Organic Pollutants

Very huge amount of industrial wastewater and domestic sewage is directly released into water bodies such as rivers and ponds with inadequate treatment, resulting in an abundant source of organic compounds, which are responsible for genotoxicity, mutagenicity and carcinogenic effect on living system. A nationwide study on organic pollution of drinking water and liver cancer showed that liver cancer mortality was positively correlated with the chemical oxygen demand (COD) in drinking water (Wang and Chen 1992).

12.5.1.1 Phenolics

Phenol-polluted wastewater is commonly produced by a number of industrial and agricultural activities. Phenolic compounds and their derivatives, e.g. catechols, are considered priority pollutants because they are harmful to living organisms even at low concentrations. In humans and mammals, catechols can occur as metabolites in the degradation of oestrogens or in endogenous compounds, such as neurotransmitters and their precursors (Gautam et al. 2017). Catechol is used in a variety of applications: as a reagent for photography, in rubber and plastic production and in the pharmaceutical industry. Substituted catechols, especially chlorinated and methylated ones, are by-products in pulp and oil mills. If catechols are released into the environment, they can accumulate in the soil, groundwater and surface water; thus they become an issue of great environmental concern.

12.5.1.2 Dyes

In the environment, there are different types of synthetic dyes, which have provided a large range of colour fast and bright hues. However, their toxic nature has become a serious concern for environmentalists. Presence of sulphur, naphthol, vat dyes, nitrates, acetic acid, soaps, enzymes chromium compounds and heavy metals like copper, arsenic, lead, cadmium, mercury, nickel and cobalt and certain auxiliary chemicals all collectively make the textile wastewater highly toxic (Kant 2012; Mani and Bharagava 2016). Due to its complex and synthetic nature, degradation or decolourization of dyes is very difficult, which makes it essential to remove them from industrial effluent before it discharges into aquatic bodies (Brown 1987).

12.5.1.3 Volatile Organic Carbon

Volatile organic compounds (VOCs) are the type of organic compounds that present in a gas or very volatile liquid state at ordinary room temperature. Volatile organic compounds (VOCs) are anthropogenic as well as natural in origins and highly reactive hydrocarbons. A majority of VOCs are created from anthropogenic activities consisting of manufacturing industries, petrochemical industries and vehicular emissions (EPA 2012). Most VOCs are photochemically sensitive and, when exposed to oxides of nitrogen and sunlight, would form ozone and other products as represented in equation

$$NO_X + VOC + Sunlight \rightarrow O_3 + NO_X + \text{other products}$$

VOCs are not only outdoor pollutants as high concentrations have been recorded indoors as well. Indoor sources include solvents used in the production and maintenance of building materials, furnishings or equipment, e.g. paint, carpets, plastics and photocopying machines (Berenjian et al. 2012). Many types of VOCs are toxic or even deadly to humans and can be detrimental to the environment.

12.5.2 Inorganic Pollutants

12.5.2.1 Suspended and Dissolved Solids

Dissolved and suspended solids from municipal and industrial sources are of great concern primarily because of their local impact. Inorganic dissolved and suspended solids from industrial wastewaters such as those from the sugar industry, paper manufacture, textiles, tanneries, distilleries and fish hatcheries are often composed of oxidizable organic matter, which can, through biodegradation, reduce the oxygen content of receiving water making it unfit for desirable aquatic life (EPA 1971; EPA 2008).

Suspended solids absorb heat from sunlight, which increases water temperature and subsequently decreases levels of dissolved oxygen. Suspended solids can also harm fish directly by clogging gills, reducing growth rates and lowering resistance to disease. The settled suspended particles on soil may cause damage to soil fauna and lead to various changes in soil porosity, soil texture and water holding capacity (Chowdhury et al. 2013; Jeyasingh and Philip 2005).

12.5.2.2 Nitrogenous Compounds

Nitrogen is one of the causes of eutrophication, while some N-compounds (e.g. ammonia, ammonium, nitrite, nitrate, chloramines) can be harmful for human health. The two major chemical pollutants in wastewater are nitrogen and phosphorus. The nitrogen content of industrial wastes varies dramatically from one industry to the next. The presence of nitrogen content in some industries like meat processing plants, petroleum refineries, ice plants, fertilizer manufacturers and certain synthetic fibre plants is quite high due to the excess amount of ammonia used for scouring and cleaning operations.

The use of artificial fertilizers has also increased the nitrogen concentration in the environment that poses severe problems with regard to the public health hazard in association with nitrate form which is limited principally to groundwater where high concentration can occur. Water that is high in nitrate concentration is used for preparing infant formulas, which is reduced to nitrite in the stomach after ingestion, and this nitrite reacts with haemoglobin in the blood to form methaemoglobin, which is incapable of carrying oxygen (EPA 2008).

12.5.2.3 Sulphides

Sulphide is one of the major components of the industrial wastewater. It causes an irritating, rotten-egg smell above 1 ppm (1.4 mg/m^3), and at concentrations above 10 ppm, the toxicological exposure limits are exceeded. It is highly toxic to human beings and can cause headaches, nausea and affect central nervous system even at low levels of exposure. It causes death within 30 min at concentrations of only

800–1000 mg/L and instant death at higher concentrations (Speece 1996). The results reveal that the wastewaters of liming and unhairing stages contained very high concentration of sulphate. This was due to the use of significant amount of sodium sulphide salts. The high concentrations of sulphate in the tannery wastewater may also result from many auxiliary chemicals used in the industries (Chowdhury et al. 2015).

12.5.2.4 Chlorides

The major source of chloride ions in industrial wastewater is sodium chloride, which is used in large quantities for the preservation of products in industrial processing. Being highly soluble and stable, chloride ions remain unaffected by wastewater treatment process and, thus, remain as a burden on the environment. However, considerable quantities of salts are produced by the industry, and the increased salt content in groundwater, especially in areas of high industrial density, is now becoming a serious environmental problem (Yadav et al. 2016).

12.5.2.5 Heavy Metals

Heavy metals are ubiquitous environmental contaminants in an industrialized society, and thus, the concern over the possible health hazards and ecosystem effects of heavy metals has been increased in recent years (Yadav et al. 2017). Different types of industrial wastes (solid and liquid) containing a number of toxic metals such as copper (Cu), cadmium (Cd), chromium (Cr), zinc (Zn), nickel (Ni), mercury (Hg), arsenic (As), lead (Pb), etc. are directly or indirectly discharged into the environment without adequate treatment in developing countries.

Several industries such as metallurgical, chemical, refractory brick, leather, wood preservation, pigments and dyes are the major sources of toxic metals contamination in environment. In this way, millions of people worldwide working in various industries such as pigment production, chrome plating, stainless steel welding, leather tanning, etc. are being exposed to various toxic metals leading to the development of various types of serious environmental problems and health hazards (Mishra and Bharagava 2016; Yadav et al. 2017).

12.6 Adverse Effect on Environment

The day-by-day growth of human population and industrial and agricultural practices are the major causes of water pollution that adversely affect the environment (Eguabori 1998). Water scarcity and water crisis-related problems become inferior as a result of overcrowding in urban areas. Agricultural, domestic and industrial wastes are the major pollutants of agnatic habitats. The public need to be made aware of the dangers with using open unprotected water sources and the direct benefits of paying for a safe water supply. The contaminated wastewater mainly contains some major pollutants such as toxic metalloids, nitrogen, phosphorus, detergents, pesticides, hydrocarbons, etc. Out of these pollutants, the two main nutrient limiting ones are nitrogen and phosphorous (Larsdotter 2006). The presence of nitrogen in wastewater discharge can be undesirable because it has ecological impacts and also affect public health. Surface waters can also contain levels of phosphorus in various compounds, which is an essential constituent of living organisms. Hence, phosphate content is found to be the limiting component for growth in many ecosystems, and emission of phosphate in surface waters causes eutrophication and algae bloom, thus having negative impacts on nature conservation, recreation and drinking water production; it is necessary to control the emission of phosphates from discharges of wastewater (Van Larsdrecht 2005).

12.6.1 Toxic Effects on Aquatic Region

From the industrial wastewater and other anthropogenic sources, several types of pollutants were generated and it affects aquatic ecosystem. However, the hot water generated from cooling engines increase the water temperature, and it lowers metabolic activities of organisms; due to this, oxygen demand increases. Wastewaters generated from industries, which are normally considered as the main industrial pollutants containing organic and inorganic compounds, are release into the nearby water bodies. It makes the water bodies toxic as various industries discharge the suspended solids, toxic chemicals, oils, greases, dyes, radioactive wastes and thermal pollutants. As a result, the high level of pollutants mainly organic matter in river water causes an increase in BOD, COD, TDS, etc. It makes the water unsuitable for drinking, agricultural as well as other uses. The effects of pollution are greater in shallow, enclosed or slow flowing streams. Excess fertilizer, herbicides and pesticides when washed by rain into rivers causes toxic effects for living beings. Some insecticides like DDT are particularly dangerous when allowed into water bodies, because its higher concentration disturbs the food chain system. The effects of water pollution in some areas have been to an extent of irreversibly changing aquatic ecosystems. This is dangerous to plants and animals including humans (Owa 2013).

The toxic metalloids pollution is a big challenging issue for environmental safety especially in aquatic water bodies. Among these some are very toxic or carcinogenic even at very low concentration and are, thus, risky for animals as well as humans if they present in food chain. These toxic metalloids are mainly dissolved into the water bodies through natural or anthropogenic activities (Nagajyoti 2010). Toxic metalloids are distributed widely during their transport in various compartments of aquatic system in biotic or abiotic region like fishes, water, sediment, plants discharge from fertilizer industry has not undergone any type of treatment, is found a major source of contamination to water reservoirs like ocean, lake, ponds and rivers. The discharge contains certain toxic components such as metals, nitrates and ammonia, which might be responsible for causing metabolic impairment in the aquatic organisms. At times, the toxic components could even cause fatality in aquatic living organism (Yadav et al. 2007).

The rivers situated nearer the industrial discharge point have causes adverse impact on the environment as well as to macro-benthic communities. Toxic contaminants from surface runoff, sewage discharges and industrial discharge have caused negative impacts towards the freshwater macro-benthic communities (Camargo 1992). The presence of substance chemical such as ammonia, chlorine, cyanide, metals, PCBs, pesticides and phenols would cause a decline pattern on the number of species and changes in the species composition. Furthermore, when industrial discharge and river regulation interact, benthic macro-invertebrates will be highly exposed to the toxic contaminants (Ho et al. 2012).

12.6.2 Toxic Effects on Terrestrial Region

The terrestrial regions get contaminated due to the uncontrolled and unplanned disposal of industrial waste onto the soil surface. The contaminated groundwater may severely affect soil surface and interrupt daily human activities causing adverse effect on the growth of plants and human health. Unplanned disposal of industrial waste directly on the land is one of the factors that caused the pollution to surface water and groundwater. Industrial wastewaters, containing organic and inorganic compounds, have strong influence on the development of growth of crop plants. When the concentration of the pollutants in the wastewaters is low, the agriculture reuse of the treated wastewaters serves goals such as promoting sustainable agriculture and conservation of the scarce water resources, while high concentration of the wastewaters causes many plant growth-related problems (Bharagava and Chandra 2010).

Industrial wastewaters have heavy metals concentrations which are toxic to plants and, thus, affect the plant growth, seed germination and human health and lower the crop yield (Chandra et al. 2011; Ali et al. 2015). Soil contamination by sewage and industrial wastewaters has affected adversely both soil health and crop productivity. Sewage and industrial wastewaters are the rich sources of both beneficial and harmful elements. Since some of these wastewaters are a rich source of plant nutrients, therefore soil provides the logical sink for their disposal. But untreated and contaminated sewage and industrial wastewaters may have high concentration of several heavy metals such Cd, Ni, Pb and Cr (Arora et al. 1985; Narwal et al. 1993). Their continuous disposal on agricultural soils reduced its fertility and accumulation of some of the toxic metals in soil (Antil and Narwal 2008; Kharche et al. 2011), which may pose serious human and animal health.

The wastewaters of a leather industry have marked increased concentrations of Cu, Fe, Mn, Zn, Al, Cr and Ni in sewage water, and irrigation with the contaminated sewage water increased the concentration of these elements in soils. Hence, Mn, Cr and Ni are more likely to be the elements that may cause health hazards for consumers of the crops grown in sewage-water irrigated fields (Brar and Malhi

2000). Continuous application of wastewater appears to deteriorate soil quality in some areas. They recommended the urgent management practices of wastewater for irrigation purpose. Metal-contaminated soils can cause health problems to animals and human beings when such plants are consumed (Mishra and Bharagava 2016; Yadav et al. 2017). It has been found that the growth, yield and soil health get reduced when the farmers use the wastewaters for irrigation of the cultivated land (Nandy and Kaul 1994). Heavy metals are being released from various sectors of industries, and accumulation of these heavy metals in plants causes physiological and biochemical changes. It reduces the germination percentage of seed, seedling growth and chlorophyll contents with a gradual decline as the increase in the wastewater concentration (Narain et al. 2012).

12.6.2.1 Toxic Effect on Human Health

The industrial wastewater contamination of water is maybe the most serious threat to current human benefit. Environmental pollution is an ‘externality’ in welfare economics (Govindrajalu 2003). Bad quality of freshwater or drinking water plays a key role in contributing the health issues of the population. Discharge of pollutants from industrial and agricultural area can spread pollutants to wide downstream areas. Worldwide, the effluents that are released from effluent treatment system represent one of the main sources of environmental contamination. The adverse impact of these effluents to aquatic bodies and human, from harmful substances found in them, has been documented both at national and international levels. The problems arising from these wastewaters include death of aquatic flora and fauna, algal blooms, destruction of habitat from sedimentation, debris, huge water flow and other short- and long-term toxicity from pollutants, in combination with chemical accumulation and interference in higher level in food web (Canada Gazzette 2010).

Enhanced concentrations of organochlorine pesticides day by day and toxic metals like arsenic have been found in human milk, blood, hair and urine of the exposed population. Due to the contamination, water may act as a source of various types of life-threatening diseases such as typhoid, tuberculosis, cholera, etc. (Owa 2013). Urban and industrial wastes from industries like distilleries, tanneries textiles and pulp and paper are often characterized by numerous toxic and carcinogenic chemicals, such as heavy metals, and also organic matter, loaded with microflora, which can contaminate water and enter the food chain, posing considerable danger to public health (Chowdhary et al. 2017a, b). Number of waterborne pathogens can spread resulting in diseases and degradation of receiving water bodies. There are a number of waterborne microbes that cause human disease, which come from animal and human faecal wastes (Tables 12.3 and 12.4). These contain a wide variety of viruses, bacteria and protozoa that may get washed into drinking water supplies or receiving water bodies (Akpor 2011).

Contaminated water is a vehicle for several waterborne diseases, such as cholera, typhoid fever, shigellosis, salmonellosis, campylobacteriosis, giardiasis, cryptosporidiosis and hepatitis A (WHO 2004). In addition, many microbial pathogens in

Table 12.3 Diseases caused by contaminated water and their transmission source

Disease category	Diseases	Infection type	Transmission
Diarrheal diseases	Diarrhoea, cholera, dysentery, typhoid, amoebiasis, giardiasis, rotavirus gastroenteritis	Gastrointestinal infection	Faecal-oral route; drinking water contaminated with faecal matter
Vector borne diseases	Lymphatic filariasis, malaria	Parasitic infection	Borne by black flies and mosquitoes which breed in stagnant water
	Dengue, Japanese encephalitis, yellow fever	Viral infection	Borne by black flies and mosquitoes which breed in stagnant water
	Schistosomiasis	Parasitic infection	Borne by aquatic snails
Blindness	Onchocerciasis	Nematode infection	Borne by black flies
	Trachoma	Bacterial infection	Person-to-person contact; water deficits result in poor personal hygiene and increased risk of transmission
Cutaneous diseases	Dracunculiasis	Nematode infection	Drinking water contaminated with nematodes
	Scabies	Parasite infection	Person-to-person contact; water deficits result in poor personal hygiene and increased risk of transmission
Paralysis	Poliomyelitis	Viral infection of the central nervous system	Faecal-oral and oral-oral routes; drinking contaminated water
Liver disease	Hepatitis A and E	Viral infection	Faecal-oral route; drinking water contaminated with faecal matter

wastewater can also cause chronic diseases with costly long-term effects, such as degenerative heart disease and stomach ulcer. Bacteria are the most common microbial pollutants in wastewater. They cause a wide range of infections, such as diarrhoea, dysentery, skin and tissue infections, etc. Disease-causing bacteria found in water include different types of bacteria, such as *E. coli* O157:H7, *Listeria*, *Salmonella*, *Leptospira*, etc. The major pathogenic protozoans associated with wastewater are *Giardia* and *Cryptosporidium*. They are more prevalent in wastewater than in any other environmental source (Akpor 2011; Yadav et al. 2016).

Table 12.4 Pathogenic microorganism, and their effect on human it's their prevention & control

Sr. No	Diseases	Caused by	Effects in humans	Prevention & control
1.	*Amoebiasis*	Protozoa	Fatigue, diarrhoea, flatulence, abdominal discomfort and weight loss	Drink only filtered/bottled water Wash hands properly before eating Wash the containers daily Eat cooked, warm foods Keep your fingernails short and clean Use of proper toilets for defecation Wash food before cooking and cook food at high temperature so as to kill harmful bacteria Avoid flies by disposing animal and organic wastes properly Ensure to take proper care in disposing of infant and toddler faeces Avoid consuming foods, fruit juices and milkshakes from roadside vendors Always keep foods and beverages closed, etc.
2.	*Giardiasis*	Protozoa	Diarrhoea and abdominal discomfort	
3.	*Cryptosporidiosis*	Protozoa	Diarrhoea and abdominal discomfort	
4.	*Cyclosporiasis*	Protozoa	Cramps, nausea, vomiting, muscle aches, fever, and fatigue	
5.	*Cholera*	Bacteria	Muscle cramps, vomiting and diarrhoea	
6.	*Shigellosis*	Bacteria	Bloody stool, diarrhoea and fever	
7.	*Typhoid fever*	Bacteria	Fever, headache, constipation, diarrhoea, nausea, vomiting, loss of appetite and an abdominal rash	
8.	*Campylobacteriosis*	Bacteria	Diarrhoea, abdominal pain and fever	
9.	Botulism	Bacteria	Dry mouth, difficulty swallowing, muscle weakness, difficulty breathing, slurred speech, vomiting and sometimes diarrhoea. Death is usually caused by respiratory failure	
10.	Poliomyelitis	Virus	Muscle Weakness resulting in an inability to move	
11.	*Viral gastroenteritis*	Virus	Gastrointestinal discomfort, diarrhoea, vomiting, fever and headache	
12.	*Hepatitis*	Virus	Fever, chills, jaundice, dark urine and abdominal discomfort	

12.6.2.2 Toxic Effects on Animals

Maximum quantities of freshwater have been affected by oil spilled in huge quantities from tankers of many oil industries, which destroys aquatic life such as molluscs, seaweed, crustaceans, marine birds, fishes and many other sea lives that are a source of food for humans. Due to this our diets suffer from calcium deficiencies (Owa 2013). Improper treatment of industrial wastewater and unplanned disposal of industrial waste not only disturbs the soil quality and crop but also affects the animal, human, aquatic flora and fauna. This unplanned dumping of industrial wastes causes many severe problems in domestic animals such as foot-and-mouth and dermal disease and mastitis. Hence, animals, human being and aquatic lives are badly affected by industrial wastes, which are dumped without adequate treatment. Wastes from agriculture practices have been a serious concern with respect to water pollution resources, mainly in terms of nutrient contamination.

The toxic effect of textile mill wastewater on *Cyprinus carpio* was observed by Rajan (1990). He recorded that protein, carbohydrate and lipid contents decrease significantly in the muscle, liver and intestine when exposed to sublethal concentrations of wastewater. Heavy metal contamination can cause increased protein content in the liver, kidney, stomach, intestine, muscle, testis and ovary of aquatic fishes when exposed to high concentrations of metals and tannery wastewaters (Subramanian and Varadaraj 1993). Ambrose et al. (1994) also reported decline in carbohydrate, protein and lipid contents of the gill, liver, intestine and kidney of *Cyprinus carpio var. communis* under the toxic stress of sublethal concentration of composite tannery wastewater. It is well known that industrial waste and wastewater contain high content of suspended solids, organic and inorganic pollutants, suspended solids, BOD, COD, toxic metalloids, oils and grease, which causes adverse impact on aquatic ecosystem (Muley et al. 2007).

12.7 Prevention and Control

Water scarcity is now becoming a serious global issue that requires an urgent attention of legislative and environmental authorities in three main areas: improving efficiency of industrial, domestic and agricultural water usage to overcome from such water crisis. With concerns about water scarcity, crisis and conflicts rising, numerous major efforts have been initiated and implemented around the world to address the issues.

- Greater policies will be needed and implementation of integrated water resources management from all ministries for environmental protection, agriculture, water resources, health, local governments, municipal authorities, nongovernmental organizations and representatives for industry for safe water and sanitation.
- Identify priority areas for freshwater ecosystem conservation and strict ‘No-Go’ zones where disruptive infrastructure such as dams and diversions and large-scale water withdrawals should be prohibited.

Adequate and eco-friendly treatment technologies and plans are applied to treat the toxic wastewater of industrial discharge.

12.8 Challenges

Many problems, which are faced by industries during the wastewater treatment and waste management, are described below:

- Industries have no option to use anything else in place of water in their production.
- Due to the high strength wastewater quality, there are many problems to adequate treatment of wastewater.
- Due to the updated/recent processing and treatment technologies in developing countries.
- Government should provide financial support for the improving water quality.
- There is no proper arrangement by industries to discharge their wastewater safely.
- Lack of revised regulations and policy related to the protection of the environment and human health.
- Growing water scarcity and the potential for water reuse and its conservation.
- Lack of social and health awareness for sustainable development.

12.9 Conclusion

In this study, the following points were concluded:

- The urgent need of proper and updated guidelines for consumption and discharge of wastewater by industries.
- Several waterborne diseases caused by microbial pathogens are strongly related to contaminated water and other environmental processes.
- A limited or insufficient water supply is one of the difficult issues faced by the world's poor countries, but the populations of these countries are not the only populations to undergo the load of water deficiency.
- The diluted/low strength wastewater can be reused for irrigation.
- The public awareness regarding environment/ecosystem and unfavourable impact on human and industrial wastes needs to be built up.

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Chapter 13
Inter-basin Water Transfer and Policies of Water Resource Management

Narendra Kumar and Anjali Verma

Abstract Water is a precious natural resource for supporting life on earth, without which life is not possible. Water is necessary for all the development activities of human civilization, such as agriculture, industry, electricity production, and transportation. Owing to its multiple benefits, it should be conserved, as it is becoming scarce in certain places. In India, a water policy is necessary for the management and planning of water resource projects and for sustainable environmental considerations in regard to both quantity and quality aspects. Natural disasters affect people's livelihoods and cause socioeconomic losses. Rainfall, which varies from heavy to scanty in different parts of India, is an important part of the Indian economy. Flood and drought are the most severe natural disasters that occur due to irregular rainfall and climate change during the monsoon season. A river-linking plan is one of the best ways to improve water management and flood and drought control in India. Therefore, it is necessary to link all the rivers to fulfill the water needs of the basins that have a water deficit. The Indian government has proposed about 30 Inter-Basin Water Transfer Links over 37 rivers to study and implement a river interlinking plan in the country. The proposed river interlinking development component aims to provide water resource benefits, including increased water availability for irrigation; the recharging of groundwater; employment generation; and improvements in irrigation, power, education, water availability, water quality, agriculture, occupational choices, family income, industry, flood status, drainage systems, tourism, soils, fisheries, public health status, and other socioeconomic aspects. This chapter highlights the importance of the water resource management plans in terms of the National Water Policies in India. The chapter also focuses on the role of large-scale water transfer links in the proper management of flood and drought disasters in India.

