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Manish Kumar
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Emerging Issues in the Water Environment during Anthropocene

A South East Asian Perspective

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Dedicated to Inspirational life and achievements
of
Prof. Mihir Kanti Chaudhuri, Ph. D. (IIT KGP), Dr. rer. nat.
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Foreword

It gives me immense pleasure to note that a book project entitled *Emerging Issues in the Water Environment during Anthropocene: A South East Asian Perspective* is going to be published by Springer Nature Singapore Pvt. Ltd. under the editorship of Dr. Manish Kumar, Dr. Daniel D. Snow, and Dr. Ryo Honda. The focal theme of this book is aptly chosen as in the present era of high population growth, rapid urbanization, and climate change, the intensity of rainfall has become too unpredictable to adequately protect and manage the freshwater systems. Any pollution management plan requires an understanding of the contaminants and how are they transported from source to sink. Sustainability is the core concern of the present day and therefore "Clean Water and Sanitation" was included as the 6th Sustainable Development Goal (SDG). This is going to be a multidisciplinary book focused on the recommendation and solutions for policy making and sustainable water management approach based on case studies which will give better insight to the reader for effective management of the problems associated with emerging environmental degradation issues.

The purpose of the present book is to bring together and integrate the subject matter that deals with water quality under the changing climatic condition, hydrogeochemistry, river management and morphology, social sciences, and public policy. The book is intended to be a comprehensive reference for students, professionals, and researchers working on various aspects of science and technology development. The topic presented in this book is purely based on the research finding and lab-based experiments conducted by the subject matter experts and established researchers, so that the readers can correlate the issues addressed in this book to their associated field of science and technology directly. Language structure will be one of the main attractions of the book since fast, easy, and effective communication of the advancement of scientific innovation to the beneficiary group is the most important factor in the present era. Therefore, this book will also highlight the scientific approach of the topics in a more simplified way.

The book seeks its impact from its diverse topic coverage revealing situations of different contemporary issues, such as water quality problems, drinking water and wastewater treatment, geomorphological features, and sociological approach. The diversity of editors' experience, location, and expertise is illustrative indications of the interdisciplinary nature of this work within the scope of water supply, water quality, scenarios, and management. In my understanding, such book is the need of the time and will be unique in many senses as per the discussion above.

The technical aspects of this book are very significant, and contributions are encompassing all the envisaged scope of global human impact on world's freshwater resources with a special reference to South East Asia: A state of perplexity of aquatic ecosystem. I am pleased to know that more than 15 contributed chapters under the four sections are embedded in this book project by the domain experts. The first section is focusing on the background building of the reader and introduce the issues, problems, perspectives and challenges of world's freshwater system and its supply, risk, and distribution scenario briefly but completely in the context of Anthropocene era. The second section highlights the effect of climate change on groundwater quantity and quality. Additionally, this section also lays special emphasis on addressing the groundwater dynamics and sustainability of water under different hydro-geochemical regimes. On the other hand, the third and fourth sections cover the various aspects of water research domains with relevant techniques and management strategies, so that the subject matter covers a deep insight into the complex and concurrent "Emerging Water Quality Issues". I hope that this book will help in charting out future directions and solutions related to emerging water-environment issues. I am sure that the readers will enjoy the individual chapters and gain scientifically stimulating experience through better understanding of the background processes and the factors controlling risk management and remediation measure of water systems. This will surely contribute to the development of more efficient, sustainable technologies, and management options of aquatic ecosystems.

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This book would not have been possible without the common ground provided by financial contribution from Asia Pacific Network (APN) Grant Number CRRP2016-06MY-Kumar and Water Advanced Research and Innovation (WARI) program using which ideas were exchanged among the editors of the book. APN grant was particularly helpful under the support of which this book project was accomplished and all contributed chapters have been put together as a comprehensive reference book on emerging water quality issues. We acknowledge the constant support and cooperation of Indian Institute of Technology (IIT) Gandhinagar, University of Nebraska–Lincoln, USA, and Kanazawa University, Japan. Participation of Water Environment Technology (WET) Laboratory members, Gandhinagar, is also highly appreciated. We would like to express our sincere thanks and gratitude to all the authors for their valuable contributions. We deeply appreciate Ms. Swati Meherishi, Ms. Avni, and Mr. Maniarasan for their persistent and hard efforts in successful coordination of the present book project. Although it is impossible to list all the names, we are thankful to our colleagues, students, peers, and notable academicians without whom we would not have completed our editorial responsibilities. Last but not least, we acknowledge the constant care and support of our families and well-wishers with which this book project came to a realization.

Gandhinagar, India	Dr. Manish Kumar
Lincoln, USA	Dr. Daniel D. Snow
Kanazawa, Japan	Dr. Ryo Honda

Contents

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Dr. Manish Kumar is a Faculty at Discipline of Earth Sciences, Indian Institute of Technology (IIT) Gandhinagar, Gujarat, India. He earned his Ph.D in Environmental Engineering from the University of Tokyo, Japan, and has received several prestigious awards and fellowship, such as Water Advanced Research and Innovation (WARI) Fellowship, Faculty Research Award, Best Research Award (IWA), Japan Society for the Promotion of Science (JSPS) foreign research fellowship, Brain Korea (BK)-21 post-doctoral fellowship, Monbukagakusho Scholarship, Linnaeus-Palme stipend from SIDA, Sweden, Research Fellowship from CSIR, India. He is active in the fields of Hydrogeochemistry, Contaminant transport and modeling, Metal speciation, Isotope fingerprinting, Emerging contaminants, and Water Management. He served as Principal Investigator (PI) for International Collaborative Projects funded by organizations like Asia Pacific Network, DST-JSPS, UKIERI, etc. He is the Associate Editor of Groundwater for Sustainable Development (Elsevier) and Hydrological Research Letters and has more than 60 international journal publications and 3 edited books to his credit.

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Chapter 1
A Review on Antibiotic Resistance Gene (ARG) Occurrence and Detection in WWTP in Ishikawa, Japan and Colombo, Sri Lanka

Sulfikar, Sorn Sovannlaksmy, Ryo Honda, Tushara Chaminda and Manish Kumar

1.1 Background

The first use of antibiotics for medication in the modern era began in 1930–1932 by Alexander Fleming, who discovered and used crude penicillin to cure bacterial eye infection in patients. Ten years later, mass production of penicillin had enabled its general introduction for clinical use and saved many lives. However, resistance to penicillin was soon discovered after penicillin was widely used. The antibiotic paradox (Levy 1992) is a term that precisely describes how the use of antibiotics to kill or to inhibit bacterial growth may actually train the bacteria to resist the antibiotic if used at low doses. Hence, the wider the spread of antibiotic use, the more resistance to antibiotics is observed. As was predicted by Fleming himself in his inaugural Nobel speech in 1945 (Fleming 1945).

The emergence of multi-drug resistant bacteria, the so called superbugs, and their spread, coupled with the slow discovery of antibiotics with new mechanism has raised concern that we might again face a pre-antibiotic era in the near future. Surgery will be hard to perform without high risk of infection, and even minor injuries might kill (WHO 2014). Nowadays, antibiotic resistant bacteria

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(ARB) have spread to all parts of the world, and the spread has been accelerated by the increasing frequency of people and goods movements (WHO 2014; Alonso et al. 2017; Matamoros 2017).

Loose antibiotic prescription practices, over-the counter sales, and a misunderstanding of the usage of antibiotics for viral infections are common practices in developing (and some developed) countries. As not the entire ingested antibiotic is absorbed in the human body, much of the antibiotics used will end up in the aquatic environment (Kummerer 2009). Thus, the aquatic environment has an important role in the dissemination of ARB. In developing countries, it is uncommon that wastewater treatment is processed or even partly processed centrally. Wastewater treatment relies on the use of septic tank for each household. Quite often not all households have septic tanks, or the available septic tank is not set up or maintained properly (Lundborg and Tamhankar 2017). Greywater is dumped directly into waterways or leaks from septic tanks, contaminating groundwater. Recent reports in India, Tunisia, and Vietnam, showed grim situations where multi-drug resistant bacteria were found in rivers, lakes, and agricultural products (Hoa et al. 2008; Marathe et al. 2017; Alonso et al. 2017). However, even in developed countries where wastewater is processed centrally, antibiotic resistant bacteria and gene were found downstream of the wastewater treatment plant (WWTP), indicating that WWTPs act as sources of ARB (Rizzo et al. 2013; Berglund et al. 2015; Gomi et al. 2017; Chu et al. 2018; Kumar et al. 2019; Gogoi 2018).

1.2 WWTPs Role in the Spread of ARG and ARB

As multi-drug resistance and new antibiotics resistance are emerging rapidly in many parts of the world, and new antibiotics discovery is slow, more attention is being directed towards limiting the spread of ARB and ARG of anthropogenic origin. WWTPs can be regarded as a meeting place for many varieties of bacteria carried within the wastewater from diverse origins. The wastewater of household, hospital, animal and food farms contain ARG and ARB. Thus, WWTPs are targeted to reduce the spread of ARG and ARB.

During wastewater purification, some physical and chemical processes are applied in WWTP to remove biodegradable compounds. In sequence, the processes are: primary sedimentation applied to remove large organic particles by settling; anaerobic process applied to help the breakdown of organic compounds, thus reducing organic load for the more costly aerobic process; aerobic process where more complete removal of organic compounds occurs; a secondary sedimentation tank to remove the excess bacterial growth; disinfection to remove pathogenic bacteria. Aeration provides not only oxygen for bacterial growth, but also enhances mixing of sludge and raw water; increasing the chance of ARB and ARG from the sludge and raw water to mingle (Diwan et al. 2013; Macauley et al. 2006).

Furthermore, the mixing provided by aeration facilitates adsorption and desorption of pollutants, ARB, and ARG onto and off the sludge, which provides the material and conditions for gene transfer. Disinfection by chlorination has been found to increase the proportion of resistant bacteria in the effluent (Macauley et al. 2006; Huang et al. 2011) and in drinking water (Shi et al. 2013), and has been found to be ineffective in reducing the number of antibiotics resistance genes (Yuan et al. 2015). Thus, WWTPs are also suspected as a significant location for the generation and dissemination of antibiotics resistant bacteria.

Previous studies on ARB and ARG in WWTP investigated the abundance of ARB and ARG in different or all stages of the purification process to infer the role of WWTPs in dissemination of ARB and ARG. The findings of these studies vary, from no change (18), increased transfer (19–22), to reduction in ARG (Munir et al. 2011; Laht et al. 2014; Karkman et al. 2016; Zhang et al. 2009) from influent to effluent. These findings suggest that WWTPs act merely as a conduit, or as a meeting place facilitating gene exchanges between bacteria, or have some role in reducing ARG. However, some studies showed that ARGs were reduced mainly by adsorption onto sludge (Xu et al. 2017; Mao et al. 2015). Thus, although this process can reduce ARGs contained in the influent, ARGs accumulate in the sludge and are still present even after anaerobic digestion of the sludge, preventing the use of sludge for e.g. on agricultural land (Calero-Cáceres et al. 2014). Removal of ARG and ARB from the sludge did not completely remove all type of ARG (Burch et al. 2013), and most cost bear by WWTP is in processing the sludge (LaPara et al. 2011).

1.3 Between Countries Distribution of Antibiotic Resistance Gene in WWTP and in Aquatic Environment

A survey of antibiotic resistance genes in WWTP raw water found that antibiotic resistance gene profiles (the resistome) are different between countries (1). However within countries, the influent of WWTP resistome did not differ geographically, as suggested by a study conducted at 32 WWTPs influent across 17 major cities in China (2). The differences between countries might be influenced by each government policy in controlling the use of antibiotics. In comparison, the resistome in water bodies differed geographically between North China and South/Central China (3). These contrasting observations might be because the municipal WWTP influent resistome to some extent is driven by genes from bacterial and fungal species with an origin in the human gut (4, 5), while the resistome in the water bodies are influenced by a more diverse population of microbiota. Nonetheless, several studies have reported increases of resistance rate or antibiotic resistance genes quantity in water bodies in closed vicinities to anthropogenic activities (Hoa et al. 2008; Pruden et al. 2012; Honda et al. 2015; Marathe et al. 2017).

1.4 Antibiotic Resistance Gene Screening in WWTP in Japan and Sri Lanka

We conducted this investigation to find out which genes are common in the wastewater treatment plants in Japan, Sri Lanka. We also compare our results to results of other studies surveying antibiotic resistance gene in influent WWTP located in other countries or cities. We specifically chose WWTP that only process municipal wastewater to get a better idea of the antibiotic resistance gene pattern derived from human use of antibiotics.

1.4.1 Method

1.4.1.1 Sampling Locations

Four WWTPs in Ishikawa prefecture were surveyed in April–May and September 2017, two WWTPs in Sri Lanka in October 2017. As the WWTPs are privately run commercial operations, the real names of the facilities have been substituted with alphanumeric identifiers to maintain commercial in confidence privacy. WWTP J operates the conventional activated sludge process. WWTP D, M, and S operate the anaerobic-aerobic activated sludge process. The WWTPs in Sri Lanka (SL1 and SL2) processed mixed raw water from municipal areas, industry, and road seepage. Samples were taken from the influent of the primary sedimentation tank (Influent PST), anaerobic tank (An), the mixed liquor of the aeration tank (AS), and the return sludge (RS). For WWTP J, the samples were taken at Influent PST, AS, RS, and effluent of the secondary sedimentation tank (FST). For SL1 and SL2, only influent PST was collected. The samples were stored on ice in Schott bottles that had been pre-baked at 200 °C for four hours. The sample volumes were 250 mL for influent and effluent PST, 100 mL for AS and RS, and 1-L for FST, while for SL1 and SL2, 50 mL samples were collected in 50 mL DNase/RNase-free conical tube. Sampling locations and conditions are summarized in Table 1.1.

1.4.1.2 DNA Extraction and PCR

All samples were kept in the dark and kept on ice during transport to the laboratory. Upon arrival, the samples were then sub-sampled for DNA extraction. For samples collected in Ishikawa, 50-mL of the Influent and Effluent PST samples was centrifuged in DNase/RNase-free conical tubes at 10,000 rpm for 15 min at four degrees. For AS and RS, 1.5-mL and 1.0-mL of sample was centrifuged in 2-mL DNase/RNase-free tube under the same conditions as the PST samples. For the FST

Table 1.1 Sampling locations and conditions and volume of samples collected

Location	WWTP	Process applied	Wastewater source	Sampling point	Sample volume (ml)
Ishikawa, Japan	J	Conventional activated sludge	Municipal	Inf PST, AS, RS, effluent of FST	Inf PST = 250; AS and RS = 100 FST = 1000
	D, M, S	A/O activated sludge	Municipal	Inf PST, AS, An, RS	Inf PST = 250; AS, An and RS = 100 FST = 1000
Colombo, Sri Lanka	SL1 and SL2	A/O activated sludge	Municipal, industry and road seepage	Influent of PST	50

Inf PST = influent of the primary sedimentation tank, AS and An = mixed liquor in aeration tank and anaerobic tank, respectively, FST = effluent of the final sedimentation tank. A/O = anaerobic/aerobic activated sludge process

samples, 1-L of sample was filtered through polycarbonate membrane filters with a pore size of 0.2 μm. The supernatant was discarded, and DNA was extracted from the pellet using FastDNA™ spin kit for soil following the kit protocol (MP Biomedicals, LLC, Ohio, USA). For SL1 and SL2, upon arrival in the laboratory, 2 mL of the samples were taken and let stand in the fridge until the supernatant looked clear. The supernatant was discarded, and the sediment was sent frozen to Japan for DNA extraction using the same DNA extraction kit. DNA extracts were stored at −20 °C until PCR amplification. The quantity and the purity (A260/280 and A260/230) of the DNA were determined using an Eppendorf spectrometer. The DNA extracts were further purified using the ethanol purification method if the absorbance ratio Abs λ260/λ280 is below 1.8 and λ260/λ230 is below 1.

Twelve genes that confer resistance to five classes of antibiotics mechanisms of action were amplified from the DNA extracts. The five types are inhibition of DNA gyrase: qnrB, *qnrS*, aac(6′)-1b, parC for fluoroquinolones; inhibition of cell-wall synthesis bla-CTX, bl-TEM, bla-SHV, ampC for β-lactams, and vanA for vancomycin; inhibition of folate synthesis: *sul1* for sulphonamides. Gene amplification was performed for 30 cycles at with initial denaturation at 95 °C for 3 min, denaturation at 30 s, annealing at optimum annealing temperature for 30 s, elongation at 72 °C for 1 min, and final elongation at 72 °C for 7 min. The reaction was performed using an Applied Biosystems 2720 thermocycler. The primer sequences and annealing temperatures (Ta) are listed in Table 1.2. The presence of antibiotic resistance gene amplicons in the PCR products was identified using the electrophoresis gel method. We used 2% w/v agarose to run the PCR product for 60 min at 50 V.

Table 1.2 ARG primers and annealing temperature

Primers	Sequence 5′–3′	Amplicon size (bp)	Annealing temp. (°C)	References
qnrS	F: GCAAGTTCATTGAACAGGGT	428	54	Cattoir et al. (2007)
	R: TCTAAACCGTCGAGTTCGGCG			
qnrB	F: GATCGTGAAAGCCAGAAAGG	476	56	Kim et al. (2009)
	R: ATGAGCAACGATGCCTGGTA			
aac(6′)-Ib	F: TTGCGATGCTCTATGAGTGGCTA	482	55	Rodriguez-Martinez et al. (2007)
	R: CTCGAATGCCTGGCGTGTTT			
parC	CTGAATGCCAGCGCCAAATT	168	54	Rodriguez-Martinez et al. (2007)
	GCGAACGATTTCGGATCGTC			
sulI	F: CGCACCGGAAACATCGCTGCAC	163	69.5	Pei et al. (2006)
	R: TGAAGTTCCGCCGCAAGGCTCG			
vanA	F: TCTGCAATAGAGATAGCCGC	377	63	Klein et al. (1998)
	R: GGAGTAGCTATCCCAGCATT			
ampC	F: CCTCTTGCTCCACATTTGCT	189	61.2	Szczepanowski et al. (2009)
	R: ACAACGTTTGCTGTGTGACG			
blaTEM	F: GCGGAACCCCTATTTG	964	55	Olesen et al. (2004)
	R: ACCAATGCTTAATCAGTGAG			
blaCMY	F: ATGATGAAAAATCGTTATGCT	1146	60	Kojima et al. (2005)
	R: TTATTGCAGCTTTTCAAGAATGCG			

1.4.2 Results and Discussion

Out of nine genes tested, *qnrS* and *sul1* were detected in most samples, including in samples from the WWTP in Sri Lanka, and in both seasons (Tables 1.3 and 1.4). The genes *vanA* and *blaCMY* were not detected at all in both seasons. In other studies, sul and tet genes were the most common genes found at the influent of WWTP (Table 1.5). This is not surprising as tetracyclines and sulfonamides are old antibiotics that have been widely used for a long time and the genes encoding resistance for these antibiotics were found to be persistent along WWTP processes (Yang et al. 2014; Calero-Cáceres et al. 2014; Wang et al. 2015; Xu et al. 2017). Although sulfonamides are not used anymore in humans because of its toxicity, it is still used in agriculture. In a study by Yang et al. (2014) in a WWTP in China which applied metagenomic technique to identify ARG, genes encoding for resistance to amino-glycosides and tetracyclines were the most abundant genes, followed by sulfonamides (Yang et al. 2013).

Table 1.3 ARG detection results in influent wastewater samples

WWTP	qnrB	qnrS	aac(6′)-Ib	parC	sulI	vanA	ampC	CMY
Autumn								
D	+	++	nd	nd	+	–	++	–
S	++	++	++	++	++	–	++	–
M	nd	nd	++	++	+	–	++	–
J	+	++	++	++	++	–	–	–
Spring								
D	nd	++	nd	nd	++	–	–	–
S	nd	++	nd	nd	++	–	++	–
M	nd	++	nd	nd	++	–	++	–
SL1	nd	++	nd	nd	++	nd	nd	nd
SL2	nd	++	nd	nd	++	nd	nd	nd

Note ++ = sharp band, + = weak band, – = no band, nd = not data, CMY = blaCMY

Table 1.4 ARG detection results for samples collected in Ishikawa WWTPs, Japan

WW TP	Samples	qnrB	*qnrS*	aae(6′)-Ib	parC	sulI	vanA	ampC	CMY
Spring									
D	Inf PST	nd	++	nd	nd	++	–	–	–
	An	nd	++	nd	nd	++	–	–	–
	AS	nd	++	nd	nd	++	–	–	–
	RS	nd	nd	nd	nd	++	–	–	–
S	Inf PST	nd	++	nd	nd	++	–	++	–
	An	nd	++	nd	nd	++	–	++	–
	AS	nd	++	nd	nd	++	–	–	–
	RS	nd	++	nd	nd	–	–	–	–
M	Inf PST	nd	++	nd	nd	++	–	++	–
	An	nd	++	nd	nd	++	–	–	–
	AS	nd	nd	nd	nd	++	–	–	–
	RS	nd	++	nd	nd	++	–	–	–
Autumn									
D	Inf PST	+	++	nd	nd	+	–	++	–
	An	–	++	nd	nd	+	–	++	–
	AS	–	++	nd	nd	+	–	++	–
	RS	–	nd	nd	nd	+	–	++	–
S	Inf PST	++	++	++	++	++	–	++	–
	An	+	nd	++	++	++	–	++	–
	AS	+	nd	++	++	++	–	++	–
	RS	nd	++	++	+	++	–	++	–
M	Inf PST	nd	nd	++	++	+	–	++	–
	An	nd	nd	nd	–	+	–	++	–
	AS	–	nd	++	–	nd	–	+	–
	RS	–	nd	++	–	nd	–	+	–
J	Inf PST	+	++	++	++	++	–	–	–
	AS	+	++	++	+	++	–	–	–
	RS	+	++	++	+	++	–	–	–
	FST	–	++	+	+	++	–	–	nd

Note ++ = sharp band, + = weak band, – = no band, nd = no data, CMY = blaCMY

Table 1.5 Antibiotic-resistance gene detection in municipal WWTPs in various countries

Year	Location	Method	Influent	Aerobic	Final effluent	sludge	References
2003	Bielefeld-Heepen, Germany	Plasmid sequence		*blaOXA, aadA1, sul1, dfr, aacC1*			Tennstedt et al. (2003)
2009	Massachusetts, USA	qPCR universal *blaTEM*	*blaTEM*		*blaTEM*		Lachmayr et al. (2009)
2009	Bielefeld-Heepen, Germany	qPCR		*Aminoglycosides, ESBL, blaTEM, shv, ctx*, except *vim-4*	*Aminoglycosides, ESBL, blaTEM, shv, ctx except aacA1, aacA7, aadA9, aph(2')-Ib, per2, veb1*		Szczepanowski et al. (2009)
2011	Northern Portugal		*qnrS, gyrA, aac(6')-Ib-cr*				Figuira et al. (2011)
2012	China, Singapore, USA, USA, Canada	qPCR		*blaOXA1,2,10, ampC, TEM, IMP*			Yang et al. (2012)
2014	Barcelona, Spain		*blaTEM, sul1, qnrA, blaCTX*			blaTEM > *sul1* > *qnrS*; blaCTX-M and qnrA decreased; *qnrS* decreased, *sul1* and blaTEM constant	Calero-Cáceres et al. (2014)

(continued)

Table 1.5 (continued)

Year	Location	Method	Influent	Aerobic	Final effluent	sludge	References
2014	Hongkong, China	Metagenome	*tet > aminoglycoside > macrolide-lincosamine, streptogramin (MLS)*	*tet* and *MDR* the most abundant, *sul* increased	*qnr* and *sul* increased, *tet, MDR, aminoglyside* decreased	tet > MLS > acriflavine	Yang et al. (2014)
2015	Zabrze, Poland	PCR		*dhfrA, sul1, erm, mef*			Ziembińska-Buczyńska et al. (2015)
2015	Beijing, China	qPCR	*tetA, tetB, tetE, tetM, tetz, tetW; sul1, sul2, sul3; gyrA, qnrC, qnrD, parC*				Xu et al. (2015)
2016	Helsinki, Finlandia	qpcr array 300 genes	MLSB (macrolide, lincosamide, streptogramin B); ARG richness chloramphenicol > multidrug = sulphonamids abundance was highest		*sul* genes were highest than in influent and sludge	MLSB highest than influent; ermF enriched 25X than in sludge, tet enriched 20X	Karkman et al. (2016)
2016	Monastir, Central-Eastern Tunisia	qPCR	*sul1 >>> erm, Int1, qnrA, blaTEM, qnrS*		*sul1* >>> erm, *Int1, qnrA, blaTEM, qnrS*		Rafraf et al. (2016)
2017	17 major cities, China	Shotgun metagenomics Hiseq 2500 Illumina	*sul1 tet40, aminoglycoside 6-N-acetyltransferase*, chloramphenicol resistance gene the most abundant				Su et al. (2017)

(continued)

Table 1.5 (continued)

Year	Location	Method	Influent	Aerobic	Final effluent	sludge	References
2017	Guangzhou, China	qPCR	*tet, ampC* B-lactamase genes	*tet* and *ampC* genes	Only *tetA tetM tetS*	Most tet genes and all ampC genes	Xu et al. (2017)
2017	Romania	qPCR	*sul1 > tetW*		*sul1* > tetW		Lupan et al. (2017)
2018	USA	qPCR	*sul1, blaSHV/TEM*	*sul1, blaSHV/TEM*	*sul1, blaSHV/TEM*		Quach-Cu et al. (2018)
2018	Michigan, USA	Shotgun metagenomics			Genes confer resistance for aminoglycoside beta lactam, chloramphenicol, fluoroquinolone, tetracycline, trimethoprim, macrolide, streptogramin, sulfonamide		Chu et al. (2018)
2018	Warmia and Mazury District, Poland	qPCR	*Intl2, blaSHV, blaTEM, sul1, tetA, tetM, aac(6)-Ib-cr, qepA*		*qepA, sul1, tet* are highest; *blaTEM* n *blaSHV* lowest. *aac(6)-Ib-cr, Intl2*		Korzeniewska and Harnisz (2018)
2018	Beijing, Qingdao, Wuxi, China	qPCR, MiSeq of *sul1* and *16S rRNA*		*sul1* was highly abundance			Wei et al. (2018)

The genes listed were the genes detected. This mean that other genes were absent or were not studied

Although quinolones are relatively new antibiotics, however genes conferring resistance to this antibiotics are also commonly found in WWTP. This is might be because quinolones are the drug of choice for treating urinary tract infection. Among the six quinolones resistance genes that we tested, only *qepA* was not identified (Kaplan et al. 2015; Kanamori et al. 2011; Tennstedt et al. 2003).

Our results also showed that almost all genes were detected in all samples, indicating that these ARG persisted along the processes (Table 1.4). Seasonal variation was only found for *ampC* where it was detected in spring, but not in autumn. Of the genes that were investigated, all four WWTP in Ishikawa showed a similar set of amplified genes, except for *ampC* which was not detected at WWTP J but was detected at the other three WWTPs.

1.4.3 Conclusions

We found that *qnrS* and *sul1* were the most common genes in all samples in both seasons. Most WWTPs had similar gene patterns, except for one WWTP. Another finding is that *qnrS*, *aac(6′)-Ib*, *parC*, and *sul1* were detected in the effluent of the final sedimentation tank of WWTP J operating conventional activated sludge. This result indicated that these genes were not completely removed during the processes chain.

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Chapter 2
Two Sides of a Coin: Targets and By-Products of Water and Wastewater Treatment

Bhagwana Ram, Divya Sharma and Manish Kumar

2.1 Introduction

Water plays the most vital part in the human body. Water intake is essential for the survival of every being. Contamination of drinking water is thus a prominent issue. To fulfill the demand for safe drinking water, there is a requirement of water treatment, i.e., primary and secondary; also, in some cases tertiary treatment. Also, with increasing population, new developments are done in the water treatment study ensuring safe drinking. However, recent researches show that these methods with the pros have their cons. Researches in the past show that these methods result in harmful by-products. The fact of utmost concern is that the amount of such harmful substances is less in raw water than in the treated water. Hence, it is realized that it is not just important to develop methods to clean water but also to authenticate them regarding repercussions, so for safe water, it is necessary to do the sensitivity analysis of these by-products. This review summarises the nature and harmful effects of these by-products.

Talking about the methods, chlorination, ozonation and UV radiations remove the pathogenic microorganisms in the name of disinfection treatment. Among all the methods mentioned above, chlorination is the cheapest, realistic and most effective method for achieving the best results. According to the basic the knowl-

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Table 2.1 Disinfection by-products (DPB)

	Before	Now
Treatment	Chlorination	Chloramination
DPB	Trihalomethane (THM), Haloacetic acid (HAAC)	*N*-nitrosodimethylamine NDMA), *N*-nitrosodiethylamine (NDEA)
Cause	Dissolved Organic Matter (DOC), free radicals	Nitrogen-containing compound
Health effect	Cell damage, carcinogenic and heart diseases	mutagenic, carcinogenic, teratogenic, hepatotoxin

edge it is a sufficient treatment, but according to the advanced research reports its results in harmful disinfection by-products (DBP). The harmful effect of these DPB and their formation potential is the highlight of this chapter. Chlorination uses any form of chlorine to disinfect whereas chloramination involves chloramine, i.e., chlorine with the addition of ammonia. There is also a difference in the DPB products of both the methods (Table 2.1). The primary concern is about the most commonly detected nitrosamine, perfluoro octane sulfonate (PFOS) and perfluorooctanoic acid (PFOA) as they are hazardous products of many such treatments (Fig. 2.1).

In addition to that, the *N*-nitrosodimethylamine (NDMA), trihalomethanes (THM) and *N*-nitrosodiethylamine (NDEA) are detected in water treated samples which are cancerous to human beings. The formation of these compounds in

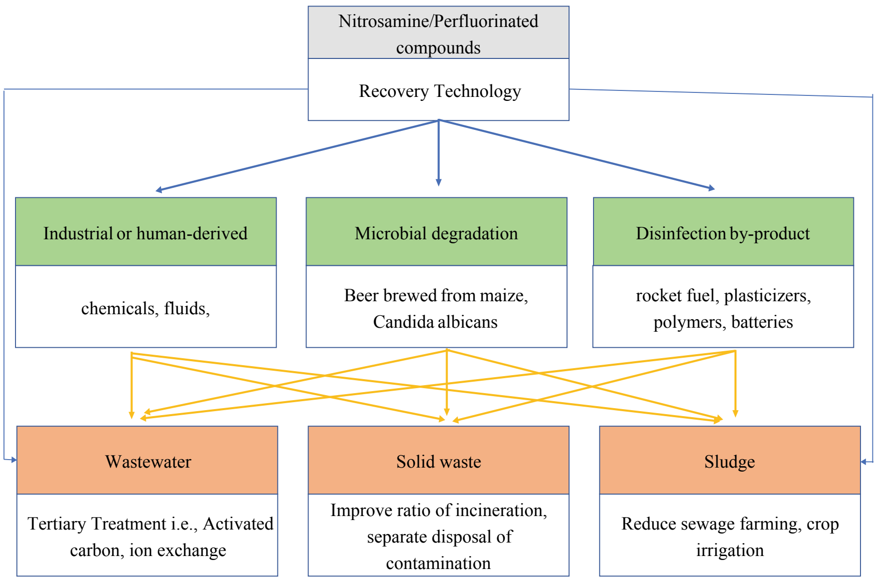

Fig. 2.1 Environmental activities responsible for Nitrosoamine and perfluorinated compounds in drinking water-causes of disinfection by-products (DBP)

disinfection of water depends upon amount and nature of precursor as well as the strategy of treatment. NDMA is covering almost all researchers in the past regarding the disadvantages of wastewater treatment techniques. NDMA is formed in low to high concentrations in the methods as it is easily formed in reactions involving chemicals and breakdown by light. Also, pH affects the formation of NDMA as the rate of formation is maximum in pH range 7–8, which is also the pH range of the treatment plant (Yang et al. 2009). NDMA is immortal as it cannot be removed by aeration because Henry's constant is very small. It is not bioaccumulated (polar compound), but it is hardly biodegradable due to strong hydrophilicity. The chloramination is also a source of NDMA. The chloramine reactions are slow in nature which are responsible for nitrosamine formation, so there is an increase in concentration with increasing distance from the treatment plant (Mhlongo et al. 2009). The reason that chlorination or chloramination responsible is that due to the oxidation, the tertiary amine oxides convert to a secondary amine which in turn becomes the precursor of nitrosamines.

THM is also similarly very popular regarding the search for its availability, fate, and removal from groundwater treatment sources. The low-cost replacement chloramines are used in place of chlorination for reduction of formation potential of THM in the treatment of water. However, it results in the formation of the new carcinogenic product. As it is a highly hazardous, concentration in parts per trillion is required for highly sensitive analysis. Moreover, as they are polar compounds (soluble in water), it is difficult to remove them by organic solvents (non-polar). Because of the low absorbability and recalcitrant nature, it is a high risk for groundwater. Many methods and their efficiency of DPB have been discussed here.

2.1.1 Trihalomethanes (THMs)

Methods like chlorination have resulted in forms of THMs. These forms are bromodichloromethane (BDCM), trichloromethane (chloroform), tribromomethane (bromoform) and dibromochloromethane (DBCM) (Gopal et al. 2007). The suggested reason for the same is a reaction between the chlorine and natural organic matter in Water treatment plants. THMs if consumed in more amount can reciprocate in adverse health effects such as cancer and adverse reproductive outcomes. As humans are associated with everyday tap water use, inhalation and dermal absorption can result in more blood THM concentrations than directly drinking the water does.

2.1.2 Haloacetic Acid (HAAs)

Likewise, haloacetic acid is found to be a common by-product in wastewater treatment with almost the same levels as THMs. Apart from trihalomethanes, several other classes of by-products are formed during water treatment. Haloacetic acid has various kinds of classes which include HAA9, HAA5, and HAA6Br (for example dibromoacetic acid, monochloroacetic acid, chlorodibromoacetic acid, bromodichloroacetic acid and chlorodibromoacetic acid). It is the second most prevalent compound among the classes of DBPs after THMs. The intake of haloacetic acid in contrast to TMHs depends only on the activity of drinking water, i.e., direct intake rather than by indirect activity like absorption through the skin. Also, the association between HAA compound and risk for stillbirth are relatable to drinking water (Rodriguez et al. 2004). However, if the THM levels are controlled, there is no link between HAA exposures and pregnancy problems in women especially stillbirth. Hence, to conclude HAA is terrible for human health and that there is a solid relationship between the occurrence of such a phenomenon with harmful by-products of disinfection.

2.1.3 Nitrosamine

The DPB nitrosamine is drawing attention as it a highly mutagenic, teratogenic and hepatotoxin product. IARC reported that it is very carcinogenic, as exposure to high levels of nitrosamines can lead to increased rates of cancer. There are more than 300 different nitrosamines, and out of that 90% are responsible for tumors (Mhlongo et al. 2009). The origin of this problem is due to the presence of ammonia during the process of water and wastewater treatment with chloramines (Mitch et al. 2003). The nitrosamine is formed by using amine-based coagulants (quaternary) in coagulation and wastewater-impaired water source. Several types of researches show that water which has been treated with ion-exchange leads to *N*-nitrosodimethylamine (NDMA) production. The anion-exchange resins in which there are functional groups of quaternary amines have been serving as NDMA precursors. The polymers used in the treatment of water such as poly(diallyldimethylammonium chloride) (polyDADMAC) and poly (epichlorohydrin dimethylamine) (polyamine) may form NDMA when in union with chloramine water disinfectants. The main thing observed is its low concentration in water, but its high concentrations in recycled water after treatment.

Choi and Valentine proposed the following nitrosation process (Choi and Valentine 2003). Dimethylamine (DMA) is not a most effective precursor of NDMA in WWTPs due to pH nearby neutral. The maximum yield at pH 3.9 (Yang et al. 2009). The DMA react with nitrate or nitrite in an acidic environment. During disinfection by chlorination, monochloramine (NH_2Cl) has been an important oxidant for NDMA formation by DMA (Bond and Templeton 2011; Choi et al. 2002).

$$(CH_3)_2NH + NO_2^- \rightarrow (CH_3)_2NNO + H_2O$$

$$(CH_3)_2NH + NH_2Cl \rightarrow (CH_3)_2NNH_2 \rightarrow (CH_3)_2NNO$$

The dissolved O_2 and dichloramine ($NHCl_2$) are the culprits responsible for NDMA formation (Schreiber and Mitch 2006).

$$(CH_3)_2NH + NHCl_2 \rightarrow (CH_3)_2NNHCl \rightarrow (CH_3)_2NNO$$

nitrosation pathway

$$(CH_3)_2NH + \text{nitrosating agent}(\text{e.g.}, NO^+, HNO_2, N_2O_4) \rightarrow (CH_3)_2NNO$$

In the nitrosation process, the presence of free chlorine (HOCl) enhances the formation of *N*-nitrosodimethylamine (NDMA) by conversion of dimethylamine (DMA). The free chlorine oxidizes the nitrite rapidly forming nitryl chloride and hydroxide ions. These products then become reactants for nitrate, proton and chloride ions. During the formation of monochloroaminethe solution is made alkaline by adding NaOH which is followed by a mixture of sodium hypochlorite solution into ammonium sulfate solution. Hypochlorite oxidation of nitrite is completed by the transfer of Cl^+ to NO_2^- via HOCl to give NO_2Cl (nitryl chloride) as an intermediate. Then by the formation of N_2O_4 as an intermediate product, nitryl chloride reacts with the last NO_2^-. Also, nitryl chloride hydrolyzes into nitrate. These are complex series-parallel reactions where N_2O_4 forms via a series of reactions. It was reported that HOCl and NO_2Cl compete for nitrite in parallel. Furthermore, hydrolyzation of NO_2Cl also occurs along with N_2O_4 formation. Thus, massive production of nitrite acts as a catalyst in the formation of N_2O_4.