Keywords Flood · Drought · Water resource management · Policy · Inter-basin water transfer plan

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13.1 India's Water Health

India accounts for only 4% of the world's water resources. According to the Intergovernmental Panel on Climate Change, India is treated as a "water stressed region". Less than 1% of the total water in India is available for human consumption. Water availability is a major social and economic concern. A study of the problems and potential of water pricing in India was carried out by Saleth (2009). Due to the rapid population increase in the country, water resources may become scarce in future. Barbier (2004) studied water scarcity in river basins in India; scarcity is increasing very rapidly and is related to economic growth (Table 13.1). Studies of economic development and water demand in India were performed by Iyer (2007) and Chapagain et al. (2005). Most of the developmental planning in India has been done to increase the amount of water in river basins for industrial, domestic, agricultural, and economic uses. Floods and droughts occur periodically in India. In the National Water Policy of India, several recommendations have been made for the conservation and management of water (Table 13.2).

13.2 Water Resources of India

The water distribution on the Earth's surface is extremely irregular, Only 3% of water is present as fresh and the remaining 97% of water is in form of ocean. Out of this, approx 69% of fresh water is present in form of glaciers, 30% as underground water and only 1% is available in form of lakes and rivers.

India has several small and major rivers, which provide livelihoods for growth and culture and which are strongly influenced by the monsoon. The seven major Indian rivers, along with their tributaries, are the Narmada, Tapi, Krishna, Indus, Brahmaputra, Godavari, and Mahanadi.

According to the Indian Water Resources Society (IWRS), river basins are also known as catchment areas. The catchment area of the major river basins in India is approximately 20,000 km^2. All the river basins account for approximately 80% of the total geographical area of the country. Indian river basins are classified as either Himalayan or peninsular.

Rivers included in the Himalayan classification, such as the Ganga, Indus, and Brahmaputra, pass through the Himalayas. Some rivers included in the peninsular classification are the Narmada, Tapi, Krishna, Cauvery, and Mahanadi.

India has several beautiful lakes, which serve as sources of fresh water for various useful purposes. Lakes play an important role in recharging water, and as flood cushions and sewage absorbers. They act as an ecosystem for a variety of birds and

Table 13.1 Comparison of Indian National Water Policies 1987, 2002, and 2012

Series no.	Sector	National Water Policy (1987)	National Water Policy (2002)	National Water Policy (2012)
1.	Water resources planning	National perspectives	National perspectives	Considering local, regional, state, and national contexts
2.	Information system	Standardized National Information System	Standardized National Information System	All water-related data should be integrated with well-defined procedures and formats to ensure the transfer of data on the proper management of water
3.	Water resources planning	Hydrological units such as drainage basins or sub-basins	Hydrological units such as drainage basins or sub-basins	Integrated water resources management, in terms of basins or sub-basins, should be the main principle for the planning, development, and management of water resources
4.	Institutional mechanism	Organizations should be established for the planned development and management of river basins	Organizations should be established for the planned development and management of river basins or sub-basins, wherever necessary	Comprehensive legislation is required for the development of interstate rivers and river valleys and to enable the establishment of basin authorities with appropriate powers to plan, manage, and regulate the utilization of water resources
5.	Water allocation priorities	Drinking water, irrigation, hydropower, navigation, industries, etc	Drinking water accorded the highest priority, followed by irrigation, hydropower, ecology, navigation, industries, etc	Safe drinking water and sanitation defined as major needs, followed by high-priority allocation for other domestic needs, food security, the support of sustenance agriculture, and minimum ecosystem needs

(continued)

Table 13.1 (continued)

Series no.	Sector	National Water Policy (1987)	National Water Policy (2002)	National Water Policy (2012)
6.	Project planning	Water resource development projects should, as far as possible, be planned and developed as multipurpose projects	Water resource development projects should, as far as possible, be planned and developed as multipurpose projects	All water resources projects, including hydropower projects, should be planned to the extent feasible as multipurpose projects with the provision of water storage to derive maximum benefit
7.	Environmental flow in rivers	No specific actions, except for providing for the preservation of the quality of the environment and ecological balance	Minimum flow should be ensured in perennial streams for maintaining ecology, taking social considerations into account	A portion of river flows should be kept aside to meet ecological needs, ensuring that the proportional low- and high-flow releases correspond closely in time to the natural flow regime
8.	Groundwater development	Exploitation of groundwater resources should be regulated so as not to exceed recharging possibilities, and also to ensure social equity	Exploitation of groundwater resources should be regulated so as not to exceed recharging possibilities, and also to ensure social equity	Declining groundwater levels in over-exploited areas need to be arrested by introducing improved technologies for water use, incentivizing efficient water use, and encouraging community-based management of aquifers
9.	Access to safe drinking water	Adequate drinking water facilities should be provided to the entire population in both urban and rural areas by 1991	Adequate safe drinking water facilities should be provided to the entire population in both urban and rural areas	It must be ensured that the minimum quantity of potable water essential for health and hygiene must be available to all citizens within easy reach of their households
10.	Inter-basin water transfer	Water should be made available by transfer from other areas, including	Water should be made available to areas of water shortage by transfer from	Inter-basin water transfers are not only for increasing production but also

(continued)

Table 13.1 (continued)

Series no.	Sector	National Water Policy (1987)	National Water Policy (2002)	National Water Policy (2012)
		transfers from one river basin to another, based on a national perspective, after taking into account the requirements of the areas or basins	other areas, including transfers from one river basin to another, based on a national perspective, after taking into account the requirements of the areas or basins	for meeting basic human needs. Inter-basin transfers of water should be considered according to the merits of each case after evaluating the environmental, economic, and social impacts of such transfers
11.	Water use efficiency	The efficiency of utilization in all the diverse areas of water usage should be improved, with the awareness of water as a scarce resource	The efficiency of utilization in all the diverse areas of water usage should be optimized and an awareness of water as a scarce resource should be fostered	The "project" and the "basin" water use efficiencies need to be improved through continuous water balance and water-accounting studies
12.	Water pricing	Water rates should be adequate to cover annual maintenance and operation charges and part of the fixed costs	Water charges should cover the operation and maintenance charges of providing the service initially and part of the capital costs subsequently	A Water Regulatory Authority should be set up to fix water tariffs, with the provision of differential pricing for pre-emptive and high-priority uses of water.
13.	Participatory water management	Efforts should be made to involve farmers progressively in various aspects of the management of irrigation systems, particularly in water distribution and the collection of water rates	Water Users Associations and local bodies should be progressively involved in the operation and management of water infrastructure facilities at appropriate levels, with a view to eventually transferring the management of such facilities to the user bodies	Water Users Associations should be given statutory powers to collect and retain a portion of water charges, manage the volumetric quantum of water allotted to them, and maintain the distribution system in their jurisdiction
14.	Flood management	Emphasis on non-structural measures, such as flood forecasting and warning, and flood	Emphasis on non-structural measures, such as flood forecasting and warning, flood plain	Every effort should be made to respond to water-related disasters such as floods and droughts

(continued)

Table 13.1 (continued)

Series no.	Sector	National Water Policy (1987)	National Water Policy (2002)	National Water Policy (2012)
		plain zoning, so as to reduce the recurring expenditure on flood relief	zoning, and flood-proofing, so as to reduce the recurring expenditure on flood relief	through structural and non-structural measures. However, emphasis should be placed on the rehabilitation of natural drainage systems
15.	Gap between created irrigation potential and its utilization should be removed	Concerted efforts, such as command area development, should be made to ensure that the created irrigation potential is fully utilized and the gap between the potential created and its utilization is removed	Concerted efforts should be made to ensure that the created irrigation potential is fully utilized. For this purpose, the command area development approach should be adopted in all irrigation projects	All components of water resources projects should be planned so that intended benefits start immediately and there is no gap between the potential created and the potential utilized

Source: Press Information Bureau, Government of India, Ministry of Water Resources (http://mowr.gov.in/policies-guideline/policies/national-water-policy)

animals. Many lakes are categorized under the Ramsar Convention on Wetlands (1971), and, with other natural water bodies, are an important source of livelihood for many people.

In India, groundwater availability in the valleys is limited. In rural areas, about 80% of the groundwater is utilized for irrigation and drinking purposes. Excessive drilling of the groundwater in some areas has led to these areas being declared ‘dark zones’. In India, some of the worst affected states in this regard are Gujarat, Rajasthan, and Madhya Pradesh.

Rainwater, consisting of condensed droplets that fall from the atmosphere under gravity, is a major part of the hydrological cycle as it replenishes both surface and underground water sources. According to the IWRS, rainwater is the most commonly used fresh water on Earth; in India, almost 80% of the rainfall occurs mainly in the 4 months from June to September.

13.3 Water Resources: Issues and Challenges

Increasing demand for water resources, deterioration of water quality, waterlogging of land, overexploitation and depletion of water, soil salinity, increasing pollution, river flow regulation, land use, degradation of watersheds, and limited efforts at

Table 13.2 Changes in India's Water Policy over the years

Issue	National Water Policy (1987)	National Water Policy (2002)	Draft Policy (2012)
Allocation priority	1. Drinking water 2. Irrigation 3. Hydropower 4. Navigation 5. Industrial and other uses However, these priorities may vary in particular regions	1. Drinking water 2. Irrigation 3. Hydropower 4. Ecology 5. Agro-industries and non-agricultural industries 6. Navigation and other uses	Explicit priorities no longer categorized. "Water, over and above the pre-emptive need for safe drinking water and sanitation, should be treated as an economic good so as to promote its conservation and efficient use". "After meeting the minimum quantity of water required for survival of human beings and ecosystem, water must be used as an economic good with higher priority towards basic livelihood support to the poor and ensuring national food security"
Service provision	No mention	Private sector participation should be encouraged in the planning, development, and management of water resources. Depending upon the specific situations, various combinations of private sector participation in the building, owning, operating, leasing, and transferring of water resource facilities may be considered	"Water needs to be managed to achieve food security, livelihood, and equitable and sustainable development for all". Water-related services should be transferred to communities or the private sector, with an appropriate public/private partnership model

Source: Down to Earth; https://www.downtoearth.org.in/news/national-water-policy-2012-silent-on-priorities%2D%2D35952

conservation are the major water challenges today. In India, various government departments are making efforts to conserve, control, and manage the water resources.

India has a great diversity of climate and weather conditions, ranging from extremes of heat and cold in arid areas to areas of excessive rainfall. Climate change refers to alterations in weather patterns, which are affected by many factors, including natural processes and human factors involving pollution, increasing populations, increasing water crises, and urbanization. Climate change has an impact on water resources, affecting vulnerable land use, as well as affecting people and their infrastructures, including ecosystems and resources.

Because of the uneven distribution and regional and temporal variation of rainfall in India, in some places there is heavy rainfall during the normal monsoon season. Valli et al. (2013) and Jain and Kumar (2012), using the data on rainfall pattern and the precipitation concentration index from the Indian Meteorological Department, explain climatic variations in several areas of India.

A flood is an overflow of water in an area that is dry. The major cause of flooding in India is heavy monsoonal rain, and floods generally happen when large amounts of rain or snow melt cause rivers to rise and produce tidal waves. Some flood-affected areas in India are Punjab, Haryana, Orissa, Kerala, Uttar Pradesh, Andhra Pradesh, and Assam. Every year floods cause billions of dollars worth of damage, affecting vehicles, buildings, roads, sewer systems, and canals (Nautital and Bhandari 2012).

Drought is a deficiency in water supply that results in water scarcity in the river basins, climate change, loss of biodiversity, and the degradation of natural resources that disrupts socioeconomic conditions (Pai et al. 2010). Several zones in India are drought affected, such as Gujarat, Madhya Pradesh, Karnataka, Tamil Nadu, Maharashtra, and Andhra Pradesh.

Pollution of water is the contamination of water bodies, such as lakes, rivers, groundwater, oceans, and aquifers, owing to the presence of heavy metals, chemicals, and micro-organisms, that leads to the degradation of the ecosystem and has negative effects on public health.

Waterlogging of an area is caused by factors such as excess rainfall, floods, water seepage, drainage problems, and over-irrigation. Such a condition results in delayed crop production, with other impacts occurring as the water dries, such as salt accumulation, causing soil salinity.

Most parts of India are semi-arid regions whose water has a high salt content, with the high percentage of sodium being dangerous for agriculture. Regular use of such water results in the accumulation of sodium salts, producing alkaline soil.

Water sanitation relates with the impurity of water is another issue in India, and efforts are being made at various levels of government to improve the situation.

There is competition for the water available in interstate rivers such as the Cauvery, Krishna, Godavari, Narmada, Tapti, and Mahanadi.

13.4 Water Resource Management Plans in India

Water management is one of the major concerns of any country and needs planning on a long-term basis. The Indian federal government has undertaken various initiatives for long-term water management and conservation.

To solve the problem of scarce water resources and various forms of degradation, it is essential to focus our attention on natural drainage units, called watersheds. The United Nations (UN) Food and Agriculture Organization (FAO), UN Development Programs (UNDPs), the National Remote Sensing Agency (NRSA), and the Indian Space Research Organization have instituted several awareness programs to manage water resources in various sectors in India.

Groundwater levels are falling day by day. To tackle the water resources problem, rainwater harvesting is an effective method of storing rainwater and increasing the recharge of groundwater; this has been the best rainwater storage method for dry areas. Simple local techniques, such as ponds and earth embankments, can help in the storage of rainwater for the restoration of streams, fisheries, and natural ecosystems and for other water uses in urban and rural areas.

According to the Indian Water Resources Information System (WRIS), water resources projects are classified into irrigation and hydroelectric projects. The Central Water Commission (CWC), set up by the Indian Government in 1945 for flood control and the utilization of water for beneficial purposes such as irrigation and hydropower generation, has been responsible for major and medium irrigation projects incorporated in the XIth Plan of the WRIS.

In 1996–1997, the Union Government of India launched an Accelerated Irrigation Benefit Programme (AIBP) to provide loans to state governments to complete ongoing irrigation projects.

Hydropower is the electricity produced by water resources and it is one of the most widely used forms of renewable energy. Hydropower in India represents about 70% of all renewable electricity, and the percentage may increase by up to 3.1% each year for the next 25 years.

Under the sponsorship of the WRIS, a Command Area Developmental Programme was launched in 1974 to improve a large number of irrigation projects, increasing efficient water management for agricultural production.

Several expert committees have suggested various approaches to minimize flood problems, and various steps have been undertaken in instituting flood management policies.

The Brahmaputra Board was set up under the Brahmaputra Act, 1980, by the Government of India, under the Ministry of Water Resources, for flood management for the rivers Brahmaputra and Barak and also for the construction, operation, and management of dams. In 1972, the Government of India set up the Ganga Flood Control Commission for flood control in the Ganga Basin. The Farraka Barrage Project was set up to carry out river bank protection works to prevent erosion near river banks.

In 1954 the Union Ministry for Planning, Irrigation and Power announced a Policy Statement, along with the two following statements: "Floods in India – Problems and remedies" and "The Floods in the country" for managing flood situations. In 2005, the Government of India set up a National Disaster Management Authority to manage the effects of disasters, including flood disasters.

The National Flood Commission submitted a report in March 1980, with 207 recommendations covering the flood problem in the country to manage life and property in flood-affected areas. In October 2001 a committee of experts set up another National Flood Commission, under the Ministry of Water Resources of the Government of India, for flood damage assessment from year to year.

The CWC set up the Water Quality Assessment Authority, and this organization's Gazette, in a notification dated June 18, 2005, suggested that water quality parameters, such as color, nitrate, nitrite, dissolved oxygen, chemical oxygen demand, biochemical oxygen demand, and temperature be identified.

In October 1986, the Inland Waterways Authority was set up for the development and regulation of shipping and navigation. It also carries out feasibility studies for National Waterways for the transportation of cargo and passengers.

In June 2005, The Ministry of Water Resources proposed the concept of Intra-State Links. The National Water Development Agency (NWDA) is preparing pre-feasibility reports for the Intra-State Links as proposed by state governments such as those of Maharashtra, Jharkhand, Orissa, Rajasthan, and Tamil Nadu.

India has abundant water resources through its numerous small and large rivers. In 1979, the CWC provided agreements on the development of interstate and international rivers. Examples of the main legal instruments involved in these agreements are the constitutional provisions relevant to interstate rivers, and agreements, laws or regulations, awards, notifications, resolutions, and orders issued by the central government.

The interest shown by many researchers engaged in the management of water resources has led to the concept of large-scale water transfer. A National Perspective Plan (NPP) was formulated by the Ministry of Water Resources and the CWC, in 1980, for identifying a number of large-scale Inter-Basin Water Transfer Links to transfer surplus water to basins with water deficits and to minimize the water problems of flood and drought in India. Such a plan is one of the best methods of water management for proper water distribution. The proposed River Link Canal Project, with economic and environmental feasibility and irrigation benefits, can help to raise productivity. About 30 major river link canals over 37 rivers throughout the country have been proposed.

The NPP consists of two components, Himalayan and peninsular. The Himalayan component consists of 14 proposed links and the peninsular component consists of 16 proposed links, as shown in Fig. 13.1.

The proposed links for development of the Himalayan rivers may help in controlling floods in the Ganga and Brahmaputra basins by transferring surplus flows of water from the east toward the west in India and may help to provide water in many states of the country.

The Himalayan component envisages the interlinking of the Mahanadi-Godavari-Krishna-Cauvery Rivers of the western coastal areas in Maharashtra, Ken-Chambal in Rajasthan, Madhya Pradesh, and Uttar Pradesh states for the diversion of water to meet all the requirements of Kerala state (Fig. 13.1).

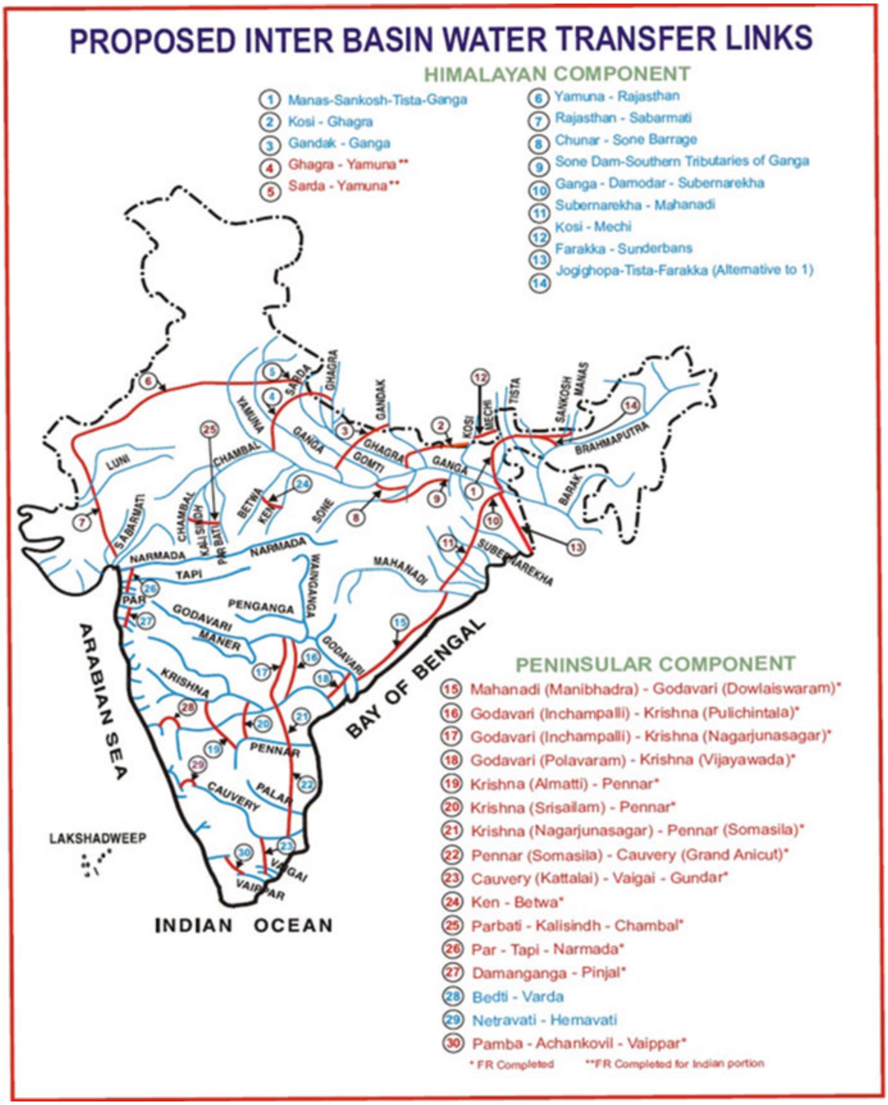

Fig. 13.1 Proposed inter-basin water transfer links. (Source: National Water Development Agency; www.nwda.gov.in)

13.5 Inter-basin Water Transfer: The Need

The Government of India has developed proposals for "Large Scale Inter-Basin Water Transfer" or "Interlinking of Rivers" for transferring surplus water to water deficit regions (Urfi 2004). The concept of the interlinking of rivers is one of the best ways to achieve the regular distribution of surface water in India and will also deliver economic and ecological benefits for sustainable development (Shah et al. 2006). The need for the proposed Interlinking of Rivers (ILR) is to make water available to river basins with a water deficit after fulfilling the water requirements of the surplus basins and also to solve the problems of droughts and floods (Bandyopadhyay 2005). Studies on drought management, including drought mitigation, were carried out by Rathore et al. (2014) and Gupta et al. (2011). Zlatanovaa et al. (2014) examined information related to flood management. Mann (2012) described flood disaster management in the Uttarkashi district.

13.6 Water Constitution in India

The Indian Water Constitution covers legislation of the Union, state, and local governments regarding water. The Constitution has a specific article (Article 263), dealing with matters of interstate rivers and valleys with respect to the use, distribution, and control of the water in any interstate river. The National Commission for Integrated Water Resource Development Plan, constituted in 1996, made several recommendations for the transfer of water to water deficit areas and also for the development of water resources, such as resources for drinking, washing, agriculture, industries, and electricity, as well as making recommendations for flood control, and submitted its report to the Union government in December 1999.

13.7 National Water Policy

According to the NWDA, India accounts for about 253 billion m^3 of water storage capacity, which is approximately 4% of the total world water resources. India is very rich in water availability, but owig to the exploitation of water resources by humans there is a problem of water pollution. Impure water is the world's biggest health risk and affects both the quality of life and public health. Demand for water is becoming more and more challenging day by day owing to the demands of agriculture, expanding urbanization, increasing industrialization, and many other factors. Narcisse (2010) explained the importance of policy-making for water security in the lives of poor people and also investigated the relation of poverty and socioeconomic conditions. Our country faces frequent floods and droughts, often at the same time in different regions, because of the uneven distribution of rain. Thus, water resource needs should be considered through the linking of rivers. The National Water Policy was framed for the planning of all the developmental water projects in basins or subbasins. Such a policy should take into account multidisciplinary aspects for the proper management of water according to the needs of each basin. Cleaver and Franks (2008) examined the relation of water governance, poverty, and water policy and favored water governance arrangements and their outcomes. They focused on knowledge generation regarding water policy. Several river basin organizations have been established for the development, investigation, and survey of basin water resources. The Government of India enacted the River Boards Act in 1956 for the management of river basins.

Some existing river basin organizations, created for the implementation of plans for specific purposes, are listed below:

1. Damodar Valley Corporation
2. Tungabhadra Board
3. Bhakra-Beas Management Board
4. Ganga Flood Control Commission
5. Bansagar Control Board
6. Narmada Control Authority
7. Sardar Sarovar Construction Advisory Committee
8. Brahmaputra Board

1. Damodar Valley Corporation

An Act of parliament in 1948 established the Damodar Valley Corporation, with responsibilities for designing and administering programs for the development of the river basin, including irrigation, water supply, drainage, power generation and transmission, flood control, afforestation, soil erosion, agriculture, and industrial and economic matters.

2. Bhakra-Beas Management Board

The Ministry of Works, Mines and Power constituted the Bhakra-Beas Management Board in 1950 for ensuring the efficient, economical, and early execution of the Bhakra-Nangal project in Punjab. This board was tasked with the maintenance and operation of irrigation and power generation, and the regulation of water supply in the states of Haryana, Rajasthan, and Punjab.

3. Tungabhadra Board

The Tungabhadra Board was constituted under the Andhra State Act, 1953, for completion of the project that comprises the Tungabhadra dam, reservoirs, low-level canal, high-level canal, and bank power houses in the states of Andhra Pradesh and Karnataka.

4. Ganga Flood Control Commission

The Ministry of Irrigation and Power constituted the Ganga Flood Control Commission in 1972 to prepare plans for flood control in the Ganga basin.

5. Bansagar Control Board

The Bansagar Control Board was constituted in 1976 in the states of Madhya Pradesh, Bihar, and Uttar Pradesh for the construction of the Bansagar Dam on the Sone River.

6. Brahmaputra Board

The Government of India established the Brahmaputra Board under the Brahmaputra Board Act, 1980, with protocols to prepare a plan for controlling flood drainage in the Brahmaputra Valley.

7. Narmada Control Authority

The Government of India set up the Narmada Control Authority in 1980 with the responsibility of securing the implementation of water resources decisions and directions in some states, including Rajasthan, Gujarat, and Madhya Pradesh.

8. Sardar Sarovar Construction Advisory Committee

The Indian Government set up the Sardar Sarovar Construction Advisory Committee in 1980 for the efficient, economical execution of dam works in some states, including Gujarat, Madhya Pradesh, and Rajasthan.

The first National Water Policy of the Government of India was legislated in 1987, and was updated in 2002 and 2012.

13.7.1 National Water Policy in India (1987)

Under the auspices of the NWDA, a meeting of The National Water Resources Council, held on September 9, 1987, framed the National Water Policy for the formulation of policies and management programs and recommended that an "adequate flood cushion should be provided in the water storage projects to facilitate better flood management" and better uses of water resources. This policy also recognized that "physical flood protection works like embankments are necessary" and emphasized such factors as the minimization of flood losses, forecasting, warnings, and flood plain zoning.

13.7.2 National Water Policy in India (2002)

The National Water Policy was revised on April 1, 2002, with modifications titled "National Water Policy-2002" for the proper planning and operation of systems; this included ecology, drinking water, hydropower, agriculture, non-agricultural industries, and navigation. The National Water Resources Council adopted this policy for the implementation of many effective water resources plans.

The relevant modifications agreed upon and action taken by the NWDA recommended the following principles of the National Water Policy-2002:

1. Water availability in the various river basins should be assessed and surplus water is to be transferred to needy areas.
2. Preservation and maintenance of quality water resources can be improved by rainwater harvesting and groundwater recharge.
3. Rainwater harvesting and groundwater recharging are two interlinked processes of water conservation.
4. Watershed management is a useful method of soil erosion control and water conservation for providing sustainable irrigation.
5. Participation by state governments is necessary for the optimum utilization of water resources, including irrigation management.
6. There should be proper management plans for flood control in flood-prone basins.
7. Flood management includes long-term planning for effective water storage, dispersion, and early evaluation of waterlogging in areas in flood-prone regions.
8. Flood cushions should be provided to facilitate better flood management plans for feasible water projects.
9. Some flood management works, such as embankments and other measures, e.g., flood plain zoning, warnings, flood-proofing, and flood forecasting, are necessary for flood relief.
10. There should be plans for the regulation of settlements and economic activity for flood-affected people.
11. Areas in coastal regions affected by soil erosion should be managed to protect coastal strips from exploitation, including economic activities.
12. Coastal land management plans should be prepared for each coastal state, taking into account other environmental and ecological impacts.
13. The interlinking of rivers is another significant proposal for the proper distribution of water in a countrywide network.

13.7.3 National Water Policy in India (2012)

The National Water Council framed the National Water Policy on June 7, 2012, under the auspices of the Ministry of Water Resources, to meet the challenges of water resources. This policy stipulates evaluation of the environmental, social, and economic impacts of the inter-basin transfer links.

The main emphases of the National Water Policy of 2012 recommendations are:

1. To ensure the availability of potable water for essential health and hygiene needs for poor people.
2. To ensure that the set-up of water regulatory authorities includes recycling and re-use options.

3. To regulate the exploitation of groundwater.
4. To adapt planning for water resource management in view of climate change.
5. To enact comprehensive legislation for the development of rivers and river valleys.
6. To support a National Water Framework Law.
7. To recognize the ecological needs of rivers for ensuring natural regime flow.
8. To maintain water charges for water distribution systems in the relevant jurisdictions.
9. To manage water resources projects to meet service delivery protocols and to apply penalties for failure to meet such protocols.
10. To provide adequate grants for water resource technologies, designs, planning, and management practices.
11. To focus on a Standardized National Information System, including data banks and databases.
12. To provide guidelines for the safety of water-storage dams.
13. To ensure that projects benefit the rehabilitation and resettlement of affected people.
14. To create awareness programs that include the participation of farmers, and address such factors as the conservation of water and flood and drought management.

13.8 Need for the National Water Policy In India

The National Water Policy plays an important role in the management of water resources for maintaining economic and ecological development. According to the Ministry of Water Resources, water is a basic need, with various aspects, such as its requirements for such areas as agriculture, electricity, and industry. Public awareness and efficient utilization of water is necessary for water conservation. Several innovatory techniques and strategies are needed to improve water quality, with recycling and re-use options. A successful water policy may depend on overall development and the efficient planning of water resources according to relevant underlying principles and objectives.

13.9 Conclusion

The aim of the National Water Policy in India is to follow proper protocols and consider proper management plans for water resources. The proposed Large-Scale Inter-Basin Water Transfer is an efficient water management plan. The Indian Ministry of Water Resources and the CWC have planned approximately 30 water links under the NPP for transferring surplus water from one basin to another after fulfilling the requirements of Enrouted (areas across the inter-basin water transfer links) and Command (surrounding) areas. During and after the construction phase, such links are also proposed to overcome the problem of irregular water distribution, and to help in the management of water crises, and in the sustainable use of water. The increases in water availability provided by surplus water may further provide other additional benefits, such as increases in the intensity of irrigation and improvements in cropping patterns and agricultural practices. Other benefits may also be provided, such as the recharging of groundwater, the generation of employment, and the development of tourism, agro-based industries, and fisheries. Infrastructure facility improvements, navigational benefits, increases in the availability of water for drinking and industrial purposes, and increases in household income, food production, and power generation will be further advantages of these links. The monsoon flood waters should be utilized and should be transferred to areas of water deficit after the river basin requirements are fulfilled. It is considered that the ILR project in India will provide for the country's water resource needs, with proper water distribution and appropriate flood and drought management.

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Chapter 14
Policy Interventions in Achieving Water Security in India

Jaya Tiwari Dubey, V. Subramanian, and Narendra Kumar

Abstract Burgeoning world population, climate change at a rapid rate, a huge shift in global financial systems, and international conflicts are some of the biggest obstacles of the twenty-first century in ensuring water security. Since the globe is interconnected, any adverse or negative changes in one part of the world have a cascading effect in other nations also, and India is no exception of it. India too faces the global as well as local challenges in tackling the water security issues. In recent years it has been realized that it is not the issue of population explosion, climate change, international conflicts, but a major part of the problem is corruption and poor governance. Hence, it is imperative that the utilization, allocation, distribution, exploitation, regeneration, and preservation of water are done at all levels and monitored at the highest level in transparent and logical way; this process must include the opinions of most of the stakeholders and policymakers alike to fulfill the demands of industry and individual to also preserve this precious resource. The issue of water security is not limited to availability only, but it goes beyond it, which ranges from the individual's fundamental right to national sovereignty rights over water, and it also includes the role of government in equitable sharing and affordability of water.

Thus, there is a need to have an appropriate policy and legal framework to regulate and distribute water resources of India. Keeping this in mind, the current chapter comprehensively reviewed the role of policy in resolving various water-related issues in India and ensuring water security.

Keywords Equitable sharing · Judicial activism · Policy · Water rights · Water scarcity

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14.1 Introduction

The prosperity of a nation depends on how successfully it is able to utilize its natural resources like minerals, water, metals, human resources, etc. Water is a natural resource that is basic to the existence of human, animal, and plant life (Gylfason 2006; Prabhakar et al. 2014). However, water is a resource that is connected to every aspect of life be it in drinking, cooking, washing, commercial or industrial use, e.g., in mining industry water is necessary to extract minerals and for various other processes. Hence, it is imperative that the utilization, allocation, distribution, exploitation, regeneration, and preservation of water are done at all levels and monitored at the highest level in transparent and logical way; this process must include the opinions of most of the stakeholders and policymakers alike to fulfill the demands of industry and individual to also preserve this precious resource (Mianabadi et al. 2015; Kumar et al. 2018).

As it is evident that any resource which is connected to some many aspects of human life will have many claimants to its use, in the same way there will be many who will like to get a major share of water resources to exploit it for their own benefit, thereby creating a rift among the users. At this point, the issue of water security arises, because water resource being a priceless commodity gives power to a nation, which renders it as a strategic commodity of that nation, and it should not be overlooked in geopolitical framework. The security of water is not limited to availability, but it goes beyond it, which ranges from the individual's fundamental right to national sovereignty rights over water, and it also includes the role of government in equitable sharing and affordability of water (Singh 2015). Thus, there is a need to have an appropriate scientific and policy framework to regulate and distribute water resources of India. Keeping this in mind, the current chapter comprehensively reviewed the role of science and policy in resolving various water-related issues in India and ensuring water security.

14.2 Water Crisis and Related Issues

It is always a topic of debate whether water crisis is "myth or reality." The water experts from worldwide have reached to a general consensus that it is not physical water scarcity, rather mismanagement of water resources (Rogers 2006). Though water is considered as the renewable resource, which is present in a fixed quantity on our planet, but due to excessive population, the distribution of this portion of water is at stake among potential users. Approximately 70–90% of water is consumed by the agricultural sector. To support irrigation for feeding the increased population, the groundwater is overpumped and due to climate change rivers are drying up; all these facts are indicating towards global water crisis.

Water stress and shortage clearly explain the issues of its availability. As the nation's water demand increases, the burden on its available supplies increases.

When supplies cannot meet the demands, scarcity sets in. Availability of water is thus primarily a physical and technical problem. Problems on availability and use, on the other hand, are brought about by political, social, and economic factors and necessarily involve similar responses. Interminably, water policy is connected with other key social concerns like health, pollution, land use, and agricultural policy. Around 663 million individual—1 in 10—lack access to safe water. Around 3.575 million people die each year from waterborne diseases. Forty-three percent of water-related deaths are because of diarrhea. Eighty-four percent of water-related deaths are in children of age group between 0 and 14. It has been observed that 98% of water-related deaths occur in the developing world (WHO/UNICEF 2015).

The water and sanitation crisis claims large number of lives through waterborne diseases than any war claims through guns. At any given time, majority of the world's hospital beds are occupied by patients suffering from a water-related illness. An American uses more water in taking a 5-min shower than the typical person living in a slum of a developing country uses in a whole day. About one third of people without access to an improved water source live on less than $1 a day. More than two thirds of people without an improved water source live on less than $2 a day. Poor people living in the slums often pay 5–10 times more per liter of water than rich people living in the same city. A person can live without food for weeks, but without water we can hope to live just a couple of days.

14.3 Qualitative: Water Pollution

The issue of water pollution has its significant impacts on availability. According to water experts, water scarcity in the twenty-first century is more of environmental, poor water management, and socioeconomic problem (Gleick 2000; Rogers 2006). Both the surface and groundwater quality are degraded due to contamination of chemical and biological agents and various anthropogenic activities. The water becomes unavailable once it is contaminated with salts, municipal and industrial effluents, heavy metals, etc. The water quality degradation led to exploration and exploitation of other water resources, which ultimately creates the water crisis-like condition.

For instance in Japan, water pollution is chiefly due to chlorinated solvents from industries (UNEP 1996). In Jakarta, Bangkok, and Manila, unlawful dumping of liquid effluents and solid wastes were responsible for the outbreaks of cholera, typhoid, and other water-related diseases (Foster et al. 1996). In most of the developing nations worldwide, it is estimated that approximately 90% of wastewater is discharged into the water body without proper treatment. This prompted the Asian Development Bank (1998) to make a list of water pollutants, which renders water scarcity as the most serious environmental problem in Asia. China is also facing severe water crisis, especially in the northern part of the country. China's water scarcity is due to limitations of local water resources as well as reduced water quality due to increasing pollution. Water crisis and substandard water quality problems are closely associated with each other and threatening the food security, economic development, and improved living standards of China (Jiang 2009).

According to the WHO, CPCB, BIS, and ICMR, the water quality of about 70% Indian rivers has deteriorated due to various pollutants, and some of the river has turned into a big drain (Ramakrishnaiah et al. 2009; Jindal and Sharma 2010; Gupta et al. 2017). River Gomti (tributary of river Ganges) and Yamuna are the live examples of it (Singh et al. 2004; Tiwari and Kisku 2016; Bharadwaj et al. 2017).

The surface water quality could be improved by better water management practices, but the revival of groundwater quality is the herculean task which may continue generation after generation. This task becomes almost impossible in arid and semiarid regions where demand is high and recharge is limited (Pereira et al. 2002). Therefore, there is a need of paying considerable attention toward protection and preservation of water quality and avoidance of human-induced water scarcity, which could be achieved only through proper policy framework and science and technology.

14.4 Quantitative: Potable Water Scarcity

Common misconception "water is everlasting and could be easily replaced as 2/3rd of earth's surface is surrounded with water" remains in the minds of the citizens of developed as well as developing nations. This impression of surplus water laid the foundation for the water crisis worldwide. It is the high salinity level and low nutritional value which render the majority of the water unfit for drinking as well as irrigation. Consumable water is just 2.6% of the total world's water, and 2/3 of it is trapped in glaciers and ice caps thus left us only with 0.01% easily accessible potable water (Table 14.1). The 20% of easily accessible water is available either at faraway places or during erratic pattern of monsoons and floods. In short, for drinking, irrigation, washing, etc., human beings are left with even less than easily accessible water, i.e., 0.01%. Thus, it is clear that the population growth in the coming years will put human beings in major crisis of useable water (Kelley 2009). Despite the fact that India has low per capita water consumption, it lags in the efficient use of water across sectors. In the recent past of burgeoning population growth, temperature rise of Indian Ocean due to greenhouse gas emissions has altered the monsoon pattern, which puts enormous pressure on water resources. The groundwater reservoirs are badly affected due to lack of water conservation and planning and huge wastage of rainwater. Since 1950 the groundwater consumption has increased manifolds, 10–20 cubic kilometers each year in 1950 to 240–260 cubic kilometers each year in 2009. It is also evident from the satellite images (Asoka et al. 2017).

Table 14.1 Distribution of water in various reservoirs

Water source	Water volume, in cubic miles	Water volume, in cubic kilometers	Percent of freshwater	Percent of total water
Oceans, seas, and bays	321,000,000	1,338,000,000	0%	96.5%
Ice caps, glaciers, and permanent snow	5,773,000	24,064,000	68.7%	1.74%
Groundwater	5,614,000	23,400,000	0%	1.7%
Fresh	2,526,000	10,530,000	30.1%	0.76%
Saline	3,088,000	12,870,000	0%	0.94%
Soil moisture	3,959	16,500	0.05%	0.001%
Ground ice and permafrost	71,970	300,000	0.86%	0.022%
Lakes	42,320	176,400	0%	0.013%
Fresh	21,830	91,000	0.26%	0.007%
Saline	20,490	85,400	0%	0.006%
Atmosphere	3,095	12,900	0.04%	0.001%
Swamp water	2,752	11,470	0.03%	0.0008%
Rivers	509	2,120	0.006%	0.0002%
Biological water	269	1,120	0.003%	0.0001%
Total	332,500,000	1,386,000,000	100%	100%

Source: Gleick (1996)

14.5 Food Issues

Increasing water scarcity is continuously constraining food production, bringing about antagonistic effects on the objectives of achieving nourishment security and human prosperity (Rosegrant et al. 2009). Water security has an extreme significance, particularly in the agricultural field: agribusiness utilizes roughly 70% of inexhaustible water assets around the globe (Taylor 2015) and will keep on being the biggest user of freshwater assets through 2050 across the world (Rosegrant et al. 2009). Moreover, in water-scarce nations, water system is very crucial to improve crop production (Jhorar et al. 2009). In any case, the increasing water shortage is putting pressure on irrigation systems' (Forouzani et al. 2012) yield and quality. Also, water uncertainty has irreparable impacts on crude material production, rural business openings, rural development, etc. Thus, any planning and discussion about agribusiness are incomplete without thought of water availability (Taylor 2015). As per Food and Agriculture Organization (FAO), global agricultural production growth is expected to decline by 1.5% every year to 2030 and then a further fall by 0.9% to 2050, in contrast to 2.3% growth per year since 1961 (FAO 2003). In reality, the growth by 2009 has dropped as compared to the growth in 2000. A deceleration in agricultural production would influence the food security across the globe (Narayanamoorthy 2007).

The key drivers which have impacted on recent past and will impact on food production and supply include (a) water (and to some extent land) crisis, (b) climate change crisis, (c) energy crisis, and (d) credit crisis. Water shortages are reflected in the per capita decrease in irrigation water used for irrigation purpose for food production across the world in the last 20 years. Water resources, critical for irrigation, are under tremendous pressure as populous cities, states, and countries need and withdraw more water from rivers, lakes, and aquifers consistently (Gleick 2003). A major concern in maintaining future water supplies is the continuous exploitation of surface water and groundwater resources (Loehman 2008). As a result, there is scarcity of available surface water and groundwater for irrigation (Shah et al. 2006). For instance, in Australia, CSIRO estimated that there will be a drastic decline in irrigation water for diversions in the MDB (Murray-Darling Basin) which is the food basket of Australia (CSIRO 2008).

The analysis revealed that population and per capita income growth will increase the demand for food and water. Irrigation will be the first sector to get affected as water consumption by nonagricultural uses increases and water scarcity intensifies. Increasing water scarcity will have many implications, e.g., food security, hunger, poverty, and ecosystem health and services. Feeding the 2050 population will require some 12,400 km^3 of water, up from 6800 km^3 used today. This will leave a water gap of about 3300 km^3 even after upgrading the efficiency in irrigated agriculture, improving water management and rain-fed agriculture (de Fraiture et al. 2007; Molden 2007; Molden et al. 2010). This gap will lead to a food gap unless concrete actions are taken today. Disrupted access to energy can additionally create the food production gap.

Hanjra and Qureshi (2010) also analyzed that the water for food security scenario is critical and might get challenging, if no action is taken. Investments are needed today for enhancing and improving future food security; this requires action on several fronts, including addressing the problem of climate change, conserving water and land, reducing the energy footprint in food systems, developing and adopting climate-resilient varieties, equipped irrigation infrastructure with modern technologies, strengthen domestic food supplies, redesign international food trade, and counter other global challenges.

14.6 Health Issues

Disposing of untreated waste into surface water is a cheap, easy unscientific way of removing waste locally; it also deteriorates quality of groundwater, particularly for the users of downstream. In developing nations today, more than 80% of municipal wastewater is discharged into rivers, lakes, and coastal areas without treating them (Schwarzenbach et al. 2010). Consumption of such contaminated water is responsible for a large number of health problems (e.g., waterborne diseases). Annually, poor quality of water and waste management causes 1.5 million deaths from diarrhea, 100,000 deaths from helminth infections (intestinal parasites), and 15,000 deaths from schistosomiasis (a parasitic disease due to ingestion of trematode flatworms) (Gleick 1996; Kosek et al. 2003). The link between adequate sanitation and safe drinking water supply is examined by Johnston et al. (2011) and Oelkers et al. (2011).

Potable water contaminated with microorganisms play an important role in causing waterborne diseases like diarrhea, nausea, gastroenteritis, typhoid, dysentery, and other health-related issues (PCRWR 2005; Shar et al. 2008), especially in children and persons with fragile immune systems (PCRWR 2005). Microbial contamination of water is one of the potential threats to nation's public health and needs special attention to take necessary remedial measures to stop its further aggravation (Azizullah et al. 2011).

The available resources of freshwater are associated with human health in several ways: they need water for ingestion, water for hygiene and cleanliness, and water for food production. In 1977, Bradley observed that most of the "waterborne" diseases are actually "water-washed" diseases due to insufficient quantity of water available for washing clothes, hands, food, and cooking utensils (Bradley 1977). The necessary step to prevent these diseases, such as shigellosis, trachoma, and scabies, is to increase the water quantity rather than improve water quality. This intervention includes providing connections or closer public standpipes at household level and construction of handwashing stations and communal bathing and cloth washing facilities. The detailed review of the impact of water, sanitation, and hygiene interventions by Esrey et al. (1991) observed that increase in water supply and hygiene interventions was closely associated with a 20 to 33% median reduction in diarrheal disease morbidity (Esrey et al. 1991). A very recent study and meta-analysis of the impact of increased water supply and hygiene interventions concluded that water supply interventions in developing countries were associated with a 24% decline in diarrheal disease and hygiene interventions were associated with 42% reduction in diarrhea morbidity (Fewtrell and Colford 2004; Moe and Rheingans 2006).

Researchers and experts of the United Nations expect alterations in the water cycle ensuing from climatic changes to multiply the number of human ailments including death (Lydersen 2008), particularly in developing countries. Such health outcomes would occur through waterborne and vector-borne maladies, particularly in nations where precipitation increases and flooding events inundate several houses in rural area and shake existing sewer and treatment systems. As a consequence, bacteria, parasites, and algal blooms would flourish, including the protozoan parasites, *Cryptosporidium*, hepatitis A viruses, *E. coli* bacteria, and several other pathogens. International organizations, like the World Health Organization (WHO), calculated that malnutrition causes the annual deaths of 5.62 million children under the age of 5, while diarrheal diseases take the lives of another 1.8 million young children every year across the globe. Overall, nearly 3 million deaths annually are mainly because of insufficient and impure water, poor standards of sanitation, and improper hygiene. As temperatures increase, many experts expect vector-borne diseases like malaria and dengue fever to expand their geographic range into regions which were previously not their home (Eckstein 2009). The WHO suggests that erratic pattern of climate like global warming and precipitation since the mid-1970s have already been responsible for more than 150,000 deaths annually. By 2030, the number of deaths would be directly associated with climate change and is expected to rise up to 300,000 per year. In addition to this, global warming has been connected with food-borne infectious diseases; 30% of reported cases of salmonellosis in continental Europe have been associated with temperature higher than average temperatures (Patz et al. 2005; Jack 2007).

14.7 Current Policy Framework for the Water Security

14.7.1 The Indian Policy Framework

As we are aware that all policies draw their legal power from the Indian Constitution, it is a good start point for doing a detailed study about policies with regard to water. As per the Indian Constitution, water is a state subject; however, since no river generates in a single country or state, overarching authority has been given to the central government for smooth coordination and communication control, between states and neighboring countries as well. The constitution of India gives the right to parliament to frame laws as per article 246 however, since water is a state subject, state legislature also has power to frame laws (Saleth 2004). Important provisions of laws are as given below:

- As water is included in List II of Seventh Schedule (referred to as state list) of the Indian Constitution, therefore legislature of any state has exclusive power to make laws for such state or any part thereof.
- Indian parliament has power to make laws with respect to any matter in the concurrent list.

In case of any dispute relating to waters of interstate river or river valley, Article 262 provides:

- Parliament can make laws applicable for settling any kind of dispute or complaint with respect to the usage, allocation, distribution, or control of the waters of any interstate river or river valley. For example, Interstate River Water Disputes Act 1956 has created specific tribunals to resolve interstate water disputes. The provisions of this act were widely applied in resolving the water sharing disputes of Cauvery river between Karnataka and Tamil Nadu, Krishna-Godavari dispute, Narmada dispute, etc. (D'Souza 2006).
- In addition the parliament can make laws to prevent judicial intervention or exercise of judicial powers in respect to dispute or complaint as referred in Clause (1).17 under List II of Seventh Schedule.

Entry 17 under List II of Seventh Schedule includes all kinds of water, that is, water supplies, irrigation and canals, drainage and embankments, water storage, and water power, and these are subjected to the provisions of Entry 56 of List I of the Indian Constitution.

Thus, as illustrated above, the central government has been provided adequate powers in the constitutional scheme of things to control, regulate, and formulate various policies as required from time to time to meet this goal of water security and management.

14.7.2 Recent Policy Initiatives of the Central Government

To manage the whole gamut of issues related to water security, the Indian government is operating a whole slew of policies and missions; these are targeted at various facets of water management but are contributing in individual way to water security. They are different in application and formulation with each other, but all of them contribute to the single goal of water security and management in their own area of application. The major policies are listed along with a short note to have a grasp of the focal subject of the policy, all such policy and programs are very elaborate in themselves and a detailed discussion will be beyond the scope of the chapter. Some of the policy initiatives taken by the government are as follows.