NDMA occurrence in water treatment plant at 32 California WTP and 179 Ontario WTP was analysed by Nawrocki and Andrzejewski 2011 (Table 2.2).

Significant attention is drawn to the sources of nitrosamines and NDMA in the upcoming section.

Table 2.2 NDMA occurrence in water treatment plant by Nawrocki and Andrzejewski 2011

Disinfection		32 California WTP		179 Ontario WTP	
		No. of sample	Sample > MDL	No. of sample	Sample > MDL
Chlorine	Influent	11	3	851	245
	Effluent	11	3	1429	794
	Distribution	12	4	282	100
Chloramine	Influent	27	9	142	53
	Effluent	31	21	277	166
	Distribution	34	27	76	60
O3/ chlorine	Influent	7	2	2	0
	Effluent	10	5	2	0
	Distribution	10	3	2	0

The sources highlights for NDMA are as follows:

- Industrial invasion or human contamination
- Degradation of microorganisms
- By-products of disinfection treatments

2.1.3.1 Industrial Invasion or Human Contamination

Factories dispose of all kinds of waste, i.e., chemicals, fluids, carcinogens in the environment, especially, in the water bodies nearby. NDMA was thus detected in the wastewater surrounding the industrial areas. Mainly the hydrazines are disposed of in water near the factories producing or using unsymmetrical dimethylhydrazines (UDMH). Moreover, such hydrazines on oxidation produce nitrosamines, which is highly toxic. Not just this, NDMA is also present in cigarette smoke, foods, rubber treatment plants, exhaust and air-drying heaters as they all contain NOx. Similarly, the removal of nitrosyl cation is a significant issue as it forms NDMA. Dimethylamine (DMA) is a primary reactant in this reaction (Choi and Valentine 2003).

$$\mathrm{DMA} + \mathrm{N_2O_4} \rightarrow \quad \mathrm{NDMA}$$

However, the nitrosyl amine reduction has been reported by adjusting the pH conditions as it only forms around 3.4 pH scales.

2.1.3.2 Degradation of Microorganisms

NDMA formation in traditional beer, brewed from maize polluted with NDMA, and Candida albicans (oral yeast infection) could be responsible for the high level of oesophageal cancer and oral cancers respectively (Krogh et al. 1987). Such microbial sources are difficult to control. While some nitrates and nitrites appear to be converted to NDMA in the stomach and by bacteria in the gastrointestinal tract (Mirvish 1975). However, until today, there are no proofs for levels of NDMA in the environment by microorganisms.

2.1.3.3 By-Products of Disinfection Treatments

Industries like batteries, rocket fuel, polymers, and plasticizers give origin to the contaminant, NDMA. They have also been discovered to form DBPs in drinking water treated with chloramines or chlorine (Richardson 2003). UDMHbeing an intermediate during chlorination given rise to NDMA in drinking water (Choi and Valentine 2002). UDMH, as discussed earlier, is a primary culprit. Levels of NDMA in drinking water following disinfection treatment in the late 1990s and late 1980s prompted surveys of 19 in California and 145 drinking water plants in

Ontario, respectively (Mhlongo et al. 2009). These surveys estimated the NDMA concentrations at almost all treatment plants were below the notification levels of 9 ng/ℓ (recently changed in California to 10 ng/ℓ for NDMA and other nitrosamines) and that none were near the response levels of 100 ng/ℓ. Also, a study result was consistent with those of a recently released WHO (2006) report, in which the ADD of NDMA from ingestion of drinking water for a 60 kg adult with a drinking water intake of 2 L/day was estimated. It was 3.0 £ 1025 to 1.0 £ 1023 mg/kg-day, based on a mean NDMA concentration of 0.012 mg/L and a maximum concentration of 0.04 mg/L obtained from 20 samples from water treatment plants in Canada (Fristachi and Rice 2007).

2.1.3.4 NDMA Formation During Ozonation

Ozonation of dyes which includes a dimethylamine group produces large amounts of NDMA. Alternatively, the results of studies performed by (Muñoz and von Sonntag 2000; Von Gunten 2003), recite a different story that ozonation is not a cause of NDMA formation. However, (Andrzejewski et al. 2008) detected NDMA after ozonation and other oxidation treatments of aqueous solutions of DMA. Taking the same into consideration, a reinvestigating study was done to study the formation of nitrosamine during ozonation and its link with the same process being catalyzed by formaldehyde which is a normal by-product of ozonation. Hydroxylamine and dinitrogen tetroxide (reactive inorganic nitrogenous intermediates) are responsible for this. During oxidation processes, hydroxylamine is a possible inorganic precursor. After doing advanced oxidation processes (AOP) of some waters using H_2O_2/UV, it was realized that more NDMA was found in treated water as compared to untreated water. However, Zhao et al. confirmed that efficiency of ozonation and chlorine dioxide for the elimination of NDMA formation purely depends on the nature of the nitrosamine presence in the source water (Nawrocki and Andrzejewski 2011).

2.1.3.5 Degradation of NDMA

Now that it is known, drinking water containing NDMA is very harmful, researches have been done to destroy this futile compound in water. Since nitrosamines are rather persistent chemicals, the methods currently being examined for it are advanced oxidation processes (AOPs), radiolytic destruction, photolytic methods, biodegradation and chemical reduction. Following are some methods proposed for the destruction of NDMA:

1. Photolytic reactions and advanced oxidation processes
2. Reverse osmosis (RO)
3. Biodegradation and phytoremediation
4. Chemical reduction of NDMA.

2.1.3.6 Photolytic Reactions and Advanced Oxidation Processes

'Photo' means light and 'lysis' means disintegration suggesting that photolytic reactions decompose a compound with the help of light. On exposure to light, each substance absorbs a particular wavelength of the radiation which is associated with it uniquely. The light decomposes the substance, and this is a prevalent method to destroy any futile compound (degradable by light). Likewise, this specific wavelength for NDMA is 225–250 nm. For the destruction of nitrosamine, acidic pH is required. Thus it is well understood that alkaline pH will result in retardation of the same process (Xu et al. 2009). Acidic conditions favor the photolytic destruction of NDMA. It is observed that UV irradiation was successful in degrading NPYR and NPIP readily. The factor pH always plays an essential role as NPYR degradation is pH independent while NPIP photolysis is pH dependent. Parent amines were the main by-products of the photolysis. Lateral degradation led to simple primary alkylamines. Methods like the free radical destruction of NDMA, ozonation, reaction with hydrated electrons and electron pulse radiolysis of NDMA have not proven to be efficient ways for removal. However, Electron-pulse radiolysis is one method which could yield better results in this matter (Landsman et al. 2007). Ozonation along with UV is also a suitable process. UV irradiation has the same efficiency as the UV/O_3 process in NMDA decomposition. However, there are vast differences between the by-products of the two processes. Mainly nitrates are the resultant of the AOP process while DMA and nitrites are the main products of irradiation. Therefore, UV-irradiated fluids have a great NDMA regeneration potential, if chlorination is done subsequently. NDMA photolytic destruction in oxygen-saturated solutions appeared to be more efficient than destruction in N_2-saturated water. The photocatalytic degradation of ammonium salts (quaternary) in TiO_2 suspensions (Kim and Choi 2002). Photolytic destruction of nitrosamines was also examined by (Plumlee and Reinhard 2007). According to their model, photolysis seems to be a much more efficient method of NDMA destruction than biodegradation, even at relatively low levels of solar radiation. The WWTP effluents (tertiary) in solar radiation channels in approximately 90 min can destroy 42% of NDMA (Plumlee and Reinhard 2007).

2.1.3.7 Reverse Osmosis (RO)

Reverse osmosis is a method used in a lot of water filters available in the market as it is an easy and efficient method for removal of impurities. The studies showed that reverse osmosis with an efficiency of 50–65% is an excellent method for NDMA degradation (Plumlee et al. 2008). However, UV treatment with RO helps for the further treatment so reverse osmosis alone can't be more efficient as this enabled the achievement of NDMA concentration less than 10 ng/L. With a reverse osmosis system, the drastically reduce the unwanted contaminants like arsenic, copper, fluoride, microbes, and many more (Kumar et al. 2019; Patel et al. 2019a, b; Das et al. 2016; Das et al. 2017; Kumar et al. 2017). The vast majority of microscopic organisms and heavy metals are removed by the special membrane which is the component responsible for the whole success of this treatment. However, in the case of nitrosamines, the 74.08 g/mol (low molar mass of the NDMA molecule, a high degree of rejection cannot be expected by such membranes. Thus to remove this disadvantage if there is an increase in the molar mass, the rejection will automatically increase (Nawrocki and Andrzejewski 2011). By this partial removal may be expected for NDEA and a complete removal for NPIP, NMOR or NDBA. Another flaw of this method is that with the removal of contaminants it also removes some minerals essential for human intake.

2.1.3.8 Biodegradation and Phytoremediation

With the help of an organic substance (source of energy and carbon), when the micro-organisms decay the materials, it is called as biodegradation. The wastewater treatment plant treats the sewage where many of the organic compounds are broken down. It is observed that some are merely biotransformed (changed), while others are entirely mineralized. Biodegradation can occur under both aerobic and anaerobic conditions. The difference that oxygen is an electron acceptor in the aerobic state while areas, where sulfate, nitrate and similar substances are the electron acceptor, is mainly anaerobic is observed definitely. Before 2003, there were remarkably fewer reports about the degradation of NDMA in groundwater by biodegradation as reported. However late results show some evidence showing the removal of a substantial amount of NDMA through aerobic biodegradation. 80% of NDMA discharged with the effluents were biodegraded by a 600-day experiment in anaerobic conditions also (Zhou et al. 2009). Contrarily, there was no destruction of NDMA and NMOR under anaerobic conditions (Patterson et al. 2010). Also, the half-life of NDMA was a debatable issue as it varied from 70 to more than 100 years in different works. It has been reported that pre-ozonation can prove to be a better method for the treatment program. However, wasting the ozone on other compounds which are naturally biodegradable is a shortcoming.

Phytoremediation is fundamentally based on degradation of pollutants in water by plants (aquatic, semiaquatic and terrestrial) satisfying the green, eco-friendly technologies. It helps to degrade or immobilize contamination (organic and inorganic) with different enzymes from the soil by removing, retaining and transforming. Several bacteria like Pseudomonas mendocina KR1, Rhodococcusrubber ENV425 (Fournier et al. 2006) and Rhodococcus (heterotrophs of the order Actinomycetes) were found to transform NDMA to less harmful compounds in both aerobic and anaerobic conditions (Sharp et al. 2007). By oxidizing (with atmospheric oxygen) NDMA to *N*-nitrosodimethylamine, which was then converted to *N*-nitromethylamine. Aerobic biodegradation of NDMA results in the products of like formate, nitric oxide, methylamine, nitrate, and nitrite. Since concentrations of NDMA in the environment are deficient, the bacteria is unlikely to sustain the growth on nitrosamine as the primary substrate. Thus, rather than metabolic degradation, co-metabolic degradation should act as the dominant degradation mechanism. An interesting observation is the high hydraulic conductivity of soils that contain NDMA that may lead to the contamination of water as the compound does not get absorbed by the soil (Nawrocki and Andrzejewski 2011).

2.1.3.9 Chemical Reduction of NDMA

To remove the WWTP effluents and NDMA in wastewater, the chemical reduction is used worldwide. It was reported that Ni-plated iron gave better results than zero-valent iron in this type of reduction method, resulting in DMA and ammonia as the main by-products (Gui et al. 2000). Using hydrogen gas with the help of Raney Ni as a catalyst following (Frierdich et al. 2007), NDMA can be reduced. However, this catalyst is very doubtful as it is susceptible to air oxygen (Nawrocki and Andrzejewski 2011). Chemically enhanced primary process (CEPP) does not affect the removal of NDMA, considerable variability was observed in the removal of NDMA (19%–85%) and NDMA (16%–76%) in WWTPs with secondary treatment processes. DMA was well removed in all the six surveyed WWTPs. In the process of CEPP, the removal efficiency was higher than 97%. For the removal of tertiary amines, biologic treatment processes with nitrification and denitrification had better removal efficiency than conventional activated sludge process (Wang et al. 2014). The various chemicals used for NDMA reduction are iron, chlorine, ozone and hydrogen gas. Bicarbonates could decrease the rate of nitrosamine reduction by half of the cent. Additionally, very high concentrations of nitrates could be unfavorable for NDMA removal (Nawrocki and Andrzejewski 2011). A different form of nitrosamine in the wastewater treatment plant are given in Table 2.3.

2.1.4 Perfluorinated Compounds

Perfluorinated compounds (PFCs) also be called as global environmental contaminants (Arvaniti et al. 2012), have been widely utilised since a long time in

Table 2.3 Different form of nitrosamine in wastewater treatment plant

Nitrosamine	Abb.	Formula	Molecular weight (g/mol)
N-nitrosodimethylamine	NDMA	$C_2H_6N_2O$	74,082
N-nitrosomethylethylamine	NMEA	$C_3H_8N_2O$	88,108
N-nitrosodiethylamine	NDEA	$C_4H_{10}N_2O$	102,135
N-nitroso-di-n-propylamine	NDPA	$C_6H_{14}N_2O$	130,188
N-nitroso-di-n-butylamine	NDBA	$C_8H_{18}N_2O$	158,241
N-nitroso-di-phenylamine	NDPhA	$C_{12}H_{10}N_2O$	198,221
N-nitrosopyrrolidine	NPYR	$C_4H_8N_2O$	100.1
N-nitrosopiperidine	NPIP	$C_5H_{10}N_2O$	114.15
N-nitrosomorpholine	NMOR	$C_4H_8N_2O_2$	116.12

industrial and commercial applications, such as stain repellents for furniture coatings, pesticide formulations, paints, fume suppressants, fire-fighting foams, semiconductors, alkaline cleaners, shampoos, photographic films, food packaging, carpets, upholstery, denture cleaners, masking tape, electroplating and non-stick cookware (Brooke et al. 2004; De Voogt and Sáez 2006). Air and water are abundant in such ubiquitous environmental surfactants (Kannan et al. 2002, 2001; Saito et al. 2003). PFOA/PFOS can enter the human body by breathing air, eating food or drinking contaminated water some through contact with skin. Surfactants containing fluoride derivatives lead to the observed accumulation of perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) in the environment by their large-scale production and industrial utilization. Due to their strong carbon-fluorine bonds, they present significant physicochemical properties such as biological stability, extraordinary thermal, radiation, chemical, and high surface-active effect (Boulanger et al. 2005; Lindstrom et al. 2011). During the biological treatment, the second phase involves the production of PFOA/PFOS by conversion of the primary compound PFCs (Arvaniti and Stasinakis 2015). The concentration of PFCs in Wastewater treatment plants (WWTPs) effluent is often higher than that in influent (Wang et al. 2017). After secondary treatment, the mass flow of PFOS and PFOA increased significantly (Sinclair and Kannan 2006). The regular increase in the application of these compounds has been attributed to their contamination in wastewaters. The serious environmental concern due to multiple toxic effects including their biotic and abiotic persistence immunotoxicity, hepatotoxicity, carcinogenicity and chronic developmental toxicity (Lindstrom et al. 2011; Prevedouros et al. 2006).

WWTPs have the been a pathway for the release of PFCs to water resources. PFOA/PFOS was detected in almost all water samples after treatment collected from water treatment plants in the river watershed (Tabe et al. 2010). The concentrations of PFCs in treated wastewater are higher compared to raw sewage (Arvaniti et al. 2012). The digestion of sludge aerobic and anaerobic of the sludge also has been increasing the concentration of PFOA/PFOS (Hamid and Li 2016). This abnormal behavior may be due to a decrease of volatile solids and increment in sorption capacity of digested sludge, degradation of precursor compounds (Guerra et al. 2014). EPA established PFOA/PFOS combined concentration in drinking water should less than 0.07 μg/L.

2.2 Conclusions

The contaminated water collected from all setups like industries, houses, and landfills are treated in the wastewater treatment plants. For the conversion of this water into drinking water, methods like coagulation, pre-oxidation, GAC and UV irradiation are prevalent (Fig. 2.2). However, they are the parent of Disinfection by-products (DBP). After reviewing the causes, degradation, and efficiencies of DBP precursors, it is suggested to minimize disinfection with an oxidizing agent

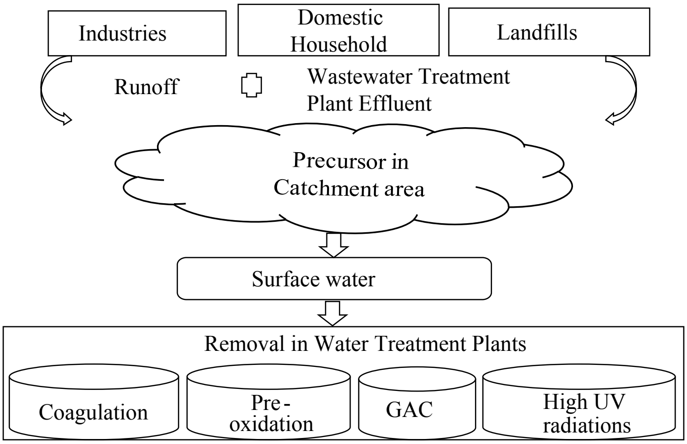

Fig. 2.2 The transport of precursor from sources to water treatment plant

like chloramine and chlorine. To check whether disinfection treatments are the reason behind these DBPs the observed is that the pollutants were higher concentration present in the treated water compare to raw water. Thus it is concluded that it is a treatment generated consequence. Use of adsorbing technology to remove DBP precursors and DOCis highly recommended. The groundwater gets polluted with ammonia in chlorination which becomes the primary source of nitrosamine. NDMA removal is achieved by photo-degradation also. The removal method of nitrosamines is described briefly. Developing treatment processes that remove nitrosamine precursors within WTP and use of polymers that do not contribute to nitrosamine precursors should be developed. Following the three-step process, reverse osmosis ensures safe drinking water by degrading NDMA to some levels which are the requirement of the hour. In the aquatic environment, photodegradation is the primary method for removing NDMA. The water environment is the parameter on which the efficiency of NDMA removal depends.

Ultimately, the research needs the sequence for the addition of chemical their reaction times for disinfectant chloramination for only or with ammonia. The use of existing facilities to oxidize precursors and removal of precursors from water should be evaluated. Developing treatment processes that remove nitrosamine precursors within WTP and use of polymers that do not contribute to nitrosamine precursors should be developed.

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Chapter 3
Water Quality Under the Changing Climatic Condition: A Review of the Indian Scenario

Nilotpal Das, Chandan Mahanta and Manish Kumar

3.1 Introduction

The IPCC defines climate change as an alteration in the climate over a specific time, either due to natural phenomena or human activities, or a combination of both. Principal among the human influences is the release of greenhouse gases like CO_2, CH_4, N_2O etc. Recently the level of atmospheric CO_2 has increased to an all-time high of about 410 ppm (Kahn 2017). Based on the IPCC report of 2007 as well as the “Conference of the Parties to the United Nations Framework Convention on Climate Change”, Bali (UNFCCC 2008), both scientists and policy makers agree on the fact that anthropogenic or human induced climate change is a highly important phenomenon. Although the rise in temperature is the most noticeable among the various changes under the umbrella term “climate change”; other important variations include an increase or decrease in precipitation and wind speed. The impact of climate change will be felt the greatest in the developing countries, especially those relying on primary production for their GDP (Kumar et al. 2006). Despite, a wide body of scientific work, there are still uncertainties regarding the implications that climate change will have on variables like precipitation, evaporation, and hydrology, on the local or regional scales (Whitehead et al. 2009). In this regard, climate models have shown great potential in predictive analysis of the impacts of the resulting changes on resources like water (Kundzewicz et al. 2007; Bates et al. 2008; Whitehead et al. 2009). However, outputs of individual models may differ; also effectiveness and the efficiency of the said models are important considerations. It

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has been speculated that, even after their increased efficiencies in recent times, global climatic models (GCMs) have major constraints as they do not take into consideration local variabilities (Kumar et al. 2006).

Presently, climate change is predicted be the cause of about 20% of the projected increase in global water scarcity (Sophocleous 2004). As mentioned earlier, the sustainability of water reserves in terms of both their quality and quantity in relation to climate change has currently become a vital issue to reckon with. India despite being endowed with a vast glacier fed surface water reserves in the form of numerous rivers, lakes, is already experiencing a shortage of water. In the state of Jammu and Kashmir, the glaciers have been recorded to recede at a fast pace of 0.7 m per year, which is alarming (Kääb et al. 2012; Laghari 2013). Despite receiving a high average annual rainfall of 1200 mm, India still faces water scarcity due to the wide spatio-temporal variation in precipitation (Mujumdar 2008). With a share of about 60% of the total water resources of the country, the Ganga-Brahmaputra-Meghna (GBM) system is the chief contributor of water in India (Mujumdar 2008). Hence, drying of the glaciers will put undue pressure on the water availability scenario for the country as a whole. Another cause of concern is that most of the agricultural activities take place in the plains of the GBM region. Agricultural intensification will lead to increased use of agrochemicals like fertilizers and the consequent influence of fertilizer runoff to surface water and leaching to groundwater will lead to undesirable consequences like eutrophication (Paerl and Huisman 2009).

In a country like India, where the majority of the population is dependent on groundwater for consumption and daily activities, it is imperative to give it priority. Groundwater remains safe from anthropogenic activities to a much greater extent than surface water, due to its partly isolated existence (Khanikar et al. 2017). However, it is important to mention that, groundwater once polluted can be very difficult to treat because of its slow recharge and discharge rates (Smedley and Kinniburgh 2002). Sea level rise is poised to cause salt water intrusion in the coastal regions (Sherif and Singh 1999), while excessive abstraction will not only deplete the aquifers, but also alter the physico-chemical properties like pH, ORP etc., which ultimately will have bearing on the availability of contaminants like arsenic (As) and other trace elements (Smedley and Kinniburgh 2002). Incidences of geogenic As (Shamsudduha and Uddin 2007; Pal et al. 2009; Kumar et al. 2010) and F^{-} (Mondal et al. 2009; Raju et al. 2012) contamination in India has already been widely reported, along with other trace elements like U (Tripathi et al. 2008, 2011; Sethy et al. 2014). Anthropogenic influences like agrochemicals and toxic wastes from industries are also making their presence felt in groundwater, along with a new class of pollutants termed emerging contaminants (Gani and Kazmi 2017). However, how and to what extent climate change will ultimately impact groundwater is not known.

While the number of studies, especially in India, highlighting the effect of climate change on water quantity is large, less focus has been given to water quality and even lesser to groundwater quality. With this view in consideration, the current work aims to summarize the recent findings and developments on climate change induced water quality degradation in India, along with the possible consequences. The review also lays special emphasis on addressing the sustainability of water under climate change regime.

3.2 Overview of the Work

The authors have compiled a review of 180 selected studies to present their views on the status of water quality corresponding to climate change in India. Mostly peer reviewed international publications were selected, apart from a few books, chapters, conference proceedings and online articles. The outline as well the theme of the work has been summarized in Fig. 3.1, which also graphically explains the current work. All maps were prepared using ArcGIS 9.3 (ESRI, Redlands, CA, USA).

3.3 Acidification of Aquatic Reservoirs and Dissolved Oxygen Content

Acidification of water bodies is mostly an anthropogenic influence. Climate change, however, has the ability to enhance its effect (Whitehead et al. 2009). The climate related variables, which have the ability to influence acidification rates include temperature rise, increased incidences of summer drought, wetter winters, reduced snow cover, alterations in hydrological pathways and increase in events of sea salt deposition (Whitehead et al. 2009). Increase in rainfall and wetter winters will lead to higher deposition of acids (Evans et al. 2008; Wright 2008; Whitehead et al. 2009). Rapid loss of snow cover will release the acidic oxides to the water bodies as well (Laudon and Bishop 2002; Whitehead et al. 2009). Assessment of Asian and European acidification scenarios by utilizing the Regional Air Pollution Information and Simulation (RAINS) model has revealed that under both "no control" and 50% reduction scenarios, SO_2 emission in Asia would increase from 1990 to 2100, to comprise 50% of the global anthropogenic sulphur emission (Posch et al. 1996). Acid deposition would likely to affect almost the entire eastern China, South Korea, Thailand, Sumatra and also large parts of India (Posch et al. 1996). The combined effects of anthropogenic SO_2 emission and climate change will be felt hard in these regions, which also include India.

Increase in dry periods combined with the excessive abstraction of groundwater leading to oxic conditions in the aquifers will also lead to the development of acidic conditions due to the oxidation of sulphur to sulphide (Wilby 1994; Dillon et al. 1997; Whitehead et al. 2009). Such acidic anions may eventually be transported to surface water and other reservoirs. In India, the regions most likely to be effected are the arid regions of the West like Rajasthan, where evapo-transpiration rates are

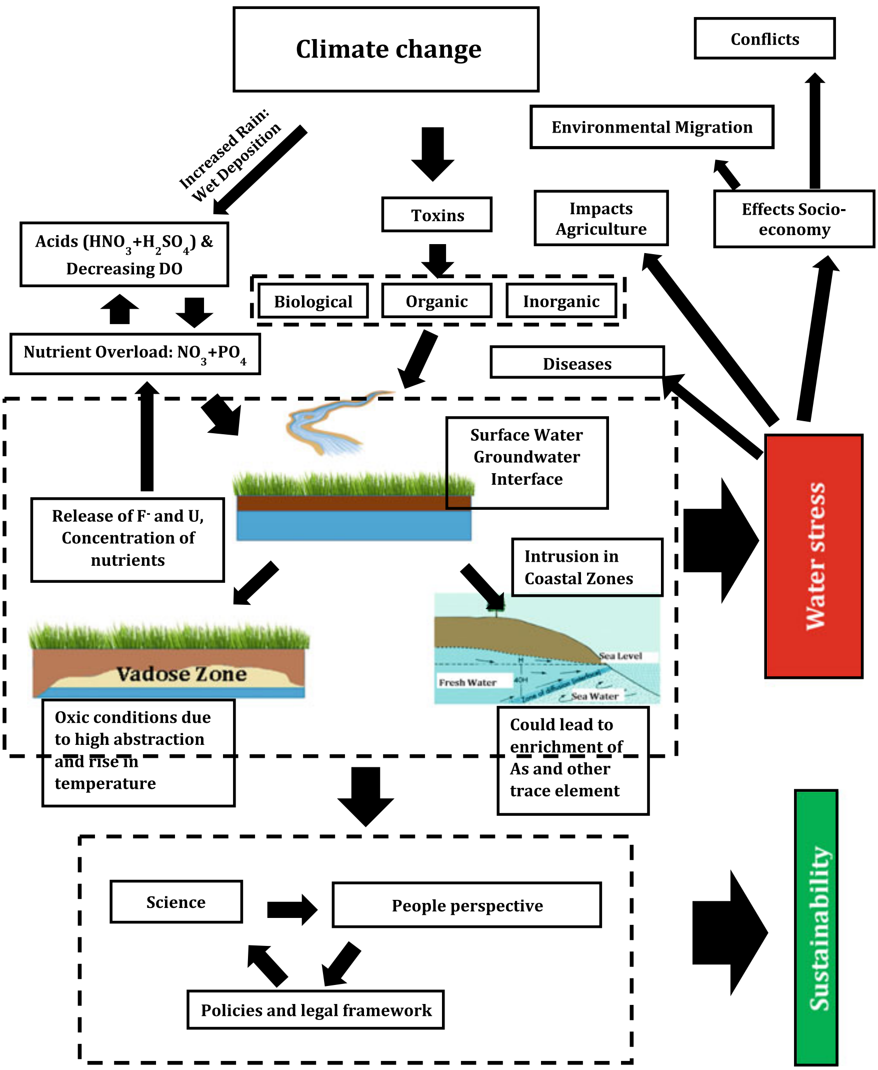

Fig. 3.1 Outline and graphical representation of the work

high (Goyal 2004). Also at risk will be central India, where rainy days are predicted to be less frequent but more intense (Krishna Kumar et al. 2011), potentially leading to both oxidation of sulphur in the aquifers, and also to wet deposition of SO_2. Acidification could also occur via the addition of NO_3 to the atmosphere, oxic aquifers could also lead to a reduction in denitrification and therefore accumulation of NO_3, leading to subsequent acidification of groundwater and ultimately surface water. Urban regions in north India like Delhi are at higher risk, as it has already been shown that NO_3^- and NH_4^+ levels in rain has increased by 486 and 283%

respectively from 1994 to 2013 (Singh et al. 2017). Most of the emission is due to anthropogenic activities, which combined with climate variables would lead to a more severe condition (Singh et al. 2017).

One of the first implications of climate change will be a shift in the dissolved oxygen (DO) content of water bodies along with their biochemical oxygen demand (BOD). The effects will be felt more on the surface water bodies like rivers and lakes. The use of models to simulate a hypothetical climate change scenario in the Tunga Bhadra river system, India reveals that under an extreme condition of a 2 °C rise in temperature and stream flow reduction of 20%, there would be a maximum reduction in DO by 1.06 mg/L per 171 km (Rehana and Mujumdar 2011). Reduced DO, will be coupled with an increase in BOD and river temperature, leading to an overall decrease in water quality in the coming years (Rehana and Mujumdar 2011). In shallow lakes, the temperature rise has the potential to generate permanent anaerobic zones, the cause of the anoxic condition has been speculated to be (1) reduction in the amount of oxygen dissolving into the lakes due to temperature rise and (2) density stratification could become stronger in the water columns preventing the aeration of the "near-bottom" (Golosov et al. 2012). Higher altitude lakes in the Himalayan region of India could be particularly vulnerable in this regard, as a rise in temperature could lead to the development of stratification in them.

3.4 Climate Change and Nutrient Flux

The Ganga-Brahmaputra-Meghna (GBM) river catchment system drains 1.612 million km^2 spread over India and Bangladesh (Whitehead et al. 2015a). Due to the dense population in the GBM catchment region, and the resultant agricultural expansion, rapid urbanization, and industrialization; climate change is predicted to have huge implication here (Whitehead et al. 2015a). Based on prediction using the INCA-N model, it was shown that simulated nitrate levels in Brahmaputra river were much lower than those in the river Ganga (Whitehead et al. 2015a). Thus, the Ganga River would be more severely hit by nutrient pollution compared to the Brahmaputra. However, the study also predicts that the actual nitrate levels in the rivers may decrease due to the predicted increase in precipitation after 2050 leading to dilution. Rising temperature combined with extended periods of low flow and droughts would also increase the rates of denitrification by prolonging the residence time of the pollutant in water (Whitehead et al. 2015a).

On the contrary, as atmospheric nitrogen pollution is poised to become more serious, it is probable that both wet and dry deposition of nitrogen based pollutants will degrade the water quality (Central Pollution Control Board 2003; Whitehead et al. 2015a). A lot of uncertainties exist regarding the ultimate fate of the water reservoirs due to the shift in the nutrient balance, resulting from the climate change. How climate change will impact nutrient flux will also depend on a number of important factors, including soil type, aquifer characteristics, and type of nutrient (Narula and Gosain 2013). A study in the northern Yamuna catchment area (Narula and Gosain 2013) has revealed that increase in temperature and precipitation is bound to increase evapotranspiration rates due to a net decrease in snow cover in the upper reaches, as snow contributes much less to evapotranspiration compared to rain. It could mean a lot of things, an increment in surface runoff is predicted in the future, leading to the quick removal of bound nutrients like phosphate, trace metals, and even nitrate resulting ultimately in reduction of nutrient availability for the plants, and increase in the nutrient load of the surface as well as groundwater (Narula and Gosain 2013). The same study also reports that in the future, increase in soil moisture stress will lead to an oxic condition, resulting in a reduction in denitrification rates, which would lead to leaching of more N bearing waste to groundwater as well as surface water. The ORP of the aquifers also play important roles, oxic aquifers are more likely to preserve NO_3 than reducing aquifers. Thus, it is likely that high abstraction of groundwater due to increase in agricultural demands in the possible climate change scenario could lead to the development of an oxic condition in aquifers, leading to the reduction in rates of denitrification (Narula and Gosain 2013).

3.5 Climate Change and Diseases

Increase in average temperature due to global warming will lead to higher microbe related health hazards in humans. A study in the Hubli-Dharwad region of Karnataka, India has revealed that the prevalence of water borne diarrhea due to *Cryptosporidium* and *Escherichia coli* was bound to increase due to an elevation in average temperature (Mellor et al. 2016). The results were based on quantitative microbial risk assessment (QMRA) modeling coupled with stochastic weather simulator (LARS-WG) modeling, which also concluded that with an increase in precipitation, the rate of diarrhea will decrease, as rainfall would bring about a depression in average temperature. Human activities and involvement is also going to influence the condition to a great extent, the installation of intermittent water supply (IWS) mainly in developing countries like India could be vulnerable to microbial contamination (Kumpel and Nelson 2016; Mellor et al. 2016). Suspended solids, biofilms of microbes and, inorganic and organic matter in the supply pipes during the intermittent period have been suggested as the main cause of this problem (Kumpel and Nelson 2016).

Cholera epidemics appear to have an association with the prevalent climate (Pascual et al. 2002; Nasr-Azadani et al. 2016); previous studies have also shown that rise in sea temperature in the coastal region was linked to major outbreaks of the disease (Epstein et al. 1993; Colwell 1996; Pascual et al. 2002). The onset of El Niño Southern Oscillation (ENSO) event in South American countries like Peru has been found to mark the beginning of intense cholera epidemics (Pascual et al. 2002; Patz et al. 2005). In the Indian context, a strong relation has not been observed (Pascual et al. 2002), however, the bacteria (*Vibrio cholerae*) laden coastal sea water has been linked to the onset of seasonal cholera in India (Pascual et al. 2002;

Nasr-Azadani et al. 2016). Under low flow river conditions of spring, the intrusion of contaminated sea water can not only pollute the groundwater, but also the surface water, resulting in spring cholera, while during autumn high flow, inundation and cross contamination results in autumn cholera (Nasr-Azadani et al. 2016). With the increase in precipitation and sea level rise, it is possible that autumn cholera may become more prevalent, especially in the Ganga-Brahmaputra deltaic region, which has previously been identified as a native habitat of cholera (Hirsch 1883).

Climate Change will predictably increase the prevalence of a number of zoonotic and vector borne diseases in the near future (Singh et al. 2011). Diseases like dengue and Japanese encephalitis, which are directly linked to water quality may take epidemic proportion in India due to unplanned and uncontrolled urbanization, poor environmental sanitation, poor household/water storage practices and so on (Singh et al. 2011). Along with predicted elevation in rainfall due to climate change, extreme events like droughts could also increase, and it has been anticipated that drier spells followed by heavy rainfall could not only lead to the flushing of fecal matter to surface water, leading to contamination but also likely to increase the frequency of diseases like echinococcosis, taeniosis, and toxoplasmosis (Singh et al. 2011). Several other diseases like melioidosis, leptospirosis and *Hepatitis E* virus infection (HEV), which are emerging water borne pathogens of potential zoonotic origin are poised to become major threats due to climate change in India (Vasickova et al. 2007; Chugh 2008; Singh et al. 2011).