14.7.2.1 National Water Mission (NWM)

The National Water Mission (NWM) of India is one of the eight missions created under the National Action Plan on Climate Change; NWM has attempted to conserve water, reduction in wastage of water and equitable sharing among the states, which could only be achieved by integrated water resources development and management (Warrior 2017). The following are five major objectives of the NWM:

(a) To create comprehensive water database in public domain and evaluate effect of climate change on resources of water
(b) To promote actions of citizen and state for conservation and protection, improvement, and preservation of water resources
(c) To focus on vulnerable areas including water overexploited areas
(d) To increase efficiency of water usage by 20%
(e) To promote integrated water resource management at basin level

Various strategies for accomplishing the objectives have been recognized which lead to integrated planning for sustainable development and water security (Warrior 2017).

14.7.2.2 National Water Policy (NWP)

A comprehensive National Water Policy 2012 has been drafted by GOI, in which the measures to be adopted for enhancing water security in the country are elaborately given. One of the major areas that can contribute to the area of ensuring water security is to adopt such universal measures in policies and regulations that can be used universally, i.e., by users and policymakers alike. Various aspects have been listed down by the NWP relating to integrated water management, strategies for climate change adaptation, water pricing, demand management, water infrastructure, institutional mechanisms, and groundwater management. The policy has prioritized the usage of water in the following sectors: drinking water, irrigation, hydropower, navigation, industrial, and other uses. NWP 2012 also highlights the fact that the role of the state has to be gradually shifted from service provider to that of a regulator of services and facilitator for strengthening the relevant institutions (TERI 2015).

The National Water Policy 2012 of India clearly states that water needs to be treated as an economic good and, therefore, may be priced to encourage efficient utilization and maximizing value from water. Water pricing is a disputable issue, particularly in the context of equality and meeting minimum needs, especially for the poor. However, appropriate water pricing ensures more efficient utilization, which definitely leads to increase water availability. The NWP also advocated the significance of groundwater. Groundwater is often considered as private/individual property, and there are no specific rules which regulate the amount of water which can be withdrawn. Therefore, the Central Ground Water Board (CGWB) was constituted to conserve and preserve the groundwater (Balani 2012).

14.7.2.3 Central Ground Water Board (CGWB)

The Central Ground Water Board (CGWB) is the top most national agency which works under the Ministry of Water Resources, River Development and Ganga Rejuvenation, Government of India; gives scientific suggestions; and inputs for the management, exploration, monitoring, assessment, improvement, and control of groundwater resources of the country. This board has powers to regulate excess withdrawal of groundwater in critical water-scarce and overused regions and to discourage construction of groundwater structures or drilling of tube wells in areas notified as critical or overexploited (Ramesh 2012).

14.7.2.4 Central Water Commission

It is a pioneer technical organization of India in the field of water resources. It is presently attached to the Ministry of Water Resources, River Development and Ganga Rejuvenation, Government of India. The responsibility of the central water commission is to initiate, coordinate, and assist in consultation of the concerned state governments, projecting to control, conserve, and utilize water resources throughout the nation, for the purpose of flood control, irrigation, navigation, drinking water supply, and power development. It also takes the responsibility of investigations, construction, and execution of any such schemes as required (Ministry of water resources, GOI 2011).

Thus, there are plenty of policy framework and reforms in water sector available in India, but it needs to deliberate and clarify a couple of issues regarding its execution and feasibility. To make these policies more effective, they should be interpreted as citizen's "water right" by the constitution of India, and the Indian judiciary has played a vital role in this regard by judicial activism.

14.8 Impact of Judicial Activism in India Towards Water Security

Fundamental right to water for every citizen of India has been evolved by "judicial activism" over the years in different water-related cases. The right to "pollution-free water" and the right of access to "safe drinking water" have been interpreted as a part of "right to life" under Article 21 of the Constitution of India. This is a liberal and social reformer interpretation of the fundamental right to life by the Supreme Court as well as the High Courts of the country in several cases before them. Cases like Narmada dam, Tehri dam, etc. are evidence that the Indian legal system has moved from the typical legal justice to natural justice by constitutional law; a shift from criminal to torts to constitutional is clearly visible in the pattern of cases. Some of the cases need to be highlighted, were private companies that have tried to get windfall profits from a natural resource, i.e., water, and impinge upon natural rights of locals, and for the purpose of social equity and justice, such restraint orders have been passed which give effect to inherent water security (Upadhayay 2011). One of such cases is discussed below.

14.8.1 The Coca-Cola Cases in India

In a several districts of India, there is accusation on Coca-Cola and its subsidiaries for creating severe water shortages for the community by extracting huge quantity of water for their factories, affecting both the quantity and quality of water. Coca-Cola has the largest soft drink bottling units in India. Water is the essential component of the products manufactured by the company. There have been numerous public protests against the Coca-Cola company's operations throughout India, involving thousands of Indian citizens and several nongovernmental organizations (Upadhyay 2005).

"Water right," a judicially evolved right, is not explicitly incorporated under the Constitution of India. The closest that we came to directly incorporating this right was the time when the National Commission that reviewed the Constitution suggested in its report in 2002 that a new Article 30D be inserted in the Constitution; thus, "Every person shall have the right—(a) to safe drinking water . . . ." There is no reason why drinking water being more fundamental and important than even elementary education—and similarly judicially circumstanced as education—should not follow the same route (Upadhaya 2011).

14.9 Challenges of Water Security Policy at Global and National Level

Water security is an issue which affects 80% of the world population, especially in the poor countries; the rich countries are not as affected by the water security issues. In addition it is also connected to the biodiversity risk. When we closely analyze the definition of water security, it says it is a permissible level of water-related risks to human health and ecosystems coupled with availability of water of sufficient quantity and quality to support livelihoods; national security, multiple levels, i.e., national, local, environmental; etc. The spirit of this definition presents the following challenges:

(a) Challenges of food security in terms of water security
(b) Integration of policy at global and local level
(c) Challenges of adequate funding for all government programs
(d) Academic incentives to carry out quality research
(e) Integration of policy with research at all levels, i.e., lateral and vertical integration
(f) Integration of interdisciplinary sciences toward a common goal
(g) Migration of policy-based approach to science-based approach
(h) Integrated approach which includes local population and stakeholders

Thus, we see that the challenges we face are multiple, but water security must cope with the complexity, and the policymakers also must learn to combine all levels to solve the challenges. These policies must cater for adequate financial resources. Implementing policies should be according to actual situation. Thus, these challenges of water security policy need to be framed in such a way that science can marshal interdisciplinary data and evidences to find solutions.

The twenty-first century water security policy challenge over the next generation is to guarantee tolerable water-related hazards to society, at all scale and levels; this requires:

(a) Ensuring efficient water-related services to 9 billion people
(b) Managing water-related threats to society, i.e., quality tipping points
(c) Monitored exploitation of water both fresh and ground by private industries
(d) Keeping contamination within permissible levels to prevent pollution of all types of water sources
(e) Formulation of water laws at global and local levels

Finally, water security can only be achieved if nations are able to make such policies and laws which do not treat water just as a resource but as part and parcel of human existence, something which is a natural part of our society rather than just a commodity of use. Our attitude must change and such education must be part of our holistic societal education.

14.10 Recommendations

From the above comprehensive review about all water security-related issues and associated challenges, it is recommended that all these issues could be addressed through carefully formulated policies backed up by penal provisions of law. The policies must address the genuine concerns of all stakeholders and allow no exploitation which leads to imbalances in the ecosystem and biodiversity. The concept of "water pricing" is applicable to societies having high per capita income and minimum disparity between minimum and maximum income groups. In case of India, this disparity will lead to complicated social problems if "water pricing" is implemented as suggested in "NWP 2012." However, minimum cost as per the intended user's monetary capacity can be levied in some selected cases like piped drinking water in urban areas. Our country being a welfare state proliferating of natural resources like water is not available especially where the lower strata of the society are affected. However, this concept of "water pricing" is successful in developed nations where the disparity in income and various socioeconomic indicators are not as pronounced as in India.

Groundwater must be accorded and treated as a limited resource like any other mineral resources which are present underground. Corporations and individuals must not have unlimited access rights to this resource; this would prevent wastage, maintain balance, and ensure adequate resources of groundwater at any given time. Thus, access rights must be formalized through legal provisions of law. Like right to education and right to life, the right to safe and clean drinking water must be enshrined in the constitutional scheme of things. This experiment has been successfully carried out in some water-deficient countries.

14.11 Conclusions

Water security relates to the fundamental nature of human existence; it is a basic requirement of sustaining life on this planet, which includes the animal, plant, and human life. It is one common natural element that connects all the ecosystems with each other, and hence it is imperative that we should understand the challenges that it faces. These challenges are at global as well as local level, which are also linked to each other, and interdependence exists between the two. The global-level challenges are independent of national boundaries and include those factors which work in one geographical area and affect the other geographical area also as nature does not recognize the nation's boundaries. The nations which are industrialized or have enough monetary capacity are able to deal with such problems due to availability of technologies and resources, but on the other hand, the poor nations not having access to these technologies have to face serious challenges. Developed nations and fast developing nations like the USA and China indulge in such activities giving rise to pollution and harmful emissions. These activities have a significant effect on the overall climate of the globe, which leads to water crisis in smaller unindustrialized nation. The sources of freshwater, of glaciers, etc. get severely affected; this is due to activities in other countries. Thus, rich countries have access to such advanced technologies which minimize the effect of same in their own country. But the poor nation gets affected severely, thereby endangering their water security. Hence, to face such challenges at a global level, there is a requirement of an umbrella policy and initiatives which are equally applicable to all i.e., rich and industrialized as well as poor and small nations. Another challenge is availability of finances to deal with requirement of poor countries. Technology availability with rich countries is also required to be transferred at minimum cost to poor nations. Since the globe is interconnected, the adverse effect or negative changes in one part of the world have a cascading effect; hence, the solution to such global challenges has to be of universal nature. Piecemeal approach fails to deliver results.

The water security issues at the nation level are similar to global issues with differences in some aspects only. Water security of any nation is related to its food and energy security also. In our country, the biggest challenge that we face is of equitable sharing of water resources among the states. Disputes between states like Cauvery, Narmada, and Sutlej are extremely severe and can lead to wide unrest if not handled properly. Exploitation of water for irrigation is an activity which needs detailed planning and deliberations; otherwise, it is easily exploited by vested interest. Maharashtra is a good example of how sugarcane farming created a water crisis due to improper distribution of planning. The similar way of exploitation of water for industrial use by corporates like Coca-Cola and Pepsi, the leather industry has created local level challenges which need to be addressed immediately. Such activities have an immense potential to disrupt and pollute local ecosystem and fragile natural balances, thereby disrupting eco-chain and delicate environmental balances.

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Chapter 15
Conservation of Energy Resources for Sustainable Development: A Big Issue and Challenge for Future

Vishal Chand

Abstract Energy is a form of power that we require to light our houses, buildings, offices, streets, to run our vehicles, to run industries, and for many other functions. There are two main sources of energy: renewable and nonrenewable. Our energy demands are mostly fulfilled by nonrenewable energy. Most of the nonrenewable energy we use comes from fossil fuels, such as coal, natural gas, and petroleum. Uranium is another nonrenewable source, but it is not a fossil fuel. Uranium is converted into a fuel and used in nuclear power plants. Once these energy sources are used up, they are gone forever. The combustion of fossil fuel releases a huge amount of greenhouse gases and this excessive amount leads to environmental concerns such as global warming and acid rain. Many renewable forms of energy are available, such as solar energy, wind energy, hydro energy, biomass energy, and geothermal energy. These are forms of energy that can be used over and over again, and produce less pollution during production and storage in comparison with non-renewable energy resources. Solar energy comes from the sun, wind energy is used to run windmills to produce electricity, hydro-energy is used to produce electricity by constructing dams on rivers. All these forms of energy no doubt fulfil our energy needs, but all of them have a negative side, which leads to environmental concerns because wherever these energy generation plants are launched, they disturb the local flora and fauna, and also affect the habitat of the local population. Now, rehabitation is becoming a social concern in those areas. This chapter focuses on different kinds of energy resources, their production, future prospects, and social and environmental concerns.

Keywords Energy sources · Renewable energy · Nonrenewable energy

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15.1 Energy Sources

Many different types of energy sources are used to perform work, and these are classified as renewable and nonrenewable energy resources. Renewable and nonrenewable energy can be converted into many different secondary energy sources such as electricity and hydrogen (US energy information 2018). Energy is one of the most important components that makes any country become popular. It is an important component for the economic development of any country (Indiacore energy review 2018). All over the world, the main forms of energy used come from nonrenewable energy sources, for example, coal, petroleum, and natural gases. Electricity is the essential component made from these sources that are mostly used to move our vehicles and to run industries.

The different physical units used to measure the energy sources are barrels or gallons for liquid fuels, cubic feet for natural gas, short tons for coal, and kilowatts and kilowatt hours for electricity. In some countries such as the USA, British thermal units (Btu), a measure of heat energy, is mainly used to compare different types of energy. The latest report in 2017 suggested that total US primary energy consumption was equal to about 97.7 quadrillion (97,728,000,000,000,000) Btu and there are five major primary energy-consuming sectors (US energy information 2018). Their shares of the total primary energy consumption in 2017 are shown in the table below.

1. Electric power – 38.1%
2. Transportation – 28.8%
3. Industrial – 22.4%
4. Residential – 6.2%
5. Commercial – 4.5%

The broad vision of the whole world is to make energy available at a low price cost with safe, clean, and convenient energy. Since the year 2000 in India, the need for energy has almost doubled, although per capita consumption is only one third of the global average. From there three quarters of its energy demand is met by nonrenewable sources such as fossil fuels (Joslyn 2018). These fossil fuels accounted for about 77.6% of US primary energy production.

It is important for energy statistics to separate primary and secondary energy. To set up the Energy Balance, the new energy flow is recorded, entering the system of national energy supply system, and its transformation and losses until its end use (Annual energy outlook 2015). To avoid error counting, it is necessary to separate new energy entering the system (primary) from the energy that is transformed within the system (secondary). It is important to know the clear difference between primary and secondary energy, which would be useful in energy planning. It is necessary to develop long-range policies for energy analysts concerned with broader energy or environmental issues, such as conversion losses, transmission losses, distribution, energy efficiency measures, and carbon emissions from energy sources (UNSD and Oslo group Secretariat 2008).

15.1.1 Primary Energy Sources

"Primary energy should be used to designate those sources that only involve extraction or capture, with or without separation from contiguous material, cleaning or grading, before the energy embodied in that source can be converted into heat or mechanical work" (UN, Concepts and Methods in Energy Statistics, New York 1982).

The manual does not provide a formal definition, but it explains the related term "primary energy commodities." "Energy commodities are either extracted or captured directly from natural resources (and are termed primary) such as crude oil, hard coal, natural gas, or are produced from primary commodities" (OECD/IEA/Eurostat, Energy Statistics Manual, Paris 2005).

Primary (or indigenous) indicates "The extraction or capture of primary fuels or heat and electricity which are retained for sale or use. Quantities reported exclude amounts of inert matter or impurities removed before sale or use and any amounts returned to the natural reserve. However, amounts of the fuel/energy consumed during the production process are included" (InterEnerStat, Tim Simmons, 1st proposal for consultation, August 2008).

The first concept of primary energy used as in the UN definition specifically refers to the energy in a source and not the source in itself. The proposed class is then "energy embodied in sources." The second option includes waste in addition to natural resources in the definition. Waste is a surplus component from any other process that has no further use in the process from which it comes. One way to see waste is as a non-energy commodity flow that enters the energy commodity flow as "new" energy.

Another very important distinguishing characteristic of primary energy is the process of extraction. This energy is extracted or captured from different sources, and during this process of extraction or capture, the physical and chemical characteristics of the energy are not changed, for example, hard coal, which is extracted from the ground, cleaned, and separated from rocks and other non-energy substances, and the physical and chemical properties of the energy in the hard coal itself have not changed. So, according to the UN definition, the extraction, separation, capture, and grading of the energy components in a source are not energy transformation processes; therefore, the energy in hard coal is not secondary energy.

Finally, we propose a new definition for primary energy: "Primary energy is energy embodied in sources which involve human induced extraction or capture, that may include separation from contiguous material, cleaning or grading, to make the energy available for trade, use or transformation."

15.1.2 Secondary Energy Sources

"Secondary energy should be used to designate all sources of energy that result from transformation of primary sources" (UN, Concepts and Methods in Energy Statistics, New York 1982).

"Secondary energy comes from the transformation of primary or secondary energy" (OECD/IEA/Eurostat, Energy Statistics Manual, Paris 2005).

"The generation or manufacture of energy or fuels from other (usually primary) fuels/energy" (InterEnerStat, Tim Simmons, 1st proposal for consultation, August 2008).

In the UN manual for secondary energy, the class currently used is "sources." The other manuals of OECD/IEA/Eurostat refer not to class but to commodities. Therefore, now the argument is started to think about secondary energy not as an energy source, but rather as an energy commodity. Thus, when any primary energy source is transformed into what has been used for the purposes of trade, then it becomes a commodity.

For secondary energy, the main distinguishing feature is the process of transformation. Energy transformation is any process of transforming one form of energy to another. Energy of fossil fuels, solar radiation, or nuclear fuels, which are all primary, can be converted into other energy forms such as electricity and heat, which are more useful to us. All the different types of energy that have been subjected to man-made transformation are defined as secondary energy.

For secondary energy, we propose a new definition: "Secondary energy is energy embodied in commodities that come from human-induced energy transformation."

15.2 Nonrenewable Energy Sources

Nonrenewable energy sources are termed thus because of limited supplies. Petroleum is one of the examples, which was formed millions of years ago from the remains of ancient sea plants and animals (India core 2018). Major nonrenewable energy sources are described in the following sections.

15.2.1 Coal

Coal is an organically derived material. It is formed from the remains of decayed plant materials that were compacted into a solid mass because of millions of years of chemical changes under high pressure and heat. Most of the energy in coal comes from its rich carbon content. The burning of coal in the presence of air or oxygen, releases a high amount of heat energy.

This energy from coal can then be converted into other forms of useful energy. The primary applications of coal are thermal (e.g., electricity generation) and metallurgical (e.g., coking or steel-making coal). In 2015, coal made up 28.1% of the world's energy supply (Natural resources Canada 2018).

Coal is one of the most important fuel sources in the energy mix. In India, it is supposed that the major issue with coal will be resolved in the future so that it may be used in a much cleaner and also in a more efficient manner. It has been found that the generation of power through coal contributed to the generation of over 174 gigawatts (GW) of electricity in India, which covered 44% of the country's needs in 2014–2015. The third largest coal reserve in India produces almost 550 million tonnes of coal in 2013 (Joslyn 2018). In 2015, the government announced plans to more than double the country's coal production by 2020. Coal is the most abundant fossil fuel in India and also the most important source for meeting domestic energy needs (IES 2018).

In India, more than 90% of coal is extracted through open cast mining. However, this method has great disadvantages such as low production cost in mining of coal is disadvantage because with low production cost it's become possible for small traders to start mining and release huge amount of coal, utilization of which impart adverse effect. It is only possible beacuse of easy aviability if production cost is high then coal is not be utilised as commonly which is advantageous.

Despite this, the demand for coal is increasing and the existing demand outstrips the supply. In the current situation, India is facing a coal shortage of about 23.96 million tons (MT). The traditional buyers of Indian coal are the neighboring countries such as Bangladesh, Bhutan, and Nepal (IEP 2018).

15.2.2 Petroleum (Crude Oil)

Petroleum is composed of hydrocarbons (a hydrocarbon is a compound made up of carbon and hydrogen) with the addition of certain other substances such as sulfur. Naturally, petroleum, when first collected, is named *crude oil*, and can be clear, green or black and sometimes either thin like gasoline or thick like tar.

Globally, there are several major oil-producing regions. Kuwait and Saudi Arabia have the largest crude oil fields, although in the Middle East many other countries such as Iran and Iraq also make a significant contribution to oil production (Petroleum 2015).

Production of petroleum increased during and after World War I; war is the real catalyst for petroleum production and a huge amount of petroleum was produced throughout the war. Nowadays, petroleum is viewed as a very important commodity, which was traded around the world in the same way as gold and diamonds. People from all over used petroleum to power internal combustion engines in the form of gasoline or petrol.

The thickest form is the almost black substance named bitumen, which is used for paving roads, forming the black surface. It is also an excellent water repellent and is therefore used in roofing. The world has a limited supply of petroleum, and the current situation tells us that after only a few decades, humankind will have completely depleted this valuable natural resource.

The production of crude oil started to decrease each year between 1970 and 2008. However, after 2008/2009, the trend reversed and production started to rise again. In 2015 and in 2017, production was the second and third highest on record respectively. Today, India has around 0.4% of the world's total proven reserve of crude oil. The production of crude oil in the country has increased from 6.82 MT in 1970/1971 to 33.38 MT in 2003/2004.

The overall quantity of crude oil imported increased from 11.66 MT during 1970/1971 to 81 MT by 2003/2004. Because of increased demand, the import of petroleum products increased from 1 MT to 7.3 MT during the same period. The export of petroleum products also increased from around 0.5 MT during 1970/1971 to 14 MT by 2003/2004. The refining capacity, as of 1 April 2004, was 125.97 million tonnes per annum (MTPA) and the production of petroleum products increased from 5.7 MT during 1970/1971 to 110 MT in 2003/2004 (NCPI 2012).

15.2.3 Petroleum Fractions

For the refining of crude oil, the first step involves separating the oil into different hydrocarbon fractions through distillation. A typical set of petroleum fractions is given in Table 15.1 below. Petroleum fractions are complex mixtures and their boiling point is influenced by a number of factors; hence, there is a different boiling point for each fraction, for example, for gasoline 500 different hydrocarbon fractions have been identified.

Table 15.1 suggests that the yield of gasoline is increased by "cracking" the hydrocarbons, which results in the production of kerosene or fuel oil fractions in smaller pieces. *Thermal cracking* was discovered as early as the 1860s. The presence of alkenes in thermally cracked gasoline increases the octane number (70) relative to that of straight-run gasoline (60), but it also makes thermally cracked gasoline less stable for long-term storage. Thermal cracking has therefore been replaced by *catalytic cracking*, which uses catalysts instead of high temperatures and pressures to crack long-chain hydrocarbons into smaller fragments for use in gasoline. About 87% of the refined crude oil went into the production of fuels such as gasoline, kerosene, and fuel oil. The remainder allocated for nonfuel uses, such as petroleum solvents, industrial grease and waxes, or as starting materials for the synthesis of *petro-chemicals*. Petroleum products serve as raw materials in the production of refrigerants, aerosols, antifreeze, detergents, dyes, adhesives, alcohols, explosives,

Table 15.1 Petroleum Fractions

Fraction	*Boiling Range (°C)*	*Number of Carbon Atoms*
Natural gas	<20	C_1 to C_4
Petroleum ether	20–60	C_5 to C_6
Gasoline	40–200	C_5 to C_{12}, but mostly C_6 to C_8
Kerosene	150–260	Mostly C_{12} to C_{13}
Fuel oils	> 260	C_{14} and higher
Lubricants	> 400	C_{20} and above
Asphalt or coke	Residue	Polycyclic

weed-killers, insecticides, and insect repellents, and can also be used to produce synthetic fibers such as nylon, orlon, and dacron, and other polymers such as polystyrene, polyethylene, and synthetic rubber (Purdue University 2018).

15.2.4 Natural Gas

Deep beneath the earth's surface, natural gas occurs. This gas consists mainly of methane, and also contains small amounts of hydrocarbon gas liquids and nonhydrocarbon gases. Natural gas was used as a fuel and to make materials and chemicals. In some places, the natural gas moved into large cracks and spaces between layers of overlying rock; it also occurs in the tiny pores (spaces) within some formations of shale, sandstone, and other types of sedimentary rock, where it is referred to as *shale gas* or *tight gas*. *Coalbed methane* is natural gas that occurs in coal deposits. The USA produces a maximum amount of coal gas from the rest of the other countries. Some natural gas is imported from Canada and Mexico in pipelines. A small amount of natural gas is also imported as liquefied natural gas.

In 2017, the second largest amount of natural gas was produced in India after the largest amount in 2015. More efficient and cost-effective drilling and production techniques have resulted in increased production of natural gas from shale and tight geological formations (Indiacore 2018). The increase in production may be responsible for a decline in natural gas prices, which in turn has contributed to increases in natural gas use by the electric power and industrial sectors (IEP 2018).

In recent years, the consumption of natural gas in India has risen faster than any other fuel, its demand has been growing at a rate of about 6.5% during the last 10 years. Most the industries, such as power generation, fertilizer, and petrochemical production, are shifting toward natural gas. In the past, in India, most natural gas consumption is fulfilled by domestic production. However, in the last 4/5 years, there has been a huge unmet demand for natural gas in the country, mainly required for the core sectors of the economy. To bridge this gap, it is important to encourage domestic production, and the import of liquefied natural gas (LNG) is also being considered as a possible solution to India's expected gas shortages.

15.2.5 Nuclear Energy

Nuclear technology uses the energy released by splitting the atoms of certain elements. It was first developed in the 1940s, and during the Second World War, research initially focused on producing bombs. In the 1950s, attention turned to the peaceful use of nuclear fission, controlling it for power generation. Civil nuclear power can now boast more than 17,000 reactor years of experience, and nuclear power plants are operational in 30 countries worldwide. In fact, through regional transmission grids, many more countries depend in part on nuclear generated power; Italy and Denmark, for example, get almost 10% of their electricity from imported nuclear power. Around 11% of the world's electricity is generated by about 450 nuclear power reactors. About 60 more reactors are under construction, equivalent to 16% of existing capacity, and an additional 150–160 are planned, equivalent to nearly half of the existing capacity.

In the fourth consecutive year (from 2012 to 2016) that global nuclear power generation has risen, output is 130 terawatt hours (TWh), which is higher than in 2012 (102 TWh) (WNA 2015).

Globally, there is a great demand for new power generation capacity to both replace old fossil fuel units, especially coal-fired ones, which emit a lot of carbon dioxide, and meet increased demand for electricity in many countries.

The OECD International Energy Agency publishes annual scenarios related to energy. In its *World Energy Outlook 2017*, there is an ambitious "Sustainable Development Scenario," which is consistent with the provision of clean and reliable energy and a reduction of air pollution. In this decarbonization scenario, electricity generation from nuclear power will more than double by 2040. The World Nuclear Association has put forward a more ambitious scenario than this – the Harmony program proposes the addition of 1000 gigawatt electrical (GWe) of new nuclear capacity by 2050; to provide 25% of electricity, then (10,000 TWh) from 1250 GWe of capacity (after allowing for 150 GWe retirements). These efforts provide one quarter of the world's electricity through nuclear power, it would substantially reduce carbon dioxide emissions, and it would have a very positive effect on air quality (WNA 2015).

India has 22 operable nuclear reactors, with a net capacity of 6.2 GWe. In 2017, 3% of the country's electricity is generated through nuclear power. Also, six nuclear power plants are under construction, which will add another 4 GW to the total. India has ambitious plans to generate 20 GW by 2020 – about 20–35% of electricity generation. Although nuclear energy is cleaner than fossil fuels, its negative impacts are huge.

15.3 Renewable Energy Sources

Renewable energy is any naturally occurring, theoretically inexhaustible source of energy that is not derived from fossil or nuclear fuel. These sources include biomass, solar, wind, geothermal, tidal, wave, and hydroelectric power.

According to a report by the International Energy Agency, there was an increase of 13% to 22% of electricity produced from renewable sources in 2012 to the following year, and it is predicted that this figure should hit 26% by 2020. The clearer needs for these sources are stated below, but these figures are encouraging from the perspective of the use of renewables alone (Mason 2017).

We divide the renewable energy types according to percentage of use as follows:

- 9% from biomass
- 2% as non-biomass heat energy

- 8% from hydro-electricity generation
- 2% of electricity generated from geothermal, biomass, wind, and solar power

Domestically, the USA produces more than 13% of its electricity from renewable sources; the country is the world's largest consumer of energy (at 11.4 kW per person per year), consuming around 25% of global production every year. Exponential growth of the production of energy through renewable sources is occurring in China, and there is equal exponential growth of coal mining there. According to a UN report, it was concluded in 2015 that renewable technology is now being produced on an industrial scale (Mason 2017).

To address energy security, renewable energy sources offer the best option. Today, India has the highest potential for the effective use of renewable energy. It is the world's fifth largest producer of wind power after Denmark, Germany, Spain, and the USA. The country has an estimated small-hydro power (SHP) potential of about 15,000 MW. The combined electricity generation capacity of hydro and wind power has increased, with a compound growth rate of 4.35% from 1991 to 2005. Other renewable energy technologies are also spreading, such as solar photovoltaic, solar thermal, small hydro, and biomass power. Greater reliance on renewable energy sources offers enormous economic, social, and environmental benefits (IEP 2018).

15.3.1 Hydro Energy

Hydropower is energy collected from flowing water that is converted into electricity or used to power machinery. Hydropower has been around for centuries, and was used to turn millwheels or drive early industrial machinery, but in modern use it typically refers to electricity generation. Today hydropower generates more electricity in the USA than any other renewable energy source, and the Department of Energy's Wind and Water Power Program promotes and accelerates its use throughout the country. For businesses, hydro offers recruiting benefits alongside a cost-effective and plentiful source of green energy. The first hydropower electrical systems were developed in the nineteenth century and used direct current technology to light Michigan theaters and shops. The USA also spearheaded the use of alternating current technology in the world's first hydroelectric plant in Wisconsin in 1882 (Kielmas 2017).

One fifth of the world's electricity is provided by hydroelectric power. The largest producers of hydroelectric power are China, Canada, Brazil, the USA, and Russia in 2004, China having the world's largest hydro plants at Three Gorges on the Yangtze River. In the USA, the biggest hydro plant is located at the Grand Coulee Dam on the Columbia River in northern Washington. More than 70% of the electricity made in Washington State is produced by hydroelectric facilities (NG 2009).

Today, hydropower is one of the cheapest ways of generating electricity, because once a dam has been built and the equipment installed, the energy source – flowing water – is free. It renews every year in snow and rainfall and is a clean fuel source.

Engineers can control the flow of water through the turbines to produce electricity and it is readily available on demand. In addition, reservoirs may offer recreational opportunities, such as swimming and boating.

However, the negative part of this source of energy is the damming of rivers, which may destroy or disrupt wildlife and other natural resources. Hydropower plants can also cause low dissolved oxygen levels in the water, which are harmful to river habitats (NG 2009). In addition to environmental concerns, dams also pose a strain on the communities around them. In China, the Three Gorges dam on the Yangtze River displaced an estimated 1.3 million people and flooded thousands of villages.

In India, 45 GW of hydrocarbon capacity is currently installed and a further 14 GW are under construction; some of the plants have been delayed by technical or environmental problems and because of public opposition. To fulfil the energy requirements, India imports 1.5 GW of hydropower from Bhutan and exports 1.1 GW to countries such as Pakistan, Nepal, and Bangladesh.

Dams were blamed for exacerbating the impact of floods in the state of Uttarakhand in 2013. Some have also irrevocably damaged wildlife and biodiversity, and others are expected to destroy livelihoods, submerge forests, and displace families – the most controversial being the Sardar Sarovar Dam (Joslyn 2018). The renowned Indian writer Arundhati Roy states: “Big dams are to a nation’s ‘development’ what nuclear bombs are to its military arsenal. They are both weapons of mass destruction.”

15.3.2 Solar Energy

Solar power is energy from the sun that is converted into thermal or electrical energy. The sun has produced energy for billions of years and is the ultimate of all energy sources. Solar energy is considered to be the most abundant and cleanest renewable energy source available, and around the world, the USA has some of the richest solar resources. Solar technologies can harness this energy for multiple uses, including the generation of electricity, providing light or a comfortable interior environment, and heating water for domestic, commercial, or industrial use (EIA 2018).

People have used the sun’s rays (solar radiation) for thousands of years for warmth and to dry meat, fruit, and grains. Over time, people developed devices (technologies) to collect solar energy for heat and to convert it into electricity (EIA 2018). For example, the first solar collection device was a solar oven used by British astronomer John Herschel in 1830 to cook food during an expedition to Africa. Nowadays, people use many different technologies for collecting and converting solar radiation into useful heat energy for a variety of purposes.

Solar photovoltaic (PV) devices, or solar cells, change sunlight directly into electricity, and were used in small PV cells to power calculators, watches, and other small electronic devices. Also, solar cell arrangements in PV panels and the use of multiple PV panels in PV arrays can produce electricity for an entire house.

Currently, these PV power plants cover many acres to produce electricity for thousands of homes (Solartech 2017).

The two major benefits of using solar energy are that solar energy systems do not produce air pollutants or carbon dioxide, and that they have minimal effects on the environment.

The main limitations of solar energy are:

- The amount of sunlight that arrives at the earth's surface is not constant. The amount of sunlight and its intensity varies according to the time of day, location, season of the year, and weather conditions.
- The amount of sunlight reaching a square foot of the earth's surface is relatively small; thus, a large surface area is necessary to absorb or collect a useful amount of energy.

The amount of solar energy that the earth receives each day is many times greater than the total amount of energy that people consume. The type and size of a solar energy collection and conversion system determine how much of the available solar energy we can convert into useful energy (EIA 2018).

15.3.3 Biomass and Bioenergy

Biomass is an energy resource that is derived from plant- and algae-based material, including crop waste, forest residue, purpose-grown grasses, woody energy crops, algae, industrial waste, sorted municipal solid waste, urban wood waste, and food waste. Biomass is the only renewable energy source that can offer a viable supplement to petroleum-based liquid transportation fuels – such as gasoline, jet, and diesel fuel – in the short to medium term. It can also be used to produce valuable chemicals for manufacturing, and power to supply the grid (AEO 2016).

Biomass is another type of renewable resource that can be converted into biofuels for transportation. Biofuels include cellulosic ethanol, biodiesel, and renewable hydrocarbon (gasoline, diesel, and jet) fuels. The two most common types of biofuels in use today are ethanol and biodiesel. Some other renewable alternatives, such as electricity, would require replacement of our current fleet of vehicles. In the future, renewable biofuels that are functionally equivalent to petroleum fuels will be available (Rogers et al. 2017).

Biopower technologies convert renewable biomass fuels into heat and electricity using processes similar to those used with fossil fuels. There are three ways of releasing the energy stored in biomass to produce biopower: burning, bacterial decay, and conversion to gas/liquid fuel. A key attribute of biomass is its availability upon demand – the energy is stored within the biomass until it is needed – whereas other forms of renewable energy are dependent on variable environmental conditions, such as wind speed or sunlight intensity.

Biomass is a very versatile energy resource, much like petroleum. Although it can be converted to biofuel for use in vehicles, it can also serve as a renewable alternative to fossil fuels in the manufacturing of plastics, lubricants, industrial chemicals, and many other products derived from petroleum or natural gas. These "bioproducts" can be produced alongside biofuels at an integrated "biorefinery." This co-production strategy offers a more efficient, cost-effective, and integrated approach to the utilization of our nation's biomass resources (Rogers et al. 2017).

15.3.4 Wind Energy

Wind is an alternative form of solar energy. Winds are caused by the uneven heating of the atmosphere by the sun, the irregularities of the earth's surface, and the rotation of the earth. Wind flow patterns are modified by the earth's terrain, bodies of water, and vegetative cover. This wind flow, or motion energy, when "harvested" by modern wind turbines, can be used to generate electricity.

The terms "*wind energy*" or "*wind power*" describe the process by which the wind is used to generate mechanical power or electricity. Wind turbines convert the kinetic energy in the wind into mechanical power. This mechanical power can be used for specific tasks (such as grinding grain or pumping water) or a generator can convert this mechanical power into electricity to power homes, businesses, schools, etc. Wind speed is a critical feature of wind resources, because the energy in wind is proportional to the *cube* of the wind speed. In other words, a stronger wind means a lot more power (Wind EIS 2017).

Wind energy is a free, renewable resource; therefore, no matter how much it is used today, there will still be the same supply in the future. Wind energy is also a source of clean, non-polluting electricity. Unlike conventional power plants, wind plants emit no air pollutants or greenhouse gases. The cost of wind power has decreased dramatically in the past 10 years, although the technology requires a higher initial investment than that for fossil-fueled generators. Roughly 80% of the cost is the machinery, with the balance being site preparation and installation. If wind-generating systems are compared with fossil-fueled systems, wind costs are much more competitive than other generating technologies because there is no fuel to purchase and minimal operating expenses.

Although wind power plants have a relatively low impact on the environment compared with fossil fuel power plants, there is some concern over the noise produced by the rotor blades, aesthetic (visual) impacts, and birds and bats having been killed (avian/bat mortality) by flying into the rotors. Most of these problems have been resolved or greatly reduced through technological development or by properly siting the wind plants.

The major challenge to using wind as a source of power is that it is intermittent and does not always blow when electricity is needed. Wind cannot be stored and not all wind can be harnessed to meet the timing of electricity demands. Further, good wind sites are often located in remote locations far from areas of electric power demand (such as cities). Finally, wind resource development may compete with other uses for the land, and those alternative uses may be more highly valued than electricity generation. However, wind turbines can be located on land that is also used for grazing or even farming (Wind EIS 2017).

15.3.5 Geothermal Energy

Geothermal energy is the heat from the Earth. It is clean and sustainable. Sources of geothermal energy range from the shallow ground to hot water and hot rock found a few miles beneath the Earth's surface, and down even deeper to the extremely high temperatures of molten rock called magma.

Almost everywhere, the shallow ground or upper 10 feet of the Earth's surface maintains a nearly constant temperature between 50° and 60 °F (between 10° and 16 °C). A very common use of geothermal energy is the geothermal heat pumps that help to maintain a constant temperature in buildings, offices, and industries. Geothermal heat pumps can tap into this resource to heat and cool buildings. They consist of a heat pump, an air delivery system (ductwork), and a heat exchanger – a system of pipes buried in the shallow ground near the building. In the winter, the heat pump removes heat from the heat exchanger and pumps it into the indoor air delivery system. In the summer, the process is reversed, and the heat pump moves heat from the indoor air into the heat exchanger. The heat removed from the indoor air during the summer can also be used to provide a free source of hot water (UCS 2014).

In the USA, most geothermal reservoirs of hot water are located in the western states, Alaska, and Hawaii. These hot water reservoirs are used for the generation of electricity. Some geothermal power plants use the steam from a reservoir to power a turbine/generator, whereas others use the hot water to boil a working fluid that vaporizes and then turns a turbine. Hot water near the surface of the Earth can be used directly for heat. Direct-use applications include heating buildings, growing plants in greenhouses, drying crops, heating water at fish farms, and several industrial processes, such as pasteurizing milk (UCS 2014).

Many technologies have been developed to take advantage of geothermal energy – the heat from the earth. The National Renewable Energy Laboratory (NREL) performs research to develop and advance technologies for the following geothermal applications (DOE 2018):

- Geothermal electricity production – generating electricity from the earth's heat.
- Geothermal direct use – producing heat directly from hot water within the earth.
- Geothermal heat pumps – using the shallow ground to heat and cool buildings.

In ancient times, geothermal energy was used for bathing and space heating. The biggest disadvantage with geothermal energy is that it can only be produced at selected sites throughout the world. The largest group of geothermal power plants in the world is located at The Geysers, a geothermal field in California, USA (CEF 2018).

15.3.6 Ocean Energy

Oceans cover more than 70% of Earth's surface; therefore, they represent an interesting energy source that with time may be able to provide us with energy to power our households and industrial facilities. Currently, ocean energy is a renewable energy source that is rarely used. There are only a few ocean energy power plants and most of these are very small; thus, the energy gained from the oceans is negligible on a global scale. However, in the future, more attention should be given to this renewable energy source. There are three basic ways of using the oceans for their energy. We can use the waves (wave energy, wave power), ocean tidal power (high and low tides), and we can even use temperature differences in the water to create energy (Ocean Thermal Energy Conversion, OTEC; Our energy 2015).

Ocean wave energy is a form of kinetic energy that exists in the moving waves of the ocean because waves are caused by winds blowing over the surface of the ocean. This energy can be used to power a turbine. There are many areas in the world where wind blows with sufficient consistency to provide continuous waves. Wave power is a tremendous energy source that provides vast energy potential. Wave energy is captured directly from surface waves or from different pressure fluctuations between the surfaces. The main problem with wave energy is the fact that this energy source is not the same in all parts of the world, and varies significantly from place to place. This is the reason why wave energy cannot be exploited globally, but there is much research going on to work on solutions to this variability problem. "The OCS Alternative Energy Programmatic EIS" is particularly dedicated to offshore and far-offshore wave technologies, where offshore systems are located in deep water, at depths below 40 m (Our energy 2015).

Tidal energy is another type of ocean energy that forms when the tide comes into the shore, and can be trapped in reservoirs behind dams. Tidal power is actually a form of hydropower that exploits the movement of water caused by tidal currents or the rise and fall in sea levels. For tidal energy production, there are tidal energy generators, which are large underwater turbines placed in areas with high tidal movements, and are especially designed to capture the kinetic motion of ocean tides to produce electricity. Tidal power has enormous potential for future electricity generation because of the massive size of the oceans. There are many advantages: it is a renewable energy source, it needs no fuel, and it produces electricity reliably, but there are also some negative factors as well. Cost effectiveness is still a very serious issue because building one of these power plants requires a very wide area. This also results in a number of environmental problems, as it completely changes the environment of those areas and affects the life of many ecosystems, for example, birds that rely on the tide uncovering the mud flats so that they can find food. In addition, there is limited working time of only about 10 h, when the tide is actually moving.

Ocean thermal energy conversion (OTEC) is a method of generating electricity that uses the temperature difference that exists between deep and shallow waters, as the water gets colder at greater depths. The larger temperature difference, the greater efficiency of this method, and the minimum temperature difference must be at least 38 °F (3.333 °C). At the beginning of the nineteenth century, some energy experts believed that if OTEC could become cost-competitive with conventional power technologies, it could produce gigawatts of electrical power. However, currently, an OTEC power plant still requires an expensive, large-diameter intake pipe, which is submerged a kilometer or more into the ocean's depths to bring very cold water to the surface, which is of course very expensive.

There are other great benefits to OTEC, such as air conditioning and aquaculture. Air conditioning can be produced as by-product and cold seawater from an OTEC plant can either chill fresh water in a heat exchanger or flow directly into a cooling system. Also, cold-water fish species, such as salmon and lobster, thrive in the nutrient-rich, deep seawater from the OTEC process. Similar to other oceanic energy forms there is a negative side, such cost-effectiveness and environmental concerns (Our energy 2015).

15.4 Hydrogen

Hydrogen can be produced from diverse domestic resources. Currently, most hydrogen is produced from fossil fuels, specifically natural gas. Electricity – from the grid or from renewable sources such as wind, solar, geothermal, or biomass – is also currently used to produce hydrogen. In the longer term, solar energy and biomass can be used more directly to generate hydrogen. Hydrogen is a clean-burning fuel, and when combined with oxygen in a fuel cell, it produces heat and electricity with only water vapor as a by-product. However, hydrogen does not exist freely in nature: it is only produced from other sources of energy; thus, it is often referred to as an *energy carrier*, that is, an efficient way of storing and transporting energy (CEF 2018).

Most hydrogen production today is by steam-reforming natural gas. Hydrogen has very high energy for its weight, but very low energy for its volume; therefore, new technology is needed to store and transport it. Fuel cell technology is in early development, needing improvements in efficiency and durability. Among the challenges NREL researchers are working on to help to make a hydrogen economy a reality include (Conte et al. 2009) improved versions of fuel cells and materials needed for fuel cell production, to produce cost-effective hydrogen from renewable sources, and also to develop technology for the proper storage and transport of hydrogen.

With these inventions, a future "hydrogen economy," where hydrogen is piped to where it is needed, and then converted cleanly into heat and electricity, should become a reality.

Hydrogen is a nontoxic form of fuel as it does not release harmful gasses into the environment. Some fuel sources such as gasoline, coal, oil, and nuclear energy are toxic and occur in areas with a hazardous environment. In fact, when hydrogen is combusted, the only by-product is water vapor, which is not toxic. Because hydrogen is friendly to the natural world, it can be utilized in places where other forms of fuel cannot work. The methods used to produce hydrogen yield a powerful and efficient energy source. The power and efficiency of hydrogen are the reasons why it is used in rockets and space ships. It is also preferred in space ships because it does not produce greenhouse gasses. Hydrogen is also used to get rid of contaminants such as sulfur from these fuels. Other industries also leverage hydrogen fuel, for example, chemical production, food processing, metal refining, and electronics manufacturing.

The process of extraction of hydrogen through electrolysis is extremely expensive. The main reason for this is that it is daunting to separate its basic elements such as hydrogen and oxygen. Even though hydrogen fuel cells are increasingly being used in hybrid cars, it is not yet affordable for everyone. Scientists are working to discover technologies that could make the harnessing of hydrogen much easier, but until then, the price will continue to remain high. The volatility and highly flammable attribute of hydrogen make it challenging to transport to the end consumer. Hydrogen energy has not been fully explored; thus, storage and support infrastructures have not been extensively developed (CEF 2018).

15.5 Electric Energy

Electricity is a convenient and controllable form of energy that we use every day to power our appliances, provide light, and cool our homes. Electricity is a secondary energy source, meaning it is generated from the conversion of primary sources of energy, such as fossil fuels (coal, natural gas, and oil), nuclear power, and renewable sources (wind, hydro, solar, geothermal) (JE 2018).

Electricity is now an integral part of our lifestyle. Take it away and most of the things we are used to would change dramatically. Those changes would not be perceived as positive by most people. Scientists from many fields of study, including chemistry, geology, physics, and biology, are working to support the technology behind electricity generation using both renewable and nonrenewable resources (Ausgrid 2017).

Electrical energy is created by the flow of electrons, often called "current," through a conductor, such as a wire. The amount of electrical energy created depends on the number of electrons flowing and the speed of the flow. Energy can be either potential or kinetic. A lump of coal, for example, represents potential energy that becomes kinetic when it is burned (Sunshine 2018).

Electrical energy can be found from various sources. We use many of these sources unknowingly, yet we continue to avail ourselves of such electricity to cater to our needs. Here are some examples of electrical energy (EE 2018).

- *Electrical energy is used to power up a light bulb*. The current moves from the outlet to the light bulb through the wire. Light energy is then created when the electrical charges slow down in the filament so the bulb can be lit.

- *Lightning is another example of electrical energy*. The negatively charged particles are separated from the positively charged particles. A charge potential develops from this separation. When the separation is fairly high, discharge takes place. This leads to the flow of current in the atmosphere.
- *Batteries are also sources of electrical energy*. In car batteries, the moving charges resulting from a chemical reaction provide electrical energy to the circuits of the car. In phone batteries, chemical energy is supplied to electric charges. The electrical energy supplies the power so that the phone operates.
- Other specific examples of electrical energy include *alternating current* (AC) and *direct current* (DC), capacitors, and the energy produced by electric eels.

15.6 Magnetic Energy

A magnet is a piece of metal that has the ability to attract iron, nickel, cobalt, or certain other specific kinds of metal. Every magnet contains two distinct regions, the north pole and the south pole. As with electrical charges, unlike poles attract and like poles repel each other (Barnett 1912).

A study of magnets allows the introduction of a new concept in energy, the concept of a field. An energy field is a region in space in which a magnetic, electrical, or some other kind of force can be experienced. The English physicist James Clerk Maxwell (1831–1879) in the late nineteenth century found that the two major forms of energy known as *electricity* and *magnetism* are not really different from each other, but are instead closely associated. That is, every electrical current has a magnetic field associated with it and every changing magnetic field creates its own electrical current (Free energy 2018). The properties of magnets are used to make electricity. Moving magnetic fields pull and push electrons. Metals such as copper and aluminum have electrons that are loosely held. Moving a magnet around a coil of wire, or moving a coil of wire around a magnet, pushes the electrons in the wire and creates an electrical current. Electricity generators essentially convert kinetic energy (the energy of motion) into electrical energy (EIA 2018).