3.6 Environmental Toxins

Climate change is likely to have a profound impact on the distribution and availability of environmental toxins to a great extent. These toxins can be categorized based on their origins to biological, organic and inorganic. Cyanobacteria, one of the oldest known photosynthetic organisms on earth are very persistent and some species of these microbes have been found to produce large growths on water surface called "blooms", which produce toxins, increase turbidity, reduce the dissolved oxygen content and can even alter the food chain (Paerl and Huisman 2009). Toxins released from various cyanobacteria (Table 3.1, modified from Paerl and Huisman 2009) have been found to effect both humans and animals by causing diseases of the liver, digestive system, skin, nervous system, and in some cases resulting even in death (Carmichael 2001; Cox et al. 2003; Paerl and Huisman 2009; Huisman et al. 2013). Rising temperature has been found to be favorable for cyanobacteria (Paerl and Huisman 2009; USEPA 2013). Projections have shown that in India, climate change will bring about a temperature rise of about 2.5–5 °C, coupled with about 1–4 mm/day increase in rainfall intensity, except for certain areas in north-west India (Singh et al. 2011). Moreover, increase in CO_2 levels in the atmosphere is also bound to favor cyanobacteria and algal growth, climate change induced droughts leading to increased salinity may result in salt stress and

Table 3.1 List of toxins produced by cyanobacteria

Toxin	Produced by
Neurotoxins	
Anatoxin-a	*Anabaena*, *Aphanizomenon*, *Oscillatoria* (*Planktothrix*)
Homo-Anatoxin-a	
Anatoxin-a(s)	*Anabaena*, *Oscillatoria* (*Planktothrix*)
Paralytic shellfish poisons (saxitoxins)	*Anabaena*, *Aphanizomenon*, *Cylindrospermopsis*, *Lyngbya*
Liver toxins	
Cylindrospermopsin	*Aphanizomenon*, *Cylindrospermopsis*, *Umezakia*
Microcystins	*Anabaena*, *Aphanocapsa*, *Hapalosiphon*, *Microcystis*, *Nostoc*, *Oscillatoria* (*Planktothrix*)
Nodularins	*Nodularia* (*brackish to saline waters*)
Contact irritant-dermal toxins	
Debromoaplysiatoxin, lyngbyatoxin	*Lyngbya* (*marine*)
Aplysiatoxin	*Schizothrix* (*marine*)

release of toxins from the cyanobacteria (USEPA 2013). Increased salinity could also lead to conditions favorable for the invasion of freshwater bodies by marine algae (USEPA 2013).

Eutrophication rates have also been predicted to increase, especially in developing countries like India, which has a high dependence on agriculture due to a fast growing population (Singh et al. 2011). Increase in nitrogen flux to water bodies due to eutrophication will ultimately lead to more harmful algal blooms (HAB) (Singh et al. 2011). Groundwater, with high residence time, may preserve nutrients and on reaching surface water may aggravate the phenomenon of algal bloom. Recent studies have shown that the estuarine and the “exclusive economic zones” (EEZ) of India are under the threat of HAB, which could be partly due to the influence of changing the climate (Padmakumar et al. 2012). In the period from 1998 to 2000, eighty algal blooms were recorded in the EEZ of India, of which thirty one were due to dinoflagellates, twenty seven due to cyanobacteria, eighteen were due to diatoms (Padmakumar et al. 2012). This report suggests a clear increase in the occurrence of algal blooms in the Indian EEZ. *Alexandrium* spp., *Gymnodinium* spp., *Dinophysis* spp., *Coolia monotis*, *Prorocentrum lima*, and *Pseudo-nitzschia* spp. were recorded to be the potentially toxic microalgae in the Indian waters (Padmakumar et al. 2012). Rise in temperature due to climate change has been cited as one of the key factors leading to the increase in algal blooms. It was also suggested that the Dinoflagellates will be able to move towards deeper layers for nutrition once thermal stratification occurs in the upper layers due to climate change (Padmakumar et al. 2012). Another study has revealed that decrease in flow of the Godavari river due to climate change induced drying and damming has resulted in an intensification of phytoplankton blooms in the estuary of the river (Acharyya et al. 2012).

The fate of organic and inorganic pollutants in water may be affected in different ways due to climate change. The degradation of organic pollutants like persistent organic pollutants (POPs) and many pesticides based on organic compounds appear to increase due volatilization as temperature rise is predicted in the future (Noyes et al. 2009; Nadal et al. 2015). In fact, the rate of degradation is bound to increase two to three time for every 10 °C rise in temperature (Macdonald et al. 2005). Temperature increase is also bound to cause faster degradation of the organic pollutants in the water. More the reduction in rainfall, greater will be the degradation, whereas increased, rainfall will enhance wet deposition of such pollutants (Nadal et al. 2015). The partitioning or switching of pollutants into solid (soil, sediment, rocks), liquid (water) and gas (atmosphere) is likely to be effected due to the increase in average temperature and rainfall (Noyes et al. 2009). Some POPs like hexachlorocyclohexane (HCH) and toxaphene will partition more into liquid phase or aquatic bodies due to increase in precipitation (Noyes et al. 2009). Places in higher altitudes are going to be effected more, as long ranged atmospheric transport (LRAP) of POPs and other toxic contaminants may become more prominent as volatilization increases (Macdonald et al. 2003; Noyes et al. 2009; Deka et al. 2016). More POPs and other organic pollutants could be released into the soil and eventually reach surface and groundwater in the upper reaches, as the snow cover decreases since ice and snow particles provide good surface areas for the adsorption of such pollutants (Noyes et al. 2009). Most of the glaciers around the world, including the Indian (Barnett et al. 2005; Laghari 2013) ones are receding as temperatures continue to rise. The Himalaya-Hindu-Kush Region of Asia appears to be most critically effected glacial region due to rise in temperature (Barnett et al. 2005). These glaciers supply water to about 50–60% of the world's population, thus this region and catchments below are at a high risk of having surface and groundwater contamination due to the release of adsorbed pollutants from snow and ice.

POPs and other organic contaminants like pesticides could contaminate surface and groundwater through another mechanism called solvent depletion, in which the solvent or water volume decreases leading to the concentration of the pollutants above thermodynamically possible levels (Brubaker and Hites 1998; Sinkkonen and Paasivirta 2000; Macdonald et al. 2002, 2003; Ma et al. 2004; Sweetman et al. 2005; Meyer and Wania 2008; Noyes et al. 2009). As the temperature is predicted to rise and extreme weather events like droughts become more common, both surface and groundwater contaminants will become more concentrated with contaminants (Macdonald et al. 2003; Meyer and Wania 2008; Noyes et al. 2009). In this regard, groundwater could be much more effected than surface water, due to its slow recharge and discharge. Increasing pressure on groundwater due to irrigation combined with leaching of contaminated surface water could worsen the scenario. However, POPs and the other organic contaminants will also be removed at a faster rate from surface water bodies due to volatilization induced by higher temperature, photodegradation and transport (Brubaker and Hites 1998; Beyer et al. 2003; Ma et al. 2004; Scheyer et al. 2005; Noyes et al. 2009), thus it remains to be seen, exactly how the scenario unfolds in the future. Anthropogenic interference is going to worsen the situation; as India is an agrarian economy, pesticide usage is quite high. India is reportedly the largest producer of pesticides in Asia and ranks twelfth in the world in terms of pesticide (Abhilash and Singh 2009). As a country, it is already battling the “residual effects” of chemical fertilizers, and pesticides like DDT (Rekha et al. 2006; Agoramoorthy 2008; Abhilash and Singh 2009). The states of Punjab and Haryana, where the use of agrochemicals is very high could be the most vulnerable, as the climate in these states is semi-arid prompting high abstraction of groundwater for irrigation. This will ultimately result in solvent depletion of the groundwater which coupled with leaching of the agrochemicals could lead to a very hazardous condition in these states. Incidences of various maladies like cancer, still births, kidney failure, infertility and others have been reported to increase in Punjab in response to the high usage of pesticides (Battu et al. 2004a, b; Abhilash and Singh 2009). Temperature rise will also lead to the appearance of previously undetected pests and weeds in newer areas prompting greater usage of pesticides, this could be an indirect pathway for the contamination of surface and groundwater in the future in response to climate change (Delcour et al. 2015).

Inorganic contaminants like trace elements are going to behave differently compared to organic pollutants, the same variables like temperature and precipitation may exert different effects on such pollutants. Arsenic is one of the most toxic inorganic environmental contaminants with a fairly low permissible limit for drinking water (10 μg/L, WHO 2017). A microcosm experiment on the release of As through reductive hydrolysis of Fe (hydr)oxides has revealed that reducing the experimental temperature from 23 to 14 and finally to 5 °C also slowed the reduction process and thus the release of As (Weber et al. 2010). Thus, the rise in temperature will most likely have a positive impact on As release. The regions most likely to be effected are As effected aquifers of the West Bengal and, north and northeast India. These regions lie in the greater Ganga-Brahmaputra flood plains of India (Kumar et al. 2017; Das et al. 2015; Patel et al. 2019a, b; Kumar et al. 2017). As already mentioned, the problem of arsenic contamination will effect mainly the groundwater, where the conditions are favorable for its release, compared to the highly oxic conditions of surface waters (Smedley and Kinniburgh 2002). Increase in groundwater based irrigation will only aggravate the situation, as it will deplete the aquifers leading to solvent depletion and also to possible leaching of As contaminated water from rice fields back to the aquifers (Neumann et al. 2011).

Fluoride, another common inorganic pollutant has been reported to occur in drier aquifers, where higher rock-water interaction or mineral dissolution is possible (Saxena and Ahmed 2001, 2003; Brunt et al. 2004). The F^- dominant aquifers of south, central and western India (Kundu et al. 2001; Gupta et al. 2005; Mamatha and Rao 2010; Paya and Bhatt 2010; Subramani et al. 2010; Arveti et al. 2011; Subba Rao 2011), will be the most effected due to temperature rise, as drying up of aquifers and anthropogenic groundwater based irrigation will only lead to higher concentrations of dissolved F^- in the aquifers due to solvent depletion. Previous studies have already shown that F^- release is positively influenced by the rise in temperature (Saxena and Ahmed 2003). An Indian study conducted in Tirupattur region of Tamil Nadu also revealed that with increase in temperature, fluorite (CaF_2), gypsum ($CaSO_4 \cdot 2H_2O$) and halite (NaCl) moved towards under saturation, while calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$) became more saturated enabling the release of more F^- into the groundwater (Sajil Kumar et al. 2015). In places where higher concentrations have previously not been detected like the Brahmaputra flood plains (BFP) despite the presence of F^- bearing minerals (Das et al. 2017), the rise in temperature could lead to elevated concentrations in the future. The same can be said for uranium, which is a radioactive contaminant, as studies have revealed that U occurrence is higher in drier oxidized aquifers (Wu et al. 2014). It has also been found that extensive use of phosphate fertilizers (ATSDR 2013) and over abstraction of groundwater (Jurgens et al. 2010) could increase U content in groundwater. With increasing instances of extreme weather events, together with expansion in agricultural activities, the threat of U contamination will loom large over the Indian aquifers. Although U has been detected from many parts of India like Singhbhum district of Jharkhand (Tripathi et al. 2008, 2011), Punjab, Himachal Pradesh (Kaul et al. 1993; Singh et al. 2003, 2005) and Meghalaya from the Northeast (Gupta and Sarangi 2011), ultimately the contamination of groundwater will depend on the availability of U bearing minerals like uraninite (UO_2), pitchblende (U_3O_8), autunite ($Ca(UO_2)_2(PO_4)_2 \cdot 10\text{–}12H_2O$), uranophane ($Ca(UO_2)_2SiO_3(OH)_2 \cdot 5H_2O$) etc., which are not very widespread compared to As and F^- bearing minerals.

As already mentioned earlier, due to its limited recharge and discharge, groundwater is very difficult to treat once polluted. An important issue, which a number of current studies have focused on is the geogenic co-contamination of groundwater by more than a single pollutant. Table 3.2 (modified from Mitchell et al. 2011) gives us an overview of naturally occurring co-contamination among toxic metals in the groundwater across the world. It can be observed that the Indian scenario is quite severe, As has been reported to occur along with Pb, Al and Cd (Buragohain et al. 2010), with Mn and Fe (Bhattacharjee et al. 2005), with Fe (Chakraborti et al. 2003); while Pb was found to co-exist with Fe (Jain et al. 2010), and Mn with Zn (Rajmohan and Elango 2005). Recently it has been speculated that As and F^- may occur together in drier isolated aquifers of the Brahmaputra flood plains (BFP) where rock-water interaction is higher (Fig. 3.2) (Kumar et al. 2016). Potential cases of As and F^- co-contamination may also be observed in certain parts of West Bengal, Jharkhand, Bihar, Uttar Pradesh, Punjab and Haryana (Pal et al. 2002; Pillai and Stanley 2002; Chakraborti et al. 2003; Rahman et al. 2005; Kumar et al. 2010; Shah 2010; Brindha et al. 2011; Das et al. 2015) (Fig. 3.2). The figure, also highlights the existence of elevated levels of naturally occurring As (Pal et al. 2002; Chakraborti et al. 2003; Samanta et al. 2004; Rahman et al. 2005; Kumar et al. 2010; Shah 2010; Das et al. 2015), F^- (Pillai and Stanley 2002; Brindha et al. 2011) and U (Gupta and Sarangi 2011) across India, which can also be termed as hotspots. Exposure to these contaminants is likely to be much higher in the regions within the hotspots.

Table 3.2 Co-contamination of multiple contaminants around the world

Country	Reported co-contaminants
China	Arsenic, selenium (Mandal and Suzuki 2002)
	Arsenic, manganese, uranium, iron (Smedley et al. 2003)
	Arsenic, nickel, iron (Virkutyte and Sillanpää 2006)
Taiwan	Arsenic, manganese, iron (Nath et al. 2008)
Malaysia	Arsenic, manganese, uranium (Kato et al. 2010)
Mekong River Delta (Cambodia and Vietnam)	Arsenic, manganese, cadmium, lead, nickel, selenium, barium (Buschmann et al. 2008) Arsenic, manganese, lead, barium (Luu et al. 2009) Arsenic, manganese, barium (Agusa et al. 2006) Arsenic, manganese, iron (Nguyen et al. 2009) Arsenic, manganese (Buschmann et al. 2008; Feldman et al. 2007)
Bangladesh	Arsenic, manganese, uranium, boron (British Geological Survey 2001; Frisbie et al. 2009) Arsenic, manganese, nickel, chromium (Frisbie et al. 2002) Arsenic, manganese (van Geen et al. 2007)
India	Arsenic, lead, aluminium, cadmium (Buragohain et al. 2010) Arsenic, manganese, iron (Bhattacharjee et al. 2005) Arsenic, iron (Chakraborti et al. 2003) Lead, iron (Jain et al. 2010) Manganese, zinc (Rajmohan and Elango 2005)
Iran	Arsenic, cadmium, selenium (Barati et al. 2010)
Uganda	Manganese, uranium, cadmium, lead, nickel, barium, iron (Taylor and Howard 1994)
Burkina Faso	Arsenic, manganese, molybdenum (Smedley et al. 2007)
Mali	Manganese, uranium (British Geological Survey 2002)
Ghana	Arsenic, manganese, iron (Buamah 2009)
Finland	Arsenic, selenium (Lahermo et al. 1998), uranium (Muikku et al. 2009; Prat et al. 2009), manganese, iron (Hatva 1989)
Italy	Arsenic, vanadium (Vivona et al. 2007)
Greece	Arsenic, manganese, uranium (Katsoyiannis et al. 2007) Arsenic, manganese, antimony (Kelepertsis et al. 2006)
Canada	Arsenic, manganese, iron (Environment 2010) Arsenic, uranium (Scotia 2010)
United States	Arsenic, manganese, uranium, selenium, molybdenum, boron (Robertson 1989) Arsenic, manganese, uranium, iron (Ayotte et al. 1999; Colman 2011; Stanton and Qi 2006) Arsenic, manganese (Kresse and Fazio 2003) Selenium, boron (Hudak 2004)
Argentina	Arsenic, uranium, vanadium, selenium (Nicolli et al. 1989) Arsenic, lithium, cesium, boron (Concha et al. 2010) Arsenic, vanadium (Ayerza 1918)

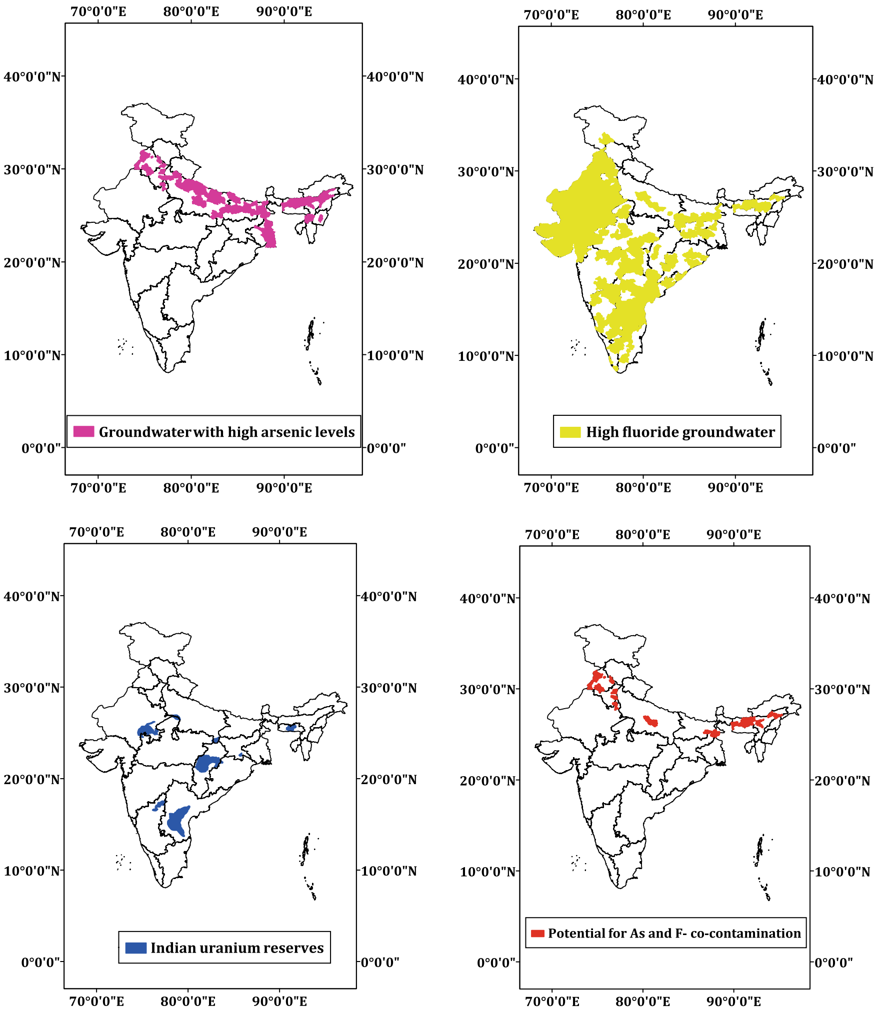

Fig. 3.2 Map showing the geographical extents of arsenic, fluoride and uranium hotspots in India, along with regions with possibility of arsenic and fluoride co-contamination

Climate change will put a lot of pressure on populations from the coastal regions, sea level rise could lead to the migration of people from these effected regions to drier places, exposing them to the contaminated groundwater the drier areas (Mitchell et al. 2011). The groundwater of coastal regions themselves may not be safe from metallic contaminants under the climate change regime. Sea water intrusion will not only increase salt concentration of groundwater but will also enhance inorganic contaminants. It has been reported that As levels in groundwater will be positively impacted by sea water intrusion (Sherif and Singh 1999; Lin et al. 2006; Mitchell et al. 2011). As gets enriched in the groundwater due to anion exchange with Cl^- in the shallow aquifers (<30.5 m; Mitchell et al. 2011). Sea water intrusion also has the potential to release a number of other ions like U^{4+}, U^{6+}, Mn^{2+}, Ni^{2+}, Cr^{2+} and Pb^{2+} into the groundwater through ion exchange (Mitchell et al. 2011).

In fact, sea water intrusion can also contaminate the deeper aquifers with As, which at the moment are As safe (Mitchell et al. 2011). Moreover, surface flooding of alluvial crop fields due to rain will release even greater amounts of As and other metals like Mn, due to the creation of stronger reducing conditions, anion exchange and mixing of deeper and shallow aquifers (Mitchell et al. 2011). The coastal regions in the state of West Bengal, India are bound to be the most severely affected in this regard. Considering the threat of sea water intrusion, another highly vulnerable region is the Godavari delta of India (Bobba 2002). A simulated study using a "Saturated-Unsaturated Transport" (SUTRA) model predicts that due to the combined effects of climate change induced sea level rise and anthropogenic abstraction, a significant advancement in sea water intrusion can be expected in the Godavari deltaic region (Bobba 2002).

3.7 Implications for Agriculture

Due to water quality degradation, there may be an unprecedented change in the agriculture patterns of the country. Greater evapotranspiration due to rising temperature could lead to the development of saline groundwater in drier regions of India (Misra and Mishra 2007; Subba Rao 2008). In the Guntur district of Andhra Pradesh, south India, extensive irrigation, saline groundwater recycling, return flow due to irrigation coupled with higher fertilizer usage has further increased the groundwater concentrations, slowly making it unfit for irrigation or drinking (Subba Rao 2008). Similarly, in north India, the alluvial plains of Ganga, which bears the burden of a significant portion of our agricultural produce is slowly experiencing a case of increasing salinity (Misra and Mishra 2007). The problem has equally affected the shallow as well as the deeper aquifers of the region. The main reasons have been reported to be the canal network and climate change, while irrigation induced salinity has also been detected in some parts of the Ganga plains (Misra and Mishra 2007). Coastal regions with the additional danger of salt water intrusion may experience more hardships in the future in relation to agricultural productivity (Tajul Baharuddin et al. 2013).

Climate change leading to extreme events of rainfall could lead to the washing off of bound nutrients in the soil like phosphates and trace elements, leading to the loss of nutrients for agricultural purposes (Narula and Gosain 2013). The washed off nutrients ending up in surface water bodies may eventually result in unwanted after effects like Eutrophication and algal blooms. The excess of fertilizers could also result in the growth of unwanted weeds, detrimental for the economy of the country. In addition, rise in temperature will lead to the growth and establishment of previously unencountered species of weeds (Peters et al. 2014).

3.8 Socio-Economic Implications

Degrading water quality due to climate change has the ability to change the face of existing geopolitics. One of the most serious outcomes could be the transboundary environmental migration of illegal populations (Reuveny 2007). A good example is the illegal migration of Bangladeshi natives into India under a number of environmentally induced conditions related to water quality (Reuveny 2007). Prominent among them would be the As epidemic, which has degraded a number of Bangladesh aquifers (Chakraborti et al. 2002; Ravenscroft et al. 2005), and also the salt water intrusion in the coastal aquifers of Bangladesh due to sea level rise (Rahman et al. 2000; Bahar and Reza 2010).

Water quality degradation can also lead to disputes at national and international levels. Irrigation has been traditionally the most important source of agricultural water source in the drier south India (Anand 2007). In this regard, one of the most prominent conflict, which has constantly made to national headlines is the Cauvery river water dispute between the states of Karnataka, Tamil Nadu, Kerala and Puducherry (Anand 2007). As the number of droughts has increased since the 1980s, the positions of the states, especially Karnataka and Tamil Nadu have been hardened. When the Cauvery Tribunal was constituted in June 1990, it asked the Karnataka government to release 250 TMCft (thousand million cubic feet) of water to Tamil Nadu, leading to widespread violence and the death of 25 people in Karnataka (Anand 2007). As climate change will bring more weather extremes of dry spells and intense rainfall, which could degrade surface water quality, it will greatly affect the future of water policies and the fate of common man in India.

India's plan to connect the water surplus rivers of North and Northeast with the water deficient rivers of the Western and Peninsular region (National River Linking Project) has been making a lot of headlines (Wirsing and Jasparro 2007). Although the primary focus is on the water quantity, the project also aims to provide better quality water to every part of India to remove the water scarcity. However, if this project comes to fruition, the water availability in neighbouring countries will be severely affected (Wirsing and Jasparro 2007; Whitehead et al. 2015b). Declining water quality due to climate change will severely affect the current status of existing treaties like the Indus Waters Treaty (IWT) of 1960 signed between India and Pakistan (Wirsing and Jasparro 2007). Both countries are already hostile towards each other, and recently, there has been growing dissent against the IWT; critics from both countries point that the treaty is outdated and should at least be amended if not completely scrapped (Wirsing and Jasparro 2007).

3.9 Steps to Be Taken

Sustainability of water resources in the context of climate change is a challenge, one of the reasons being that the number of stakeholders involved is high, including displaced populations, farmers, environmental agencies, economic development organizations, the scientific community and also the government (Mujumdar 2008). Another important factor is to identify and address the lacunae that exist currently in the broader sphere of water sustainability in the context of climate change. It is imperative that different stakeholders act as partners while working to address the various existing shortcomings. Taking the above factors into account, the current review would like to divide water quality sustainability initiatives under three broad subcategories.

First and foremost, scientific research and developments will continue to play a vital role in the future sustainability of our water resources. Traditionally, the majority of the studies on water quality has highlighted a single contaminant or at best a few contaminants. For example, the arsenic problem in India and in many other parts of the world is already documented (Smedley and Kinniburgh 2002; Harvey et al. 2005; Ravenscroft et al. 2005; Kumar et al. 2010), similarly others like fluoride (Gupta et al. 2005; Fordyce et al. 2007; Rao 2009; Fantong et al. 2010; Reddy et al. 2010; Sarma and Sunil 2010; Raju et al. 2012) and uranium (Tripathi et al. 2008; Jurgens et al. 2010; Gupta and Sarangi 2011; Sethy et al. 2014) have received widespread attention. However, the need of the hour is getting a deeper insight into the behavior of different classes of contaminants with each other in response to climate change induced alterations in water and soil parameters like pH, organic matter, temperature, microbial community etc.

An important class of pollutants called emerging pollutants has recently received some attention. These are described as new chemicals, which do not have any regulatory status and the impact of which on environment and human health is still poorly understood (USEPA 2008). As per review on the Indian scenario, more than half of the studies concerning emerging contaminants are on pesticides (57%), followed by pharmaceuticals (17%), surfactants (15%), personal care products (PCPs, 7%) and phthalates (5%) (Gani and Kazmi 2017). Cities like Hyderabad have been found to be severely affected by pharmaceuticals; some of them like triclosan and parabens have been reported to represent high risk out of the PCPs (HQ > 1). The review also reveals that only five classes of emerging contaminants have been studies in India, others like estrogen have not been reported anywhere (Gani and Kazmi 2017). More focus should be laid on the study and understanding of such pollutants, especially in the context of climate change, as they are going to be important pollutants to rekon with in the near future.

Models can go a long way in presenting a predictive analysis of the different scenarios, which may arise due climate change. As such, they can be of great assistance to scientist in carrying out future research, and policy makers in forming decisions (Mondal and Mujumdar 2015). However, there are serious limitations. First of all, models are not a reality, most of the models used are based on economics, which give broad assumptions by analyzing patterns of global fossil fuel usage over a timeline (Maslin and Austin 2012). However, economies can fail anytime, as seen during the economic collapse of 2008, and therefore it is very difficult to make predictions solely based on economy (Maslin and Austin 2012). One of the key aspects is that different models give different predictions based on their designs, and how the key processes like effect of clouds etc. are "parameterialized" (Maslin and Austin 2012). Often outputs of the general circulation models are used to run regional models, resulting in large scale uncertainties due to difference in precipitation over smaller scale of time and space. The same study also concludes that the "projected regional models" form the basis for 'impact models' in estimating the quality of human life. However, in the long run, it is the relative resilience of a particular society that matters more than the magnitude of environmental change (Maslin and Austin 2012).

The ability of climatic models to predict extreme events has also been widely debated, some arguing that with time, climate prediction models are getting better at predicting extreme events, while others state that climatic models are just too stable to fail and therefore would never be able to predict such changes (Maslin and Austin 2012). However, in spite of all the shortcomings, models will always be an important part of climate research. A good example is that predicted rise in global temperatures with doubling of CO_2 emission has not changed a lot in the last 20 years (Maslin and Austin 2012). With time and research, climate models should continue to improve and help in making better predictions, the rule of uncertainties notwithstanding.

More effective treatment and purification options for water can go a long way in its conservation. Although the domain has progressed tremendously, there is still a lot of scope to improve existing techniques and develop better ones. At present the most commonly used techniques are membrane filtration technologies like ultrafiltration, reverse osmosis and nano filtration (Fu and Wang 2011). Focus should be on the development of materials which can remove more than a single class of pollutants, for example, "perfluorous conjugated microporous polymers" (PCMP) can remove a wide variety of pollutants like oils, dyes, trace elements etc. The aforementioned study showed that a synthetic PCMP named PFCMP-0 had higher adsorption efficiencies for Congo red, a known carcinogen (1376.7 mg/g), Pb (II) (808.2 mg/g) and As (V) (303.2 mg/g) than majority of the porous materials described previously. Therefore, a major component of sustainable water use under the effect of climate change is to develop better technologies for water purification.

Policies and legal framework will always be important, as they provide the structure and guidance to the people across different platforms, ranging from the local community in a township to the entire world. Any act, law or policy will have serious implication on the status of water in the future. For example, although initiatives like the National River Linking Project promise to solve the water crisis of the country, it is important to analyse the outcome pragmatically. Waters of different rivers have different physico-chemical properties. Currently, not much thought has been given to the outcome of mixing such different river waters. Probable negative outcomes could be on the existing biodiversities of the different rivers, which depend on the unique physico-chemical characteristics of each water system. While pollutants from more contaminated rivers could be transported to less polluted ones, change in physico-chemical properties could also lead to the release and mobilization of trace elements and other contaminants. Moreover, overall recharge of other reservoirs like groundwater etc. could be affected or get limited due to net decrease in water quantities of water surplus rivers. As temperature increases and precipitation patterns become extreme, there is every possibility that regions with water surplus like the Northeast may be affected. Lastly, downstream countries who are reportedly affected by water stress, may face various implications. This in the longer run could result in higher incidences of undesirable events like environmental migration, which could be detrimental for India.

Use of agrochemicals like fertilizers and pesticides is very high in India, being mainly an agricultural economy. One review concludes that the India is one of the highest contributors of persistent organic pesticides in the world (Yadav et al. 2015). To tackle the problem, India has taken a number of steps. India introduced the integrated pest management (IPM) approach first in cotton and rice crops (Swaminathan 1975). Government of India has implemented various regional level IPM programs under three stages: (1) in the first phase the emphasis is on the authenticity of the technology involved, and on expanding the pilot scale initiative among the farmers, (2) the second phase deals with training and human resource development under a full time training program for the farmers called 'IPM FFS' and lastly (3) the third phase involves institutionalizing the IPM approach into the government structures (Yadav et al. 2015).

India has also developed a National Implementation Plan (NIP) as per the requirement of the Stockholm Convention on persistent organic pollutants (SCPOPs). Some of the top priorities of the NIP include: (1) developing and implementing non-persistent organic pesticides as alternatives to DDT, (2) developing separate mechanisms to deal with POP pesticides, (3) implementing best available technique (BAT) and best environmental approach for eliminating and reducing unintentional POP pesticides from industries, (4) promotion of neem based bio-pesticides, (5) identification of sites contaminated by POP pesticides and potential hotspots, (6) raising and creating awareness on POP pesticides in India, (7) implementation of a national POP pesticide monitoring program has been suggested and (8) institutes involved in pesticide research and capacity building should be strengthened to enable efficiency and effectiveness of the NIP (Yadav et al. 2015).

Six internationally legally binding treaties have been negotiated and concluded, but India has signed and ratified only three of them (Table 3.3, Yadav et al. 2015). Most important among these is the UNECE protocol on POPs, on Long Range Trans boundary Air Pollution (CLRTAP), adopted in June 1998, but India is yet to become a member. India is a signatory to the Stockholm Convention on Persistent Organic Pollutant (SCPOPs), and since 1998, has involved itself actively on various negotiations under the SCPOPs. Despite setting up a National Steering Committee (NSC) under Ministry of Environment and Forest (MoEF) to ensure its participation in the Intergovernmental Negotiating Committee (INC) involved in international

Table 3.3 India's status on conventions on POPs

International conventions	Parties	Rationale	India's status	Adopted	Ratified
Virtual Elimination of Persistent Toxic Substances in the Great Lakes	Canada, United States	To promote emissions reductions of toxic substances	–	–	–
North American Agreement on Environmental Cooperation (NAAEC)	United States, Canada, and Mexico	To develop regional initiative on the sound management of chemicals	–	–	–
Basel Convention on the Transboundary Movement of Hazardous Waste and the Subsequent 1995 Ban Amendment (Basel Ban)	163 nations	Import and export of hazardous waste	Signed and ratified	1989	1992
United Nations Economic Commission for Europe (UNECE) on POPs under the Convention on Long-Range Transboundary Air Pollution (LRTAP)	United States, European countries, Canada, and Russia	Elimination of production and reduction of emissions of POPs in the UNECE region	–	–	–
Rotterdam Convention on the Prior Informed Consent (PIC) Procedure for Certain Hazardous Chemicals and Pesticides in International Trade	United States, along with 71 other countries	Import and export of hazardous chemicals	Signed and ratified	2002	2004
Stockholm Convention on Persistent Organic Pollutant	149 countries	Production, use, and disposal of persistent organic pollutants	Signed and ratified	2002	2006

action on POP pesticides, India is yet to take progressive decisions, foremost being the unabated use of DDT, which has been banned internationally in a majority of countries. In other words, our laws and regulations are in need of amendments and there should be stricter enforcement. Farmers are the most vulnerable to pesticide pollution as usage directions are rarely followed, safety equipments are lacking and most of the users are highly untrained (Yadav et al. 2015). Stricter regulation will definitely reduce the burden of POPs and other contaminants on water in the long run.

Water must be assigned due priority on the international platform. While major focus is on clean and sustainable energy, pollution etc. sustainability of water resources has not received due attention. A standalone Sustainable Development Goal on water and sanitization (SDG 6) was adopted on 25th September 2015 as part of the Paris Accord. But closer examination reveals that there was no clear mention of water resources in the climatic change negotiations (Damkjaer 2015). The lives of millions will be at stake due to degrading water quality as a consequent of climate change, and it could also be the cause for future conflicts (Baten and Titumir 2016).

The greatest onus, however, will lie on the general population, the ones who will be affected the most by water degradation and scarcity in the future. Increasing awareness among farmers about correct doses of fertilizers, about banned pesticides, protective clothing/gear and the overall dangers of using excess agrochemicals will not only protect their health but will also help in protecting our water bodies (Yadav et al. 2015). Currently, use of pesticides has relatively decreased in India, after many of them were banned. Yet, residual levels in air, water and soil are still remains high due to previous unrestricted use (Yadav et al. 2015). Conscious efforts by the farming community will directly bring down the frequency and intensities of algal blooms, eutrophication and accidental exposure to pesticides and other agrochemicals.

It is very important to optimize the use of water in industries, as it can lower the withdrawal and put lesser pressure on the reservoirs. It has also been revealed that industries put more pressure on water bodies by wastewater discharged than by the amount of fresh water used during production (UNESCO 2009). These wastewaters not only contain toxic trace elements, microbes etc. but can also cause thermal pollution due to their higher temperature (Kennish 1992). One of the first things industries can do is to create awareness among the employees themselves. The training protocols have to be updated constantly. In fact, a number of for-profit companies and universities are currently engaged in designing competitions and "feedback mechanisms" to create awareness among users about water and energy use in the real time (Melton 2011). Operational changes involving updates to machinery and replacing faulty equipment on regular basis should be made essential. Lastly greater emphasis on recycle and reuse would not only reduce the burden on water bodies but will also lead to lesser pollution.

In today's world, the society is unified by common interests and collective activities which determine their future. Such a group of individuals are together termed a civil society (Bouman-Dentener and Devos 2015). Civil Society pillar of the 2015 UN Water Annual Conference (Bouman-Dentener and Devos 2015), can be very helpful in making the post-2015 development agenda on water a success. The main aim of the civil society initiative is on the developing countries. The highest impact that a civil society will have on the rural scene is by improving sanitation, and the ecosystems in the watershed (Bouman-Dentener and Devos 2015). This is an important consideration as traditional indigenous tribal communities have access to 22% of the world's land surface which hold 80% of the total biodiversity (Sobrevila 2008). Civil Society as a whole can help in reaching sustainability goals by the following ways: (1) by holding the government accountable and enabling that the needs of the local communities are addressed in national policies and plans. They can also ensure the mobilization of necessary resources so that local communities can take adaptive actions. (2) Civil Society organizations can be involved in technology intervention necessary for sustainable solutions. (3) By building capacity of the local communities and (4) facilitating financing.

3.10 Conclusion

One of the first influences of climate change will be the increased acidification of water bodies, as wetter winters and higher intensity of rainfall is predicted to increase SO_2 deposition in India. Industrialized cities like Delhi are at greater risk. Temperature rise will reduce the dissolved oxygen content while BOD will continue to rise. Shallower lakes, especially high altitude lakes may develop permanent anaerobic zones due to stratification brought about by temperature rise.

Fertilizer usage in India is already high, increased intensity in rainfall will wash off excess nitrate and phosphates to surface water, which has already observed in the northern Yamuna catchment area. Both wet and dry deposition of various oxides of nitrogen is bound to increase, while, degradation of nitrates and sulphates will be prevented by the prevalent oxic condition. Potentially the Ganga River system appears to be at greatest risk from anthropogenic activities.

Diseases and toxins will become major problems under the changing climate regime. Intrusion of *Vibrio cholerae* contaminated sea water during low flow conditions, and inundation by the contaminated water during high flow conditions could occur in coastal regions. Dengue and Japanese encephalitis are predicted to take epidemic proportions in India, mainly due to uncontrolled urbanization, poor environmental sanitation, poor household/water storage practices etc. Drier periods followed by heavy rainfalls would lead to flushing of fecal matter to surface water bodies, which may ultimately leach to groundwater. As such there will be an increased frequency of diseases like echinococcosis, taeniosis, and toxoplasmosis.