With such huge stores of invisible power, is it not likely that magnetism could be a source of efficient, green energy? Harnessing magnetism to produce energy is an idea that has been around for years. New research suggests that magnetism might play an important role in a number of other emerging clean technologies. Recently, scientists at the University of Michigan concluded that it may be possible to use magnetic fields to collect solar energy directly, without the need for semiconductors, potentially reducing the cost of solar power (EPonline 2011).

Researchers are also working on a number of other green technologies involving magnetism. Someday soon, we may be able to recharge magnetic batteries with a few vigorous shakes. Yale researchers have also invented a lead-free solder that uses a magnetic field to melt a tin–silver alloy. Removing lead solder from household electronics would make them considerably cleaner, greener, and more recyclable (Science.howstuffworks 2011).

15.7 Chemical Energy

Chemical energy is stored in the chemical bonds of atoms and molecules. It can only be seen when it is released in a chemical reaction. When chemical energy is released, the substance from which the energy came is often changed into an entirely different substance (Your dictionary 2018).

Many substances and objects store and release chemical energy.

- Batteries: a battery can be connected to a circuit, a reaction between chemicals takes place inside the battery, and it produces electricity. The energy in the battery cannot be seen when the battery is just lying around; it is when the electricity is produced that the energy is seen.
- Petroleum: a combination of oil and natural gas, petroleum is made of hundreds of molecules containing carbon and hydrogen.
- Wood: dry wood stores chemical energy. This chemical energy is released as the wood burns, and it is converted into heat energy, which is also called thermal energy, and light energy. As a result of burning, the wood turns into an entirely new substance – ashes.
- Explosives: when an explosive goes off, chemical energy that was stored in the explosive is changed and transferred into sound energy, kinetic energy, and thermal energy. These are observable in the sound, motion, and heat that are created.
- Food: the chemical energy in food is released while the food is being digested and the molecules of food are broken down into smaller pieces. As the bonds between the atoms of the food break or loosen, new substances are created as a result of the chemical reactions taking place.
- Bleach and ammonia: when these two substances are mixed, an entirely new substance – a toxic chemical called chloramines vapor – is produced.
- Heating packs: these handy packages, which are used to warm up cold hands or sore muscles, have chemicals inside them. When the pack is cracked open for use, the chemicals are activated. These chemicals mix together, and the chemical energy that they release creates the heat that warms up the pack.
- Vehicle air bags: these bags are activated by a chemical reaction inside the bag. A sensor turns on an electrical circuit, and then sodium azide is ignited. The reaction that occurs generates nitrogen gas, which fills the bag at an extremely rapid rate.
- Baking soda and vinegar: when these two substances are mixed in a container, carbon dioxide gas is produced. As this gas grows in volume, it puts pressure on the container, and will erupt out of an opening in the container, creating a volcano effect.

In today's world, chemical energy is the most widely utilized source of energy. However, we should not forget that it is a nonrenewable source of energy. Therefore, we must use it sensibly, so that we can save it for future generations.

15.8 Future of Different Energy Resources and Sustainable Development

The world has now become a global village in which the daily requirement of energy for the whole population is increasing, whereas the energy sources on Earth are limited. The future problem with nonrenewables is climate change because of the huge production of greenhouse gases due to the combustion of fossil fuel. Renewables are sustainable and can help to reduce climate change and its impact.

Energy is required to meet basic human needs such as heat, lighting, cooking, mobility, and communication (Edenhofer et al. 2011). On the road toward a sustainable future, the two major challenges of the energy sector are to maintain the energy supply and to meet the climate change attributed to energy sources (Kaygusuz 2012). Eighty-five percent of the population live in rural areas and depend on the traditional use of biomass. This is projected to rise from 2.7 billion today to 2.8 billion by 2030. The dominance of fossil fuel-based power generation (coal, gas, and oil) and exponential increases in the energy demands result in global challenges that are associated with the growth of CO_2 emissions (Asumadu-Sarkodies and Osusu 2016). The significant climate change has become one of the greatest challenge of the twenty-first century.

Many countries, in their recent national policies, strategies, and development plans, have focused on sustainable development. The UN general assembly launched a set of global sustainable development goals (SDGs), including 17 goals and 169 targets, in New York. In addition, a preliminary set of 330 indicators was also introduced in March 2015 (Lu et al. 2015). To address the climate change, renewable energy, food, health, and water resources require global monitoring, along with the modeling of many factors that are socially, economically, and environmentally oriented (Hák et al. 2016).

It is evident from the literature that replacing fossil fuel-based energy sources with renewable sources such as bioenergy, solar energy, geothermal energy, hydro power, wind, and ocean energy would gradually help the world to achieve the idea of sustainability. Globally, every government, agency, party, and individual look forward to achieving a sustainable future by replacing fossil fuel-based energy sources with renewable energy sources.

Climate has been changing but the alarming situation is that in recent years, the speed of change has been threatening the Earth. The rate of CO_2 emission increased by an average of 1.9 ppm per year before 1995 and 2.0 ppm per year thereafter (Earth system research laboratory 2015). Climate change defines directly or indirectly the human activities that alter the composition of the global atmosphere (Fräss-Ehrfeld 2009). The objectives of keeping global warming below 2° has been a key focus of international climate debate.

The recent launch of a set of SDGs has had the purpose of ensuring that climate change in the twenty-first century and its impact are overcome and that a sustainable future is guaranteed (Edenhofer et al. 2011 Lu et al. 2015).

Tester (2005) defines sustainable energy as a “dynamic harmony between the equitable availability of energy intensive goods and services to all people and preservation of earth for future generations.” The continual use of fossil fuel-based energy sources has become problematic by creating problems, such as the depletion of fossil fuel reserves, greenhouse gas emissions, environmental concerns, geopolitical and military conflicts, and continual fuel price fluctuations. These problems create an unsustainable situation, which results in a threat to human societies (UNFCC 2015). In 2012, renewable energy sources supplied 22% of the world’s total energy generation, which was not possible a decade ago.

For renewable energy to be sustainable, it must be limitless and provide the nonharmful delivery of environmental goods and services. In spite of the great advantages of renewable energy sources, there is also a certain negative side, such as the discontinuity of energy production, because of seasonal variation (most are climate-dependent); thus, for this we require complexity and optimization difficulties to be overcome by technological advances in computational resources that are applicable to both renewable and sustainable energy (Baños et al. 2011).

There is a direct relationship between renewable energy and sustainable development that has an impact on human development and economic productivity (Asumadu et al. 2016g). It also provide opportunities in energy security, access to energy to overcome climate change, and health impacts.

Renewable energy provides a continuous supply of energy that gives an idea of energy security. This provides the interdependence of economic growth and energy consumption. It reduces energy imports, economic vulnerability, volatility, and provides an opportunity to enhance security.

The sustainable development goal 7, which is affordable and clean energy, seeks to ensure that energy is clean, affordable, available and accessible to all, and this is achieved by renewable energy.

For energy generation, the use of renewable sources reduces the greenhouse gases, which overcome the problem of climate change, also reducing environment and health problems associated with pollutants generated from fossil fuel sources. There was a 14% decline in greenhouse gases in 33 European Environmental Agency (EEA) countries during the period 1990–2012 (EEA 2016).

The major challenges with regard to the use of renewable energy are each country’s policies and policy instruments, which affect costs and technological innovations.

15.9 Conclusions

Energy is a requirement in our everyday life. It is one way of improving human development, leading to economic growth and productivity. Today, we have a number of renewable and nonrenewable energy sources. The advantage of nonrenewable energy sources is that the technology used to harness energy from these sources is well developed and these are cheapest sources of energy. However, there are a number of disadvantages: they contribute to the greenhouse gases responsible for climate change, they will very soon be exhausted, they are unsustainable energy sources, they are a cheaper source of government incentives, and there have been a number of accidents reported during the production, storage, and transport of these sources. In contrast, the renewable energy sources are clean, renewable, and therefore sustainable, and they will never run out. These energy sources require less maintenance and fewer traditional generators for energy production. They have a minimal impact on the environment and projects provide economic benefits to various regions. Increased research into renewables is reducing the risk associated with these energy sources. Efforts in developing countries aimed at improving institutional training, strengthening institutions, and improving the capacity of research on climate change will increase awareness, and promote adaptation and sustainable development. The least well-developed countries should advance and test tools and methods with the global support of direct policy- and decision-making for climate change mitigation, adaptation, and early warnings.

Achieving the sustainability of renewable energy sources requires a guarantee of affordable, reliable, sustainable, modern energy for all, and of combating climate change and its impact.

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Chapter 16
Alternative Fuels for Sustainable Development

Chandra Bhan, Lata Verma, and Jiwan Singh

Abstract As the demand for energy increases, reserves of fossil fuels are steadily declining. The growing consumption of energy is responsible for the world's dependence on non-renewable energy sources, such as petroleum, gas, and coal. The burning of fossil fuels increases greenhouse gases, resulting in increasing global temperatures. To overcome these problems, there is an urgent need for alternative and advanced fuels. Bioethanol, biodiesel, and biogas are the best fuels generated from biomass, and there are also emerging fuels that could minimize the overloading of non-renewable fuels and decrease pollution levels. Bioethanol is a plentiful new source of fuel for the future and has the capacity to conserve petroleum resources. Biodiesel is also clean and is generated from renewable sources. It can be used in diesel engines either directly or as an additive in diesel fuel. It has the capacity to replace petro-diesel fuel and to reduce pollution levels. Apart from biodiesel, hydrogen is also a clean source of energy and has huge potential to minimize the load of imported energy sources. Alternative fuel production and use play major roles in economic growth, biomass waste management, producing a cleaner environment, decreasing gaseous pollutants, and ultimately developing sustainability. This chapter discusses the energy problem, the current status of conventional fuel sources, and the role of alternative fuels in sustainable development.

Keywords Energy · Alternative fuels · Sustainable development · Biodiesel · Bioethanol

16.1 Introduction

Energy is the backbone of economic development in any country. Without energy multidirectional development of the nation cannot be achieved. Fast-increasing populations have resulted in the rapid growth of energy requirements for

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industrialization, transportation, agricultural practices, and residential use. There are three main sources of fuel: coal, petroleum, and natural gas, but these sources are limited in nature (Koh and Ghazoul 2008; Anand et al. 2017). Additions to the world population are huge in number (200,000 people per day) and this is responsible for large increases in energy demand, while reserves of fossil fuel are finite. Annually about 11 billion tons of petroleum from fossil fuel is consumed worldwide. The consumption rate of conventional fuels is increasing very rapidly with the growing global population and the rise in living standards; these factors will lead to a rapid decline in fossil fuels, so in this condition our world will face a major fuel problem (Demirbas 2001).

The world is facing a major energy problem associated with global energy demand; the dependence on fossil fuels for electricity production and transportation; and the rapidly growing world population. Over-combustion of petroleum and gas is exhausting the natural resources and increasing carbon dioxide emissions, resulting in increasing global temperatures (Omer 2008). This increasing of global temperature has major adverse effects worldwide, on local and global climates, health, agriculture, and nations' economies. To reduce conventional fuel use and carbon dioxide emissions, and to manage future energy demands, it is mandatory to use renewable sources of energy and technologies (Demirbas 2009).

It is estimated by the United States Energy Information Administration that 80% of energy is obtained from fossil fuels, specifically 35.30% from petroleum, 26.8% from natural gas, and 19.6% from coal (Jacobson et al. 2015). For the production of electricity, the conventional energy sources for generation are coal, petroleum, natural gas, and nuclear reactors. In India the main energy sources used for electric power production are coal, natural gas, petroleum, and nuclear reactors. Nuclear energy accounts for 8.3% of India's energy requirements and renewable energy accounts for 9.1% (Panwar et al. 2011).

16.2 Current Status of Conventional Fuels

Coal has played a crucial role in the development of the industrial revolution worldwide. At present coal is used for electricity generation by thermal power plants, for steel production, and for cement manufacturing (Gartner 2004). Thermal power generation is the largest contributor to electric power generation in India. The fuels used in thermal power plants are mainly coal, natural gas, and diesel. Around 41% of total electricity generation across the globe relies on coal-fired power plants (International Energy Agency 2013).

Coal fuels yield high percentages of electricity in China (79%), India (69%), the United States (49%), Poland (92%), and South Africa (97%), and coal supplies in excess of 40% of global electricity generation requirements, including Germany and much of Central Europe (www.ecotricity.co.uk).

According to the World Energy Council, the global production of coal decreased by 0.6% in 2014, with a further decrease of 2.8% in 2015. As stated above, coal-based electricity production accounts for about 40% of global electricity generation requirements. However, demands for climate change mitigation, the transition to cleaner energy forms, and increased competition from other resources are presenting challenges for the sector. About 66% coal consumed by Asia of total global coal consumption (World Energy Resource 2016). About 717 million short tons of coal were consumed in 2017 by the United States; this is equal to 14% of the total United States energy consumption. Consumption of coal reached its highest point in the year 2007, but with the use of other energy sources for the production of electricity, coal consumption has decreased (www.eia.gov).

India is the fourth largest coal producer in the world, after Australia, in third place. It is estimated by ? that India has coal reserves of around 277 billion tons, whereas the total estimated coal resources in the country, as noted in "The inventory of Geology of India (www.indoasiancommodities.com), are 315.149 billion tons.

Natural gas also contributes to electric power production and it is the second largest energy source for this purpose after coal, accounting for almost 22 % of the energy source in electricity production worldwide. Thus, a large proportion of fossil fuels is used in power production. These fuels are the main source of energy in growing global industrialization. Natural gas is used both as a fuel and as feedstock in various industries (Milano et al. 2016). Natural gas has been used in various sectors, such as transportation; cooking; heating; and in ceramics, cement, and glass manufacture; as well as in tea plantations, and as a chemical feedstock in the manufacture of fertilizers, plastics, petrochemicals, and other commercially important compounds. Owing to the high calorific value of natural gas, the demand for it is increasing, for the heating of water and for electricity generation (Al-Fattah and Startzman 2000). About 80% of the world's total natural gas source is found in ten countries, including the United States, Russia, Iran, and Qatar as the highest producers. It is estimated that a quarter of the world's total natural gas reserves are in the United States and Russia. Worldwide natural gas reserves were estimated at 120 Tcf in 1995, 156.9 Tcf in 2005, and 186.1 Tcf in 2014 (Abas et al. 2015).

Oil is an important source of energy for different sectors. Oil remains the world's primary fuel; it fulfills nearly 33% of global energy demand. It is roughly estimated that the transport sector consumes 63% of oil production. India is the third largest importer of petroleum crude oil (Table 16.1), after China and the United States. India's imports of crude oil amounted to USD 60869 million in 2016. At present, India holds fourth position globally in the consumption of petroleum products. With the increasing demand for petroleum in India, the requirement for crude oil and refining capacity will increase to nearly 355–360 MMT (million metric tons) by the year 2025. But the refining capacity for crude oil depends on the consumption and economic growth of the country (Energy Scenario in India, Raghuraman and Ghosh 2003).

Almost 21.3 billion tons of carbon dioxide is emitted into the environment every year by the combustion of fossil fuels, which is the major cause of increasing global temperature and the greenhouse effect. About half of the above amount of carbon dioxide is absorbed by natural processes and the remaining 10.65 billion tons of carbon dioxide increases in the atmosphere per year (Dukiya 2013). Large amounts of gasoline and gas oil are used in the industrial and transportation sectors, but liquefied petroleum gas and kerosene oil are consumed mainly for commercial and

Table 16.1 India's importation of petroleum crude oil by country

Name of country	Percentage of petroleum crude oil imports
Saudi Arabia	19.9%
Iraq	16.2%
Iran	11%
Nigeria	10.9%
United Arab Emirates	9.3%
Venezuela	8.3%
Kuwait	4.5%
Qatar	2.8%
Malaysia	2.8%
Angola	2.8%
Mexico	2.4%
Brazil	1.6%
Egypt	1%

Source: www.exportgenius.in

residential purposes in India. Owing to the over-consumption of these fossil fuels, India's current energy use is unsustainable. Energy sources in India, including fossil fuels, hydropower, nuclear reactors, and combustible dry mass and non-traditional resources, contribute one-quarter of the country's energy requirement. India is dependent on conventional energy sources, and this is responsible for unsustainability. So alternative energy sources may play a major role in sustainable development (Ellabban et al. 2014).

16.3 Alternative Fuels

There are two main types of energy sources, renewable and non-renewable, as shown in Fig. 16.1. In the condition of over-consumption and increasing energy demand, we must move toward alternative fuel sources. Fuels other than conventional fuels, e.g., petroleum, coal, and natural gas, are known as alternative fuels. These alternative fuels include biodiesel, bioethanol, natural gas, non-fossil methane, and hydrogen gas. Fuels that are produced from biomass are known as biofuels (Hosseini and Wahid 2016). Biofuels, in liquid or gaseous form, are produced from biomass resources and are used in addition to conventional fuels in the transportation, power production, and commercial sectors, as well as in other sectors. Biofuels play an important role in the promotion of sustainable development, as they are produced from renewable biomass resources such as sugarcane, crop residues, and other waste materials. Biofuels may also be advantageous for the supplementation of fossil fuels, the need for which is increasing day by day, for transportation and commercial applications. Thus, to achieve better economic growth and fulfill

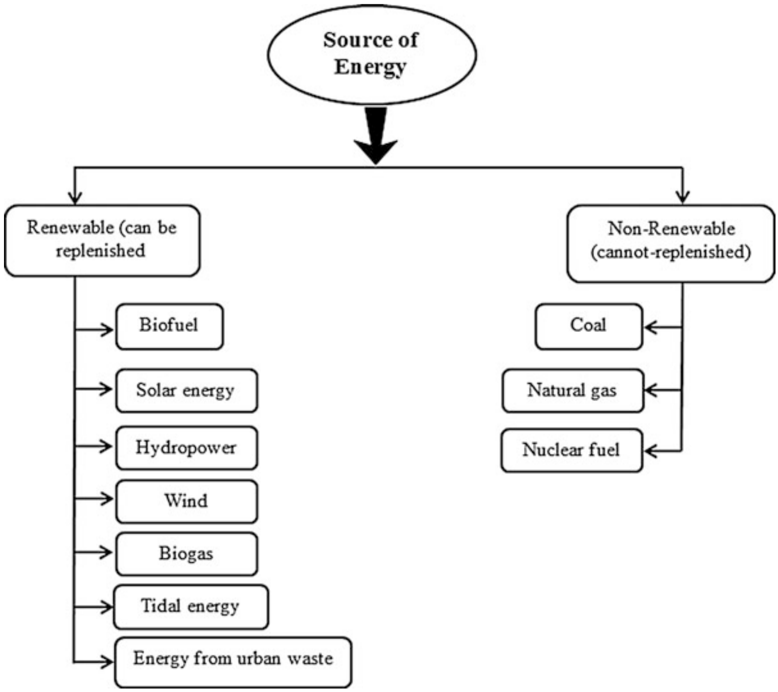

Fig. 16.1 Renewable and non-renewable sources of energy

energy requirements for the large urban and rural population of India, biofuels will be helpful.

Biofuels are categorized on the basis of the raw materials used (Said et al. 2015). First-generation biofuels are derived mainly from food crops such as grains (wheat and maize), sugarcane, vegetable oil, and animal fats. Biodiesel and bio-ethanol are first-generation biofuels, while second-generation biofuels are produced from agricultural waste and forestry residues or co-products, such as rice husks, wheat straw, and woody biomass, which contain cellulosic, hemi-cellulosic, and lignin materials (Saini et al. 2015). The use of these materials in biofuel production is a method of waste management and leads to sustainable development. Owing to some limitations of first-generation biofuels, second-generation biofuel technologies are gaining in importance. To increase the production of second-generation biofuels, it is necessary to create governmental and non-governmental policies for the production of raw materials that involve local people. The production of nonfood crops may be increased by providing financial support and subsidies to farmers to enable commercial biofuel plantations. The second-generation biofuels are more suitable for sustainable development as they are affordable and have greater environmental advantages (Renzaho et al. 2017).

Hydrogen production by the conversion of biomass is a third-generation biofuel.

Another third-generation biofuel is produced by algae, regarded as an engineered crop for an energy source. Algae are grown in suitable conditions with well-developed techniques and oil is extracted from them. The extracted oil can be converted into biodiesel through a trans-esterification process, and the resultant biodiesel is used in diesel engines with or without blending as petro-diesel. The use of algal biofuel is a sustainable alternative for petroleum crude oil and decreases petroleum crude oil overload.

Algal hydrogen is a fourth-generation biofuel, produced by algae cultivated in the presence of high solar efficiency (Aro 2016). There are various environmental, social, and economic advantages of biofuel. The vehicular pollutants that produce greenhouse gas emissions are reduced by the use of biofuels. Carbon dioxide, sulfur dioxide, carbon monoxide, and particulate matter are emitted in lower amounts by the combustion of biofuels than with the combustion of fossil fuels.

16.3.1 Biodiesel

Biodiesel is a liquid fuel produced by renewable sources such as vegetable oils, jatropha oil, animal fats, and waste cooking oil. It also known as carbon-neutral biofuel because the carbon dioxide released after the combustion of biodiesel is absorbed by the growing oil crops. In the United States and the rest of the world, biodiesel is an accepted fuel for diesel engines as an additive to diesel fuel. It can be used as fuel in diesel engines either by blending with diesel fuel or without changes. Biodiesel is a renewable source of energy that can help reduce greenhouse gas emissions. It acts as a safe alternative fuel, substituting for conventional petroleum diesel (Ak and Demirbas 2016). Biodiesel fuel is registered by the United States Environmental Protection Agency. The United States, Brazil, Germany, Indonesia, France, and Thailand are leading producers of biodiesel, at 5.5, 3.8, 3.0, 3.0, 3.0 and 1.5 million tons per annum, respectively. Biodiesel is a clean-burning alternative fuel produced from domestic and renewable resources. In India, the amount of biodiesel production is very low, at nearly 1% of global production, although India has great possibilities for biodiesel production by using jatropha oil and waste cooking oil; however, much research and governmental and political support is required (Speight and Radovanović 2015). Biofuels, because of their biodegradable nature, reduce the environmental impact of petroleum fuel, which arises mainly from oil spillage. Biodiesel is a 75% cleaner energy source than petroleum diesel; it contains no sulfur, with minimal amounts of incompletely burned hydrocarbon, and minimal amounts of carbon monoxide and particulate matter. The combustion of biodiesel produces nearly 50% less particulate pollution than the combustion of petroleum fuel. Biodiesel is usually used as a conventional diesel supplement to reduce the levels of particulate matter, carbon monoxide, hydrocarbons, and toxic agents in the exhaust fumes of diesel-based vehicles. The advantages of vegetable oils, such as the availability of feedstock, their low hydrocarbon content, and no sulfur content, as well as their biodegradable and renewable nature, make these oils a significant replacement for diesel fuel (Hari et al. 2015).

At present, higher market values for biodiesel production are challenging its uses and restricting crops for commercial utilization. Biodiesel is produced by a chemical method called trans-esterification. In this process oil or fat reacts with alcohol, such as methanol and ethanol, in the presence of a chemical catalyst (sodium hydroxide and potassium hydroxide), resulting in the formation of methyl esters or ethyl ester (biodiesel). Currently, research is focusing on enzymatic trans-esterification, because of some disadvantages with chemical catalysts. Enzymatic biodiesel production is carried out with the use of lipase (Cubas et al. 2016).

There are a number of oil sources that are used to produce biodiesel, the most common feedstocks worldwide being soybean, palm oil, and rapeseed oil. Other feedstock can come from waste vegetable oil, *Jatropha curcas* oil, sunflower oil, mustard, flax, palm oil, safflower, and hemp. For the manufacturing of biodiesel, food vegetable oils such as soybean oil, palm oil, and rapeseed oil are used as the large-scale raw material. Various types of raw materials are used for the production of biodiesel in the United States, and these feedstocks are soybean oil (52%), corn oil (13%), and canola oil (13%). Instead of these raw materials, cooking oil and yellow grease, with 12% and 10% animal fat content, respectively, were used in 2017.

However, there have been many objections, by non-governmental organizations and the public, to the use of edible oils as a biodiesel source. Against this background, the production of non-edible oils such as *Jatropha curcas* and other crops can be increased for large-scale biodiesel, thus avoiding the food problem. Therefore, non-edible oil sources appear to be an attractive alternative raw material for the production of biodiesel (Mujeeb et al. 2016).