Biological toxins from algal blooms will increase as nutrients become more concentrated in the water bodies. The estuarine and the "exclusive economic zones" (EEZ) are currently under threat from harmful algal bloom, the cause of which has been speculated to be climate change to some extent. As temperatures rise, Dinoflagellates will be able to move towards deeper layers seeking nutrients once thermal stratification occurs in the upper layers as a result of climate change.

The states of Punjab and Haryana are expected to be hit most severely by solvent depletion induced POP and pesticide concentration of groundwater, as the climate of the region is already semi-arid and groundwater use is high due to high agriculture activities. Wet deposition of POPs will rise under increased intensity and periods of rainfall. POPs like hexachlorocyclohexane (HCH) and toxaphene will be partitioned more into the aquatic bodies under higher rainfall. Places at higher altitudes will be affected by long ranged atmospheric transport (LRAP) of POPs and other toxic contaminants as volatilization increases with temperature. Temperature rise will release the adsorbed POPs from the glacier ice, as they melt. The Himalaya-Hindi Kush region of Asia, which supplies water to about 50–60% of the world's population will be the most critically effected by this phenomenon.

Temperature rise could also enhance the release of higher amounts of inorganic toxicants like As from Fe (hydr) oxides. The most likely regions to be effected are those in the Ganga-Brahmaputra flood plains of India, where As has already been detected, while, drier aquifers will favor the release of F^- and U, in groundwater. But the contamination due to U will also depend on the availability of its minerals like uraninite (UO_2), pitchblende (U_3O_8), autunite ($Ca(UO_2)_2(PO_4)_2 \cdot 10–12H_2O$), uranophane ($Ca(UO_2)_2SiO_3(OH)_2 \cdot 5H_2O$) etc., which are not as widely distributed as As and F^- bearing minerals. In the coastal regions, sea water intrusion due to climate change could also lead to release of As and other trace elements through ion exchange, it has been predicted that both shallow and deeper aquifers will be equally affected. The regions along the coast of West Bengal are especially vulnerable in this regard.

Degrading water quality could also put pressure on agriculture. The northern plains of Ganga, which is a major agricultural zone of India, have been slowly experiencing increased salinity in response to rise in temperature and the massive network of canal. Coastal regions also suffer from the same plight due to salt water intrusion, making the groundwater unfit for irrigation. Increased intensity of rainfall is also likely to wash off essential nutrients from the crop fields, thus decrease their availability for essential activities.

Climate change will also increase conflicts over water sharing, and water constraint related migration, both at the national and international levels, high As contamination combined with sea level rise and subsequent salt water intrusion of the Bangladesh aquifers will increase the influx of illegal environmental migrants to India. Similarly, the Indus Waters Treaty (IWT) signed between India and Pakistan in 1960 has come under increased scrutiny as there is decrease in the quantity and degradation of quality of the river water, and the problem is compounded by the fact that there is spurt in population growth and water demand increase in both the countries. In India, Cauvery river dispute has time and again led to conflicts among stakeholders.

Thus, climate change is predicted to have drastic impacts on the quality of the Indian water reservoirs, which will lead to far flung changes. Sustainability will be possible through the collaborative efforts of the scientific community with policy makers and the common people, which would include farmers, industrialists and their employees and, finally the general public. Scientific advances will continue to improve our knowledge and understanding of the situation, resulting in the development of better modelling techniques for future prediction and also helping us directly through the improvements in water purification and treatment technologies. Focus of current and future studies should be placed on understanding co-contaminant behaviours in aquifers along with emerging contaminants. Lastly policies and legislature should be updated with time to deal with the legal framework, moreover, handing the community greater power to control the various natural resources would lead their better management and conservation.

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Chapter 4
Review on Occurrence and Toxicity of Pharmaceutical Contamination in Southeast Asia

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4.1 Introduction

Pharmaceuticals include any substance or mixture of substances manufactured, sold, or represented for use in the diagnosis, treatment, mitigation, or prevention of a disease, disorder, abnormal physical state, or its symptoms in human beings and/or animals. Their widespread use results in the entry of a wide palette of pharmaceutically active compounds into wastewaters around the globe (Bartelt-hunt et al. 2009; Karthikeyan and Meyer 2006; Lin et al. 2018; Loos et al. 2013). These pharmaceutically active compounds encompass a rather large umbrella of drug classes, ranging from over the counter drugs such as analgesics and non-steroidal anti-inflammatory drugs, to drugs that require a prescription such as, antibiotics, anti-epileptics, anti-anxiety and anti-depressants, contraceptives, drugs for lifestyle diseases, and anti-cancer drugs (Enick and Moore 2007). Other than drugs used in human healthcare, pharmaceuticals are also widely used for maintaining livestock,

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poultry, and aquaculture. Veterinary medicines also contribute to the total pharmaceutical loading in wastewater (Halling-Sorensen et al. 1998).

Pharmaceuticals are designed to induce various physiological and biological alterations in the body, so it comes as no surprise that they are toxic at high concentration, i.e., concentration of the order of mg/L. Acute effects caused by various pharmaceuticals are well documented. Discharges from wastewater treatment plants (WWTP) and the final concentration of pharmaceuticals in surface water after substantial dilution were earlier thought to be negligible. Detection of such low concentration of pharmaceuticals in complex environmental matrices also posed a challenge (Mohapatra et al. 2018). Hence, these compounds were not part of environmental monitoring policies until recently. However, since the last decade there is growing concern regarding the chronic effects of pharmaceuticals due to observation of sex reversal in male fish communities near sewage treatment plant discharge points and rivers in the U.K. and the U.S. The World Health Organization (WHO) designated these under "emerging pollutants" or "micropollutants", which consisted of a wide array of organic pollutants including certain pharmaceuticals, pesticides, ingredients in cosmetics, and personal care products and plasticizers. These pollutants were observed to be recalcitrant, persistent in the environment, and exhibited long-term toxic effects even when present at low concentration (Mishra et al. 2018).

Southeast Asian countries are a hotspot for pharmaceutical manufacturing and also have a growing market for pharmaceutical consumption. The countries of Southeast Asia, especially the members of the Association of Southeast Asian Nations (ASEAN: Brunei, Burma, Cambodia, Indonesia, Laos, Malaysia, the Philippines, Singapore, Thailand, and Vietnam), have been keen since the past decade towards seeking proper and holistic regulation of pharmaceutical and medical-device industries. Since these countries vary significantly in their stages of development, there are huge voids in the availability of monitoring, toxicology and fate data. Regulation of pharmaceuticals may be feasible only when there is ample toxicology data, especially for indigenous species and/or for universally accepted biomarker species. However, a major pitfall while using universal biomarkers is that these species are innate to American and European waters. Southeast Asian countries, being tropical may harbor hardier and more resistant aquatic organisms. In this regard, very few universal biomarkers, such as zebrafish (*Danio rerio*), are indigenous to Southeast Asia and hence, the studies may not be exhaustive or conclusive. Numerous chronic effects have been reported in the literature and the feminization of male species of fishes (Zhang et al. 2011) gained maximum public attention (Connor 1994; Hagerman 2009; Ian Johnston 2017; Konkel 2016). Other effects include deformation of limbs, and incomplete metamorphosis in amphibians and reproductive failure in planktons, cnidarians, mussels, mollusks, insects, fishes (Ferrari et al. 2003), and amphibians. These effects would not be immediately detectable. However, these may eventually cause gradual extinction of species (Mills and Chichester 2005).

The International Union for Conservation of Nature (IUCN) red list classifies most of the aquatic species indigenous to Southeast Asia as "no known major widespread threats" and are hence, considered more or less safe. However, due to lack of chronic eco-toxicological data for micropollutants other than some phthalates, personal care products, and pesticides, these species may be experiencing chronic effects, which may be unknown. There is, therefore, an urgent need to conduct a more holistic monitoring of occurrence, fate and toxic (acute and chronic) effects of pharmaceutical residues in Southeast Asian countries. This section aims to collate the available data on the occurrence of selected pharmaceuticals in various aquatic compartments, such as, wastewater influents and effluents, surface water and marine environment.

Using the available occurrence data, a comprehensive literature review on the eco-toxicological impacts on various freshwater species ranging from freshwater algae, rotifers, planktons, cnidarians, fishes, molluscs, mussels, and amphibians is conducted. Since accurate measurements of toxicity in aquatic animals of Southeast Asia are currently not exhaustive, universal biomarker studies were used to plot species sensitivity distributions (SSD) for the selected pharmaceuticals. SSDs are models that depict the sensitivity of various species to a particular contaminant. The species that are affected based on the concentration of selected pharmaceuticals reported in wastewater effluents and surface water in Southeast Asian countries were subsequently determined.

4.2 Consumption of Pharmaceuticals

With increasing clinical trials, Southeast Asia has become a hub for pharmaceuticals in recent years. With a population of about 620 million, 43% of the region's population live in urban areas, however, there is considerable dissimilarity between the countries (from 15% in Cambodia to 100% in Singapore) (Hashim et al. 2012). In addition to export of consumer electronics and information technology products, Singapore's economy is primarily controlled by growing exports from the pharmaceutical sector. The middle-income country, Malaysia has recently attracted investments in medical technology, and manufacturing of pharmaceuticals (JGCRI 2009). An overview of the total population and expenditure towards the health sector in various Southeast Asian countries is shown in Table 4.1. Among Southeast Asian countries, Vietnam (7.1%), followed by Singapore (4.9%) has the highest percentage contribution of their GDP in the health sector. However, the total per capita expenditure is highest for Singapore ($4047) followed by Malaysia ($1040). The household consumption on health sector followed the order; Indonesia ($3236), Thailand ($1614), Vietnam ($1471), and Philippines ($1185) (World Bank 2018). Globally, US has the largest market for pharmaceuticals with a value of $339,694 million followed by Japan ($94,025 million) and China ($86,774 million).

Despite major changes and improvements in the healthcare industry, infectious diseases are of major concern in Southeast Asian countries due to the growing number of deaths than in other parts of the World. In addition to poverty, overpopulation, increased bacterial resistance, and inadequate preventive health care system has increased the incidence of bacterial infections. According to WHO, infectious and

Table 4.1 Health profile of various Southeast Asian countries (WHO 2018)

Parameters	Malaysia	Singapore	Thailand	Indonesia	Philippines	Vietnam
Total population (2016) (million)	31	6	69	261	103	95
Gross national income per capita (PPP international $, 2013)	22	76	13	9	7	5
Life expectancy at birth M/F (years, 2016)	73/78	81/85	72/79	67/71	66/73	72/81
Number of individuals per 1000 dying between 15 and 60 years, M/F	156/86	65/38	203/91	205/146	244/141	182/66
Total expenditure on health per capita (Intl $, 2014)	1040	4047	600	299	329	390
Total expenditure on health as % of GDP (2014)	4.2	4.9	4.1	2.9	4.7	7.1
Household consumption on health (Nation, $) (2010)	–	–	1614	3236	1185	1471
Ischemic heart disease (%)	20.1	18	13.1	8.9	–	–

parasitic diseases account for 19% of total deaths in Southeast Asia, and only 3% in Europe and 5% in the Americas (Gupta and Guin 2010). The number of deaths due to communicable and not communicable diseases in Southeast Asia until 2002 was 5762 and 7423, respectively (Bandara 2005). Currently, there is a growing concern regarding the development of antibiotic resistance in these regions. An increase in resistance to doxycycline and chemoprophylactic treatment was reported in Southeast Asia (Papadakis et al. 2017). A shift from *Mycobacterium scrofulaceum* to more resistant *Mycobacterium avium* causing cervical lymphadenitis in children was reported to be of major concern (Sarma 2017). Again, an increase in resistance of malaria parasites to chloroquine, sulfadoxine/pyrimethamine, mefloquine and artemisinin was also reported (Sarma 2017). Similarly, development of antimicrobial resistance to infection causing bacteria, such as, *Acinetobacter baumannii*, and *Salmonella enterica* in Southeast Asian countries was reported to be of prime importance (Horby et al. 2013, Kumar et al. 2019).

With intensive aquaculture, agriculture, and animal husbandry (Kookana et al. 2014) there is evidence of potential input of pharmaceuticals, especially antibiotics to the aquatic environment. However, globalization has led to changes in lifestyle in

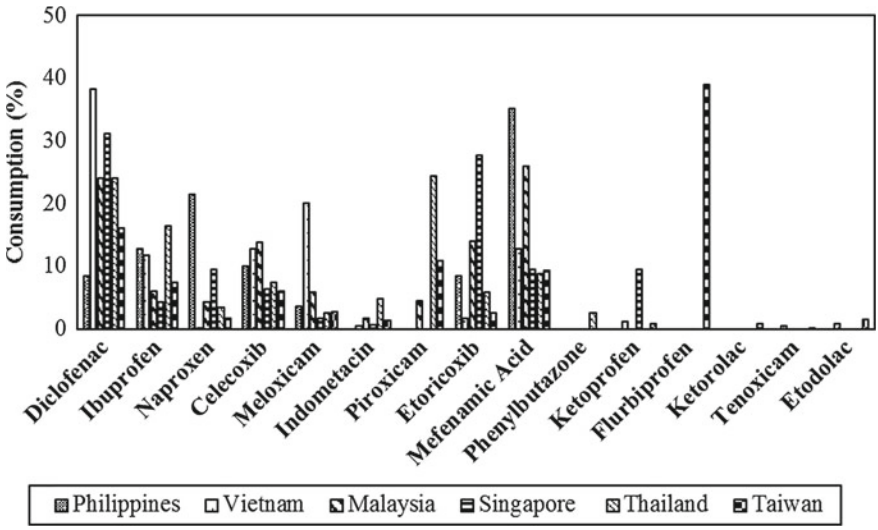
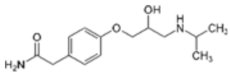
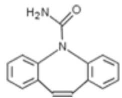
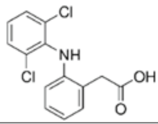
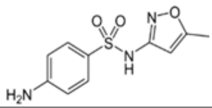
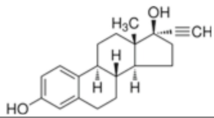


Fig. 4.1 Consumption pattern of NSAIDs in Southeast Asian Countries. Consumption of each NSAID is reported as % of total consumption of the listed NSAIDs in any country. This figure is prepared based on data reported by McGettigan and Henry (2013)

many Southeast Asian countries where a shift in food consumption pattern was seen, especially among Malaysians, Indonesians, and Philippinos (Lipoeto et al. 2013). Due to growing lifestyle-related diseases a variety of next-generation medicines have found their way into the environment. The percentage of deaths due to Ischaemic heart disease in Malaysia and Singapore were 20.1 and 18%, respectively (Table 4.1). Another study also reported widespread consumption of carbamazepine (CBZ) to treat childhood epilepsy in Singapore (Lester 2009). The consumption of CBZ in Vietnam was 2.8 g/day/1000 people (Nguyen et al. 2018). An extensive survey on consumption of Nonsteroidal anti-inflammatory drugs (NSAIDs) was conducted by McGettigan and Henry (2013) in various part of the world. Among various countries surveyed, the highest consumption of diclofenac (DCF) was observed in Vietnam, followed by Singapore and Malaysia (Fig. 4.1).

The tropical regions comprising of Southeast Asia, Africa and South America are known as biodiversity hot-spots for species richness, threatened species and diversity in endemic species. Hence, rapidly growing economy, growing aquaculture and livestock industries, increased incidence of infectious disease, and change in lifestyle in the Southeast Asian countries may result in increased load of pharmaceuticals being released into those hotspots. Such effects have previously been reported in the mangrove forests (Bayen et al. 2016). A detailed discussion on the occurrence of pharmaceuticals is discussed in the next section where the discussion is restricted to only 5 pharmaceuticals covering a wide range of classes. They belong to β-Blockers (atenolol), antiepileptics (carbamazepine), antibiotics (sulfamethoxazole), anti-inflammatory drugs (diclofenac), and hormones analogues

Table 4.2 Physicochemical properties and structure of selected pharmaceuticals

Pharmaceuticals	Molecular weight	Chemical formula	pKa	Log K_{ow}	Structure
Atenolol	266	$C_{14}H_{22}N_2O_3$	9.6	0.16	
Carbamazepine	236	$C_{15}H_{12}N_2O$	13.9	2.45	
Diclofenac	296	$C_{14}H_{11}Cl_2NO_2$	4.15	4.51	
Sulfamethoxazole	253	$C_{12}H_{14}N_4O_4S$	5.7	0.89	
17 α-ethinylestradiol	296	$C_{20}H_{24}O_2$	−1.7, 10.33	3.67	

(17 α-ethinylestradiol). These pharmaceuticals are widely reported across the world (Karthikeyan and Meyer 2006; Lin et al. 2018; Loos et al. 2013; Padhye et al. 2014, Kumar et al. 2019). The structure, chemical formula, pK_a values and log K_{ow} values are shown in Table 4.2.

CBZ is an anti-epileptic drug and about 72% of this compound and its metabolites are excreted via urine. This compound is reported to be very persistent in nature. CBZ, has a Log K_{OW} of 2.45, suggesting that its potential for bioconcentration in aquatic organisms is low. However, CBZ is fairly persistent in nature (Bouissou-Schurtz et al. 2014). Several researchers have reported the occurrence of CBZ in surface water in Southeast Asian counties.

Atenolol (ATN) is the most frequently prescribed medication for lowering blood pressure and for other cardiovascular diseases. It is prevalent in wastewater effluents and surface waters globally. Chinnaiyan et al. (2018) found that ATN was one of the most consumed pharmaceuticals. It was identified by the authors as one of the compounds that add substantially to the toxic load in the water. This conclusion was based on the number of prescriptions, reduced removal in WWTPs, and inherent toxicity. DCF and sulfamethoxazole (SMX) belonging to the category, nonsteroidal anti-inflammatory drug, and antibiotics respectively, were also considered along with 17 α-ethinylestradiol (EE2), a major component in birth control pills. Being a synthetic analog of the natural hormone, EE2 has gained much research interest as a potent endocrine disruptor. EE2 is an orally bioactive pharmaceutical and widely used in human and sometimes in veterinary medicine and aquaculture (Aris et al. 2014). Additionally, EE2 is resistant to biodegradation and can sorb to sediments, bioaccumulate in adipose tissues of animals and biomagnify along the food chain (Wit et al. 2010). All these selected pharmaceutics pose both acute and chronic toxicity as discussed later.

4.3 Occurrence of Selected Pharmaceuticals in Environmental Matrices

4.3.1 Wastewater Treatment Plants

Only limited research has been carried out on the occurrence of pharmaceuticals in Southeast Asian WWTPs. Out of 14 studies, 8 monitoring studies were conducted in Singapore and Malaysia. Two studies were conducted in Vietnam. Only one study each from Taiwan, Indonesia, Thailand and the Philippines are available. For the WWTP in Thailand, the reported influent and effluent concentration of ATN varied from 0.09 to 0.30 μg/L, and 0.005 to 0.06 μg/L, respectively (Tewari et al. 2013). However, in Singapore, the influent and effluent concentration of ATN varied from 3.19 to 4.62 μg/L and 0.15 to 0.35 μg/L, respectively (Tran and Gin 2017). The influent concentration of CBZ for the WWTPs in Singapore, Malaysia, and Vietnam varied from 0.004 to 2.02 μg/L (Tran et al. 2014; Tran and Gin 2017), 0.01 to 0.02 μg/L (Yacob et al. 2017), and 0.03 to 0.19 μg/L (Kuroda et al. 2015; Nguyen et al. 2018), respectively. Being resistant to biodegradation, there was no appreciable removal of CBZ at the selected WWTPs. Presence of CBZ in surface water is an indication of river water pollution caused by pharmaceutical discharges. DCF was detected in WWTPs located in Singapore (Tran et al. 2014; Tran and Gin 2017), Taiwan (Fang et al. 2012), Thailand (Tewari et al. 2013), Indonesia (Shimizu et al. 2013) and Philippines (Shimizu et al. 2013). Among Southeast Asian WWTPs, WWTPs in Singapore experienced DCF load in the range 0.003 to 0.95 μg/L (Tran et al. 2014; Tran and Gin 2017). Such a high concentration in the WWTP in Singapore was attributed to the lower per capita water consumption (151 L/day) compared to France (290 L/day), Norway (300 L/day), Spain (320 L/day), Italy (385 L/day) and the United States (500 L/day) (Tran and Gin 2017). It was also interesting to note that in Singapore, out of the various sources investigated, i.e., residential, hospital, commercial and industrial, a major portion of the total pharmaceuticals at WWTPs were primarily contributed by residential sources due to its high population density and separate sewer system. Except for WWTPs in Singapore and Taiwan, SMX was detected in all WWTPs for studies conducted in Southeast Asia. The highest influent concentration of SMX was reported in Vietnam WWTPs (1.72 μg/L) (Shimizu et al. 2013). Similarly, another WWTP

Table 4.3 Occurrence of pharmaceuticals in the WWTPs from various Southeast Asian countries (μg/L)

Countries	Inf./Eff.	Atenolol	Carbamazepine	Diclofenac	Sulfamethoxazole	17 α-ethinylestradiol
Malaysia	Inf.	n.d.	0.0092–0.018[a]	n.d.	0.01–2.23[a]	n.d.
	Eff.	n.d.	0.00549–0.125[a]	n.d.	0.004–0.028[a]	0.077–1.75[b]
Singapore	Inf.	3.185–4.602[c]	0.323–0.339 0.004–2.023[d]	0.318–0.390[c] <0.003–0.950[d]	n.d.	n.d.
	Eff.	0.155–0.355[c]	0.262–0.336[c]	0.271–0.394[c]	n.d.	n.d.
Taiwan	Inf.	n.d.	n.d.	0.152–0.185[e]	n.d.	n.d.
	Eff.	n.d.	n.d.	0.100–0.131[e]	n.d.	0.019[f]
Thailand	Inf.	0.092–0.304[g]	n.d.	0.058–0.367[g]	0.003–0.035[g]	n.d.
	Eff.	0.005–0.062[g]	n.d.	0.025 –0.182[g]	0.0025–0.089[g]	n.d.
Indonesia	Inf.	n.d.	n.d.	n.d.	0.282[h]	n.d.
Philippines	Inf.	n.d.	n.d.	n.d.	0.802[h]	n.d.
Vietnam	Inf.	n.d.	0.03–0.19[i], 0.041, 0.057[j]	<0.28[j]	1.720[h] < 2.6[j]	n.d.
	Eff.	n.d.	<0.05[b]	–	–	n.d.

Inf. Influent, *Eff.* Effluent, *n.d.* not detected
[a]4 different types of WWTPs (Yacob et al. 2017)
[b]Grab sample, extended aeration (Al-Odaini et al. 2013)
[c]Grab sampling, activated sludge process (Tran and Gin 2017)
[d]Grab sampling from the sewerage pipe, residential source wastewater (Tran et al. 2014)
[e]Composite sampling, preliminary WWTP (Fang et al. 2012)
[f]Grab sampling, activated sludge process (Chen et al. 2007)
[g]Grab sampling, activated sludge process (Tewari et al. 2013)
[h]Grab sample (Schimizu et al. 2013)
[i]Grab sample, activated sludge process and aerated ponds (Nguyen et al. 2018)
[j]Grab sampling, sequential batch reactor type WWTP (Kuroda et al. 2015)

in Malaysia reported the highest effluent concentration for EE2 (Al-Odaini et al. 2013). The occurrence of pharmaceuticals in various Southeast Asian countries is summarised in Table 4.3.

4.3.2 *Surface Water and Groundwater*

The occurrence of pharmaceuticals in surface water (river and lake water) in Southeast Asian countries is shown in Table 4.4. Among the pharmaceuticals studied, ATN and CBZ were only detected in Thailand (Tewari et al. 2013), and Singapore (Tran et al. 2014; Bayen et al. 2016). The concentration of DCF in surface water for Singapore and Thailand varied from 0.04 to 21 ng/L and 81.1 ng/L, respectively. Except for Singapore, SMX was detected in all other

Table 4.4 Occurrence of pharmaceuticals in surface water from various Southeast Asian countries (ng/L)

Pharmaceuticals	Malaysia	Singapore	Taiwan	Thailand[a]	Vietnam	Philippines
Atenolol	n.d.	n.d.	n.d.	49.5	n.d.	n.d.
Carbamazepine	n.d.	0.06–4.63[b] <0.3–53.5[c]	n.d.	n.d.	n.d.	n.d.
Diclofenac	n.d.	$\leq$0.04–1.7[b] <1.5–21[c]	n.d.	81.125	n.d.	n.d.
Sulfamethoxazole	76[d]	$\leq$0.06–6.26[b]	n.d.	21.75	26.25[e] 111[d]	44[d]
17α-ethinylestradiol	n.d.	n.d.	15.3[f] 0.35	n.d.	n.d.	362.5[g]

[a]Grab sample (Tewari et al. 2013)
[b]Year-long sampling (Bayen et al. 2016)
[c]Grab Sampling in the sewered catchment (Tran et al. 2014)
[d]Grab sample (Shimizu et al. 2013)
[e]Grab sampling (Managaki et al. 2007)
[f]Grab sampling (Chen et al. 2007)
[g]Grab sample from a lake (Paraso and Capatain 2012)

Southeast Asian countries with the highest concentration in Vietnam (111 ng/L) (Shimizu et al. 2013). As high as 362.5 ng/L of EE2 was detected in lake waters of Philippines (Paraso and Capatain 2012).

A comparative study on the occurrence of pharmaceuticals in groundwater from two catchment areas in Singapore: with and without sewerage connection was studied by Tran et al. (2014). The concentration of CBZ and DCF in groundwater of the sewered catchment ranged from <0.3 to 9.3 ng/L and <1.5 to 17 ng/L, respectively. However, lower concentrations of CBZ (<0.3 ng/L), and DCF (<1.5 ng/L) was reported in the Nation's non sewered catchment area. The concentration of CBZ in the samples collected from groundwater, tap water and bottled water in Vietnam varied from 0.25 to 0.49 ng/L (Kuroda et al. 2015). An attempt was made by Yang et al. (2014) to detect these compounds in tap water and fountain water. While the concentration of DCF was below the detection limit, the concentration of SMX was between 2 and 13 ng/L during a three year sampling period.

4.3.3 Marine Water and Sediment Samples

Only DCF and EE2 were detected in marine water samples from Taiwan at a concentration of 8.46 ng/L (Fang et al. 2012), and 0.43 ng/L (Chen et al. 2007), respectively. The concentration of CBZ and DCF varied between <0.3 to 10.9, and <2.2 to 9.1 ng/L, respectively (Bayen et al. 2013). In addition to direct discharges from the WWTPs, localized hydrodynamic flushing, and also hydrodynamic residence time of the contaminants strongly influences the retention time of pharmaceuticals in subsurface marine systems.

Several attempts were made to study the concentration of pharmaceuticals in sediment samples. The concentration of CBZ in sediment samples from Singapore varied from 0.001 to 1.3 ng/g (Bayen et al. 2016). Similarly, the concentration of CBZ and EE2 in samples from Malaysia and Taiwan varied from <0.12 to 5.88 ng/g (Omar et al. 2018) and 1.93 ng/g, respectively (Zhang et al. 2011). The concentration of DCF and SMX in river sediments from Malaysia were varied from 0.35 to 13.88 ng/g and <1.73 ng/g, respectively (Omar et al. 2018). Such concentrations were majorly contributed by domestic and industrial wastewater discharge and livestock activities along the river.

From the above discussion, it is evident that while few data are available relating to the occurrence and fate of the selected pharmaceuticals in Southeast Asian countries, studies related to eco-toxicological effects need more emphasis and is discussed in details in the following section. This realm has not been examined adequately.

4.4 Chronic Effect of Pharmaceuticals

Sub-lethal concentration of pharmaceuticals is sufficient to impart several chronic effects in aquatic organisms (Enick and Moore 2007). Additionally, due to their hydrophobic nature, pharmaceuticals can sequester in adipose tissue of animals and biomagnify along the food chain (Halling-Sorensen et al. 1998). The chronic exposure effects due to pharmaceuticals include endocrine disruption in aquatic organisms (Balakrishna et al. 2016; Shanle and Xu 2011) and creation of antibiotic resistance in bacteria (Balakrishna et al. 2016). However, a comprehensive approach towards chronic toxicity testing for pharmaceuticals is still scarce and these are difficult to detect, evaluate and manage under the current risk assessment policies in Southeast Asia (Enick and Moore 2007).

Hormone systems that can be affected by chronic exposure to pharmaceuticals include those in the hypothalamic-pituitary axis, including thyroid stimulating hormone, follicle stimulating hormone, adrenocorticotrophic hormone, prolactin, and growth hormone (Diamanti-Kandarakis et al. 2009). Pharmaceuticals are also reported to target and disrupt the neuroendocrine system, and male and female sex hormones, by mimicking them and binding to the corresponding receptors (Mills and Chichester 2005). The major chronic, as well as transgenerational effect of pharmaceuticals, is reproductive failure, stemming from endocrine disruption of reproductive hormones. Pharmaceuticals, owing to their similarity in structure to natural estrogen is mainly characterized by the presence of phenolic or benzene groups (Mishra et al. 2018; Ohko et al. 2002). Thus, they can bind to estrogen and androgen receptors and can act as mimics or antagonists of natural hormones, subsequently hampering normal hormone metabolism and synthesis (Soto et al. 1995). In this regard, it is important to point out that studies pertaining to reproductive effects in indigenous species of Southeast Asia are rather scarce and hence the data for universal biomarker species was used for generating toxicity estimates. These data points were further used to generate species sensitivity distributions (SSD) for selected pharmaceuticals. This aspect has been discussed in the final section. A description of the various chronic effects of selected pharmaceuticals on aquatic organisms is elaborated in the following section.

4.4.1 Atenolol

There are very few in-vivo toxicity studies for atenolol (ATN). Adverse histopathological alterations in the heart of *Oncorhynchus mykiss* (rainbow trout) in response to varying ATN dosage was studied by Steinbach et al. (2016). Moreover, since ATN undergoes negligible degradation in the human body, and has absorption of only 10%, a significant fraction is excreted as the parent compound. However, chronic exposure data, with emphasis on reproductive failure due to ATN is scarce. Some data is available for freshwater fishes that are primarily found in U. S. In one such study on fathead minnows (*Pimephales promelas*) (Winter et al. 2008), varying concentration of ATN (10–0.1 mg/L) was reported to cause negligible reproductive failure after an exposure duration of 21 days. However, as the exposure duration was increased from 21 to 28 days, the no observed effect concentration (NOEC) was reduced from 10 mg/L to 3.2 mg/L. This clearly indicates an exposure duration dependent effect of ATN on reproductive toxicity. However, the NOEC reported are orders of magnitude higher than environmentally relevant concentrations reported in Southeast Asia. More studies are required to validate this observation. Studies also indicate that ATN shows a very high acute to chronic toxicity ratio (ACR) >35 (Winter et al. 2008). Therefore, ATN may not be involved in endocrine disruption mediated reproductive failure in fishes.

4.4.2 Carbamazepine

Carbamazepine (CBZ) is reported to have anti-estrogenic effects and in-vitro studies with estrogen receptor positive human breast cancer cell line, MCF-7, have shown an inhibitory effect (IC_{50}) value of ~ 10.5 mg/L (Mishra et al. 2018). Many studies have reported that CBZ and its metabolites, after partial biodegradation, can have significantly high-risk quotient (RQ, determined as a ratio of measured environmental concentration to the predicted no effect concentration) in fish exposure studies (Chinnaiyan et al. 2018; la Farré et al. 2008). In a comprehensive study across WWTPs in France, Greece, Italy, and Sweden conducted by Ferrari et al. (2003), both acute and chronic toxicity was tested for a wide array of species ranging from bacteria, algae, microcrustaceans, and fishes. Chronic toxicity assays were conducted in algae (growth inhibition), rotifers, crustaceans and fishes (reproductive failure), and the NOEC and LOEC (lowest observed effect concentration) for CBZ were determined. Acute and chronic toxicity studies conducted with *Chlorella vulgaris*, *Daphnia magna* and the plant *Allium cepa* indicated that while CBZ may be classified as non-toxic with respect to acute toxicity, its chronic toxicity stemming from endocrine disruption poses a substantial risk (Jjemba 2006; Jos et al. 2003). For instance, Jjemba (2006) reported that in the same species, *Daphnia magna*, mobility inhibition under acute exposure occurred at a CBZ concentration of 77.7 mg/L for a 48 h exposure study, while that under chronic exposure occurred at 0.025 mg/L for a study with 25 day exposure. In a 10-day survival analysis of freshwater benthic organisms, viz., *Hyalella azteca* (amphipod) and *Chironomus tentans* (midge) exposed to CBZ, chronic effects (LC_{50}) of CBZ was obtained at 9.9 and 47.3 mg/L, respectively (Dussault et al. 2008). In general, amphipods were seen to be more sensitive than insects. Inhibition of antioxidant enzyme activity, glutathione levels and K^+-Na^+ ATPase activity in the gills of *Oncorhynchus mykiss* were reported after exposure to CBZ at environmentally relevant concentrations for 42 days (Li et al. 2009). Additionally, chronic exposure to sub-lethal concentrations of CBZ (0.2–2 mg/L) was also found to inhibit antioxidant enzyme activity in the brain of rainbow trouts (*Oncorhynchus mykiss*) (Li et al. 2010b) as well as in the intestine (Li et al. 2010a), as CBZ was found to generate excess reactive oxygen species, which led to oxidation of lipids and proteins. Similarly, 35-day exposure to sub-lethal concentration of CBZ in *Cyprinus carpio* was observed to be disruptive to transaminases, such as, glutamate oxaloacetate transaminase (GOT) and glutamate pyruvate transaminase (GPT); and lactate dehydrogenase (LDH) activities in gill, liver, and muscle (Malarvizhi et al. 2012).

4.4.3 Diclofenac

Diclofenac (DCF) has gained a lot of public and scientific interest. It is highly toxic and was found to be solely responsible for the near extinction of vulture species in the Indian subcontinent (Green et al. 2004). In-vitro studies in MCF-7 cells indicated that DCF caused anti-estrogenic effects (Mishra et al. 2018). The oxidative stress and various biochemical alterations induced by the commonly used non-steroidal anti-inflammatory drug, DCF, is well documented in a wide variety of organisms, some of which are also native to Southeast Asia. Some examples of toxic effects in organisms studied for DCF are oxidative stress in *Oreochromis niloticus*, (Ajima et al. 2016) and common carp (*Cyprinus carpio*) (Nava-Álvarez et al. 2014) and phospholipid level reduction in *Channa punctata*, native of southeast Asia (Padma and Devi 2016). Other than indigenous species, DCF related toxicity has been reported for a wide variety of organisms ranging from green algae, cnidarians, rotifers, amphipods, insects, fishes and amphibians (Ferrari et al. 2003). Cytological alterations upon exposure to has been observed in the liver kidney, and gills of rainbow trout (*Oncorhynchus mykiss)*, common carp (*Cyprinus carpio*)

(Triebskorn et al. 2007) and brown trout (*Salmo trutta* f. *fario*), after 28, 28 and 21 days, respectively. In zebrafish (*Danio rerio*), developmental abnormalities, cardiovascular and nervous defects were observed due to exposure of embryos to DCF (Chen et al. 2014b). Risk quotients (RQ) for DCF was observed to be ~ 15, which is indicative of chronic effects (Bouissou-Schurtz et al. 2014). DCF is also reported to bioaccumulate in rainbow trout and zebrafish (Memmert et al. 2013).

4.4.4 17-α Ethinylestradiol

It has been reported worldwide that the major estrogenic load in wastewater effluents and surface water is due to the presence of E2 and EE2, especially in Southeast Asia (Duong et al. 2010). Estrogenic effects of EE2 include sex-reversal (Sumpter 2007) and delay in sexual maturity in both males and females (Richardson et al. 2005). EE2 is known to affect both vertebrates and invertebrates. Although the mechanism of action and effects of EE2 are well documented in vertebrates, the role played by reproductive hormones in invertebrate hormonal control is not as clear. They were not expected to affect the reproduction and survival rates of insects or crustaceans since these organisms do not contain estrogen receptor-mediated mechanisms for reproduction. However, in studies with microcrustaceans, *Chironomus tentans* and *Hyalella azteca,* with 10 days exposure, EE2 has been reported to cause havoc at environmentally relevant concentrations (Dussault et al. 2008). A number of studies report EE2 induced toxicity such as, induction of vitellogenin in male fishes, decreased egg and sperm counts and reduced gamete quality (Aris et al. 2014; Richardson et al. 2005; Sumpter 2007). EE2 can directly or indirectly reduce the survival and growth in the early-life stage of various organisms. It may even affect reproduction (e.g., fertility and hatching success), and can thus cause an impact on the population level also (Singh et al. 2010). However, such studies are scarce in Southeast Asia.

4.4.5 Sulfamethoxazole

Sulfamethoxazole is a major, non-steroidal antibiotic and is used widely in veterinary medicine. While sulfamethoxazole (SMX) related endocrine disruption is scarcely reported, some studies suggest that SMX can chronically affect growth and mobility in *Hydra attenuata* (Quinn et al. 2008) and striped marsh frogs (Melvin et al. 2014). However, the chronic effects need to be examined in more detail in Southeast Asian waters.

A literature review conducted for the current study indicates that the aquatic faunal biodiversity in these systems is poorly understood, with respect to induced endocrine disruption and reproductive failure induced by pahramceuticals. Very few studies have been reported for species that are widespread and are more representative to Southeast Asian waters. A widely studied fish species is *Channa punctata* (Malarvizhi et al. 2012; Padma and Devi 2016; Pipil et al. 2015; Rawat et al. 2013). Chronic toxic effects measured in some other native species are given in Table 4.5. However, except for very few studies, most of the studies were not focused on reproductive failure or vitellogenin induction. These endpoints are important in assessing the sustainability of a particular species in the ecosystem. Therefore, these endpoints were used to generate typical species sensitivity distributions for the selected pharmaceuticals.

Table 4.5 Chronic effects reported for freshwater organisms specific to Southeast Asia

Species	Pharmaceutical	Endpoint	Exposure duration	Reference
Corbicula fluminea (Asian clam)	Fluoxetine	Gills and digestive gland enzymes	30 days	Chen et al. (2014a)
	Carbamazepine	Siphoning behavior, heat shock protein expression	30 days	Chen et al. (2014a)
Oreochromis niloticus	Diclofenac	Lipid peroxidation and antioxidant activity	60 days	Ajima et al. (2016)
Ruditapes philippinarum	Ibuprofen	Gill acetylcholinesterase and digestive gland superoxide dismutase	7 days	Milan et al. (2013)
Clarias gariepinus	Diclofenac	Immunological markers	42 days	Ajima et al. (2015)
	Chloramphenicol	Hematological parameters	15 days	Nwani et al. (2013)
	EE2 and diethylstilbestrol	Ovary steroidogenesis pathway	50 days post hatch	Sridevi et al. (2009)
Clarias batrachus	Flutamide and E2	Ovary-specific transcription factors, gonadotropin-releasing enzymes in the brain	50 days	Chakrabarty et al. (2012)
	EE2 and methyl-testosterone	Sex reversal	50 days	Mamta et al. (2014)
		Aromatase expression	21 days	Rajakumar and Senthilkumaran (2014)
Labeo rohita	E2	Aromatase expression	30 days	Gupta et al. (2017)
	Oxytetracycline	Hematological study	25 days	Ambili et al. (2013)
	Sulfamethoxazole, Albendazole, Doxycycline, Enrofloxacin, Ivermectin	Bioaccumulation	30 days	Reddy et al. (2013)

(continued)

Table 4.5 (continued)

Species	Pharmaceutical	Endpoint	Exposure duration	Reference
Cirrhinus mrigala (Indian major carp)	Diclofenac and clofibric acid	Enzymological parameters	35 days	Saravanan et al. (2013)
	Diclofenac	Total protein, carbohydrates, and lipids in gills, liver, and kidney	10–30 days	Binukumari et al. (2016)
Pomatoschistus minutus (sand goby)	EE2	Vitellogenin induction in males	4 weeks	Saaristo et al. (2009)
Heteropnustes fossils	E2, keto-testosterone	Histological changes in liver, gonads and sperm motility	45 days	Singh and Singh (2008)

4.5 Species Sensitivity Distribution of Selected Pharmaceuticals

Species sensitivity distributions (SSDs) are constructed by fitting a cumulative distribution function to a plot of species toxicity data against rank-assigned percentiles (Hose and Van Den Brink 2004). The fraction of species that may be potentially affected by exposure to a contaminant as indicated by the SSDs is useful for establishing threshold concentrations, commonly referred as NOEC or hazard concentration 5 (HC5) (Garner et al. 2015; Hose and Van Den Brink 2004). HC5 is the concentration at which only 5 percentile of the species are affected. Thus, HC5 is indicative of environmental concentration of the contaminant that most species can tolerate, such that the structure and function of the ecosystem are preserved. Since there is a lack of such studies in the Southeast Asian belt, these profiles generated using the database can be useful in assessing the chronic effects of pharmaceuticals in wastewater effluents and in surface waters. SSDs have been developed for a variety of pollutants/stressors, such as, pesticides, insecticides and engineered nanomaterials (Garner et al. 2015; Hose 2005; Hose and Van Den Brink 2004; Maltby et al. 2005). However, SSDs have not been developed specifically for the chronic toxicity of pharmaceuticals.

SSDs are derived based on the assumption that species toxicity data is a random sample from a population of ecosystem toxicity data that follows a normal distribution. Thus, limited toxicity testing for only a handful of species can allow extrapolation to a community level toxicity of a specific contaminant (Garner et al. 2015). The accuracy of SSDs may be refined as more data for various species is available (Newman et al. 2000). Generation of an SSD involves three major steps. Firstly, the selection of endpoints desired, followed by the gathering of single-species toxicity data for the desired endpoint (Garner et al. 2015). The process requires a list of exposure concentrations at which different species exhibit a standard response (EC_{50}, LC_{50} or LOEC) to the selected pharmaceutical. Further, the various species are ranked based on the species-specific response concentration selected for a pharmaceutical. Subsequently, these ranks are converted into proportions (Proportion = (Rank − 0.5)/number of species). Lastly, these proportions are transformed to a probit function, such that the probit is the inverse cumulative distribution function of the normal distribution with a mean of 5 (chosen such that all log probit values are non-negative) and have a standard deviation of 1. Finally, the mean concentration of the pharmaceutical versus the probit proportion is plotted to get the central tendency. Non-linear regression analysis and minimization of the sum of squared deviation from the central tendency values can cause 5% error (Garner et al. 2015). The chronic reproductive toxicity data of pharmaceuticals were thus used as inputs in the Species Sensitivity Distribution Generator provided by the US Environmental Protection Agency (USEPA) for generating the SSDs.

The endpoints considered for the development of SSDs were vitellogenin induction (LOEC) and reproductive failure (LOEC and/or EC_{50} values). The values and species chosen to generate the SSDs are given in supplementary information. These endpoints characterize the most prevalent and harmful chronic effect: sex-reversal and reproductive failure. Obviously, these effects can be instrumental in creating hermaphrodites and ultimately wiping out entire species (Mills and Chichester 2005). While there are other chronic effects such as neuroendocrine and thyroid dysfunction, many lower organisms do not possess the specific targets such as receptors and enzymes associated with these effects to generate the responses (Sumpter 2007). Hence, other studies relating to chronic exposure were not used for developing the SSD. The dataset consisted of a wide range of species ranging from freshwater algae (growth inhibition) to fishes, mussels, snails and in some cases, frogs. The species were selected based on the available data and also such as to include at least one species each of algae, invertebrate and vertebrates, in accordance with the European Medical Agency (EMEA) based on data availability and attempt was also made to include more holistic view of the chronic effect of the selected pharmaceutical (EMEA 2006). The single species reproductive toxicity data used were obtained from more than 40 published articles and the data included the half-maximal effect concentration (EC_{50}), median lethal concentration (LC_{50}), and lowest observed effect concentration (LOEC). The exposure time (96 h to 30 days) was dependent on the species and the endpoint chosen. Such varying time duration toxicity studies have also been used in the literature for generation of SSDs (Garner et al. 2015).

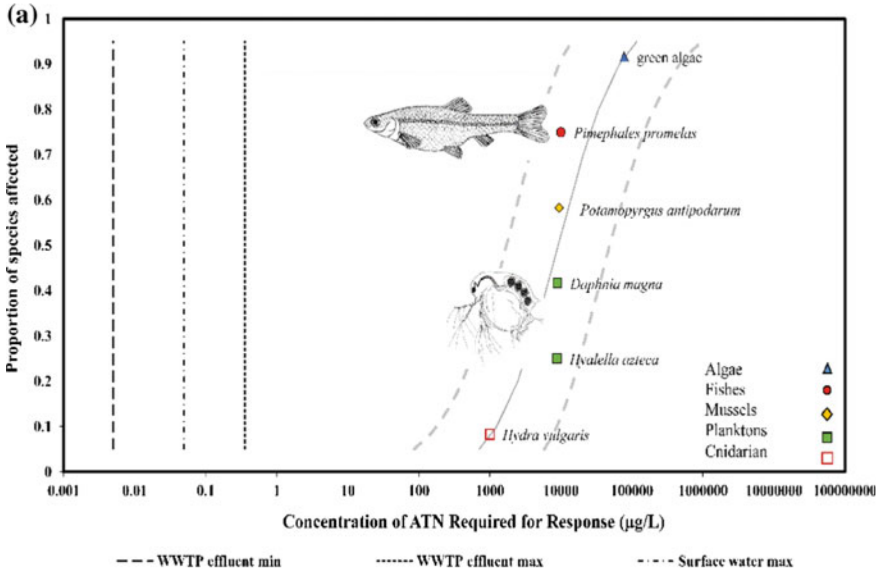
Figure 4.2a–e depict the SSDs of the selected pharmaceuticals and the species affected. The minimum and maximum concentration of selected pharmaceuticals reported in WWTP effluent and surface waters in Southeast Asia is depicted on the SSD (Tables 4.2 and 4.3). However, in some cases, the minimum values reported in case of surface waters were too low and hence, these are not shown on the SSDs. Generally, it was observed that SSDs differed according to the properties of the pharmaceutical. For instance, the range of concentration of pharmaceuticals in WWTP effluent stream and surface water for ATN and CBZ were observed to cause no effect in the species considered. However, concentration tending to maximum reported in WWTP effluents were observed to affect a small proportion of animals in case of DCF and SMX. All concentrations of EE2 reported were observed to cause reproductive failure and/or vitellogenin induction in the species selected for the study. From Fig. 4.2d, it is evident that the range of WWTP effluent concentration of EE2 reported in Southeast Asian countries can affect ~80–90 percentile of the species selected to generate the current SSD. However, due to substantial dilution in surface waters, the proportion of species affected was considerably reduced.

Additionally, for pharmaceuticals that depicted a tendency for bioaccumulation and sorption on sediments, such as CBZ and EE2, more adverse reproductive effects were seen in animals such as mussels and microcrustaceans. These benthic organisms are often found to associate with sediments. In addition to uptake from the aqueous phase, passive uptake of pharmaceuticals from resuspended sediment particles as well as from the sediment-water interface may affect these organisms. Thus, they may be affected even when the aqueous concentration is low. Further, microcrustaceans and mussels are known to have poorer detoxification machinery, as compared to fishes. Hence, bioaccumulation in such organisms may be several folds higher relative to fishes. In contrast, pharmaceuticals that are appreciably more hydrophilic, such as DCF, ATN, and SMX, are found to cause greater toxic effects in fishes compared to mussels and other sessile organisms.

It was observed that the concentration reported in WWTPs and surface waters of Southeast Asia corresponding to ATN and CBZ did not adversely affect reproduction in any of the universal biomarker species (Fig. 4.2b, c). However, the same pharmaceuticals may exhibit other chronic toxic effects that are outside the scope of this study. DCF and SMX are shown to cause vitellogenin induction or impair reproduction over the concentration range reported in wastewater treatment effluents. However, their effects were substantially reduced in surface water, owing to dilution and also partly, due to direct or indirect photolysis. Interestingly, EE2 was found to affect the largest population of organisms at the concentration of pahrmaceuticals reported to be present in both wastewater effluents and in surface waters in Southeast Asia. Endocrine disruption by EE2 is widely reported. EE2 is also known to be extremely resistant to processes, such as, biodegradation, and photolysis and can lead to significant bioaccumulation. Additionally, from the SSDs, while ATN, CBZ, DCF, and SMX are reported to cause reproductive failure and/or vitellogenin induction at concentrations of the order of µg/L, EE2 depicted such effects at 1000 fold lower concentration. There are some reports that also suggest that EE2 may be more potent than E2.

4.6 Summary

A comprehensive review on the occurrence of atenolol, carbamazepine, diclofenac, and sulfamethoxazole in Southeast Asian countries was performed and chronic toxicity of these pharmaceuticals in terms of adverse reproductive effects was discussed. Although very limited literature is available on the occurrence of pharmaceuticals in Southeast Asian countries, pharmaceutical load in surface water is expected to increase due to the growing consumption of pharmaceuticals with



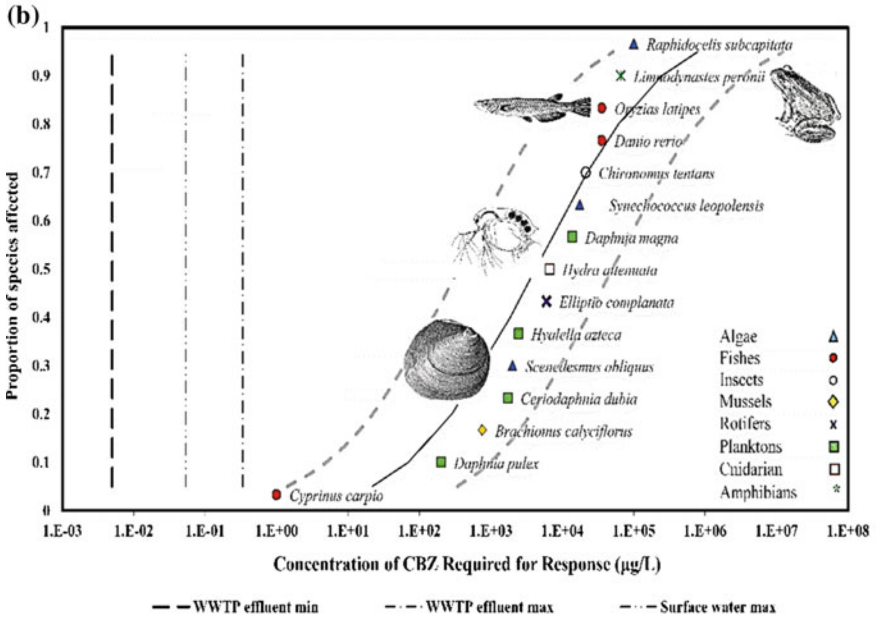
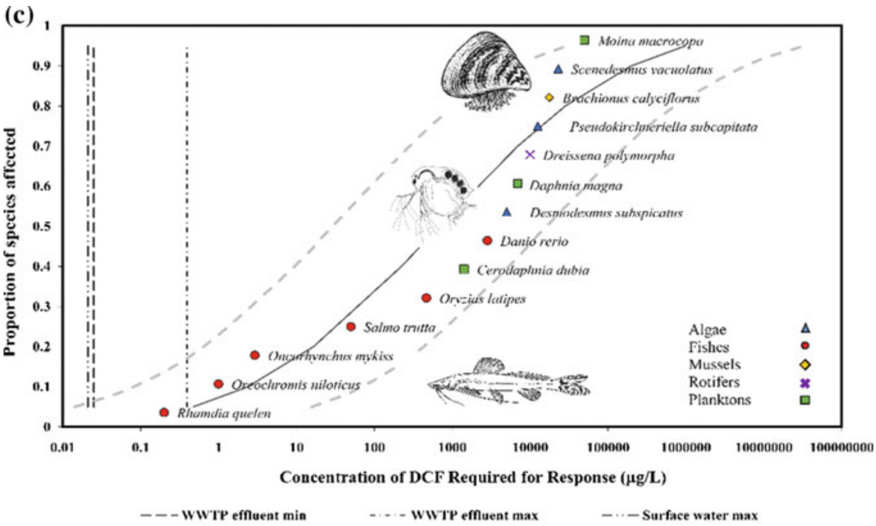


Fig. 4.2 SSD generated for **a** ATN, **b** CBZ, **c** DCF, **d** EE2, and **e** SMX showing the various species selected for SSD generation and mean environmental concentration (MEC) of selected pharmaceuticals reported in Southeast Asian waters



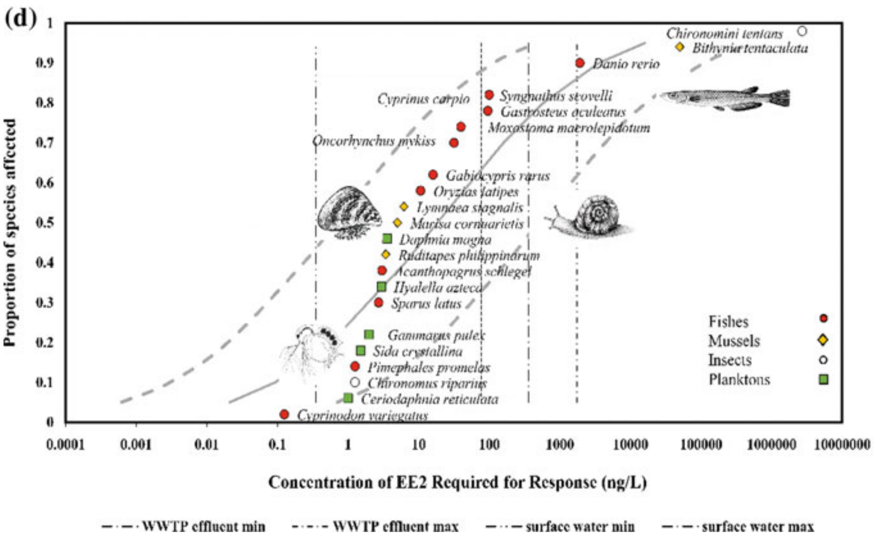


Fig. 4.2 (continued)

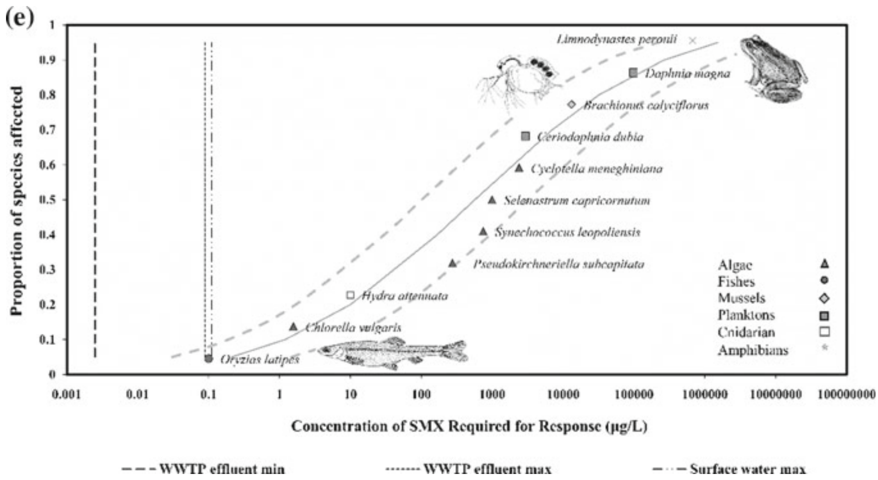


Fig. 4.2 (continued)

economic development and greater incidence of lifestyle diseases. In addition to human consumption, aquaculture and livestock production also contribute significantly to the load of pharmaceuticals in the aquatic environment in Southeast Asian countries. From the available literature, SSDs were plotted for all the studied pharmaceuticals. Among the pharmaceuticals studied, EE2 is predicted to impart reproductive failure and/or vitellogenin induction at concentrations in the order of ng/L, unlike other pharmaceuticals where similar effects were observed at concentrations in the range of μg/L.

Supplementary Information Chronic toxicity values in species used to generate SSDs of selected pharmaceuticals

Pharmaceutical	Species	LC_{50}/LOEC (μg/L)
ATN	*Potamopyrgus antipodarum*	9450
ATN	*Pimephales promelas*	10,000
ATN	*Hydra vulgaris*	1000
ATN	*Hydra vulgaris*	1000
ATN	*Hyalella azteca*	8820
ATN	*Daphnia magna*	8900
CBZ	*Synechococcus leopolensis*	17,500
CBZ	*Scenedesmus obliquus*	2000
CBZ	*Raphidocelis subcapitata*	100,000
CBZ	*Oryzias latipes*	35,400
CBZ	*Limnodynastes peronii*	65,700
CBZ	*Hydra attenuata*	5000
CBZ	*Hydra attenuata*	15,520
CBZ	*Hydra attenuata*	3760

(continued)

(continued)

Pharmaceutical	Species	LC_{50}/LOEC (μg/L)
CBZ	*Hyalella azteca*	600
CBZ	*Hyalella azteca*	9900
CBZ	*Elliptio complanata*	6000
CBZ	*Daphnia pulex*	200
CBZ	*Daphnia magna*	13,800
CBZ	*Danio rerio*	25,000
CBZ	*Danio rerio*	50,000
CBZ	*Cyprinus carpio*	1
CBZ	*Chironomus tentans*	9500
CBZ	*Chironomus tentans*	47,300
CBZ	*Ceriodaphnia dubia*	250
CBZ	*Ceriodaphnia dubia*	264.4
CBZ	*Ceriodaphnia dubia*	77,700
CBZ	*Brachionus calyciflorus*	754
DCF	*Scenedesmus vacuolatus*	23,000
DCF	*Salmo trutta*	50
DCF	*Salmo trutta*	50
DCF	*Rhamdia quelen*	0.2
DCF	*Pseudokirchneriella subcapitata*	20,000
DCF	*Pseudokirchneriella subcapitata*	10,000
DCF	*Pseudokirchneriella subcapitata*	10,000
DCF	*Oryzias latipes*	1
DCF	*Oryzias latipes*	10,100
DCF	*Oryzias latipes*	10,000
DCF	*Oreochromis niloticus*	1
DCF	*Oncorhynchus mykiss*	1
DCF	*Oncorhynchus mykiss*	1.7
DCF	*Oncorhynchus mykiss*	5
DCF	*Oncorhynchus mykiss*	5
DCF	*Oncorhynchus mykiss*	5
DCF	*Moina macrocopa*	50,000
DCF	*Dreissena polymorpha*	10,000
DCF	*Desmodesmus subspicatus*	5000
DCF	*Daphnia magna*	56,600
DCF	*Daphnia magna*	33,000
DCF	*Daphnia magna*	50
DCF	*Daphnia magna*	25,000
DCF	*Danio rerio*	8000
DCF	*Danio rerio*	1000

(continued)

(continued)

Pharmaceutical	Species	LC_{50}/LOEC (μg/L)
DCF	*Danio rerio*	4000
DCF	*Danio rerio*	2000
DCF	*Cerodaphnia dubia*	1000
DCF	*Cerodaphnia dubia*	2000
DCF	*Brachionus calyciflorus*	12,500
DCF	*Brachionus calyciflorus*	25,000
SMX	*Synechococcus leopoliensis*	30
SMX	*Synechococcus leopoliensis*	26,800
SMX	*Synechococcus leopoliensis*	520
SMX	*Selenastrum capricornutum*	1000
SMX	*Pseudokirchneriella subcapitata*	520
SMX	*Pseudokirchneriella subcapitata*	146
SMX	*Oryzias latipes*	0.1
SMX	*Limnodynastes peronii*	672,220
SMX	*Hydra attenuata*	10
SMX	*Daphnia magna*	100,000
SMX	*Daphnia magna*	25,200
SMX	*Daphnia magna*	205,200
SMX	*Daphnia magna*	177,600
SMX	*Daphnia magna*	100,000
SMX	*Cyclotella meneghiniana*	2400
SMX	*Chlorella vulgaris*	1.57
SMX	*Ceriodaphnia dubia*	250
SMX	*Ceriodaphnia dubia*	210
SMX	*Ceriodaphnia dubia*	210
SMX	*Ceriodaphnia dubia*	15,510
SMX	*Ceriodaphnia dubia*	100,000
SMX	*Ceriodaphnia dubia*	15,510
SMX	*Ceriodaphnia dubia*	210
SMX	*Ceriodaphnia dubia*	100,000
SMX	*Brachionus calyciflorus*	25,000
SMX	*Brachionus calyciflorus*	9630
SMX	*Brachionus calyciflorus*	9630
EE2	*Syngnathus scovelli*	100
EE2	*Sparus latus*	2.71
EE2	*Sida crystallina*	1.5
EE2	*Ruditapes philippinarum*	3.42
EE2	*Pomatoschistus minutus*	20
EE2	*Pimephales promelas*	0.1
EE2	*Pimephales promelas*	0.3

(continued)

(continued)

Pharmaceutical	Species	LC_{50}/LOEC (μg/L)
EE2	*Pimephales promelas*	5
EE2	*Pimephales promelas*	2
EE2	*Pimephales promelas*	1
EE2	*Pimephales promelas*	1
EE2	*Pimephales promelas*	1
EE2	*Pimephales promelas*	1
EE2	*Pimephales promelas*	1
EE2	*Pimephales promelas*	10
EE2	*Pimephales promelas*	4
EE2	*Oryzias latipes*	2
EE2	*Oryzias latipes*	5
EE2	*Oryzias latipes*	4
EE2	*Oryzias latipes*	16
EE2	*Oryzias latipes*	0.1
EE2	*Oryzias latipes*	1.4
EE2	*Oryzias latipes*	63.9
EE2	*Oryzias latipes*	488
EE2	*Oryzias latipes*	10
EE2	*Oryzias latipes*	116
EE2	*Oryzias latipes*	63
EE2	*Oncorhynchus mykiss*	63
EE2	*Oncorhynchus mykiss*	488
EE2	*Oncorhynchus mykiss*	100
EE2	*Oncorhynchus mykiss*	63.9
EE2	*Oncorhynchus mykiss*	1
EE2	*Oncorhynchus mykiss*	5
EE2	*Oncorhynchus mykiss*	32
EE2	*Nitocra spinepes*	2
EE2	*Moxostoma macrolepidotum*	20.27
EE2	*Moxostoma macrolepidotum*	78.15
EE2	*Marisa cornuarietis*	5
EE2	*Lymnaea stagnalis*	6.2
EE2	*Hyalella azteca*	1.67
EE2	*Hyalella azteca*	3
EE2	*Hyalella azteca*	15.4
EE2	*Hyalella azteca*	1
EE2	*Gastrosteus aculeatus*	53.7
EE2	*Gastrosteus aculeatus*	170
EE2	*Gammarus pulex*	2
EE2	*Gabiocypris rarus*	16

(continued)

(continued)

Pharmaceutical	Species	LC_{50}/LOEC (μg/L)
EE2	*Daphnia magna*	9
EE2	*Daphnia magna*	3
EE2	*Daphnia magna*	1.67
EE2	*Danio rerio*	1.54
EE2	*Danio rerio*	100
EE2	*Danio rerio*	6
EE2	*Danio rerio*	105,000
EE2	*Danio rerio*	105,000
EE2	*Danio rerio*	12,500
EE2	*Danio rerio*	1,800,000
EE2	*Danio rerio*	4,100,000
EE2	*Danio rerio*	10
EE2	*Danio rerio*	320
EE2	*Danio rerio*	100
EE2	*Danio rerio*	160,000
EE2	*Danio rerio*	100
EE2	*Cyprinus carpio*	100
EE2	*Cyprinodon variegatus*	0.125
EE2	*Chironomus riparius*	1.25
EE2	*Chironomini tentans*	1,600,000
EE2	*Chironomini tentans*	4,600,000
EE2	*Ceriodaphnia reticulata*	1
EE2	*Bithynia tentaculata*	50,000
EE2	*Acanthopagrus schlegel*	3.03

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Chapter 5
Geochemical Modelling of Groundwater Using Multivariate Normal Distribution (MND) Theory

B. K. Sahu

5.1 Introduction

Groundwater is becoming a very scarce commodity especially in arid and semi-arid regions where there is little precipitation and climate is extreme. However, it is essential drinking and domestic use as well as for survival of human species. It must be conserved and utilized very carefully and should not be misused for irrigation, commercial and industrial purposes. This is especially applicable to areas not having any alternate source of water such as surface water. Groundwater in soils are rain-fed and form a saturated zone with a surface called watertable (W.T.) whereas deeper aquifers can have rain-fed source if aquifer is exposed at surface or may be closed with original connate waters only. Groundwater is generally safe for drinking and domestic use unless seriously polluted by chemical fertilizers used for agriculture and or toxic waste water released from domestic/industrial units. Groundwater is rarely polluted through natural rock-water interactions except at rare localities having toxic elements such as F, As, S, Se, U etc. in host rocks. Chemical quality of groundwater can be affected by evapo-transpiration, rock-water interaction, and precipitation processes and also by composition of connate waters in deep seated aquifers.

WHO guidelines for water quality are as follows:

(i) pH range 6.5–8.5 with mean value of 7.5; for Drinking pH range is 6.68–8.00. Mean 7.15.
(ii) EC 1400 uS/cm; TDS 500 mg/l.

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It may be noted that EC and TDS are perfectly correlated and predictable if one is known; hence knowledge of only one (say TDS) need be measured. This is because electrical conductivity in water is dependent on the total number of cations and anions present in water which is same as TDS.

Recently it has been estimated that about 1/3 of world population in the underdeveloped countries live in conditions of permanent water scarcity. In the arid and semi-arid regions of central and southern India, rainfall is extremely irregular and very low. The major threats are that groundwater table is currently fast depleting at an alarming rate because of (i) indiscriminate over pumping of groundwater for irrigation or domestic use, (ii) overuse of chemical fertilizers leading to pollution as well as salt-pan formation yielding waterlogging, (iii) over-pumping of GW for industrial use and disposal of toxic wastes. This induces problems for food security, ecology, environment and survival of mankind. Therefore, groundwater professionals and policymakers must address these issues immediately and take appropriate actions so that groundwater use is restricted only for drinking and domestic purposes and domestic wastes must be properly treated and recycled. Farmers should be encouraged and induced to utilize natural manures and minimize use of chemical fertilizers. Industries must treat their wastes completely before disposal or recycling.

In order to solve these problems a clear understanding of geochemistry of groundwater is required which would help in formulation of realistic and appropriate geochemical model for estimation of required parameters, tests of hypotheses and in taking optimal decisions for management of groundwater and for taking remedial measures for pollution control as well as for improving the availability of good quality and quantity of groundwater.

5.2 Geochemical Characterization

Groundwater available at the surface from soils is renewable through annual precipitation and at underground aquifers can be renewable (if aquifer exposed at surface) or non-renewable (if aquifer not exposed at surface nor physically connected to surface by fracture/fault). In arid and semi-arid regions where surface waters may not be available, people have to depend on groundwater and therefore its quality must be suitable for drinking and domestic use. Chemical equilibrium of groundwater is necessarily heterogeneous having multiple phases (gases such as CO_2, O_2; liquid water with dissolved salts; solids such as fine clays and colloids etc.). Sample characterization of groundwater is site-specific and deal with multiple random variables in spatial (3D, 2D, 1D) and /or in time domains. From statistical theory, samples collected at wider spatial and /or temporal spacings (intervals) would be independent (uncorrelated) but collected at closer intervals would become dependent (correlated). Statistical analyses and inferences differ greatly in these two different situations and appropriate methodology must be followed to reach correct inferences for taking optimal decisions (Sahu 2003, 2005).

If a few (<100) samples are available, then it would be wiser to analyze by Multivariate methods and time series methods are to be used (sample sizes >100 along a given line) only in special cases where careful sampling has to done at regular(constant) intervals by suitable experimental design. In most groundwater studies the sampling is random in space/time and also rather small (order of 100), hence time series methods are not applicable, appropriate nor desirable. If necessary, proper sampling design must be made to apply time series in time or frequency or time-frequency (wavelet) domains but it would require at least 100 equally spaced samples at some constant interval for 1D and at least 300 samples for 2D (two orthogonal lines and diagonal line) and at least 1000 samples for 3D analyses (3 orthogonal and rest 7 diagonal lines). Geostatistical models are being used but these have technical problems of Nugget Effect (Co) should be zero from theory, if sample size is adequate (REV size or more), so that sample characteristics is representing a Homogeneous medium. Therefore, if a non-zero Co (Nugget value) is used in the variogram model, then this Co value must be shown to be statistically significant at 5% level.

Linear statistical models are preferable as these are mathematically tractable as compared to non-linear statistical models which are rather complex and very difficult to analyse and interpret. Non-linear models can be locally approximated as linear model and interpreted more simply, rather than analysed as globally non-linear system. However linear models also require a few pre-requisites for applicability as follows:

(a) Samples must be independent each other; (achieved by random locations and wide spacings (intervals) in spatial and/or temporal domains;
(b) Random variables measured from the samples must be continuous type and possess Gaussian Cumulative Probability Distribution (cdf) or Gaussian Probability Density function (pdf).

The first pre-requisite is easily achieved by sampling randomly at sufficiently wider intervals. Sample size must be sufficient (>REV size) so that it is homogeneous over the space/time sampled. The second pre-requisite is not always, in fact, never true (except for pH which is negative logarithmic (non-linear) transformation of Hydrogen ion concentration in groundwater). All other geochemical random variables require suitable non-linear pre-transformation to make them Gaussian. As most chemical constituents (TDS, cations and anions) in groundwater are present in very small (trace) quantities and have very high frequency at lower end and long tails to higher values that is high positive skewness, these random variables can be Gaussianised by simple (non-linear) logarithmic transform of their numerical concentration values. Since, the concentrations of cations/anions are in trace quantities in groundwater, closure correction needed for the constant sum (1.0 or 100%) problem in geochemistry has negligible effect, since the required non-linear transform log $(c/(1 - c))$, where c represents fractional value of the constituent, reduces to log (c) as c tends to zero or $(1 - c)$ in denominator tends to 1 (Sahu 1982a, b, 1995, 2003, 2005, 2013, 2014a, b).

Geochemical model of groundwater quantitative data should permit prediction of the numerical outcomes of geological processes and the future of geological systems. Quality of groundwater should be within safety limits of drinking, domestic, irrigation and industrial purposes. Geochemical problems include: Mass balance, Chemical Equilibria, Dynamics, and Transport etc. Modelling methods include use of Linear Algebra, Numerical Analysis, Probability and Statistics to solve these problems. Although deterministic solutions are available for these problems and often necessary, statistical and stochastic solutions are generally much more realistic and better for geochemical inferences especially when there is much uncertainty.

In groundwater there exist a large number of dissolved ionic species, and after pre-transformation of these random variables to Gaussian, it is now appropriate to use LINEAR MULTIVARIATE NORMAL(GAUSSIAN) DISTRIBUTION (MND) statistical theory for their parameter estimation, hypotheses tests, and geochemical inferences using standard multivariate methods such as Cluster, Principal Component, Factor; Multiple Linear Regression (Correlation), Partial Correlation, Canonical Correlation analyses for single Population(Group); or MANOVA, Linear Discriminant (2-group or multi-group), Quadratic Discriminant, Classification, MANCOVA analyses for multiple Populations (Groups) as given in Sahu (2005). It may be noted that simple two-group linear discriminant function (T-LDF) proposed by Fisher in 1936 (see, Sahu 1964) has been later (see, Sahu 1982a, b, 1983) extended and superseded by multi-group linear discriminant functions (M-LDF) which are more useful. The input random variables to MND can be listed as (i) pH, (ii) log(TDS)/log(EC), (iii) log $\left(Mg_2^+\right)$, (iv) log $\left(Ca_2^+\right)$, (v) log $\left(Na^+\right)$, (vi) log $\left(K^+\right)$, (vii) log $\left(Cl^-\right)$, (viii) log $\left(HCO_3^-\right)$, (ix) log $\left(SO_4^{-2}\right)$, (x) log $\left(NO_3^-\right)$, (xi) log $\left(PO_4^{-3}\right)$, (xii) log $\left(CO_3^{-2}\right)$, (xii) log $\left(F^-\right)$. So, multivariate system has a dimension of 13 random (real) variables and N (>30) samples measured for each population. This is a fairly large data matrix X ($13 \times N$ for each population) with resulting correlation matrix of size (13×13 for each population). The statistical solutions to estimation, hypotheses tests and other multivariate solutions like PCA, FA, MR/MC, CCA or MANOVA,LDF/QDF, Classification, or MANCOVA are given in Sahu (2005) but summarized below for a few simpler methods which are frequently used.

Linear time series or geostatistical analyses are much more involved and require very large number of closely spaced samples (>100 for 1D, >300 for 2D and >1000 for 3D) at regular interval along the lines of investigation. These are useful for specialized studies and are not recommended for routine work. Hence, linear and/or nonlinear methods of Time Series Analysis (TSA), (TSA needs complex variable for 2D and 3D problems) and/or geostatistical models for analyses of dependent data are not included here.

5.3 Linear Multivariate Normal Distribution (MND) Theory

This is appropriate for analyzing multiply correlated measurements (random vectors) made on one or more samples and on one or more (homogeneous) populations/groups. If a p-variate (p* 1) Gaussian random vector (X) is measured on N independent samples of a population, then the mathematical model has multivariate normal distribution (MND) which is characterized as all linear compounds of the variables are also MND as the rank of vector X may/may not be equal to its order (p). MND methods are classified on basis of number of Populations (one or more); number of sets of random vectors (one or more). Four classes thus form: (i) one population and one set of variables: MND methods are Principal Component (PCA), Factor(FA); Cluster(CA); (ii) One Population but more than one set of variables: MND methods are Multiple Regressions(correlations); Polynomial Regressions; Canonical Correlation; (iii) One set variable but more than one Population: MND methods include MANOVA, Discriminant functions(DF: linear, quadratic); Classification function(CF); and (iv). More than one Sets of variables and Populations: MANCOVA methods.