16.3.2 Bioethanol

Ethanol (ethyl alcohol) is manufactured from sugarcane, corn, and grain plants, and also from cellulosic waste material (e.g., paper waste). Ethanol is a fermented product of crushed sugarcane and grains (Pietrzak and Rygielska 2015). It is also a well-known source of fuel energy and can be used to drive vehicles; at the gas pump it is mixed with gasoline for oxygenation. The use of bioethanol decreases exhaust emission levels and reduces the consumption of classic petroleum products. Ethanol could become a cheap alternative fuel, with many countries developing new technologies based on the processing of the green mass in order to obtain bioethanol. If it is obtained from agricultural products then it represents a low-cost and ecological process. It is because of this that bioethanol can win the cost price – pollution competition, whether it is used as a single fuel or added to gasoline in the spark ignition engine (Bergthorson and Thomson 2015).

Agricultural waste material or raw material contains sugar; hence, it is mainly used to produce bioethanol. The agricultural raw waste material is categorized as a first-generation material that contains starch and sugar. Lignocellulosic sugar materials are classed as second-generation materials. Sugars from sugarcane, sugar beet, molasses, and fruits are examples of the sugars that are used to produce ethanol by a process of fermentation using yeast strains. Many processes, such as milling, hydrolysis, pretreatment, and detoxification, are used for the processing of waste materials into bioethanol, but if sugar waste biomasses like molasses or sugarcane juice are utilized for the production of ethanol via fermentation, the above-mentioned processes are not necessary (Ayarza and Cortez 2017). For lignocellulosic materials, the processes of milling, hydrolysis, and pretreatment are required, while the conversion of starch into fermentable sugar requires the use of many processes, e.g., liquefaction and saccharification.

Ethanol is produced by, first, the grinding up of crop residues or plant materials. After that, the ground-up materials are converted into sugar or starch and then, through the process of fermentation, the plant materials containing sugar are converted into ethanol and carbon dioxide. After the fermentation process is completed, the ethanol is distilled and purified to make the ethanol fit for use. The United States and Brazil are the largest producers of fuel ethanol worldwide; in 2016 these countries produced approximately 85% of the world's total ethanol. These countries use corn as a primary source for ethanol production. The whole corn plant, including its cob, leaves, and stalk can be transformed into fermentable sugars with the help of cellulose processing techniques; a high amount of starch is present in corn grains and this can be converted by hydrolysis and pretreatment to monosaccharides (Schwietzke et al. 2009).

Ethanol is a very cost-effective source of energy and can be produced by any country. Agricultural waste biomasses such as corn, sugarcane, grains, and crop residues are generated in huge amounts in all countries, and can be used for the economically efficient production of bioethanol (Gupta and Verma 2015). So this can be very useful in reducing the dependence on fossil fuels. Ethanol is more environmentally friendly than the other sources of energy, as it does not pollute the environment to the same extent as fossil fuels do. Using ethanol to drive vehicles is a very important step for lowering environmental pollution levels caused by automobiles or the transport sector. Ethanol is blended with gasoline, at a ratio of 85:15, for the conversion of ethanol into fuel. The small amount of gasoline acts as an igniter (Hsu and Robinson 2017). Separately, the burning of ethanol releases carbon dioxide and water into the environment, but when ethanol is mixed with gasoline this reduces the emission of greenhouse gases into the environment and the fuel combusts efficiently without harming the environment.

16.3.3 Biogas

Biogas is one of the cleanest fuels and is used for internal combustion engines. Biogas may serve as a secondary fuel and can be used as a substitute for fossil fuels, mainly as a substitute for diesel fuel in conditions of oil scarcity. Fumigated dual fuel

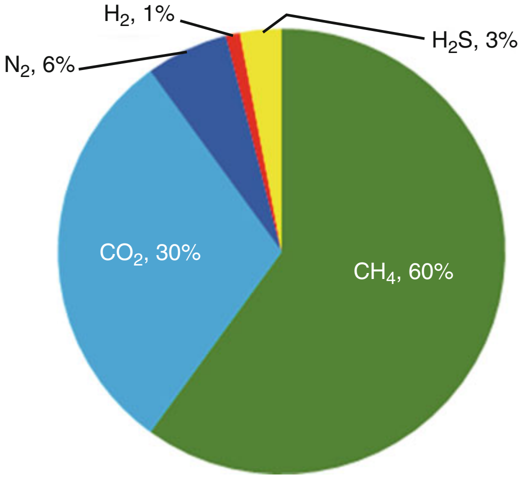

Fig. 16.2 Chemical composition of biogas

engines can be made by the easy conversion of diesel engines (Barik and Murugan 2012) and this is a very practically important way to exploit the high ignition temperature of alternative fuels (biogas). Biogas can be produced from organic waste, livestock manure, and agricultural residues through biological degradation and is a byproduct of the microbial breakdown of these wastes. Biogas contains methane (60–80%), carbon dioxide (20–40%), and hydrogen sulfide and nitrogen in trace amounts, as shown in Fig. 16.2 (Herout et al. 2011).

Various waste materials, such as animal manure (from pigs, cows, and chickens), sewage sludge from aerobic wastewater treatment, and agricultural residues are used for the production of biogas. Leaves of sugar beets and municipal biowaste from households are also used in the generation of biogas. The biogas yield from different types of substrates varies according to their origin and organic composition. Fat-containing substances produce high amounts of biogas (Weiland 2010).

Advantages of Biogas

- Biogas is an environmentally friendly, non-commercial energy source.
- It is non-polluting by reducing greenhouse gas emission.
- The production of biogas is not expensive, because it is formed from the breakdown of waste biomasses; its processing does not involve any combustion and hence its use is an important way to tackle the problem of global warming.
- The waste material remaining after the generation of biogas is highly enriched with organics, which can be used to replace chemical fertilizers.
- The technology used for the production of biogas is cost-effective and it can be started on a small scale with little investment.

Table 16.2 Biogas production varies between different substrates depending on the composition of the substrate, as shown in the table

Substrate	TS (Total solids) (%)	Biogas production (m^3/ton TS)	(m^3/ton wet weight)	Methane concentration (%)
Sludge from wastewater treatment plants	5	300	15	65
Straw	78	265	207	70
Fish waste	42	1279	537	71
Sorted food waste	33	618	204	63
Potato haulm	15	453	68	56
Liquid cattle manure	9	244	22	65
Liquid pig slurry	8	325	26	65
Slaughterhouse waste	16	575	92	63

Sources: Substrate handbook for biogas production

16.3.3.1 Biogas Production by Different Substrates

The production of biogas differs with different biomass substrates, depending on the substrate composition, as shown in Table 16.2.

16.3.4 Hydrogen

Hydrogen is said to be the fuel of the future. It has many benefits over conventional fuels and is a non-commercial energy source that exists across the year. It can be used in the transportation sector, and as a byproduct it releases only water and very small amounts of nitrogen oxides, and the emission of these products can also be eliminated by the application of hydrogen cells. Currently, world hydrogen production is approximately 38 Mt (metric tons). annually. About 3.4 Mt (metric tons). is produced by Canada per year. Hydrogen is mainly produced by steam reforming natural gas and by fossil fuel gasification. From these processes, a very small proportion of hydrogen is used in the form of fuel, while the remainder is used in the upgrading of heavy oil, oil refining, and the production of methanol and ammonia (Sustainable Development Business Case Report 2006).

Hydrogen is produced by different methods, the main ones being:

1. **Electrolysis**: The electrolysis of water results in the generation of hydrogen; when water is subjected to a direct electric current between electrodes, hydrogen and oxygen can be collected at the electrodes. By this process hydrogen can be formed anywhere by the use of renewably generated electricity (solar energy, wind energy) in a renewable way.

2. **Biomass gasification**: Hydrogen can be produced on a large scale by biomass gasification. In this process high-grade carbon is also produced as a byproduct.
3. **Thermal decomposition of water:** This process requires a very high temperature, over 20,000 °C for thermal water dissociation into oxygen and hydrogen. But with the assistance of some chemicals the production of hydrogen is possible at lower temperatures, under 7000 °C. This method has not yet been applied on a commercial level.

Some other methods of hydrogen production are still the subject of research, e.g., the photo-electrochemical cell, which directly produces hydrogen from water by artificial chemical photosynthesis.

On burning 1 kg of hydrogen, 120 MJ energy is produced, on assuming that the resultant water is released as water vapor. This amount of energy is three times more than that produced by a unit of petrol or diesel. However, despite having high energy potential, the use of hydrogen as a fuel is still not applicable owing to such disadvantages as its low energy production per unit volume at atmospheric pressure. Storage of hydrogen can be done in the following ways:

- Hydrogen can be stored in gaseous form in pressurized containers at about 300 atmospheres; the weight of these containers is a problem.
- When hydrogen is adsorbed into metals it forms metal hydrides. On heating of these metal hydrides, hydrogen is released.

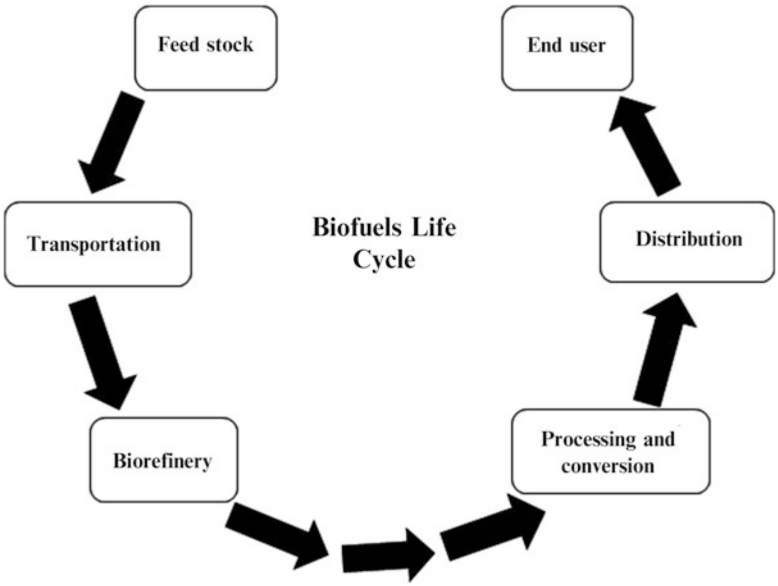

Fig. 16.3 The biofuel life cycle

- The liquefying of hydrogen requires a temperature of − 253 °C, and therefore highly insulated storage is required (Ghergheles and Ghergheles 2008).

Figure 16.3 shows the life cycle of biofuel from its production to consumption.

16.4 Contribution of Alternative Fuels to Sustainable Development

Sustainable development is a broad expression and a notion that can be defined in various forms, hence leading to different responses. Sustainable growth or development is about growing concerns related to environmental degradation/environmental disputes in relation to socioeconomic matters (Hopwood et al. 2005). The meaning of sustainable development is the use of resources present today without exploiting them in excess, so that they remain for the use of future generations to meet their needs. Industrialized development degrades the natural environment at a fast rate, and it is necessary to save the natural features of the ecosystem. This idea of sustainable development was first described in "our common future" renowned as the Brundtland report. The goals of this report came into effect in 2016; there are 17 sustainable goals to be achieved in 2030, the target year. The seventh of these sustainable goals is to provide affordable and clean energy (http://www.undp.org).

Biofuels are alternatives to natural fuels and are produced from waste biomass; their use has been trending worldwide over the past few years. These fuels are cleaner than conventional fuels, and are an ecofriendly product that is also very cost effective; the increasing price of conventional fuels makes it hard for rural areas to afford these fuels. So biofuels have a positive impact on rural development (ASA-NBB 2004). Traditionally, mainly in developing countries, various types of raw biomass waste have been used as very important energy sources for households, but recently there has been developing interest in biofuel production from waste biomass; interest was first shown after the oil crisis in the 1970s and now there is renewed interest (Acheampong et al. 2017).

The report of "World Energy Council" notes that alternative sources of energy contribute about 30% of the world's total energy supply and there is a target to increase this percentage to 80% by 2050. Earlier studies led by the Shell International Petroleum Company have stated that biofuel will be used in high amounts and its production will increase after 2020 (Kirschbaum 2003).

Some definite targets of sustainable development goal number seven are: to noticeably raise the stake of renewable alternative sources of energy by 2030; to double energy efficiency worldwide, and to increase the amount of renewable energy in all the developing countries by improving the technological structure (United Nations Sustainable Development Goals 2015).

The promotion of renewable sources of energy is very important, as these sources are greener than non-renewable energy resources and hence may be a less-polluting, low-carbon source for future energy needs. Biofuels are the best substitutes for non-renewable energy resources and it is projected that their use will help to achieve the increasing public demand for fuel. The carbon dioxide level in the atmosphere is increasing at an alarming rate, and had reached 406.69 ppm by 2017 (NASA 2017); by using alternative energy sources carbon emission can be reduced. The aim of the Paris agreement at the United Nations Framework Convention on Climate Change summit is to reduce greenhouse gases, thus removing fossil fuels as a non-renewable polluting source and replacing them by a carbon-neutral and sustainable source (Bhawmick et al. 2018). Many renewable sources of energy are available, such as biofuels. Many scientists are engaged in the development of various methods for the production of biofuel from a sustainable biomass, and this alternative technique is very effective to replace environmentally degrading exhaustible fuels (Weldemichael and Assefa 2016).

16.4.1 Advantages of Biofuels Over Conventional Petroleum Fuel (Gaurav et al. 2017)

- Biofuels are sustainable, as they have biodegradable properties.
- Biofuels can be easy to extract from biomass.
- Biofuels entail carbon-dioxide-based combustion.
- Biofuels are more ecofriendly than petroleum-based fuels.

16.5 Conclusion

All the sectors that are driven by energy are totally dependent on non-renewable fuels. The availability of these fuels is not secure for excessive energy needs. The over-consumption of non-renewable energy resources is responsible for the destruction of natural resources and the burning of these conventional fuels increases the volume of greenhouse gases, which is a very serious problem worldwide. The use of alternative fuels will decrease the demand for fossil fuels and promote sustainable development. Biofuels such as biodiesel and bioethanol are ecofriendly in nature because they are produced from biomass and are biodegradable. Alternative fuels can be developed domestically by the utilization of a country's resources, thus improving the economy of the country. Alternative energy resources are also considered to be an ecofriendly source of energy, and the ideal use of these sources will reduce the environmental impact of energy use and achieve sustainability. We note that many opportunities have opened in the field of non-commercial fuels, and non-commercial fuels are now being traded in national and international energy markets.

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Chapter 17
Microbial Remediation of Crude Oil-Contaminated Sites

Babita Kumari, Kriti, Gayatri Singh, Geetgovind Sinam, and D. P. Singh

Abstract Sustainable development becomes a need for economic growth of any country that allows the use of natural resources with minimum damage to our environment. The same is applied for the use of crude oil. The demand for crude oil can't be denied as it is a major source of energy (production of electricity, cooking gas, and facilitating transportation) and raw materials for various petroleum products like solvents, fertilizers, plastics, paints, pesticides, etc. Development of remediation technology to remediate petroleum hydrocarbon-contaminated sites due to crude oil spillage during its transportation becomes essential as it contains various hazardous, toxic, and carcinogenic compounds. Compared to physical and chemical processes of remediation, bioremediation is a highly efficient and self-propelling economic process. This review article presented a brief discussion on development of bioremediation of petroleum hydrocarbon in soil or in water. This article especially emphasizes the inherent characteristics of microbes that facilitate the bioremediation and the use of different biostimulants for fastest remediation of petroleum hydrocarbon-contaminated sites.

Keywords Crude oil · Bioremediation · Biostimulants · Cell inherent characteristics · Biosurfactants · Enzymes

17.1 Introduction

Soil and water pollution due to petroleum oil is now a prevalent ecological hazard, and hence, microbial degradation of hydrocarbons remains a topical issue as before. The world demand for crude oil in 2010 was 86.95 million barrels per day and is

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projected to increase to 98.3 million barrels per day in 2015 and 118 million barrels per day in 2030 (EIA 2006). The global transport and use of both petroleum and its derivatives have made petroleum hydrocarbons major contaminants in both prevalence and quantity in the environment.

Impact of oil spill can be understood easily by the fact that one barrel of crude oil can make 1 million barrels of water undrinkable (Ercoli et al. 2001). Oil spills involve the release of dangerous hydrocarbons, such as benzene and polynuclear aromatic hydrocarbons, into the soil and water sources. These spillages affect vast stretches of land and waterways, thus affecting the terrestrial and aquatic plants and animals. Soil contamination with hydrocarbons causes an extensive damage to life in the environment, since accumulation of pollutants in animal and plant tissue may cause death or mutations in them (Alvarez and Vogel 1991).

The technologies commonly used for soil remediation of petroleum hydrocarbons include mechanical burying, evaporation, dispersion, and washing. These remedial measures are not only cost intensive and time consuming, but also not very effective. Bioremediation method has gained acceptance worldwide as an in situ treatment of contaminated sites. It is also considered as the most promising technology as compared to physical and chemical process since it is cost-effective, self-propelling, and eco-friendly and will lead to complete mineralization.

Bioremediation of crude oil depends on various factors like physical nature of oil (light or heavy), chemical nature of oil (composition of petroleum hydrocarbons), abiotic factor of contaminated sites (temperature, pH, water and oxygen content, etc.), availability of nutrient, type of microbial species and their capability, etc.

Bioaugmentation and biostimulation are two major techniques that are being used successfully to remediate either crude oil or petroleum hydrocarbon-contaminated sites. Bioaugmentation or seeding is the addition of highly concentrated and specialized populations (single strains or consortia) to the site contaminated with recalcitrant toxic compounds (Gentry et al. 2004). This technique is best suited for sites that (1) do not have sufficient microbial cells, or (2) the native population does not possess the metabolic routes necessary to metabolize the compounds under concern. The best approach for selecting competent microbes should be based on the prior knowledge of the microbial communities inhabiting the target site (Thompson et al. 2005). On the other hand, biostimulation involves the identification and adjustment of factors, such as nutrients, that may be looming the biodegradation rate of the contaminants by the indigenous microorganism at the affected site (Swannell et al. 1996).

As bioremediation has limit due to its slow rate, bioaugmentation along with biostimulation may overcome the constraint of the bioremediation technology. Emerging formulations and products are gaining attention and application claiming for fast decontamination rates.

17.2 Fate of Petroleum Hydrocarbons

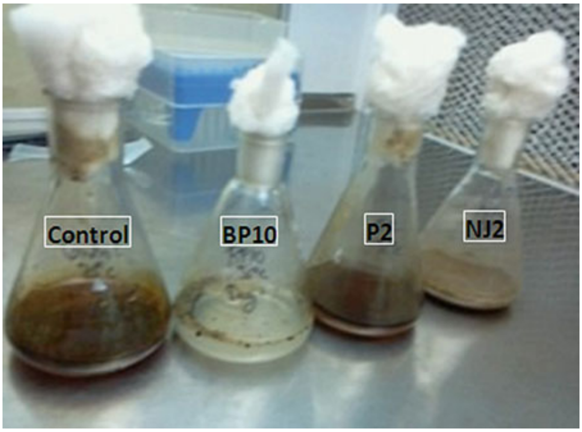
Composition of crude oil depends upon various factors like geographical origin, the raw material from which the crude oil was originally formed, and the condition that prevailed during its formation. In crude oils, asphaltenes, resins, and petroleum alkanes compose a dynamic stable system, in which the petroleum alkanes act as solvents, the asphaltenes as micelles, and the resins as stabilizers (Wiehe and Kennedy 2000). Since evaporation of the light components takes place immediately, up to 40% of crude oil gets evaporated during a short period of time, while the remaining part of the oil is loaded into the water and sorbed over soil. Possible fates of petroleum hydrocarbons in the environment are volatilization, photooxidation, chemical oxidation, bioaccumulation, interaction with the soil matrix, and biodegradation.

17.3 Bioremediation of Petroleum Hydrocarbons

Microbes make the major contribution to mineralization of crude oil pollutants (Fig. 17.1). Bioremediation utilizes the metabolic versatility of microorganisms to degrade hazardous pollutants for the ecological recovery of petroleum waste-contaminated sites.

Among the microorganisms, bacteria are usually the choice (Prakash and Irfan 2011) because of their rapid metabolic rates and because they follow numerous degradation pathways and can be genetically manipulated to improve their bioremediation capabilities. *Pseudomonas*, *Mycobacterium*, *Haemophilus*, *Rhodococcus*, *Paenibacillus*, and *Ralstonia* are some of the most extensively studied bacteria for the bioremediation of organic compounds (Haritash and Kaushik 2009).

Fig. 17.1 Degradation of crude oil in presence of microbial strains (Kumari et al. 2012)



Besides bacteria, members of fungal genera like *Amorphoteca*, *Neosartorya*, and *Talaromyces* and yeast genera, namely, *Candida*, *Yarrowia*, and *Pichia*, which were isolated from petroleum-contaminated soil were also found to be the potential degraders of hydrocarbons (Chaillan et al. 2004). Similarly, Singh (2006) also reported a group of terrestrial fungi, namely, *Aspergillus*, *Cephalosporium*, and *Penicillium* which could be potential degrader of crude oil hydrocarbons. The yeast species, namely, *Candida lipolytica*, *Rhodotorula mucilaginosa*, *Geotrichum* sp., *and Trichosporon mucoides*, isolated from contaminated water, were also reported to degrade petroleum compounds effectively (Boguslawska-Was and Dabrowski 2001). The degradation of TPH by *Phanerochaete chrysosporium*, *Pleurotus ostreatus*, and *Coriolus versicolor* has also been reported (Yateem et al. 1997).

Other than bacteria and fungi, involvement of green alga, cyanobacteria, and brown alga in degradation of petroleum hydrocarbons was also reported (Cerniglia and Gibson 1977). Walker et al. (1975) isolated *Protothecazopfi* that was capable to degrade crude oil and mixed hydrocarbon substrates.

The hydrocarbons differ in attack by the microorganism and could be ranked based on the degree of availability of these hydrocarbons to microbes for their mineralization in the following order: n-alkanes > branched alkanes > low-molecular-weight aromatics > cyclic alkanes > high-molecular-weight aromatics > asphaltenes.

LMW alkanes are still soluble enough so that a direct uptake of the alkane from water can assure a sufficient mass transfer to the cell. Because of the structural similarity of alkanes to fatty acids and plant paraffins, which are ubiquitous in nature, many microorganisms (bacteria, filamentous fungi, and yeasts) in the environment can utilize n-alkanes as a sole source of carbon and energy.

PAHs are not only carcinogenic and mutagenic but also potent immunotoxicants. It is known today that LMW PAHs are highly toxic, while HMW PAHs are genotoxic. In the past two decades, a number of bacteria have been identified as "PAH degraders," mainly members of genera like *Pseudomonas*, *Sphingomonas*, *Cycloclasticus*, *Burkholderia*, *Rhodococcus*, and *Polaromonas*, some novel genera of *Neptunomonas* and *Janibacter*, and some thermophilic bacteria of *Nocardia* and *Bacillus*, *Mycobacterium*, *Stenotrophomonas*, and *Pasteurella*. *Bjerkandera adusta* is reported to degrade dibenzothiophene, fluoranthene, pyrene, and chrysene (Valentin et al. 2007), while *Irpex lacteus* can metabolize phenanthrene, anthracene, fluoranthene, pyrene, chrysene, benzo(β)fluoranthene, benzo(k)fluoranthene, benzo(α)pyrene, dibenzo(a, h)anthracene, benzo(g, h, i)perylene, and indeno(1, 2, 3 – c, d) pyrene (Leonardi et al. 2007).

Lavania et al. (2012) reported a bacterial strain *Garciaella petrolearia* TERIG02 that was found capable of degrading 55% of asphalt, 45% of aromatic, and 25% of aliphatic fraction after 30 days of incubation under anaerobic conditions.

17.4 Consortium Versus Single Strains

Various authors supported the idea to use consortium than monoculture for higher biodegradation efficiency (Kadali et al. 2012). The cooperation between the individuals with consortium member and complementary effects of microbes on each other may result in notably enhanced growth and survivability of consortium members (Sampath et al. 2012) that directly or indirectly boost the rate of biodegradation.