Constituents of groundwater as well as of rocks/ores/soils are constrained to 1.0 or 100% which form a mathematically induced dependence structure (not geologically interpretable or meaningful) but having a Binomial/Poisson distribution with heteroskedastic variances. Gaussianisation of marginal distributions are often performed but this does not guarantee that the joint distribution of random vector belong to MND. So, MND theory must be tested through all linear combinations (esp. Principal Components, Conditional regression components) of the random measurements are MND. However, MND theory is very robust and if N is fairly large then the random vector may be accepted to have MND and this is practical also. The parameters of a multivariate r.v. can be estimated for any homogeneous population by its mean vector ($\boldsymbol{\mu}$) and dispersion (correlation) matrix (D/R) using MLE. Null hypothesis of Homogeneity of population mean vectors (H_2) conditional on homogeneity of dispersion matrices is given by T^2 test:

$$T^2 = N(m - \boldsymbol{\mu})^T D^{-1}(m - \boldsymbol{\mu}), \text{with} (N - p)T^2/(N - 1)$$

is F, p, (N − p) distributed and m being sample mean.

Homogeneity test for Covariance matrices (H_1) of different populations is more involved (Box test).

Matrix operations are essential for multivariate analysis. Matrix A is a rectangular array of numbers with p rows and q columns, where a (i, j) is its ijth element. Addition and scalar multiplication are straightforward but matrix multiplication requires that the number of columns of the pre-matrix must be equal to the number of rows of the post-matrix, otherwise multiplication is not defined. If AB = C exists, the elements c(i, j) = Sum over r (a(i, r) × b(r, j)). But in general multiplication is not commutative, AB not equal to BA, so pre- or post- multiplication of the matrix must be specified. However, multiplication is associative: A(BC) = (AB) C = ABC. Transposed matrix A^T has the rows and columns interchanged in A; so $(AB)^T = B^T A^T$. If X and Y are two conformable column vectors then their inner product is given by X* Y. If A is (m $\times$ n) matrix, the A.x is a column vector. A* is conjugate transpose of complex matrix A, then (AB)* = B* A* and so on. Rank of matrix is the number of independent columns (or rows) in the matrix. A square matrix of order m is nonsingular, if its rank (m) is less than its order (p). A unique inverse matrix A^{-1} exists if A is nonsingular, then $AA^{-1} = A^{-1} A = I$ (identity matrix). If unique inverses of A and B exist, then $(AB)^{-1} = B^{-1} A^{-1}$; also $(A)^{-1} = A^T$ and $(A^*)^{-1} = (A^{-1})^*$. For an unitary, matrix A*; we have A*. A = I = A.A* and so, $A^* = A^{-1}$. If A is a real non-singular square matrix is said to be orthogonal if $A^T A = A A^T = I$, so $A^{-1} = A^T$ and hermitian if $A^{-1} = A^*$. Elementary operations on columns (rows) of a matrix can give simpler form to interpret and compute but its rank is preserved.

Determinant of a square matrix A ($=a_{ij}$) can be obtained by expanding the element ($a_{(i,\ j)}$of a row(column) by multiplying by its cofactor and summing over all elements of the row(column) or by multiplying the eigenvalues of A. Generalised inverse of a singular matrix (rank less than its order) is denoted as A^-; then $A A^- A = A A^-$ is not necessarily unique. $A^-A = H$ with $H^2 = H$ (idempotent). If $A^- = A$, we get det A = r(A) = r(H) = trace(H). If A^- exists then $r(A^-) \geq r(A)$.

Quadratic form (Q) of matrix plays an important role in MND analysis and is given by $Q = X^T A X$ with $A = [\ (a_{(ij)} + a_{(ji)})/2\}$ this symmetric matrix. If $X^T A X$ is >0 it is positive definite(pd), 0 it is negative definite(nd) and semi-definite is 0 is included in the product. For any nonsingular linear transformation Q remain definite and invariant. Every positive definite matrix A can be decomposed into CC^T where C^T is inverse of the linear transform matrix and inverse A matrix is uniquely defined. A necessary and sufficient condition for A to be positive definite (pd) is that its determinant is positive. This summary on Multivariate Analysis is based on Sahu (2005) where more details are available.

5.3.1 Principal Component and Factor Analyses

This method is for single population and one set of random variables, Original vectors in p dimensional space are linearly transformed to a smaller m dimensional subspace of principal components which are orthogonal. Mathematically, a real symmetric covariance (correlation) matrix is diagonalised (all nondiagonal correlations become zero) s.t. the principal diagonal yields the eigenvalues (variances) along the orthogonal eigenvectors (directions). In Factor Analysis, some of the smaller non-significant eigenvalues are deleted as negligible error components without losing information. The retained eigenvectors are rotated orthogonally in the lower common factor space ($m \ll p$), so the new correlations (loadings) become easily interpretable (either near 1 highly loaded or near zero uncorrelated) as Factors. Rotation of orthogonal factors in the lower space is made by standard

VARIMAX program (Kaiser 1958). Cluster analysis can be made to obtain homogeneous groups by using similarity or distance matrices but this process is rather empirical and needs great care for accuracy.

Eigenstructure of correlation(Dispersion) matrix (R or D) is achieved through powering the matrix to a very high index(say 64 or 128) so that the largest eigenvalue dominates over the rest and corresponding eigenvector is obtained by a few iteration. The effect of the first eigenvalue is subtracted from the matrix to obtain the Residual Matrix which is again powered to high index to get next eigenvalue and eigenvector. This sequence is continued till all information of R(or D) are extracted and residual matrix becomes zero matrix. However, before running the eigenstructure analysis, null hypothesis R = I, must be tested for statistical significance by a chisquare test with $p(p - 1)/2$ d.f. at 0.05 level. The test quantity is given by $- [(N - 1) - (1/6)(2p + 5)] \ln(|R|)$.

Spectral decomposition of matrix gives:

$$R = \boldsymbol{\Lambda}_1 v_1 \left(v_1^T\right) + \boldsymbol{\Lambda}_2 v_2 \left(v_2^T\right) + \cdots + \boldsymbol{\Lambda}_p v_p \left(v_p^T\right) = \sum R_i \text{ over all } p_j.$$

If m components are found to be statistically significant then the rest (p – m) components are noise and are deleted. So, total variance explained is sum R(j) of first m components, and rank of R is now $m(\ll p)$. Multiplication of all eigenvalues gives $|R|$ and sum of all eigenvalues gives trace of R.

Principal factors (f(j); j = 1 to m) are computed dividing the retained eigenvectors by square root of their eigenvalues. Thus each factor becomes equally important as other with variance of one for all j. Factor Structure $S = V(\boldsymbol{\Lambda})^{-1/2}$ and predicted R by all factors is $S{*}S^T$; residual error is $R - S{*}S^T$.

The number of significant principal components (m) retained as factors is most important. A chi-square test of det of residual matrix; res (A) with $(p - m)(p - m - 1)/2$ d.f. is given by:

$$\begin{aligned} &-\{(N-1) - 1/6(2p+5) \\ &\quad - 2/3(m)\} \ln\left[|R|/\{\Pi \text{ of } m \text{ eigenvalues}(p - \sum (m \text{ eigenvalues}))/(p-m)\}^{(p-m)}\right] \end{aligned}$$

which is tested at 0.05 level. Another method is to plot jth eigenvalue versus j to get inflexion point giving m factors or to plot std. devn. of cum. Eigenvalues computed on independent replicate samples of size N sampled from the same population versus j to get a minimum at which cum. eigenvalue is 85% or more gives m. This second procedure is a second order criteria for deciding the common factor space (m) (see, Sahu 1973). Varimax rotation is absolutely necessary to eliminate non-interpretable intermediate loadings in the range of 0.2–0.5 in any unrotated eigenvector of principal component. Factor j is interpreted by the rotated loadings in the jth rotated eigenvector as follows: (i) absolute loadings close to unity are statistically significant and indentifies the factor in terms of the input variables and loadings near zero are non-significant and do not contribute to this factor (but may identify some other factor on which they are strongly loaded).

Correlation matrix can be computed over N samples to give R-mode R showing correlations among the random variables, or over the p variables to give Q-mode R showing correlations among N samples. However, both R or Q correlation matrices have the same information and hence give finally the same inferences/decisions. But the order of R in R-mode is $p \ll N$; hence computationally R-mode analyses are preferred/cheaper. The rotated eigenvalues are different from the variances from corresponding eigenvalues, although the total variance (=Cumulative Eigenvalue) of m retained factors is conserved by orthogonal rotations as can be easily demonstrated by matrix theory. (see, Sahu 1973).

5.3.2 *Multiple Regression (Correlation) and Canonical Correlation*

Multiple (including Polynomial) regression(correlation) yield linear prediction of dependent(criterion) variable(Y) from the knowledge of the predictors(X). The slope is given by $b = (\mathrm{Var}\ x)^{-1}\ \mathrm{Cov}(x, y)$ if X and Y are scalars (univariate analysis) which can be extended to vector random variables as $b = \mathrm{Cov}(x)^{-1}\ \mathrm{Cov}\ (x, y)$ if x is a vector random variable and Y is a scalar random variable. Multiple correlation exists if the multiple correlation coefficient R is statistically significant, and R^2 indicates the sum of squares explained by predictors and $(1 - R^2)$ indicates noise sum of squares. F test can be made with $(p - 1)$ and $(N - p)$ as degrees of freedom. However, since elements of X are mutually correlated (not independent), the effect of each element of X on Y is highly confounded and not possible to correctly interpret. Partial correlations remove the effects for other elements mathematically to give correct interpretation for correlation of Y with any element (x_i) of X.

In Canonical correlation, two or more sets are variables are needed, one set is criterion, other set predictor and third set control which can be kept mathematically constant. In contrast to Principal Component Analyses, the eigenstructure is computed along the maximum covariances (not along maximum variances). The total correlation matrix R (with y as the pth r.v.) is partioned into X of order (p-1) and hence we get the real nonsymmetric matrix as $R_{22}^{-1}\ R_{21}\ R_{11}^{-1}\ R_{21}$ which is product of two real symmetric matrices: $B = R_{22}$ and $A = R_{21}\ R_{11}^{-1}\ R_{12}$. Mathematically we solve the eigenstructure of $(A - \mathbf{\Lambda}B) = 0$ or of eigenstructure of $B^{-1}\ A\ V = V(\mathbf{\Lambda})$. Eigenstructure of B^{-1} A can be done through two stages: (i) eigenstructure of real symmetric matrix B to give $\mathbf{\Lambda}_1$ an eigenvector U_1 to compute B^{-1} and obtain $B^{-(1/2)}$ and then (ii) eigenstructure of symmetric matrix $(B^{-1/2}\ A\ B^{-1/2})$ to give $\mathbf{\Lambda}_2$ and eigenvector U_2 Eigenvalues of $B^{-1}A$ is same as that of $(B^{-1}/2\ A\ B^{-1/2})$ but eigenvector V of B^{-1} A is given by $B^{-1/2}\ U_{2.}$ Statistical significance of diagonal elements of canonical eigenvalues ($\mathbf{\Lambda}_2$) can be assessed as follows: (i) proportion explained by $\mathbf{\Lambda}_j = \mathbf{\Lambda}_j/(\mathrm{trace}\ \mathbf{\Lambda}_2)$ (ii) Bartlett Lamda statistic = Product (j = 1 to p_2)

of (1 − $\boldsymbol{\Lambda}_j$), where p_2 is dimension of predictor vector. The null hypothesis that criterion and predictor sets are uncorrelated is assessed through chi-square with $p_{(1)}$ x $p_{(2)}$ d.f. as: − [(N − 1) − (1/2) ($p_{(1)}$ + $p_{(2)}$ + 1)] ln ($\boldsymbol{\Lambda}$). If null hypothesis of no correlation is rejected, then the effects of the first canonical root ($\boldsymbol{\Lambda}_1$) is subtracted the rest $p_{(2)}$ − 1 canonical roots tested as: Product(j = r + 1 to $p_{(2)}$) (1 − $\boldsymbol{\Lambda}_j$) as a chi-square with d.f. = ($p_{(1)}$ − 1) ($p_{(2)}$ − 1).

$$\text{Chi-square} = -\left\{(\mathrm{N}-1)+1/2\left(\mathrm{p}_{(1)}+\mathrm{p}_{(2)}+1\right)\right\}\ln(\boldsymbol{\Lambda}_1\,\text{residual}).$$

This test is continued as is necessary.

(iii) A thumbrule is any canonical correlation <0.30 is statistically nonsignificant and hence dropped.

Multiple regression with standardized variables z can be written as z (hat) = b_1 z_1 + b_2 z_2 + ⋯ + b_p z_p and multiple correlation coefficients R are similar to product-moment correlation coefficient (r) having range [−1, + 1] for linear regression of scalars but *R* has range 0 to 1. R^2 explains major part of the variance of criterion and (1 − R^2) gives the error variance of regression. Therefore, F test with (p − 1) df in numerator and (n − p) df as the denominator is applicable for the quantity R^2 (N − p)/(1 − R^2) (p − 1). The (p*p) correlation matrix R can be partitioned into R_{11} with order (p − 1) and the last criterion (scalar) $z_{(p)}$ has variance 1.0. The multiple slope vector b = $R_{11}^{-1}R_{12}$. However, high values and high significance of any b_j does not imply true importance of z_j since other predictor z's confound the multiple correlation slopes. Hence partial correlation of criterion with a z_j keeping all other predictors mathematically constant is absolutely necessary for any statistical/geological inference.

Polynomial regression is similar to multiple regression but powers of predictor random variables and the interaction terms are included. High degree of polynomial regressions is very difficult to interpret and also if X is Gaussian then its powers and interactions cannot be Gaussian, precluding use of F-test for the regression equations. So, unless theory dictates such polynomial regression, it should be avoided, and in any case the degree should as low as possible (say, second order).

$$\begin{aligned}&\text{Multiple partial correlation matrix}\,\mathrm{R}_{2.1}\\&\quad=\left\{\mathrm{r}_{21.\mathrm{jk}}\right\}=\text{residual}\,\mathrm{r}_{22.\mathrm{jk}}/(\text{res }\mathrm{r}_{22.\mathrm{jj}}\times\mathrm{r}_{22.\mathrm{kk}})^{1/2}\end{aligned}$$

For a trivariate-random variable, system res r_{22} = 1 − r_{21}^2 and res $r_{23.j}$ = res $r_{23.j}$/ (1 − $r_{21}^2)^{1/2}$. So, $r_{21.}{}^{3j}$ = res r_{23j}/ (1 − $r_{21}^2)^{1/2}$, a well known result in statistical theory. The output of partial correlation analysis can be arranged as: $\mathrm{R}=\left[\,(\mathrm{R}_{21}/\mathrm{R}_{32.1})\quad(\mathrm{R}_{21.3}/\mathrm{R}_{33})\,\right]$.

An Example of Partial Correlation would clarify many concepts involved. The following random variables were measured in 33 thin-sections from 33 sandstone samples. The variables were X_1 = phi long axis of grains, X_2 = matrix percent and X_3 = porosity percent as reported in Griffiths (1967, p. 468) and the multiple correlation matrix R with r_{12} = 8813**, r_{13} = −0.7094** and r_{23} = −0.66771**.

Here, ** means statistical significance at 0.01 level. We compute partial correlation $r_{13.2} = (r_{13} - r_{12} \times r_{23})/ (1 - r_{12}^2)^{1/2}$. Partial correlations between X_1 X_3; X_1 X_2; and $X_{21.3}$ are similarly computed and we get $r_{21.\ 3} = 0.6439^{**}$, $r_{31.2} = -0.3862^{**}$ but $r_{23.1} = -0.2222^{NS}$ instead of -0.6671^{**}. Therefore, $r_{23.1}$ is non-significant indicating X_2 and X_3 are really not correlated and do not possess any negative correlation. This fallacy of multiple correlations must always be remembered and true inference sought through partial correlations.

Comments: Although X_1 has a Gaussian distribution, X_2 and X_3 possess closure constraints (range 0 to 100%, or 0 to 1 as fractions) and not Gaussian but Binomial. X_2 and X_3 can be Gaussianised by transformation log $(x_j/(100 - x_j))$ for j = 1, 2. Multiple correlations should have been computed with X_1 and, the new transformed and Gaussianised X_2 and X_3 variables (not original non-Gaussian X_2, X_3).

5.3.3 MANOVA, Discrimination and Classification

MANOVA is similar to ANOVA for vector random variable X, In ANOVA (scalar r.v) two types of tests are necessary to test equality of Main Effects: (i) when interactions are non-significant the interaction variances are pooled with error variance and a pooled error variance is calculated to yield the F test, (ii) when interaction variance is significant then its variance is used to test main effects by F test. In MANOVA, treatment variance is divided by the pooled error variance to give F test since interaction variance is non-significant. But if interaction variance is significant then MANCOVA methods are used to test main effects (F test) by dividing treatment variance by interaction variance (not error variance). Populations (groups) are not necessarily homogeneous in mean vectors and covariance matrices. Two situations can arise (a) covariance matrices homogeneous and testing done to find homogeneity of mean vectors (H2 test; LDFs and MDFs as hyperplanes) or otherwise. In second case (b) at least one covariance matrix is different we have to use nonlinear quadratic hyper-surfaces(QDF) to delineate regions of each population. If both the mean vectors and covariance matrices are utilized together, then the procedure is called classification.

We decompose a ith vector of kth group $X_{(ki)}$ from grand mean m as, $x_{(ki)} = X_{(ki)} - m = (m_{(k)} - m) + (X_{(ki)} - m_{(k)})$, where $m_{(k)}$ and m are the mean vectors for kth population and all populations, respectively. So any data is the sum of main effects (Among Group) and Within Group deviations$(X_{(ki)} - m_{(ki)})$. The SSCP are then $\Sigma\ x_{(ki)}\ x^T_{(ki)}$ = Sum $(m_{(k)} - m)\ (m_{(k)} - m)^T$ + Sum $(X_{(ki)} - m_{(k)})^T$, summed over i = 1 to $N_{(k)}$ and k = 1 to g groups. Symbolically, T = A + W, where only two matrices are independent because of closure constraint. We get $W^{-1}T = W^{-1}A + I$, having only one independent matrix, W^{-1} A, for further analysis as I(Identity matrix) is a constant. If covariance's (correlations) among the groups are equal (H_1 true), the dispersion among the groups (D(A)) = A/(g − 1) and dispersion within groups D(W) = W/(N − g) where N is total data over g populations. The null hypothesis H_2: $\boldsymbol{\mu}_{(k)} = \boldsymbol{\mu}$ for all k = 1, …, g. and m = (sum X_{ki} over all I and k)/N. Rao(1973) proposed F test as follows:

$$s = \left\{ \left(p^2 (g-1)^2 - 4 \right) / \left(p^2 + (E-1)^2 - 5 \right) \right\}^{1/2}; n_{(1)} = p(g-1);$$
$$n_{(2)} = s[(N-1) - (p^*(s-1)+1)/2] - (p(s-1)-2)/2.$$

Let y = $(|W|/|T|)^{-s}$. Then, $F(n_{(1)}, n_{(2)} = ((1 - y)/y)\ (n_{(2)}/n_{(1)})$ and tested for statistical significance. H_2 true, if F test is non-significant, means all mean vectors are equal.

Linear Discriminant Function (LDF)

For two groups, g − 1 = 1; hence there can be only one LDF(Hyperplane). But for multigroups (g − 1) is more than one, so we can have several LDFs some of which may not be significant(should be dropped) but we also need the angles between the accepted(significant) LDFs(Hyperplanes). The retained LDFs form a subspace within the original p dimensional space and samples may be projected onto this subspace for visual studies. Optimal solution is to maximize the ratio $W^{-1}A$ (nonsymmetric real matrix) in the common discriminant subspace defined by vector v s.t. the ratio($\boldsymbol{\Lambda}$) = (v^T A v/ $V^T WV$) is maximized with the constraint $v^T v$. The maximum values are the eigenvalues of W^{-1} A: that is we solve ($W^{-1}A$) V = V$\boldsymbol{\Lambda}$. Since W is full rank W^{-1} is unique and can be decomposed as U $\boldsymbol{\Lambda}_1$ U^T, so $W^{-1/2}$ = U($\boldsymbol{\Lambda}_1^{-1}$ U^T. Then, eigenvalues of W^{-1} A is same as that of $W^{-1/2}$ A $W^{-1/2}$ = B but having a different eigenvector U_2. Since B is symmetric, its eigen structure is $U_2 \boldsymbol{\Lambda}_2 U_2^T$ and the eigenvector matrix V of $W^{-1}A$ is obtained as V = $W^{-1/2} U_2$ and eigenvalue $\boldsymbol{\Lambda}_2$. The number of LDFs to be retained are obtained by statistical significance tests for elements $\boldsymbol{\Lambda}_{2,j}$ where j = 1 to (g − 1) or p whichever is minimum (=rank of $W^{-1}A$ matrix). The importance of jth discriminant function (if retained as significant) can also be judged by the ratio $\boldsymbol{\Lambda}_{2,j}$/ trace $\boldsymbol{\Lambda}_2$ where this ratio lies between 0 and 100%. Also, each $\boldsymbol{\Lambda}_{2,\,j}$ can be tested as a canonical correlation of discriminant vector v_j with any population(group) as the criterion(Y). The eigenvectors in V should be normalized (to vector with magnitude 1) and the angle between the i and jth linear discriminants $J_{(i)}$ and $J_{(k)}$ is given by: $(\theta_{(i,\,j)}) = \mathrm{Cos}^{-1}(v_{(ik)}.\ v_{(jk)})$. These angles are not necessarily orthogonal since $W^{-1}A$ is a nonsymmetric matrix. Discriminant scores can be computed as $v_{(i)}^T\ x_{(jk)}$ for each retained eigenvector j_i and x_{jk} the kth sample of j th group. These scores can be projected onto the common discriminant sub- space for visual perusal. A chisquare test of significance of discrimination amount for remaining m − k discriminants after accepting the first k significant discriminants can be assessed and tested as −(N − (p + g)/2) ln $\boldsymbol{\Lambda}^*$ with df = (p − k) (g – k − 1) and $\boldsymbol{\Lambda}^*$ is product of 1/(1 + $\boldsymbol{\Lambda}_j$) for j = (k + 1 to m). This test should be nonsignificant. Usually two discriminants are most useful for visual representation of projection of LDFs as straight lines in the discriminant space, but 3D projections can be made if three discriminants are required.

Quadratic Discriminant Function (QDF)

This procedure is nonlinear (see, Sahu and Rath 1995 for nonlinear analyses) and NOT Linear model as the others. If at least one covariance matrix is unequal among the groups, then pooling of covariance matrices to give a common covariance matrix is inadmissible. The discriminant is non-linear but hypersurface(s) given by $\boldsymbol{\mu}_{(1)}\, D_{(1)}{}^{-1}\, \boldsymbol{\mu}^{T}_{(1)} - \boldsymbol{\mu}_{(2)}\, D^{-1}_{(2)}\, \boldsymbol{\mu}^{T}_{(2)}$ which reduces to LDF if $D_{(1)} = D_{(2)} = D$ as $(\boldsymbol{\mu}_{(1)} - \boldsymbol{\mu}\ (2))\ D^{-1}\ (\boldsymbol{\mu}_{(1)} - \boldsymbol{\mu}_{2})^{T}$ as was derived under LDF theory. If number of samples $N_{(1)}$ and $N_{(2)}$ are large, LDF is sufficiently robust for applications. Also, for QDF, F test is inapplicable to find its significance.

CLASSIFICATION procedures are also nonlinear methods and hence, are not discussed here for simplicity.MANCOVA methods are useful for multi-element ores and multiple populations (groups) for discriminations and/or classification purposes.

5.4 Geochemical Inferences

5.4.1 General Geological Inferences

This summary is based on several authors and reader may refer to Albareda,F. (2001), and Fetter (1993, 2001). Geochemical inferences are based on equilibrium relations between different ions in relation to varying physical and chemical characteristics of groundwater and the associated host rocks (Patel et al. 2019a). Under acidic conditions (pH 4–6.5) CO_2 from atmosphere will be dissolved and this induces carbonate dissolutions. Under neutral conditions (pH 6.5–7.5) bicarbonates $\left(HCO_3^-\right)$ become dominant carbonate dissolution. Under alkaline conditions (pH 7.5–12) carbonate ions would be dominant inducing precipitation of carbonate minerals.

Oxidation-Reduction potential (Eh) also affect equilibrium and reaction rates and these are affected by pH as well (Patel et al. 2019b). Cations can displace other less strong cations in following order:

$Na^{+} > K^{+} > Mg^{2+} > Ca^{2+}$. However, higher valence cations are somewhat stronger.

Sodium Adsorption Ratio (SAR) is useful to quantify quality of groundwater as follows:

Little danger (2–10); Medium Hazard (7–18); High Hazard (18–26) and Very High Hazard (>26). Piper triangular diagrams are useful for comparison and classification of groundwater. Water quality and contamination (pollution) is based on both physical and chemical characteristics. A simple classification on TDS (mg/L) is as follows:

Fresh	Brackish	Saline	Brine
0–1000	1000–10000	10000–100000	>100000

5.4.2 Geochemical Inference Based on MND Theory

Multivariate statistical methodology and inferences are dealt with in details by Sahu (2005).

Groundwater reacts with associated host rocks to change its stable geochemistry. The different processes involved inducing chemical changes can be listed as (i) dissolution, (ii) hydrolysis, and (iii) evapotranspiration.

(i) Dissolution: Dissolution of soluble salts as halite, sylvite in host rocks release both cations and anions in same proportions as are present in the salt. This induces the linear correlation of log (cation conc.) and log (anion conc.) to be strongly positively correlated.

(ii) Hydrolysis: This processes substitutes H^+ ions for alkali cations (Na^+, K^+, etc.) and simultaneously produces clay minerals in host rocks. This induces high linear correlation between pH = ($-\log H^+$) and log (Na^+ or K^+ concentrations) under acidic environment. Under neutral pH, carbonates in host rocks would be dissolved, so pH and log $\left(HCO_3^-\right)$ would be positively correlated. Under alkaline conditions (pH > 8.0), CO_3^{2-} in groundwater is dominant and carbonates would tend to be precipitated out. This would induce pH and log $\left(CO_3^{2-}\right)$ to be highly negatively correlated.

(iii) Evapotranspiration: This is dominant in arid to semi-arid conditions inducing higher levels of concentrations of salts, and of ions in groundwater. Supersaturation of some salts may induce their precipitation as well. Hence, linear correlation among cations and anions in groundwater would remain unchanged. However, linear correlation between log (cation conc. and/or anion conc.) of precipitated salts and of log (cation conc. and/or anion canc.) of other solutes in solution would be weakly to strongly negative, respectively.

(iv) Rotated factor analyses would provide different homogeneous variables. Each group of variable could belong to natural environment (hostrock composition; aquifer nature; or specific anthropogenic source $\left(NO_3^-\right)$ from agriculture; toxic metals from industries; bacterial concentrations from domestic sewerage). Significant factors can yield pathfinders by using the strongly loaded variable needed for prediction of Factor Scores based on the chemical concentrations.

(v) Statistically significant multiple regression (correlation) vector can be used for quality prediction and/or mapping (by interpolation as well). Partial correlations are more useful since it yields the true linear correlation between any two random variables. Statistically significant Canonical Correlation Vectors are useful to predict criterion variable and helps in mapping this variable over space.

(vi) Multiple linear discriminant functions (M-LDFs) can provide delineation of each homogeneous population (group) and also help in classification of unknown sample (group) to a given population. This method can reduce the space from a large dimension to a smaller one without losing much information about the system. In conclusion, geochemical modeling using multivariate normal (Gaussian) distribution is shown to provide valuable geochemical/geological inferences. However, the assumptions for application of MND theory such as: (i) Input chemical constituent random variables must be Gaussian or pre-transformed to be Gaussian using log (c) transform and (ii) Covariance matrices are homogeneous among populations should be checked.

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Chapter 6
Nutrient Exchange at Water and Sediment Interface of the Largest Brackish Water Lagoon (Chilika), South Asia

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6.1 Introduction

The sediment-water interface plays a great role for exchange of dissolved substances across it and controlling the chemical composition of water column in the deep oceans (Manheim 1976; Leote and Epping 2015), coastal zone (Rowe et al. 1975; Michael et al. 2005), rivers (Helali et al. 2016) and lakes (Bannerman et al. 1975; Fillos and Swanson 1975; Holdren and Armstrong 1980; Steinman et al. 2012; Deka et al. 2016). For shallow water ecosystems like coastal lagoon, estuaries and continental shelves, the benthic domain plays an essential and very important role to regulate the nutrient exchange at sediment and water column interface. Such coastal ecosystems receive nutrients from the riverine discharge, land run-off from adjacent watershed area and atmospheric deposition. About 87% of fishery resources sustain due to occurrence of continental margin systems (Romankevich 1984; Walsh 1991). About 85% of fresh organic matter, which get deposited in sediments of coastal and continental margin, has a contribution of 15–55% of the annual primary productivity in the water columns (Jørgensen 1983; Ly et al. 2014; Patel et al. 2019).

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6.1.1 Background

The organic matter availability in coastal lagoon sediments is higher than open ocean sediments (Santschi et al. 1990; Kristensen 2000) and in shallow aquatic systems, the decomposed plankton derive organic carbon contributed as a significant sink for atmospheric CO_2. The benthic mineralization of organic debris due to the microbial activities has major role for recycling of biogenic elements. A number of factor are responsible for transportation of re-mineralized nutrients from sediment to water, which are molecular diffusion (Li and Gregory 1974), macro benthic activities (Kristensen 1985; Compton et al. 2013), and advective transport of pore water (Marinelli et al. 1998). In shallow environments, the algal nutrient demand can potentially fulfil significant level of pelagic nutrient inventory contributed by benthic inputs (Callender and Hammond 1982). It signify the role of sediment to control the biogeochemistry of such shallow coastal ecosystems. Only primary production is not able to measure the productivity for shallow systems and the contribution of benthic supply of nutrients has significant contribution for differentiating it from oceanic source (Rowe et al. 1975).

6.1.2 Literature Review

In coastal lagoons in situ incubation by using benthic chamber method has been qualified for supply of accuracy results of benthic flux (Steinman et al. 2012). This lagoon has been studied with respect to its geological background and geological features by a number researchers (Bhattacharya et al. 1994; Panigrahy 2000; Sekhar 2004). Studies related to hydrodynamics (Jayaraman et al. 2007; Mohanty and Panda 2009), water quality (Nayak et al. 2004; Panigrahi et al. 2009; Patel et al. 2019), phytoplankton diversity (Patnaik 1978; Panigrahy 1985; Raman et al. 1990; Adhikary and Sahu 1992), zooplankton diversity (Mohanty 1975; Naik et al. 2008), phosphorous speciation in sediments (Barik et al. 2016) and other faunal and floral diversity (Pal and Mohanty 2002; Panigrahi 2006; Sutaria 2007; Das 2008) has also been carried out.

6.1.3 Objective and Implication

No researcher has focused their study to quantify the in situ benthic nutrients exchange across the sediment and water interface on spatiotemporal scale for the lagoon, Chilika. This is the first kind of study in coastal lagoon in Indian subcontinent to present systematic benthic flux measurements with in situ process as well as diffusive method.

6.2 Study Area

The lagoon, Chilika (19 28°–19 54′N; 80° 05′–85° 82′E), the largest sub-elliptical brackish-water ecosystem in Asia (Fig. 6.1) and situated on the east coast of India. This has been listed as Category I of the marine protected areas and designated as a Ramsar site on the Ramsar Convention on Wetlands in 1981. The Eastern Ghat hill range surrounded the western and southern part of the lagoon (Sarkar et al. 2012). The lagoon covers the three important districts (Khurda, Puri, and Ganjam) administrative boundaries of the state of Odisha, India. The north shore of the lagoon touches the district Khurda, while western and outer zone shore are part of the district Ganjam and Puri district of Odisha. The lagoon spreads over an area of 950 km^2 during pre-monsoon, which swells up to 1,165 km^2 during monsoon (Siddiqui and Rama Rao 1995). The outer zone of the lagoon connected with the Bay of Bengal near Satapada with the artificial opening mouth made in September 2000. A 24 km long narrow and curved channel running parallel to the coast was joining the Bay of Bengal near Arakhakuda. The Chilika Lagoon surrounded by the catchment area of 4,406 km^2. The western and Mahanadi delta constituted 68 and 32% of the total catchment area respectively. The lagoon spreads with a total inflow of estimated freshwater 14,331 million km^3 per year (Panigrahi et al. 2009). The 55% of total inflow accounted by the three tributaries viz. Daya, Bargavi and Nuna of river Mahanadi and the rest 45% contribute from the western catchment (Annon 2003).

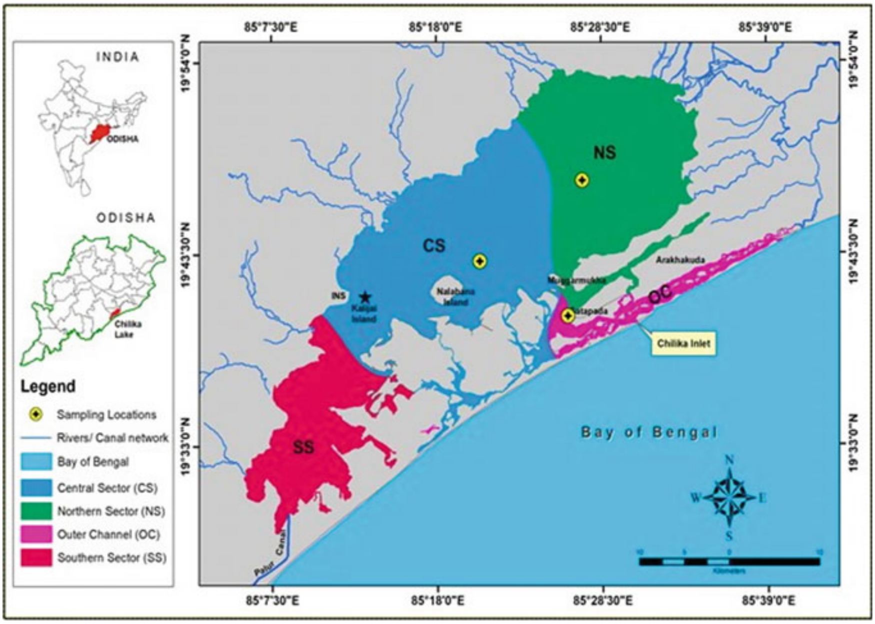

Fig. 6.1 Benthic chamber deployment locations map for the study area

6.3 Materials and Methods

6.3.1 Benthic Chamber Deployment and Sampling

The benthic chamber used for flux study was fabricated as per the Fig. 6.2. The two opposite side outer walls of the chamber attached with flanges to keep the chamber free from penetration of sediments into the chamber during emplacement. The chamber is allowed to penetrate into the sediment up to an average depth of 16 cm. The 0.16 m^2 area of sediment surface remain covered with the chamber at the moment of deployment. The benthic chamber have capacity of $\sim$56 L and it capacity an average $\sim$33 L of water after deployment. A stirrer was kept attached on a fixed to the chamber approximately 15 cm above the sediment through two opposite walls, which is used to mix the enclosed water properly. More caution is needed to avoid the disturbance of the surface sediment but to keep attention for proper mixing of the enclosed water.

The chamber was deployed in all the three sectors (Fig. 6.1) during pre-monsoon and monsoon. At the time of deployment, much attention was focused to avoid the disturbance of the surficial sediment. The chamber was fixed with two metallic weights on the opposite sides to suppress the movement by the current during incubation period. Utmost care remains required to keep the water column at a measurement of approximately 1 m over the chamber during the incubation period. Samples were collected by inserting syringes into the chamber.

The samples collection was performed on the interval of each 4 h. The first sample collection carried out immediately after deployment of chamber, it considered as at time 0. This process continued up to 24 h. It was ensued to keep the

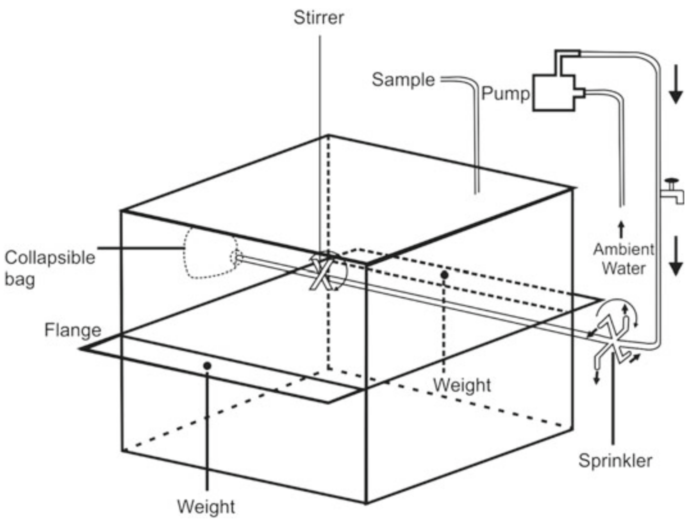

Fig. 6.2 Diagram of deployed benthic chamber

sampling tube to avoid air bubble before the sampling. Nutrient samples were sampled using filter syringes and stored at 20 °C until analysis. For sampling, at least 160 mL of sample was withdrawn to avoid the same amount sample from the plastic bag.

6.3.2 Collection of Sediment Core

The chamber was withdrawn after 24–36 h. period of incubation. Form this exact location, three sediment cores were collected, one is allotted for measurement of porosity and other two for pore water profiling using a handheld corer of length 25 cm and 55 mm ID. Utmost care has been practiced to keep the core sediment free from head space air. The collected corer were stored at 4 °C for further analysis.

6.3.3 Chemical Analysis

The stored samples were analyzed for the nutrients parameters (NO_3^-, NH_4^+, PO_4^{3-} and SiO_4^{4-}) within 24 h after collection by a UV-Visible spectrophotometer (Orion Aquamate 8000, Thermoscientific) adopting the spectroscopic methods (Grasshoff et al. 1999). Porosity is the one of the important physical properties of sediment. A known volume of accurately weighed sediment was dried at 115 °C. It is expressed as the ratio of loss of weight of sediment and that of total volume of sediment. The sediment core were sectioned at each 1 cm interval for extraction of pore-water. Immediate process was carried out for collection of pore water by centrifuging at 4,550 rpm for 15 min and after that filtered by using 0.45 µ filter and placed it for nutrient analysis following the same procedure as described earlier. The water quality checker (Aqua probe) used for the measurement of salinity of pore water.

6.3.4 Benthic (Diffusive) P Flux

Assuming steady state, diffusive (benthic). Phosphate fluxes (*Jp)* were estimated with the equation Berner 1980:

$$\mathrm{Jp} = \varnothing\, \mathrm{D_S}(c/dZ) \tag{6.1}$$

where, Ø is the porosity of the upper sediment sample, *D* the whole sediment diffusion coefficients for phosphate, and dc/dz the concentration gradient at the sediment surface, determined as the concentration difference between the uppermost interstitial water samples (1-cm depth) and the bottom water, assuming a linear concentration gradient between these two points. Whole sediment diffusion coefficients (*Ds*) ($cm^2\ s^{-1}$) can be expressed by

$$D_S = D^*/\theta^2 \tag{6.2}$$

where D* is the diffusion coefficient in seawater and θ the tortuosity. Diffusion coefficients ($7.34 \times 10^{-6}\ cm^2\ s^{-1}$) for HPO_4^{-2} at 25 °C were corrected for the in situ bottom water temperatures (Li and Gregory 1974). The tortuosity of the sediment was estimated with the equation (Boudreau 1997).

$$\theta^2 = 1 - (\varnothing^2) \tag{6.3}$$

6.4 Results

6.4.1 Benthic Nutrient Fluxes

The in situ benthic nutrient fluxes were measured in different seasons of the concerned year. A good linear correlation ($r^2 > 0.89$) was observed in between nutrient concentration inside chamber and incubation time intervals (Figs. 6.3 and 6.4). During pre-monsoon, the NO_3^- flux attained lower value and started upward flux from pre-monsoon onwards. It attained maximum value in monsoon (Table 6.1). A positive strong correlation was established in between benthic NO_3^- influx and NO_3^- value of water column (r = 0.98, $p < 0.001$; Fig. 6.5a). In Chesapeake Bay and Pattos lagoon the researchers (Boynton and Kemp 1985; Niencheski and Jahnke 2002) have recorded the similar results. The efflux of NH_4^+ conquered maximum in pre-monsoon and the minimum in monsoon (Table 6.1). No significant correlation was found between NH_4^+ flux with its value in the water column (r = 0.45, $p > 0.05$; Fig. 6.5b). Phosphate flux showed lowest and highest value during pre-monsoon and monsoon season respectively (Table 6.1). An insignificant correlation, (r = 0.45, $p > 0.05$) was observed in between the PO_4^{3-} flux with PO_4^{3-} concentration in the water column (Fig. 6.5c). The relation between SiO_4^{4-} concentration and incubation time during monsoon season (Fig. 6.4d) was not much significant. Over the period of the year, SiO_4^{4-} was always desorbed to the water column. The lowest and highest values were observed during monsoon and pre-monsoon respectively (Table 6.1). It established significant correlation ship with the concentration of SiO_4^{4-} in the water column (Fig. 6.5d).

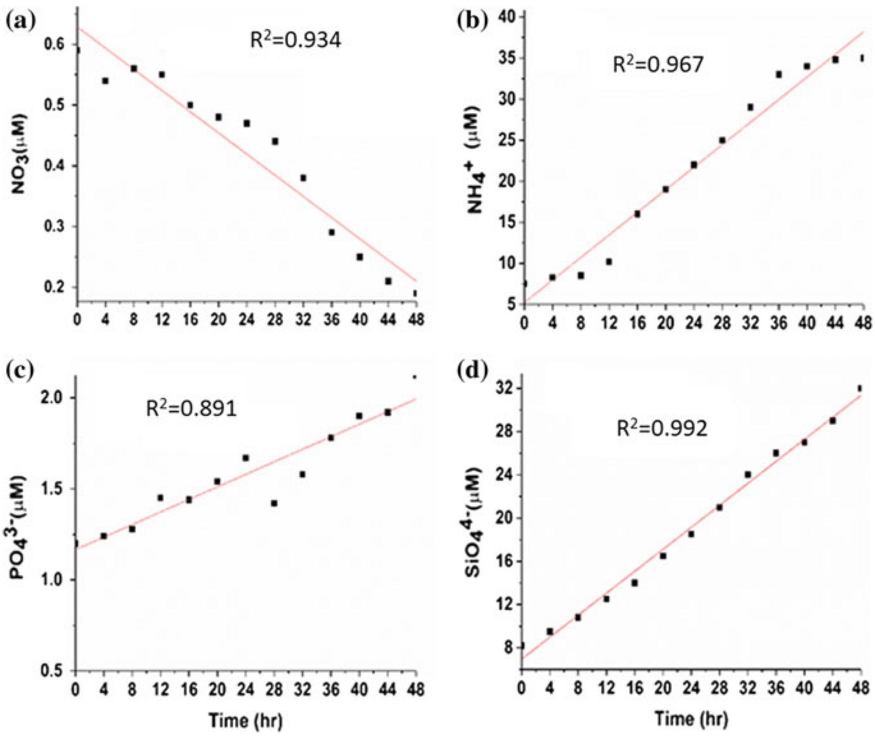

Fig. 6.3 a–d Variation in nutrient concentrations inside benthic chamber with respect to time during pre-monsoon period

6.4.2 Diffusive Fluxes

The pore water nutrient concentration is the major contributor for estimating diffusive fluxes, which are presented in the Table 6.1. The seasonal variation for diffusive fluxes were observed for the lagoon, Chilika. Both the nutrients NO_3^- and PO_4^{3-} influx recorded highest and lowest value during pre-monsoon and monsoon seasons respectively. The NH_4^+ flux attained its lowest during monsoon from the highest value during pre-monsoon season. The SiO_4^{4-} flux recorded highest during monsoon and lowest during pre-monsoon season.

6.4.3 Spatial Variability of Benthic Fluxes

The in situ fluxes was estimated for all the sectors of the lagoon sediments (Table 6.1). The spatial variation for nutrient fluxes found to be relatively higher in outer channel area compared to northern sector. The variation for nutrient fluxes

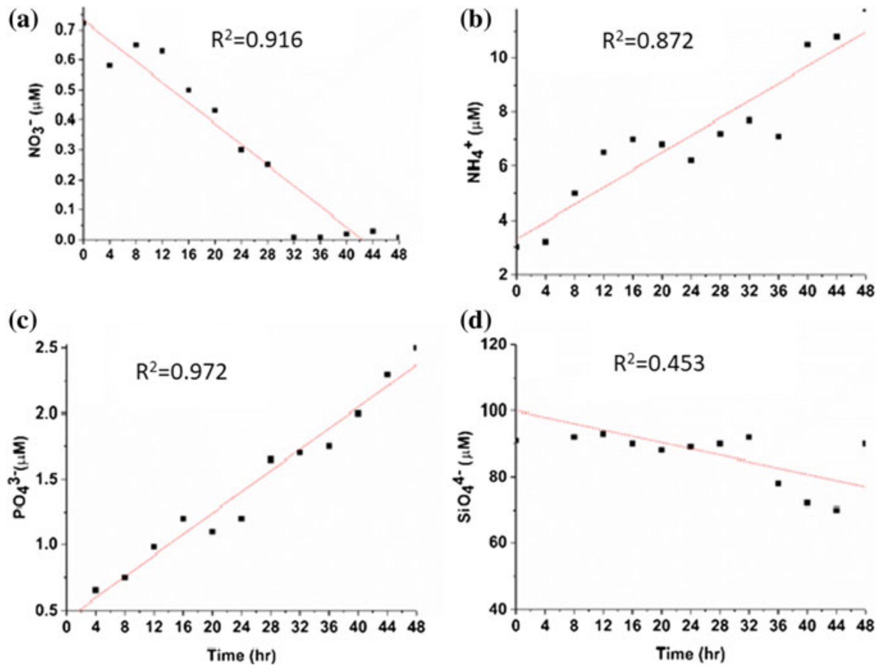

Fig. 6.4 **a–d** Variation in nutrient concentrations inside benthic chamber with respect to time during monsoon season

remained 3,000 and 14,000 μmol m^{-2} d^{-1} for NO_3^-, 2,000 and 20,000 μmol m^{-2} d^{-1} for NH_4^+, 120 and 2,400 μmol m^{-2} d^{-1} for PO_4^{3-}, 3,000 and 20,000 μmol m^{-2} d^{-1} for SiO_4^{4-} in the whole lagoon. The macro faunal abundance formed the 30–45% spatial variation of benthic fluxes of nutrient in San Fransisco Bay.

6.5 Discussion

6.5.1 Exchange of Nutrients at Sediment and Water Column Interface

Nutrient fluxes reaches a maximum level particularly during pre-monsoon. In general NH_4^+ was the only form of desorbed DIN from sediment. The benthic DIN efflux contributed with 76–100% of NH_4^+ (Blackburn and Henriksen 1983). It attributed due to low nitrification rate at this particular site (Horrigan et al. 1981). During monsoon, lowest flux observed could be due to effect of changes in salinity. The lagoon, Chilika behave saline (30–33 PSU) characteristics during pre-monsoon, however, the fresh water (1–2 PSU) characteristics prevailed during

Table 6.1 Database of the benthic flux with the benthic chamber from the respective sectors of the Chilika lagoon during pre-monsoon and monsoon seasons

Seasons	Pre-monsoon								Monsoon							
Sectors/ parameters	NO_3^- (μmol m^{-2} d^{-1})		NH_4^+ (μmol m^{-2} d^{-1})		PO_4^{3-} (μmol m^{-2} d^{-1})		SiO_4^{4-} (μmol m^{-2} d^{-1})		NO_3^- (μmol m^{-2} d^{-1})		NH_4^+ (μmol m^{-2} d^{-1})		PO_4^{3-} (μmol m^{-2} d^{-1})		SiO_4^{4-} (μmol m^{-2} d^{-1})	
Flux	Diffusive	Benthic	Diffusive	Benthic	Diffusive	Benthic	Diffusive	Benthic	Diffusive	Benthic	Diffusive	Benthic	Diffusive	Benthic	Diffusive	Benthic
NS	280	3,000	4,450	6,470	280	120	1,500	11,300	1,200	4,300	450	2,000	15	450	3,450	2,000
CS	450	4,500	4,830	8,500	245	450	4,500	14,500	2,000	12,300	780	7,530	620	2,150	3,610	4,500
OC	1,400	11,500	5,500	20,000	255	2,500	8,430	20,000	2,500	14,000	1,220	8,120	940	2,400	4,800	8,600

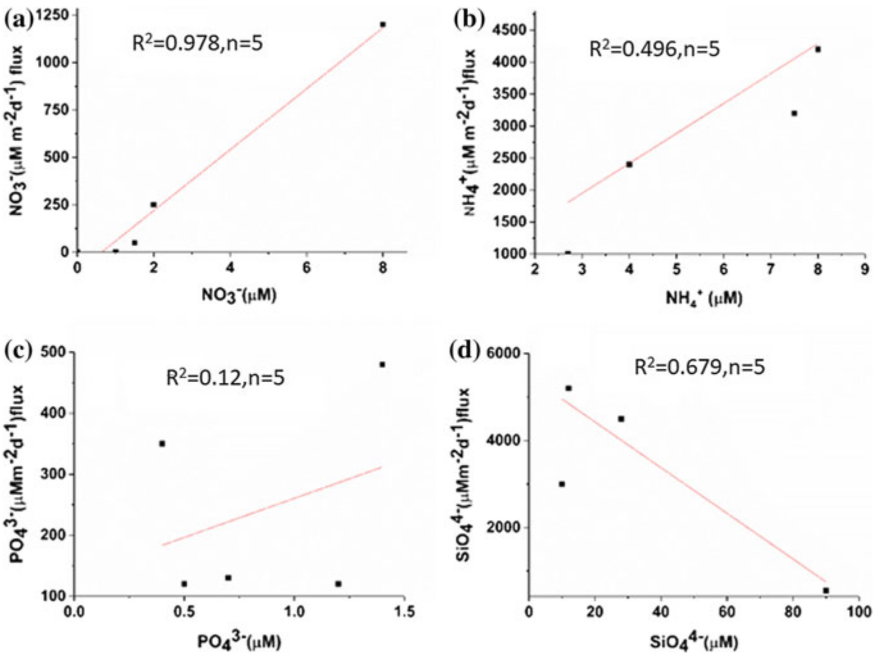

Fig. 6.5 a–d Correlationship in between benthic nutrient fluxes and nutrient concentrations in water column

monsoon season. The sediment was penetrated with low saline water. The vertical characteristics of salinity along the pore water, which gradually increases from 1 at interface to 14 at 20 cm (Fig. 6.7b). The increasing trends of salinity towards down the core could be due to the penetrating effect on NH_4^+ flux. The experimental observation also verified that the increasing salinity can boost benthic NH_4^+ release (Gardner et al. 1991). At low salinity, major portion of NH_4^+ in pore water remains loosely bound to sediment particles and is easily exchangeable. This condition favours significant nitrification in the upper oxic layer after curbing release of benthic NH_4^+. During pre-monsoon, DIN flux experienced a dramatic variation as it accomplished a highest level and substantially became negative in monsoon. This observation points towards the fact that the estuarine sediment behave as a net source of DIN in pre-monsoon and a sink in monsoon. But, the sediments serve as sink for NO_3^- in both the seasons. The benthic PO_4^{3-} release was not control by the effect of variation in PO_4^{3-} concentration in the water column (Fig. 6.5d). The higher benthic flux of PO_4^{3-} appeared for Chilika lagoon compared to other ecosystems (Table 6.2). During monsoon, the lower value of SiO_4^{4-} efflux, attributed due to the decrease in concentration in between porewater and water column, since coastal lagoon water was highly supplemented with SiO_4^{4-} Niencheski and Jahnke (2002) also reported similar trend in Patos lagoon.

Table 6.2 In situ benthic flux of nutrients (µmol $m^{-2}d^{-1}$) in coastal ecosystems on global scale

Coastal ecosystems	NO_3^- flux	NH_4^+ flux	DIN flux	PO_4^{3-} flux	SiO_4^{4-} flux	References
Marano and Grado Lagoon (northern Adriatic Sea, Italy)	−2,000.12	3,670	–	−49.00	−2,626.00	De Vittor et al. (2012)
Tjärnö area, Swedish west coast	–	–	−600 to 4,000	−60 to 200	130–6,000	Engelsen et al. (2008)
Makirina Bay (Central Dalmatia, Croatia)	375.00	575.00	–	9.05	–	Lojen et al. (2004)
Chilika, East coast of India	8,266.00	8,769.00	–	1,344.5	10,149.5	Present study

6.5.2 *Stoichiometric Ratio of Nutrient Fluxes*

The oceanic elemental cyclic largely governed by the process of mineralisation of nutrients in sediments and release back to water column. The processes involved to maintain the Redfield ratio of nutrients in water column in the steady state by assembling the ratio of C, N and P in algal cell and the ratio at which these biogenic elements are released back to water column through remineralisation. Due to some biogeochemical process like benthic nitrification and de-nitrification, and fractionation of elements occurring in the aquatic ecosystems, fail to maintain the Redfield ratio for the nutrients in the aquatic ecosystems (Suess and Müller 1980; Suess 1979; Deka et al. 2016).

The stoichiometry ratio of nutrient flux by the sediments of lagoon, Chilika was verified by equating average molar ratios of NH_4^+:PO_4^{3-}:SiO_4^{4-} obtained in diffusive fluxes, by calculating from gradients in pore water chemistry and in situ measurement of benthic flux by benthic chamber experiments. The results were presented in the Table 6.3. The nutrient ratio maintained nearly same both by calculated diffusive fluxes and in situ benthic fluxes in the northern sector. In northern sector sediments the Si:P ratios of calculated diffusive fluxes and measured in situ fluxes maintained nearly four times measurement than in central sector sediments (Table 6.3). The significant level of macro faunal irrigation and opposing

Table 6.3 Spatio temporal variations of stoichiometric ratios of NH_4^+ : PO_4^{3-}: SiO_4^{4-} calculated in diffusive fluxes and in benthic fluxes in the lagoon

Seasons	Pre-monsoon		Monsoon	
Sectors/flux ratio	Diffusive	Benthic	Diffusive	Benthic
NS	15.9:1:5.4	53.9:1:94.2	30:1:230	4.4:1:2.25
CS	19.7:1:18.4	19:1:32	1.3:1:5.82	3.5:1:2.1
OC	22:1:33	8:1:8	1.3:1:5.1	3.4:1:3.6

the flows of soluble phosphate from surface sediments possessing huge quantity of amorphous ferric oxy-hydroxides which are extractable with ammonium oxalate responsible for the significant higher measurement of Si:P ratios in fluxes from central sector sediments (Piercey 1981). The reason for strong relation in between interstitial phosphate with iron oxy-hydroxides in outer channel, supported variation of the Si:N:P ratios of both calculated diffusive fluxes and in situ benthic fluxes. The stoichiometric ratio for benthic fluxes studied by many authors to clarify the behaviour of nutrients in coastal oxic and anoxic ecosystems.

The higher (1.17) value of NH_4^+ :SiO_4^{4-} ratio observed in monsoon compared to the ratio value (0.76) during pre-monsoon season. The lower in ratio value during pre-monsoon compared to its theoretical value (1:1) represented that the lagoon, Chilika was dominated by diatoms during this period. However the reducing level of biogenic silica flux to the lagoon during monsoon resulted due to the decrease in population of diatoms. The decrease in population of diatoms has been observed in the lagoon by Adhikary and Sahu (1992). The range of variation of DIN:DIP ratio was high (17) during pre-monsoon compared to monsoon, which is declined to 9.6 attributed due to effect of the net consumption of combined N and relatively higher release of PO_4^{3-} in monsoon. Higher de-nitrification rate causes the rise in NO_3^- levels subsequently the decrease in salinity level in monsoon favours low benthic realise of NH_4^+, which allows the lagoon sediment a net sink of N in monsoon (Fig. 6.6).

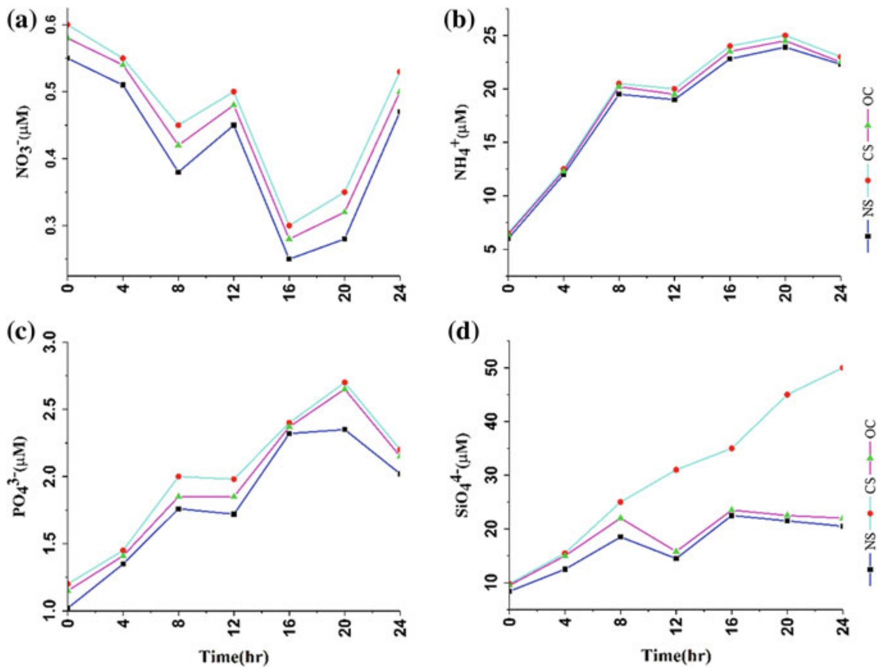

Fig. 6.6 Sectoral variation in benthic exchange rate in the study area

6.5.3 Pore Water Nutrient Profile

The variation of pore water nutrient concentrations observed particularly in upper layer of sediment in between pre-monsoon and monsoon seasons. During pre-monsoon, there is no regular trend of NO_3^-, $\mathbf{NH_4^+}$ and SiO_4^{4-} concentration observed in the sediment column could be attributed due to higher irrigational activities by benthic macro fauna (Ansari and Parulekar 1993). The activated nitrification process helped to nitrify some portion of $\mathbf{NH_4^+}$ to NO_3^-, as a result, there is sudden rise in NO_3^- and decline in $\mathbf{NH_4^+}$ concentration in the pore water observed. Somehow, other benthic organisms churning up the upper few centimetre of sediment. During pre-monsoon, the lowering in fresh organic matter flux to the sediment causes relative decrease in population density of macro faunal organisms, as a result a constant increasing trend of $\mathbf{NH_4^+}$ and SiO_4^{4-} observed.

During monsoon, the fresh water flow to the lagoon, Chilika from Mahanadi river tributaries drastically suppress the salinity level of the pore water. High riverine discharge carries silt borne particulate matter and made availability of silt clay sediment, which responded to increases the porosity at surface up to 95% compared to pre-monsoon (Fig. 6.7a). During monsoon, due to decline in level of salinity of pore water responsible for considerable decreasing in level of $\mathbf{NH_4^+}$ concentration compared to pre-monsoon values (Gardner et al. 1991). Hopkinson et al. (2001) observed that the increasing in salinity level of bottom water enhance the $\mathbf{NH_4^+}$ concentration in pore water and also responsible for considerable increase in benthic $\mathbf{NH_4^+}$ release has also been observed in Parker estuary. No much variation found for Pore water SiO_4^{4-} in between pre-monsoon and monsoon season in the upper layer. Since, the riverine water carries huge quantities of silica to the lagoon during monsoon resulted in significant increase in water column and reduced the concentration gradient across sediment water interface and also responsible for lower flux.

6.5.4 Benthic Flux and Diffusive Flux

This study focuses on the measurement of nutrient flux at sediment–water interface. Generally, two methods were employed for estimation of flux viz. diffusive flux and benthic chamber experiments. The benthic faunal studies highlighted that the sediments of Chilika are inhibited by various groups of benthic macrofauna and meiofauna such as polychaetes and copepods (Ansari et al. 2015). The seasonal variability of a benthic population, which is highest during pre-monsoon and post-monsoon periods due to increase in salinity. The availability of large number benthic population, which are responsible for increasing the benthic fluxes than diffusive flux by increasing rate of bio-turbation and bio-irrigation in the lagoon, sediment. During the pre-monsoon period, the diffusive fluxes contributed 13% of

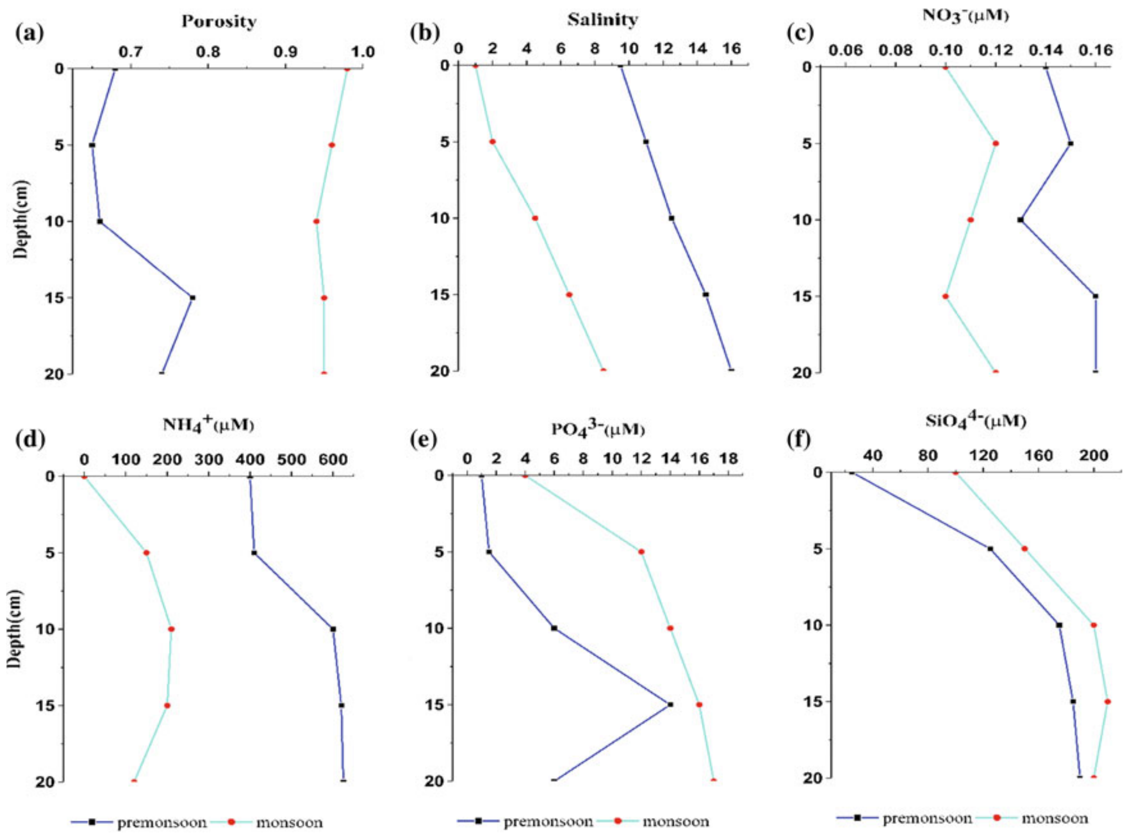

Fig. 6.7 Seasonal variations of pore water profile for porosity, salinity and nutrients of the study area

NO_3^-, 42% of NH_4^+, 25% of PO_4^{3-} and 31% of SiO_4^{4-} to the corresponding benthic fluxes measured by the benthic chamber. In monsoon diffusive fluxes of NO_3^-, NH_4^+, PO_4^{3-} and SiO_4^{4-} contributed respectively.

The ratio between in situ fluxes value and calculated diffusive fluxes resulted enhancement factors. During pre-monsoon, the enhancement factors were 8.9, 2.4, 4 and 3.17 for NO_3^-, NH_4^+, PO_4^{3-} and SiO_4^{4-} respectively. During monsoon, fluxes of NO_3^-, NH_4^+, PO_4^{3-} and SiO_4^{4-} were enhanced 1.60, 7.20, 3.17 and 1.27 times respectively, it signifies that the macrofaunal activities were still predominant in monsoon to a smaller range. Due to the activity of bio-irrigation by microbenthic organisms like polychaetes and oligochates in the sediment of the Potmac estuary, there is hiring up 20 times in ammonium and silicate fluxes (Callender and Hammond 1982). The macrofaunal activities possibly increases the fluxes of DIN 2.5–4.5 times in an estuary near Norsminde fjord (Kristensen et al. 1991). The enhancement of 2, 1.2 and 4.5 times of NO_3^-, NH_4^+ and PO_4^{3-} flux respectively in Lake Illawarra was also reported by Qu et al. (2005).

6.5.5 *Turnover Period for Benthic Flux*

The required time for benthic fluxes to replace available nutrient in overlying water column is known as benthic flux turnover period. It is expressed as the ratio of quantity of a particular nutrient in water column and the benthic flux of the same nutrient. During pre-monsoon, turnover period of DIN was calculated as 6 days (Table 6.4), which clarify that benthic flux can replace whole pelagic DIN in ~6 days. However, during monsoon, the riverine DIN flux subjected directly to the sediment makes the calculation of gross DIN i.e. overall DIN scenario in the lagoon difficult. During pre-monsoon, the contribution of NH_4^+ fractions is still higher and the net DIN efflux with an average turn over time 5.6 days. During monsoon, turnover time of DIN flux could not be calculated due to the negative contribution of DIN flux. During pre-monsoon, average turnover time for PO_4^{3-} and SiO_4^{4-} were 26.6 and 10.2 days respectively. But, during monsoon it was ~6 and 864 days respectively. During monsoon, the long turnover time of SiO_4^{4-} was observed.

Table 6.4 Seasonal status of benthic turnover period in Chilika lagoon

Seasons	Turnover period (day)			(%) benthic flux with respect to total flux		
	DIN	DIP	SiO_4^{4-}	DIN	DIP	SiO_4^{4-}
Pre-monsoon	6	26.6	10.2	52.48	3.0	44.5
Monsoon	(–)	6	864	70.60	7.3	22.1

6.5.6 Ecological Consequence of Benthic Fluxes in the Lagoon

The lagoon experiences strong seasonality with respect to saline condition, during pre-monsoon, the ecological status of the lagoon behaved like marine and during monsoon season, ecological significance of the lagoon dominated with fresh water body. The lagoon and its adjacent coastal system loaded with heavy riverine nutrients discharge from the periphery Rivers. The significant variation of benthic fluxes on spatio temporal scale largely depends on the significant variation water temperature, benthic activities and river runoff. The nutrient exchange at sediment and water column significantly varied with the effect on season. During pre-monsoon, the coastal ecosystems experiences maximum nutrient fluxes, which is attributed to the major remineralization of planktonic organic matter in the sediments. Lower nutrient fluxes observed during monsoon season, possibly due to the riverine water discharge, lowering water temperature, organic matter load and efficient microbenthic activities. The benthic turnover time of NH_4^+, PO_4^{3-} and SiO_4^{4-} were 7, 25 and 11 days respectively during pre-monsoon, which remain on higher side as compared to monsoon. This may be due to hypothesis of static condition; nutrients leached out of the sediments get redistributed in the overlying water as the lagoon remains well mixed during pre-monsoon. During pre-monsoon, productivity is high even in depletion in nitrate concentration. Which marginated the estuarine productivity from nutrient limitation. The benthic flux calculation also reveals that sediments of the lagoon act as a sink of NO_3^- during pre-monsoon. However, due to higher flux of NH_4^+ into the water column of the lagoon.

6.6 Conclusions

The benthic nutrient fluxes at the interface of sediment and water column for the lagoon, Chilika experiences variation in concentration with respect to locations and seasons. The overlying water characteristics have significant effect on the quantity of fluxes. The significant higher level of nutrient fluxes measured in situ with benthic chambers may be 1–12 times the flux estimated by the diffusion flux methodology. The irrigation of sediments of the outer channel zone by macrofauna is responsible for the large variation in benthic flux. The benthic turnover time for SiO_4^{4-} is more compared to other nutrients during monsoon season. The ecological significance of benthic flux resulted that the benthic turnover time of NH_4^+, PO_4^{3-} and SiO_4^{4-} were 7, 25 and 11 days respectively during pre-monsoon, which remain on higher side as compared to monsoon.

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Chapter 7
Determination of Anthropogenic Sources in the Groundwater Chemistry Along KT Boundary of South India

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7.1 Introduction

The Cretaceous, Tertiary (K/T) limit is exposed in five unique areas like Pondicherry, Vridhachalam, Ariyalur, Tanjore and Sivaganga locale of Cauvery basin of Tamil Nadu, with a thickness of around 6 km over the Archean formations (Baneerjee 1972; Ramarao 1960). The Ariyalur area demonstrates a huge portrayal of this arrangement (Madhavaraju and Lee 2010). The K/T aquifer framework in Ariyalur District is the main source of providing drinking water to this area. Attention for groundwater abstraction has expanded during recent decade because of the increase in water demand and rigorous increase of use of water by diversified populace, leading to the accumulation of various chemical constituents into the groundwater. Thus a thorough understanding of the physico-chemical processes leading to the increase of concentration of chemical constituents in groundwater by the people will upgrade the awareness towards safe use of groundwater. Few works were reported on anthropogenic sources and its influence on groundwater chemistry from different parts of world along with the present study area (Madhavaraju et al. 2002; Ayyasami 2006; Harrison and Safford 2006; Jirakova 2010; Perry and Paytan 2009; Ledesma-Ruiz et al. 2015; Patel et al. 2019a, b; Das et al. 2016). The hydrochemical parameter has been used to understand the recharge process and

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nitrate pollution along the KT sedimentary aquifer by Adelana et al. (2002, 2006). The layered aquifers of cretaceous and Tertiary age along the Pondicherry region and variation in their water quality was studied by Thilagavathi et al. (2012). Similar studies were also studied by Howari et al. (2005), and Johns (1968) in North Jordan and KT aquifers of south western Victoria of Australia respectively. Weathering process governs the dissolved ion in groundwater, which has been highlighted from the hydrochemical studies (Chidambaram et al. 2010). Chidambaram et al. (2007) studied on the significance of various litho units in governing the chemistry of the groundwater and stated that weathering process releases HCO_3 to the groundwater. pCO_2 which varies with lithology governs the saturation states of minerals. In any case, geochemical attributes, and in addition the anthropogenic sources of groundwater of this locale, has not been dealt in detail. Hence, the main objective of present investigation is to determine the anthropogenic exercises in the groundwater of this area by an integrated approach.

7.2 Study Area

Ariyalur, the proposed study area located along the southern part of Tamil Nadu, (Fig. 7.1) which covers an area of 1,774 km^2 within the latitudes of 11°449′ and 10°974′ N and longitudes 78°808′ and 79°275′ E. A significant stream Vellar flows within the investigation region in the northern half together with the minor tributaries like Marudiyar streams diagonally from SW to SE. There are 5 LU/LC patterns is noted i.e. Farming land, water bodies, orchard waste and scrub land. The investigation space gets notable precipitation during the NE storm period (Oct–Nov) but scanty showers received during SW monsoon (July–Aug) with a standard yearly precipitation of 1096 mm. The geology of the study space is for the most part consists of charnockites, migmatite gneiss, sandstones and limestones. The shallow marine atmosphere with a particularly rich faunal progression of Albian—Maastrichtian age is normal for cretaceous progression of this district. Ariyalur is a rift basin and splits in 3 groups as Uttatur, Trichinopoly and Ariyalur on the basis of lithology (Devaraj et al. 2016).