From an applied perspective, using a microbial consortium provides the metabolic diversity and robustness needed for the field applications (Nyer et al. 2002). Li et al. (2009) observed that adding microbial consortium of five fungi, *Phanerochaete chrysosporium*, *Cunninghamella* sp., *Alternaria alternata* (Fr.) Kessler, *Penicillium chrysogenum*, and *Aspergillus niger*, and three bacteria, *Bacillus* sp., *Zoogloea* sp., and *Flavobacterium*, enhanced the degradation rate by 41.3% as compared to control.

17.5 Genetically Modified Microbes

Genetic engineering helps in designing a microorganism capable of degrading specific contaminants (Wasilkowski et al. 2012) by artificial combination of genes that do not exist together in nature. Joutey et al. (2013) reviewed the involvement of genetically modified microbes in biodegradation. *Pseudomonas putida* PaW85 was genetically modified by introducing pWW0 plasmid to degrade oil (Jussila et al. 2007). Ripp et al. (2000) and Sayler and Rip (2000) demonstrate the use of genetically engineered strains, *Pseudomonas fluorescens* HK44, containing naphthalene catabolic plasmid pUTK21 and a transposon-based bioluminescence-producing *lux* gene fused within a promoter for the naphthalene catabolic genes for field application of bioremediation.

Even if modified microbes were recorded to boost the degradation process of petroleum hydrocarbons, ecological and environmental concerns and cost and regulatory constrains are major obstacles for testing these modified microorganisms in field. Simultaneously, the burden of maintaining all of these genes is likely to make the engineered strains noncompetitive in the natural environment (Lethbridge et al. 1994).

17.6 Microbial Inherent Characteristics: Facilitate Petroleum Hydrocarbon Biodegradation

17.6.1 Enzyme Induction

The presence of a high enzymatic capacity allows microbial communities to degrade complex hydrocarbons (Fig. 17.2). The diverse catabolic activities of microbes are mainly due to the presence of catabolic genes and enzymes (Khomenkov et al. 2008). Microbes induced both extracellular and intracellular enzyme, but extracellular enzymes play a major role in the degradation of petroleum hydrocarbons (Barnabas et al. 2013). Extracellular enzymes break down oil into simpler compounds that are easily taken/utilized by microbes. Lots of enzymes are reported by various authors (Liang et al. 2006; van Beilen et al. 2004) during the degradation of petroleum hydrocarbons. Microbial genetic diversity contributes to the metabolic versatility of microorganisms for the transformation of contaminants into less-toxic final products, which are then integrated into natural biogeochemical cycles (Alexander 1994).

Proteomics is an effective technique to identify enzymes involved in the biodegradation of petroleum hydrocarbons. Lee et al. (2007) studied fluoranthene catabolism and associated proteins in *Mycobacterium* sp. JS14. Detection of fluoranthene catabolism associated proteins coincides well with its multiple degradation pathways that are mapped via metabolites identified.

Petroleum hydrocarbons may be degraded under both aerobic and anaerobic conditions. But aerobic catabolism of hydrocarbons can be faster, due to the metabolic advantage of having the availability of O_2 as an electron acceptor (Cao et al. 2009). Under aerobic conditions, oxygenase enzymes introduce O_2 into hydrocarbons (monooxygenases introduce one oxygen atom to a substrate while

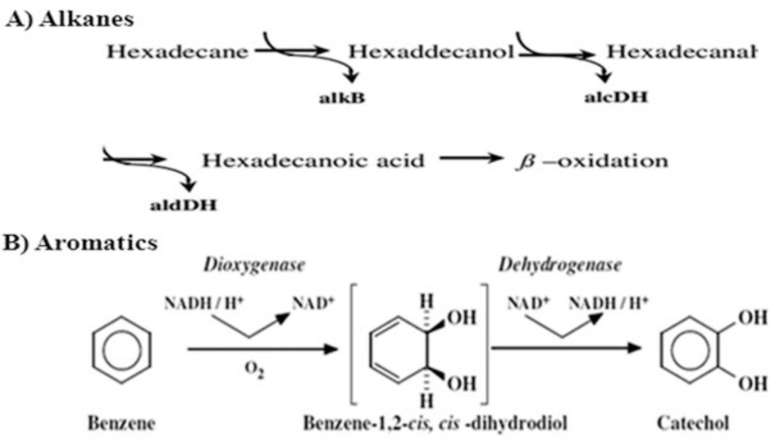


Fig. 17.2 Degradative enzymes involved in the degradation of petroleum hydrocarbons

dioxygenases introduce two). The final product of petroleum hydrocarbon oxidation is acetyl Co-A, which is further catabolized into the citric acid, together with the production of electron transport chain. The chain is repeated, and degraded hydrocarbons are fully oxidized to CO_2 (Madigan et al. 2010). Induction of various enzymes by microbes governs the different degradation pathway of petroleum hydrocarbons.

17.6.1.1 Alkanes

Microorganisms follow different pathways for the degradation of alkanes like monoterminal, diterminal, and subterminal (Fig. 17.1). Generally, alkane oxidation is catalyzed by alkane monooxygenase, resulting in an alcohol (Abdel-Megeed 2004) which is further oxidized to the corresponding fatty acid via aldehyde by an alcohol dehydrogenase and an aldehyde dehydrogenase, respectively. In some cases, both ends of the alkane molecule are oxidized through ω-hydroxylation of fatty acids at the terminal methyl group (the ω position), rendering an ω -hydroxy fatty acid which is further converted into a dicarboxylic acid and processed by β-oxidation (Coon 2005). Besides terminal oxidation, subterminal oxidation generates a secondary alcohol which is converted to the corresponding ketone and then oxidized by a Baeyer-Villiger monooxygenase to render an ester. The ester is hydrolyzed by an esterase, generating an alcohol and a fatty acid. Among terminal and subterminal, terminal oxidation was discovered as a major pathway for *n*-alkane degradation by van Beilen et al. (2003) and subsequently confirmed by Wentzel et al. (2007).

van Beilen and Funhoff (2007) have proposed three categories of alkane-degrading enzymes, such as methane monooxygenase, alkane hydroxylase, cytochrome P450 monooxygenase, aldehyde dehydrogenase, etc.

Sometimes, both terminal and subterminal oxidation may coexist in some microorganisms. However, members of *Rhodococcus* group possess all three degradation pathways, and the products of these pathways are primary alcohols, monocarboxylic fatty acids, secondary alcohols, and ketones.

17.6.1.2 Aromatics

Biodegradation mechanism of aromatics also requires the presence of molecular oxygen to initiate the enzymatic attack on PAH rings. The initial step in the aerobic bacterial degradation is the hydroxylation of an aromatic ring via a dioxygenase, with the formation of a *cis*-dihydrodiol. These dihydroxylated intermediates may then be cleaved by intradiol or extradiol ring-cleaving dioxygenases through either an ortho-cleavage pathway or meta-cleavage pathway, leading to formation of central intermediates, such as protocatechuates and catechols, which are further converted to tricarboxylic acid (TCA) through cycle intermediates (Cerniglia 1992).

In breakdown of aromatic compounds, the role of catechol dioxygenase has been studied by various workers (Kumar et al. 2011). Dioxygenases responsible for the formation of *cis* dihydrodiols from arenes of PAH substrates appear to be the most ubiquitous in the bacteria (Fig. 17.2). Multicomponent enzyme systems, involving several proteins, nonheme iron, and NADH (Resnick et al. 1994), were found to play a major role in degradation of aromatic compounds. To date, dioxygenase-containing organisms have been grown on a range of carbon sources, and these enzymes have been classified accordingly, e.g., toluene (TDO), naphthalene (NDO), and biphenyl (BPDO). Bacteria can also degrade PAH via the cytochrome P-450 pathway, with production of *trans*-dihydrodiols (Moody et al. 2004).

Besides bacteria, fungi have been found to partially or completely metabolize PAHs. Fungal degradation of PAH occurs through two different pathways. White rot fungi produce unspecific extracellular ligninolytic enzymes, peroxidases, and laccases that initiate a free radical attack by a single electron transfer, leading to formation of quinones (Cerniglia 1993). Degradation of PAH by non-ligninolytic fungi involves the activity of the cytochrome P-450 monooxygenases. These enzymes catalyze a ring epoxidation to form an unstable arene oxide, which is further transformed to *trans*-dihydrodiol by enzymatic hydration or rearranged to phenols by nonenzymatic reactions (Sutherland 1992).

For the first time, Chandran and Das (2012) reported the role of plasmid on diesel degradation by five yeast species, namely, *Candida tropicalis*, *Cryptococcus laurentii*, *Trichosporon asahii*, *Rhodotorula mucilaginosa*, and *Candida rugosa*. These microorganisms showed the presence of enzymes, such as cytochrome P450 monooxygenase, NADPH cytochrome c reductase, alcohol dehydrogenase, aldehyde dehydrogenase, naphthalene dioxygenase, catalase, and glutathione S transferase when the cells were incubated for 48 h in Bushnell Haas medium supplemented with 2% diesel oil as the sole source of carbon. Leilei et al. (2012) studied the effect of different levels of crude oil on the activities of several enzymes like dehydrogenase, catalase, urease, and polyphenol oxidase synthesized by *Rhodococcus* strain.

17.6.2 Cell Hydrophobicity

Furthermore, microbes possess other adaptation strategies, such as the ability to modify the cellular membrane to maintain the necessary biological functions (de Carvalho et al. 2009), the production of surface-active compounds as biosurfactants (Ron and Rosenberg 2002), and the use of efflux pumps to decrease the concentration of toxic compounds inside the cells (van Hamme et al. 2003). All these mechanisms and metabolic abilities make microorganisms an interesting and effective tool for the petroleum hydrocarbon bioremediation of contaminated sites. The uptake mechanism of hydrophobic substrate occurs by the direct contact between the hydrocarbon and cell surface hydrophobic interaction (Liu et al. 2016).

Bacterial cell surface properties are, in general, affected by the culture medium composition, growth conditions, and culture age (Dufrêne and Rouxhet 1996). Noha et al. (2007) observed an increase in cell surface hydrophobicity, if there was an increase in equivalent alkane carbon number (as carbon source for culture media of

Table 17.1 Biosurfactants produced by different microbes

Biosurfactants	Microorganisms
Sophorolipids	*Candida bombicola* (Daverey and Pakshirajan 2009) *Candida batistae* (Konishi et al. 2008) *Trichosporon ashii* (Chandran and Das 2010)
Rhamnolipids	*Pseudomonas aeruginosa* (Kumar et al. 2008) *Pseudomonas fluorescens* (Mahmound et al. 2008) *Serratia rubidaea* (Jadhav et al. 2011)
Trehalose lipid	*Rhodococcus erythropolis*, *Arthrobacter* sp., *Nocardia erythropolis*, *Corynebacterium* sp., *Mycobacterium* sp. (Krishnaswamy et al. 2008)
Lipomannan	*Candida tropicalis* (Muthusamy et al. 2008)
Ornithine lipids	*Pseudomonas* sp., *Thiobacillus thiooxidans*, *Agrobacterium* sp. (Desai and Banat, 1997)
Surfactin	*Bacillus subtilis* (Youssef et al. 2007)
Glycolipid	*Aeromonas* sp. (Ilori et al. 2005) *Bacillus* sp. (Tabatabaee et al. 2005)

B. subtilis T 894 and *B. subtilis* Ro 662). Also in another investigation, adsorption of rhamnolipids on *P. aeruginosa* CCTCC AB93066 and *P. aeruginosa* CCTCC AB93072 could increase cell surface hydrophobicity (Zhong et al. 2008).

17.6.3 Biosurfactants Production

Biosurfactants, synthesized by the microorganisms (Table 17.1), are surface-active molecules. These molecules solubilize and promote the uptake of hydrophobic substrates. Another mechanism through which biosurfactant enhances the biodegradation of poorly soluble molecules is by causing the cell surface to become more hydrophobic (Noudeh et al. 2010). These substances include many advantages in comparison to chemical surfactants. For instance, they have lower toxicity, higher biodegradability, better environmental compatibility, higher foaming activity and specific activity at extreme temperatures and pH ranges and the ability to be synthesized from renewable feedstocks (Noudeh et al. 2010).

The effect of biosurfactant on the bioavailability of organic compounds can be explained by three main mechanisms: (1) dispersion of nonaqueous phase liquid hydrocarbons, leading to an increase in contact area, which is caused by a reduction in the interfacial tension between the aqueous phase and the nonaqueous phase; (2) increased solubility of the pollutant caused by the presence of micelles which may contain high concentrations of hydrophobic organic compounds, a mechanism which has been studied extensively previously; and (3) "facilitated transport" of the pollutant from the solid phase to the aqueous phase, which can be caused by a number of phenomena, such as lowering of the surface tension of the pore water in soil particles, interaction of the surfactant with solid interfaces, and interaction of the pollutant with single surfactant molecules (Liu et al. 1992).

Biosurfactants have a wide diversity of chemical and molecular structures (Abdel Mawgoud et al. 2010). It may be classified as (1) glycolipids; (2) lipopeptide; (3) fatty acids, neutral lipids, and phospholipids; and (4) polymeric surfactants and particulate surfactants (Vater et al. 2002). They have typical molecular weights of 500–1500 Da, made up of peptides, saccharides, or lipids or their combinations. They may be located on the cell surface or be secreted into the extracellular medium and facilitate uptake of hydrophobic molecules through direct cellular contact with hydrophobic solids or droplets or through micellarization (Ward 2010).

Their synthesis depends on cell density, signal molecules (autoinducers) of regulatory pathway (Satpute et al. 2010), and various chemical and physical factors including carbon source, carbon/nitrogen ratio, divalent cations, and specific substrate availability (Nitschke and Pastore 2006). Further, the physical nature of the medium also affects biosurfactant production in different ways and in different strains.

P. aeruginosa has been extensively studied for the production of glycolipid-type biosurfactants. However, glycolipid-type biosurfactants are also reported from some other species like *P. putida* and *P. chlororaphis.* Biosurfactants increase the oil surface area which makes oil available for bacteria to utilize it (Nikolopoulou and Kalogerakis 2009).

17.7 Environmental Factors: Optimize the Microbial Biomass

The rate of exponential growth of microbes is influenced by various environmental factors. However, exponential growth of microbes cannot occur indefinitely. At this point, the microbial population reaches to stationary phase, where there is no net increase or decrease in microbial cell populations. The possible buildup of environmental toxins or depletion of bioavailable substrates (Yates and Smotzer 2007) may cause microbial population to enter the death phase and the viable number of microbes to decrease. Some of them can be controlled or modified, while some are difficult to control. The most salient factors are pH, temperature, moisture content, aeration, nutrient availability, etc.

The pH of soil is maintained by a natural buffering capacity that exists in most fertile native soils due to the presence of carbonates and other minerals (Robinson et al. 2009). However, this buffering capacity can be depleted over time as a result of acidic by-products of degradation (Komnitsas et al. 2004). The majority of bacteria exhibit growth optima at or near neutral pH (Andreas and Ekelund 2005). Fungi are generally more resistant to acidic soils than soil and aquifer bacteria.

Temperature affects bacterial metabolism, microbial growth rates, soil matrix, and physicochemical state of the contaminants. Generally, in situ bioremediation is carried under mesophilic condition (20–40 °C). Even for laboratory studies, bacteria with potential biodegradation ability have focused on mesophilic species because of cultivation and relatively short doubling times (Kuntz et al. 2008). The rate of biochemical reactions in cells increases with temperature up to a maximum, above which the rate of activity declines as enzyme denaturation occurs and organisms either die or become less active (Trasar-Cepeda et al. 2007). Coulon et al. (2005) found a direct relation of TPH degradation with increasing temperature from 4 to 20 °C, using sub-Antarctic soil artificially contaminated with diesel or crude oil. Low and high temperatures seldom kill the microbes that results in declining in degradation rate. Temperature also affects the physical state (rate of evaporation) and solubility of petroleum hydrocarbons.

Oxygen is used as an electron acceptor to increase bioremediation activity (Boopathy 2000). A number of anaerobic bacteria can break down a variety of aliphatic and aromatic organic compounds, both of natural and anthropogenic origin wholly or partially by denitrifying bacteria, sulfate, iron, and molybdenum reducers and methanogenic consortia. But the aerobic degradation rate was always found higher than anaerobic degradation. Salminen et al. (2004) recorded 31% and 27% degradation of lightweight fuel and lubricant oil at a boreal in aerobic condition after 3 and 4 months of incubation in microcosmic study, whereas 44% and 15% was recorded after 12 and 10 months in anaerobic condition.

Further, degradation of petroleum hydrocarbons by a given native microbial population can be favored by the presence of the required nutrients in the contaminated site (Delille et al., 2004). Spilled petroleum hydrocarbons represent a substantial C-source for the indigenous microorganisms, but availability of nitrogen and phosphorous is limited. Therefore, in most environments, an addition of one or more rate-limiting nutrients to the system, which is called biostimulation, improves the degradation potential of the inhabiting microbial population (Nikolopoulou and Kalogerakis 2009).

17.8 Biostimulants

Significant enhancement in biodegradation process can be achieved by using different types of bioaugmentation and biostimulation products (Fig. 17.3). However, these products are not panacea and need to be evaluated according to the requirements of the site before implementation.

17.8.1 Fertilizers

Nitrogen deficiency was found in oil-soaked soil that directly retards the microbial growth (Chromo et al. 2010). Therefore, nutrient addition is an important factor to achieve C:N balance for successful biodegradation of petroleum contaminants (Jin and Fallgram 2007). Fertilizer should be added gradually in soil in order to avoid

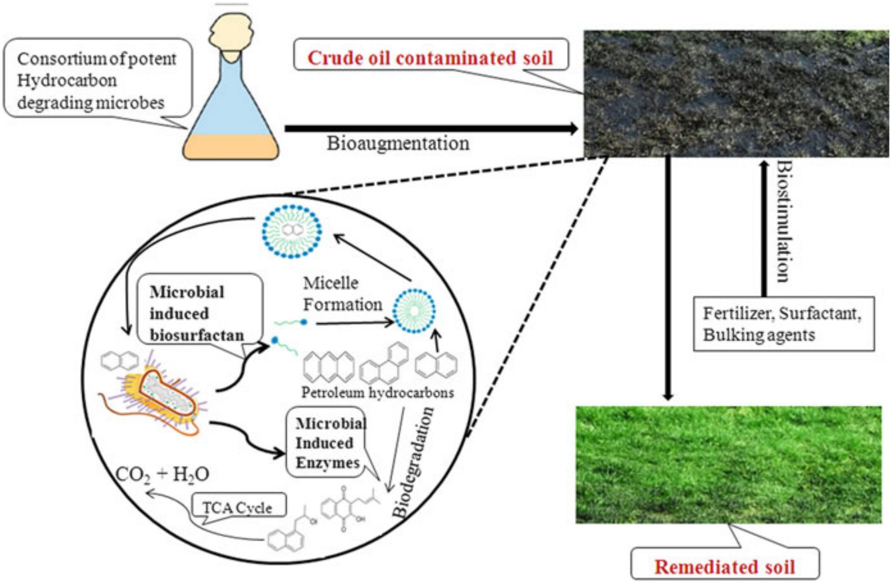


Fig. 17.3 Integrated approach of bioremediation including bioaugmentation and biostimulation

excessively high pH and high concentration of N_2 that might be toxic to soil microbes (Prince 2002).

17.8.2 Surfactant

Biodegradation is enhanced by surfactants due to increased bioavailability of pollutants (Kose et al. 2003). When surfactant concentration is above the critical micelle concentration (CMC), micelle aggregates provide an additional hydrophobic area in the central region of micelles enhancing the aqueous solubility of petroleum hydrocarbons (Li and Chen 2008) and reducing the surface tension (Fig. 17.4).

Surfactants may be classified based on the presence of polar head group. If polar head group contains ionic form, it may be categorized as anionic or cationic surfactant. In anionic surfactant, hydrophilic domain may be sulfate, sulfonate, phosphate esters, or carboxylates. Cationic surfactant may have permanently charged quaternary ammonium cation or pH-dependent primary, secondary, or tertiary amines. In the case when polar head contains both ions, surfactants are classified as zwitterionic surfactant like CHAPS. Largely used surfactant for bioremediation is nonionic surfactants that have no ionic form in polar head that makes it less toxic to microbes.

Some studies have suggested positive effects of Tween 80 and Triton X-100 (Kim et al. 2001) and of Tergitol NP-10 (Grimberg et al. 1996). However, other workers

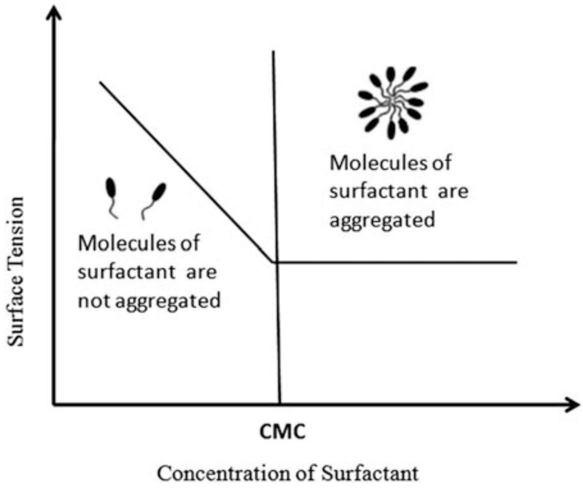


Fig. 17.4 Reduction of surface tension by adding surfactant

(Laha and Luthy 1992; Yuan et al. 2000) have reported inhibitory effects of surfactants on the bacterial biodegradation activity when the surfactants were added in concentrations over the CMC, most likely due to an excess of micelles of the pollutant and a reduction of the bioavailability (Mulligan et al. 2001). Tween 80 was found to inhibit the rate of fluoranthene mineralization by two strains of *Mycobacterium* (Willumsen 2001).

Possible reasons are bacteria-surfactant interactions which could be the competitive substrate utilization and/or toxicity of the surfactants to the hydrocarbon-degrading bacteria (Liu et al. 2001). Biodegradation experiments, using *Pseudomonas* sp. with Triton X-100 or Tergitol NP-10, did not show a significant decrease in toxicity along the whole course of both experiments (Bautista et al. 2009).

17.8.3 Bulking Agents

Bulking agents provide the optimum free air space and regulate the water contents in soil. They generally fall into two categories, i.e., structural and organic. Bulking agents are materials of low density, and when added to soils, they lower the soil bulk density, increase porosity and oxygen diffusion, as well as form water-stable aggregates. Such changes to a soil increase aeration and microbial activity (Hillel 1980). Besides, they also contain microbial biomass and have nutrient quality that improves soil fertility. In composting applications, organic bulking agents allow for successful treatment of higher oil concentration by increasing its biodegradation rate (Nakles and Ray 2002). Similarly, Koolivand et al. (2013) recorded TPH degradation increased from 67–80% with increasing immature compost ratio with sludge (1:0–1:8). Kumari et al. (2016) compared the role of different bulking agents, i.e., sugarcane bagasse, vermicompost, coconut coir, and rice husk for the degradation of crude oil and found that rice husk could degrade petroleum hydrocarbons of crude oil (82%) with faster rate than others.

Various agricultural by-products like wheat bran, sawdust, peat moss, pine wood shavings, peanut hull powder, rice husk, and bran flakes are being used as bulking agents. Bulking agents are also used as carrier material to immobilize bacteria owing to its properties of being highly granular, absorbent, biodegradable, and inexpensive. The carrier materials provide nutrients, moisture, and physical support for the increased aeration required by the microorganisms, and it can also prolong the shelf life of the microorganisms until they are applied in the field. Extended survival of the microorganisms under field conditions is essential for efficient degradation of the toxic hydrocarbons.

17.9 Conclusion

A lot of reports are available on the degradation of crude oil by a number of bacteria and fungi in isolation and combination both in vitro and in situ conditions. Besides, many degradative enzymes, e.g., laccase, catalase, dehydrogenase, mono- or dioxygenases, etc., involved in degradation of oil have been identified based on their upregulation and overexpression. In order to enhance the process of mineralization by the biological agents, natural or cultured organisms, various environmental factors were manipulated in conjugation with biostimulation and bioaugmentation at oil-contaminated sites in shortest time.

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