7.2.1 Aquifer Parameters

The KT groundwater is mainly limited to Archean, cretaceous, tertiary, and alluvial aquifer. The water level varies considerably throughout the post-monsoon (POM) and pre-monsoon (PRM). It ranges from 1–8 mbgl and 1–6 mbgl during the PRM. CGWB (2009) has reported the range of water level rise and fall varies between 0.0027–0.16 m/year and 0.05–0.07 m/year respectively and flow direction is towards the SE part of the area. Sedimentary formation has shallow aquifer,

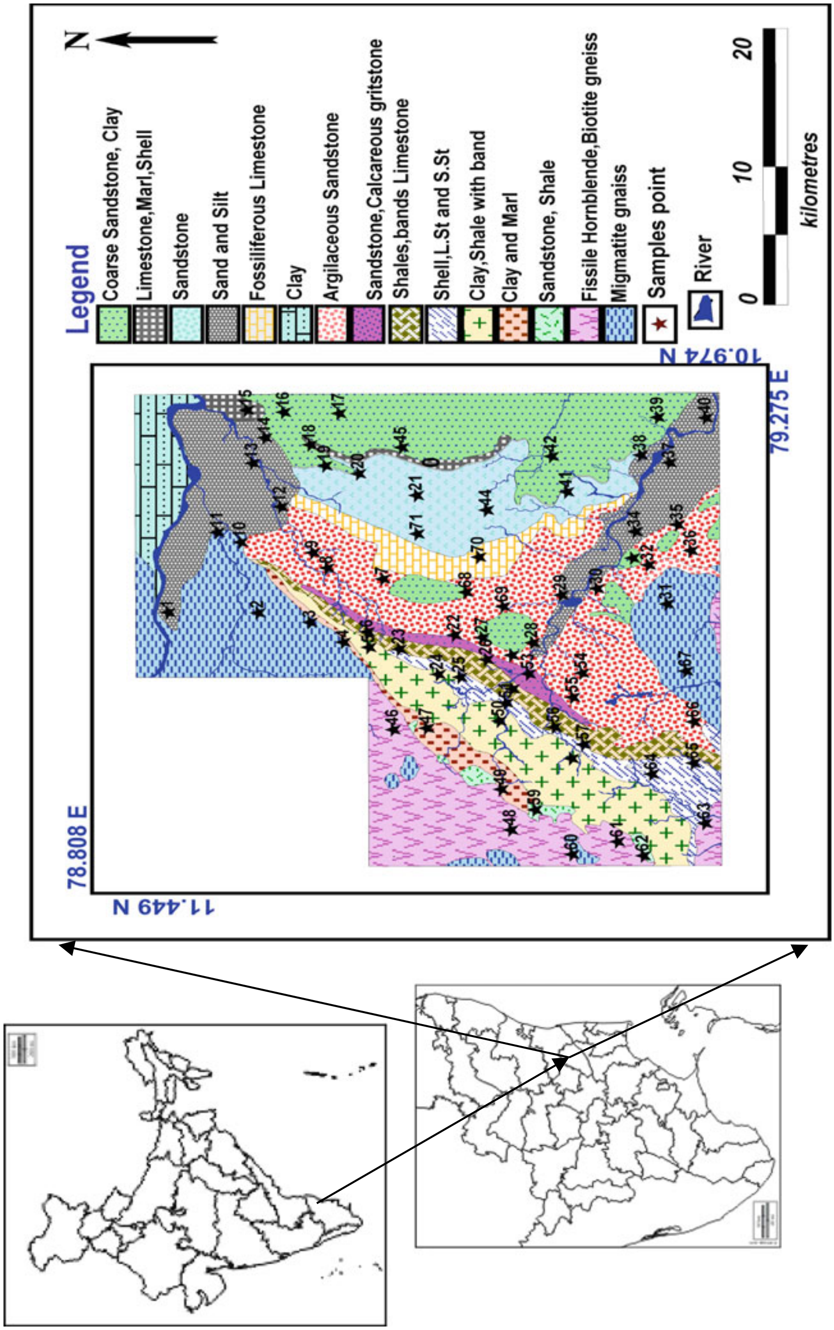

Fig. 7.1 Geology and sample location map of the study area alongside the Major rivers

however hard rock formation along the study area contained both shallow and deeper aquifer. The shallow water level within the hard rock terrains on the SW half could be due to the weathering. Weathering happens due to the interaction of water within the fractures with the formation. Shallow water level in addition noted on the southern a part of the district and e the stream flows from SW to SE course.

7.3 Materials and Methods

Seventy-one water samples were collected from hand pumps from supported spatial variance and lithological coverage. pH scale of water samples was measured by pH conductor, (Thermo Orion five-star meter). Physical parameters like pH, EC and TDS were measured in the field by using hand held water analysis kit.

Major ions like HCO_3^-, Cl, SO_4^{2-}, PO_4^{3-}, NO_3^-, H_4SiO_4, Ca^{2+}, Mg^{2+}, Na^+ and K^+, Ca^{2+}, Mg^{2+}, Cl^-, HCO_3^-, were analyzed by volumetric analysis technique (Senthilkumar and Elango 2013; Thilagavathi et al. 2013, 2014), Na^+ and K^+ by flame photometry and SO_4^{2-}, PO_4^{3-}, NO_3^- and H_4SiO_4 by spectro photometry (DR-6000). The analytical error percentage was calculated by considering total cation (Tz^-) and total anion (Tz^+) values by using the formula given in the Eq. (7.1) and that varies in between 5 and 10%.

$$((\mathrm{Tz}^- - \mathrm{Tz}^+)/(\mathrm{Tz}^- + \mathrm{Tz}^+) * 100) \tag{7.1}$$

Statistical analysis (correlation matrix and factor analysis) has been carried out by using SPSS-17. Major ion data used as input for the software, correlation matrix table has been generated. Eigen value '1' has been considered as minimum for factor extraction and factor scores are calculated for each sample. The spatial distribution diagram was plotted by using MapInfo (8.5) software with combination of vertical mapper (VM).

Water samples were collected in a 60 mL air tight plastic bottle for stable isotope analysis. The collected water samples were analyzed for stable isotope (oxygen-18 ($\delta^{18}O$)), Deuterium (δD) by using mass spectrometer (Finnigan Deltaplus Xp, Thermo electron Corporation, Bermen, Germany) adopting gas stabilization technique with a preciseness of 0.5 and 0.1‰ (2 σ criterion). Stable isotope results were expressed with respect to VSMOW (Vienna Standard Mean Ocean water) in units δ (‰) where

$$\delta = \left(\mathrm{R_{sample}} - \mathrm{R_{SMOW}}/\mathrm{R_{SMOW}}\right) \times 10^3 \tag{7.2}$$

where, R = D/H or $^{18}O/^{16}O$.

7.4 Results and Discussion

7.4.1 General Hydrochemistry

The maximum, minimum and average of chemical constituents and its comparison with WHO (2011) standard is given in the Table 7.1. Almost all the parameter falls above the permissible limit of the WHO (2011) standard for the groundwater samples except pH and Sulphate. The groundwater in this region is slightly alkaline in nature and within range of WHO (2011) standard (Table 7.1). The order of dominance of major anions and cations are:

$$HCO_3^- > Cl^- > H_4SiO_4 > NO_3^- > SO_4^{2-} > PO_4^{3-} \text{ and}$$
$$Ca^{2+} > Na^+ > Mg^{2+} > K^+ \text{ respectively.}$$

7.4.1.1 Electrical Conductivity (EC)

Higher EC is noted in southern and SW part of the study area (Fig. 7.2), and ranges from 440 to 14,430 µscm^{-1} which reflects leaching or dissolution of the aquifer

Table 7.1 The statistics of minimum, maximum and average of the chemical constituents and $\delta^{18}O$ and δD in groundwater (all values in mg/L except EC in µs/cm, $\delta^{18}O$ and δD in ‰ and U in ppb)

Season	N = 71			
Parameter	Min	Max	Avg	WHO (2011)
pH	6.42	7.81	7.07	6.5–8.5
Ca^{2+}	14.00	380.00	113.35	75.00
Mg^{2+}	9.60	139.20	55.90	50.00
Na^+	11.00	346.70	72.30	200.00
K^+	0.20	68.50	9.05	12.00
F^-	0.04	4.00	0.70	–
Cl^-	30.45	868.53	208.88	250.00
HCO_3^-	130.60	1,134.60	494.47	500.00
NO_3^-	−5.96	120.20	18.77	45.00
PO_4^{3-}	−0.09	0.51	0.03	–
SO_4^{2-}	0.30	10.97	2.59	250.00
H_4SiO_4	26.00	170.00	87.73	–
TDS	248.00	5,983.00	1,166.69	500.00
EC	440.00	14,430.00	2,657.10	1,500.00
Uranium (U)	118.70	0.06	6.44	–
$\delta^{18}O$	−6.04	−0.39	−3.55	–
δD	−40.52	−8.35	−27.95	–

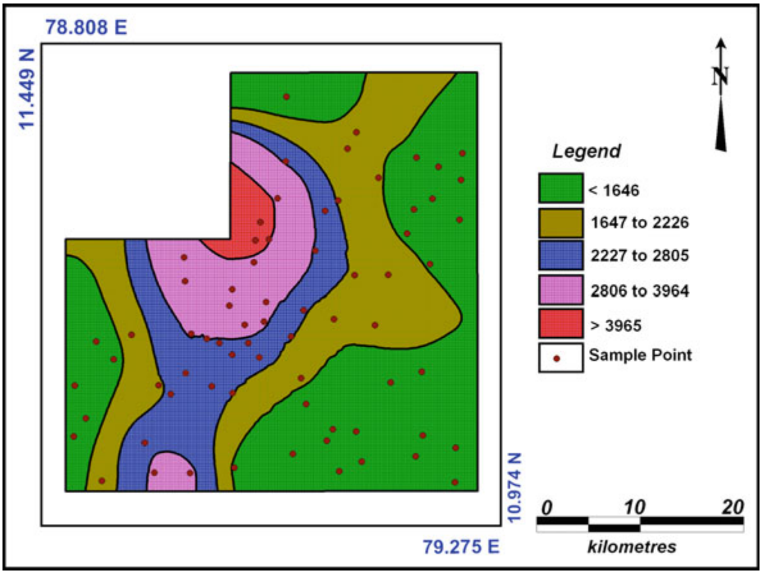

Fig. 7.2 Spatial distribution of electrical conductivity of the groundwater samples collected in POM (in µs/cm)

material or mixing of saline water. Based on electrical conductivity, waters are classified into (1) fresh (<1,500 µS/cm), (2) brackish (1,500–3,000 µS/cm), and (3) saline > 3,000 µS/cm (Saxena and others 2003). Based on the classification 18.30% of the samples are fresh.

7.4.2 *Statistical Analysis*

The geochemical characters of groundwater are studied in statistical approach by means that of variable statistical strategies like correlation analysis, correlational analysis and factor score. A matrix is established supported methodology of covariance using Pearson's coefficient of correlation between ion pairs (Swan et al. 1985). Correlational analysis offers the final relationship between measured chemical variables by elucidating and classifying the original data. Correlational analysis also can be accustomed to confirm the geographical distribution of the ensuing factors.

7.4.2.1 Correlation Among Hydrochemical Parameter

The statistical analysis shows that, good correlation noted between Ca with Na, Cl, HCO_3, PO_4, EC; Mg with Na, Cl and EC, Na with Cl, HCO_3, PO_4 and EC; Cl with PO_4, EC, HCO_3 and PO_4 shows positive correlation with the EC. Cl shows good correlation with Ca, Mg, Na, and HCO_3 (Table 7.2) indicating leaching of secondary salts and a strong correlation of HCO_3 with Ca, Mg, Na and K shows chemical weathering. Good correlation is observed for Ca, Cl, HCO_3, Na, K and PO_4 indicating the anthropogenic sources influence into the system. Uranium shows the week positive correlation between Ca, Mg and EC (Das et al. 2017; Kumar et al. 2017). pH shows negative correlation with U reflecting decrease of pH during the dissolution of soil minerals (Bruno and Casas 1992). This also leads to the inference that decreasing pH results in increasing uranium concentration in solution (Charalambous et al. 2013).

7.4.2.2 Factor Analysis

The data reduction analysis shows that 5 factors were extracted with 72.43% of Total data variability (TDV). The Factor 1 is represented by 35.83% of TDV with a strong positive loading of Ca, Na, K, Cl, HCO_3, PO_4 and EC (Table 7.3). This factor exhibits the process of dissolution of secondary salts during the monsoon into the aquifers. Factor II is represented by Mg, Cl, EC, NO_3 and U with 11.5% of TDV which reflects contamination of groundwater from agricultural areas (with dolomites used for neutralization of acid solids and agricultural additives) (Gosk et al. 2006). Factor III with the TDV of 9.2% is represented by SO_4 and Temperature indicating the predominance of temperature in the dissolution of SO_4 mineral. Factor IV with the TDV of 8.61% represented by pH and F showing the dominance of the base ion exchange and Factor V is H_4SiO_4 dominant with TDV of 7.17%, indicating the silicate dissolution (Chidambaram et al. 2008; Das et al. 2015; Das and Kumar 2015).

7.4.3 *Stable Isotopes of Water (δD and δ^{18}O)*

The Stable isotopes are ideal tracers for identifying the groundwater flow direction and processes like mixing, evaporation effect in the recharge mechanism (Coplen 1993). The maximum, minimum and average of the isotope results in permil is given in Table 7.1. The $\delta^{18}O$ and δ^2H values ranges between −6.04 and −0.39‰ and −40.52 to −8.35‰ respectively.

The association between δ^2H and $\delta^{18}O$ in atmospherically precipitation usually known as Global meteoric water line (GMWL) is outlined by the expression:

$$\delta^2H = 8^*\delta^{18}O \pm 10 \tag{7.3}$$

Table 7.2 Correlation analysis of groundwater samples

	Ca	Mg	Na	K	F	Cl	HCO_3	NO_3	PO_4	SO_4	H_4SiO_4	pH	EC	Temp
Mg	0.284	1.000												
Na	0.77	0.67	1.000											
K	0.85	0.34	0.14	1.000										
F	−0.15	0.37	0.53	0.20	1.000									
Cl	0.84	0.63	0.97	0.92	0.34	1.000								
HCO_3	0.36	0.93	0.65	0.93	0.12	0.20	1.000							
NO_3	0.71	0.77	0.04	0.55	0.59	0.34	0.76	1.000						
PO_4	0.33	0.10	0.92	0.31	0.68	0.55	0.18	0.01	1.000					
SO_4	0.88	0.59	0.10	0.29	−0.16	0.48	0.90	0.29	−0.42	1.000				
H_4SiO_4	−0.25	−0.80	−0.08	−0.15	0.98	−0.61	−0.32	−0.85	−0.39	0.15	1.000			
pH	−0.75	−0.17	0.13	−0.24	0.92	−0.98	0.54	−0.50	−0.41	−0.43	−0.55	1.000		
EC	0.98	0.83	0.11	0.27	0.05	0.31	0.97	0.35	0.83	0.94	−0.80	0.06	1.000	
Temp	0.70	−0.38	0.45	0.11	0.47	0.19	0.37	0.35	0.79	0.25	0.08	0.74	0.56	1.000
U	0.46	0.50	0.25	0.61	−0.46	0.37	0.03	0.25	−0.59	0.80	−0.98	−0.56	0.36	0.40

Table 7.3 Factor analysis of the samples (Varimax rotated)

	Fact 1	Fact 2	Fact 3	Fact 4	Fact 5
Ca^{2+}	0.54	0.45	0.01	−0.57	0.39
Mg^{2+}	0.76	0.52	−0.46	0.89	−0.86
Na^{+}	0.15	0.65	0.57	0.28	−0.40
K^{+}	0.33	−0.21	0.45	−0.76	−0.25
F^{-}	0.87	−0.86	0.58	0.83	0.10
Cl^{-}	0.96	0.64	0.69	−0.42	−0.46
HCO_3^{-}	0.18	0.03	0.31	0.00	−0.69
NO_3^{-}	0.82	0.69	−0.80	−0.10	−0.85
PO_4^{3-}	0.67	−0.47	−0.64	0.00	−0.16
SO_4^{2-}	0.17	0.80	0.08	−0.55	−0.49
H_4SiO_4	−0.52	−0.54	0.08	−0.20	0.56
pH	−0.41	0.04	0.47	0.19	−0.06
EC	0.33	0.04	0.34	0.83	−0.90
Temp	0.40	−0.27	0.39	0.45	0.73
U	−0.12	0.10	0.56	−0.29	−0.36
Eigen value	5.37	1.73	1.39	1.29	1.07
% of variance	27.27	14.29	11.36	11.16	8.34
Cumulative %	27.27	41.56	52.92	64.09	72.43

Fact factor

The bivariate plot of $\delta^{18}O$ and δD is given in the Fig. 7.3 and correlate with the GMWL. The equation of local meteoric water line (LMWL) was derived from the stable isotope values the samples collected throughout SWM of Tamil Nadu and as given as $\delta D = 7.89 * \delta^{18}O + 10$, (Chidambaram et al. 2009). The LMWL provides a baseline for groundwater investigations of a locality, that slightly differs from the global line as a result of the variations in climatical and geographic parameters.

Enriched isotopes are noted in Archean and Cretaceous formations. The lighter isotopes are ascertained within the Tertiary and Quaternary formation (Fig. 7.3). Few Cretaceous, Tertiary and Quaternary samples demonstrate depleted isotopes, that recommend that these waters are isotopically almost like the Global meteoric water line and Local meteoric water line. it's implicit that the recharge is predominant throughout infiltration instead of the lateral flow. Hence, the groundwater ought to reveal the mean isotopic composition of the watercourse or the lake or that of local precipitation (Aggarwal et al. 2004). Few samples of Archean and Cretaceous formation shows enriched isotopes, which because of the recharge from open water bodies like rivers and tanks. The enrichment is due to direct isotopic exchange with atmospherical moisture. Few samples from Quaternary, Tertiary and Cretaceous formation have depleted isotopes and noted near the GMWL, revealing the direct recharge from rainfall. There also are representations of samples from Cretaceous, Tertiary and Quaternary with enriched $\delta^{18}O$ reflective of the evaporation nature of the samples (Karmegam 2012).

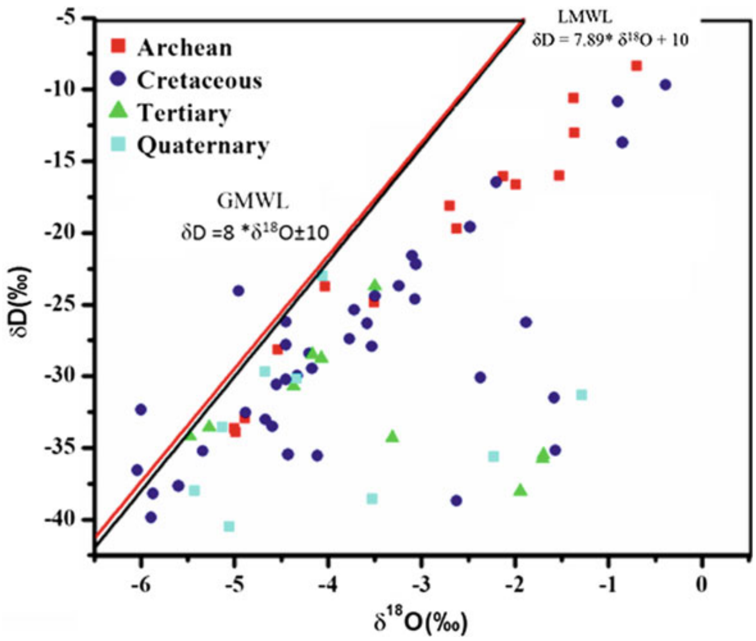

Fig. 7.3 Plot for $\delta^{18}O$ versus δD precipitation samples

7.4.3.1 The δ^{18}O—Deutrium-Excess Relationship

The variations in environmental condition like evaporation in precipitation supply areas, the fractionation of oxygen and hydrogen doesn't unremarkably occur underneath balance conditions leading to the distinction between $\delta^{2}H$ and $\delta^{18}O$. This factor was outlined as d-excess (Dansgaard 1964), it reflects both non-equilibrium method an index of evaporation rate developed as:

$$d\text{−excess} = \delta^{2}H - 8 * \delta^{18}O \tag{7.4}$$

The d-excess in precipitation depends totally on meteoric environment like humidity, temperature and wind regime within the precipitation supply (Jouzel and Vostok 1984). Hence, d-excess plays a vital role in determining the contribution of vapor from various sources to the atmosphere at a given location.

The d-excess values of the groundwater of the proposed study ranges between −22.64 and +15.6‰ (Fig. 7.4). Groundwater has undergone evaporation before infiltration if d-excess value is around +5‰ (Caro et al. 2009). Most of the Archean samples and few Cretaceous samples have lower d-excess value which reflects kinetic evaporation of precipitated water before recharge (Dalai et al. 2002; Krishnamurti et al. 1991). Elevated d-excess (>10.5%) most of the Cretaceous,

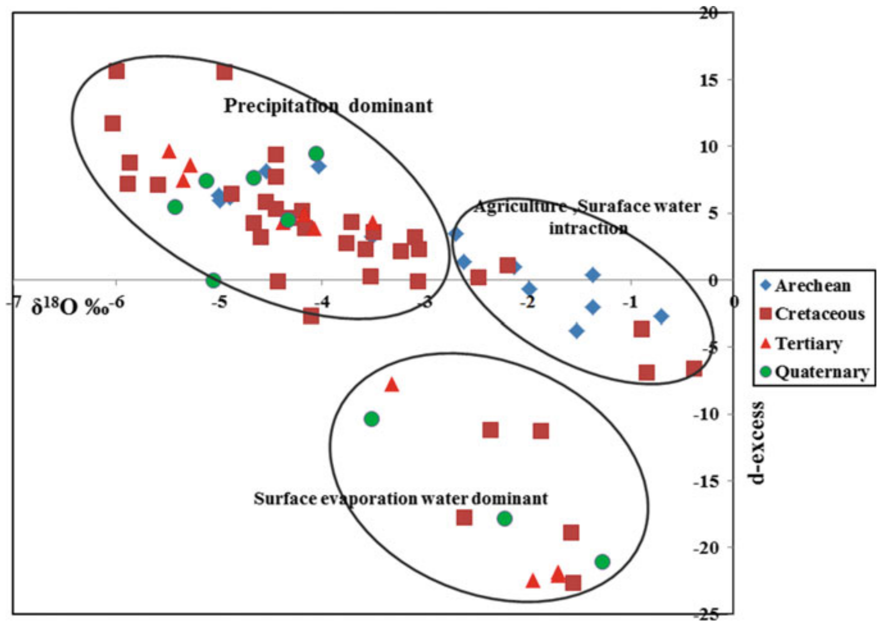

Fig. 7.4 Plot for d-excess versus δ^{18}O permil data of groundwater samples

Tertiary, Quaternary sample shows recharge directly from precipitation (Liu et al. 2010). Lower d-excess indicates the recharge either by lateral recharge or by surface runoff maintained by tanks, however 'd-excess' values (<5%), reflects significant evaporation of rainwater, leaving the residual groundwater (Negrel et al. 2011). Samples from Cretaceous, Tertiary and Quaternary with lesser d-excess worth and enriched δ^{18}O shows the evaporation dominance (Karmegam 2012).

7.4.3.2 Stable Isotopes (δ^{18}O, δD) Versus Chloride

The analysis of δD and chloride provides information about f groundwater-surface water interaction within the study area. There are variations of isotopic characters with relevance to Cl^-. The chloride against δD and δ^{18}O plot (Figs. 7.5 and 7.6) indicates that there are 3 major mechanism operatives within the study space (i) recharge from precipitation (ii) evaporated water recharge (from tank/river) and (iii) recharge of the mixed residual waters.

The chloride-deuterium plot suggests that groundwater samples with high chloride and enriched δD (Fig. 7.5) indicating seldom receive recharge from meteoric water and recharge of the evaporated waters from a unique supply. High Cl^- reveals leaching of secondary salts from the formation (Chidambaram et al. 2007). It's been reportable that few samples from Archean and Cretaceous regions are characterized by low chloride and comparatively enriched δD suggests recharge by stream waters

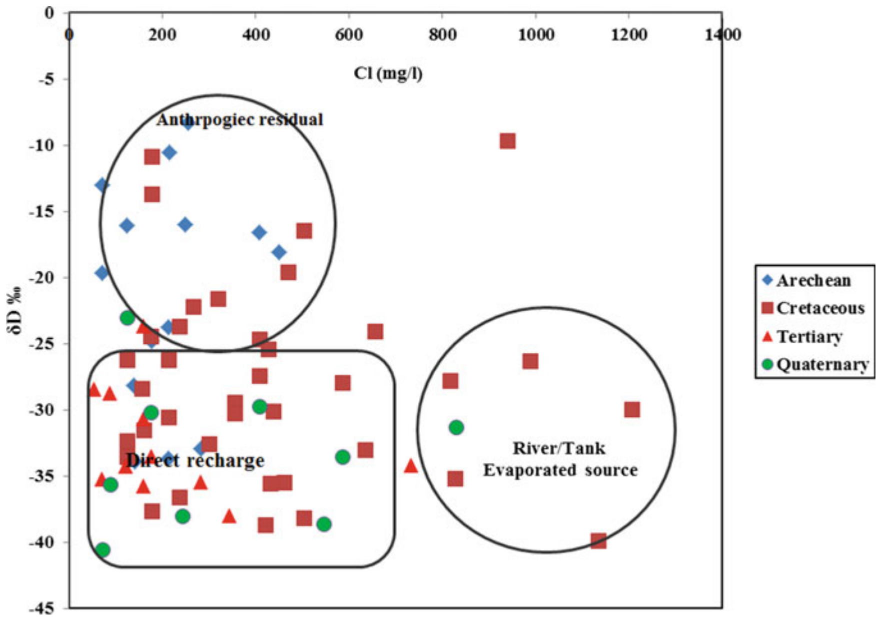

Fig. 7.5 Plot for chloride versus δD of groundwater samples

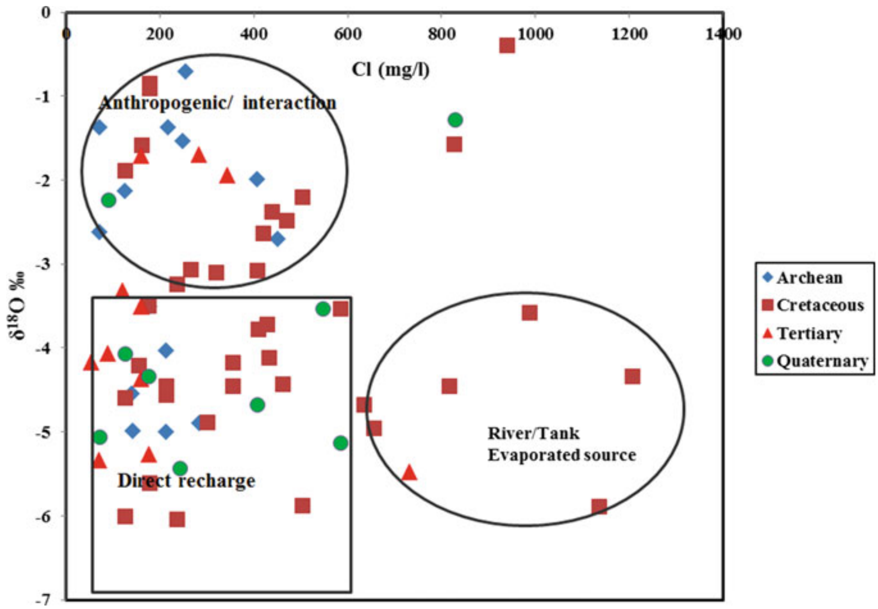

Fig. 7.6 Plot for $\delta^{18}O$ versus chloride for groundwater samples

and tanks (Prasanna et al. 2008). Certain groundwater samples in Cretaceous and Quaternary with high Cl^- and low deuterium is because of the anthropogenic supply. Samples from Quaternary, Tertiary, and Cretaceous with low Cl^- with low δD signatures shows the recharge of fresh water from less evaporated supply.

These processes may also be simply discerned from Cl^- versus $\delta^{18}O$ plot. The (Fig. 7.6) distribution of Cl^- variation with relevance to $\delta^{18}O$ in few samples from Archean, Cretaceous and Tertiary shows the dominance of stream/tank water recharge and therefore the samples from Quaternary, Tertiary, Cretaceous shows the fresh water recharge from non-evaporated sources (Fig. 7.6). Few samples from Cretaceous and Tertiary, show high Cl^- and show moderate enrichment in $\delta^{18}O$ indicating contribution of residual and evaporated surface water bodies.

7.5 Conclusion

The study revealed that the EC ranges from 440 to 14,430 μscm[1] and higher values noted along southern and SW part of the study area. The statistical analysis reveals that dissolution of secondary salts, anthropogenic activities, ion exchange are the major factors controlling the chemical composition of groundwater. The isotopic study indicates that the enriched isotopes are mostly observed in Archean and Cretaceous formations may be due to the recharge form the fresh water bodies like rivers and tanks. However, Tertiary, Cretaceous and Quaternary samples have depleted values, so the recharge is mainly from local precipitation. Lower value of d-excess along the Cretaceous and Archean formation reflects that there is little to significant kinetic evaporation of the precipitated water before groundwater recharge. Whereas, the increased value along Tertiary and Quaternary formation suggest a new source whose d-excess (>10.5%) was characterized by precipitation or storm runoff. The enriched samples with high chloride reflect the recharge from contaminated surface water sources, relatively enriched samples with low chloride indicates the recharge from an open water source, however, depleted samples with high chloride indicates recharge from anthropogenic sources.

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Chapter 8
Hydrogeochemical Investigation and Health Perspective of Arsenic in the Mid-Brahmaputra Floodplain of Assam, India

Latu Khanikar, Rashmi Rekha Gogoi and Kali Prasad Sarma

8.1 Introduction

Contamination of groundwater by arsenic (As), in recent years is a growing concern, affecting the population worldwide (Chakraborti et al. 2011; Charlet et al. 2007; Halim et al. 2009). It can impart both carcinogenic effects like cancers of skin, lung and bladder and non-carcinogenic effects like keratosis, skin pigmentation problems, hypertension, cardiovascular disease and diabetes (IPCS 2001). The problem of As contamination is well documented in countries like India, Bangladesh, China, Taiwan, Thailand, Cambodia, Vietnam and Nepal (Bagchi 2007; Berg et al. 2007; Chakraborti et al. 2004; Nickson et al. 2005; Rahman et al. 2009; Sengupta et al. 2003; Smedley and Kinniburgh 2002; Thakur et al. 2011).

The Bengal Delta Plain comprising the rivers, the Ganga, Brahmaputra and Meghna originating from the Himalayas is adversely As affected. Milliman et al. (1995) reported that these rivers carry dissolved particulates of about 173 million tonnes, suspended solids of about 1060 million tonnes and >1330 km^3 of water onto the Bengal basin. Holocene alluvium and river deposits are the characteristics of this deltaic plain. Recently such contamination has also been reported in several Indian states viz, Assam, Manipur, Nagaland, Arunachal Pradesh, Uttar Pradesh, Bihar and Tripura having identical geological conditions (Acharyya et al. 1993; Bhattacharya et al. 1999; Chakraborti et al. 2003; Singh 2004; Kumar et al. 2017; Das et al. 2015, 2016, 2017).

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8.2 Arsenic in Brahmaputra Floodplain

The Brahmaputra River is characterized by a network of channels forming several riverine islands and sandbars. It is the second largest sediment loaded river next to the Huang He in China (Patel et al. 2019a; Goswami 1985). Goswami (1985) in his study reported that the Brahmaputra river transports approximately 400 million tonnes of sediments annually and 2 million tonnes daily at Pandu which rose up to 26 million tonnes during peak flood flows. Seventeen out of 32 rivers in his study have excess rates of about 500 tonnes/sq.km/year, the highest being from the Jia Bharali basin.

Geogenic As contamination in the Northeast India was first documented by Singh (2004). The author also reported that 20 of the districts of Assam were As contaminated; Jorhat district being the worst affected with As concentration ranging from 194 to 657 μg/L. Other severely affected districts according to the study were Lakhimpur, Nalbari and Nagaon district. The study also revealed that the areas adjacent to foothills were highly As contaminated; the probable reason being erosion and deposition of sediments from surrounding hills. In regard to this, several other authors documented elevated levels of groundwater As in their works (Baviskar et al. 2011; Borah et al. 2009; CGWB 2009; Chakraborti et al. 2004, 2008; Chetia et al. 2011; Ghosh and Singh 2009; Hazarika et al. 2003; Kumar et al. 2016a; Devi et al. 2009; Mukherjee et al. 2006; Shah 2007, 2012; Singh 2004). Mahanta et al. (2011) in his study conducted in northern parts of the Brahmaputra floodplain revealed that high As concentrations were localized in certain pockets and the spread was narrower compared to the Ganga Brahmaputra Meghna floodplain in West Bengal and Bangladesh. The major As release mechanism in the study was reductive dissolution; cations like Fe, Na and Ca also played a major role in leaching of the metalloid.

Several studies conducted in the region revealed the sources of As to be the Himalayan sediment load of young Holocene alluvium, carried by the river and its tributaries (Ben et al. 2003; Bhattacharyya et al. 2003; Bundschuh et al. 2000, 2004; Sarma and Phukan 2004; Singh 2006; Smedley et al. 2002, 2003; Smedley and Kinniburgh 2002; Kumar et al. 2010a, b). Sediment deposition by the river Brahmaputra vary in accordance to the sources; the north bank fed by more sediments of recent alluvium and the south comprising of sediments from older Assam plateau having more silt fraction (Kunte 1988; Mahanta 1995). Alluvial environments are dominated by reducing conditions resulting in increased concentration of As in the aquifers. Oxidation of pyrites and arsenopyrites may even lead to As contamination in the groundwaters (Patel et al. 2019b). Presence of cations like Fe and anion like bicarbonate, phosphate and sulphate further impact the concentration of As in the groundwater (Saha et al. 2009). Source of As contamination in the floodplain is assumed to be primarily geogenic and there is lack of information on As anthropogenic contamination in the extensive alluvial stretch (Singh 2006).

8.3 Arsenic and Human Health

The ill effects of As can primarily be categorized into non-malignant and malignant manifestation. Non-malignant effects include a variety of symptoms like generalized weakness, anemia, fatigue to neurotoxicity, hepatotoxicity and chronic gastrointestinal diseases (Maji et al. 2016). Studies conducted by Chakraborty et al. (2004) and Mukherjee et al. (2005) reported anomalies relating to As exposure and pregnancy outcomes, resulting in spontaneous abortion, premature and still births, low body weight and neonatal and perinatal mortality. Sengupta et al. (2009) have observed such adverse obstetric effects during their study in West Bengal. Malignant effects include cancers in lung, bladder and the commonest being skin cancer (IARC 2004; Maji et al. 2016; Naujokas et al. 2013). Maji et al. (2016) further mentions that the As concentration of >50 mg/L, >1 mg/L and 1.08 mg/kg in urine, hair and nail corroborates for toxicity of the metalloid. Urine hair and nail are the biomarkers of As exposure. Arsenic in hair and nail give indication of past exposure to the metalloid while As in urine, expressed either as inorganic As or the sum of its metabolites generally gives the best estimate of recent exposure (EHC 2001). Several studies conducted to understand the As human body burden showed significant relationship between As concentration in the biomarkers and groundwater. Some of such studies conducted in the Ganga Brahmaputra Meghna floodplain are shown in Table 8.1.

Table 8.1 Studies conducted in the Ganga Brahmaputra Meghna floodplain (GMB) showing As exposure levels

Authors	Region/ area	Groundwater As (μg/L)	Biological sample	Methodology
Chakraborti et al. (2004)	West Bengal	Upto 700 to 1000	**Urine:** 10–3147 μg/L **Hair:** 180–20,340 μg/L **Nail:** 380–44,890 μg/L	FI-HG-AAS
	Bangladesh	Upto >1000	**Urine:** 24–3086 μg/L **Hair:** 280–28,060 μg/L **Nail:** 260–79,490 μg/L	
Hata et al. (2012)	Bangladesh	<0.5 to 332	**Urine:** As III (7.7–32.3 μg/L), As V (0.5–3.3 μg/L), MMA (5.6–25.0 μg/L, DMA (47.9–153.4 μg/L)	HPLC-ICP-MS
Tokunaga et al. (2003)	West Bengal	0.66 to 75.5	**Urine:** As III (0–166.1 ng/ml), As V (0–1624.5 ng/ml), MMA (0–132.7 ng/ml), DMA (0–127.4 ng/ml)	HPLC-ICP-MS
Sengupta et al. (2009)	West Bengal	<3 to 3700	**Urine:** 5–9375 μg/kg **Hair:** 70–31,770 μg/kg **Nail:** 80–44,890 μg/kg	FI-HG-AAS

(continued)

Table 8.1 (continued)

Authors	Region/ area	Groundwater As (μg/L)	Biological sample	Methodology
Rahman et al. (2005)	West Bengal	<3 to >1000	**Urine:** 33–2353 μg/L **Hair:** 535–8453 μg/L **Nail:** 851–9706 μg/L	FI-HG-AAS
Goswami et al. (2014)	Assam	<3 to 468	**Urine:** 20.8–697.5 μg/L **Hair:** 224–5461 μg/L **Nail:** 426–11,725 μg/L	FI-HG-AAS

The present study aims in understanding the dominant hydrogeochemical processes favouring the mobilization of As with emphasis on human body burden of the metalloid. Biomarkers viz. urine, hair and nail collected from affected population have been used for evaluating the exposure levels in the study area. Health study being carried out for the first time in the study area, though preliminary, will give an idea of the extent of this metalloid contamination.

8.4 Materials and Methods

8.4.1 Study Area

The study was conducted in the Dhekiajuli area (26.7º N; 92.5º 5E) of Sonitpur district of Assam, India (Fig. 8.1). The eastern region of Himalayas lies on its north and the mighty Brahmaputra river on its south. Demographically, the township has a total population of 21,579 as per 2011 India Census. The region is elevated at around 100 meters above the mean sea level. The region is characterized by sub-tropical humid climate along with heavy rainfall. Rainy season prevails during June to September which is highly influenced by the south-west monsoon. During summer the temperature may rise up to 37.5 °C while it may fall to 7.6 °C in winter.

Hydrogeologically, the region may be classified into three sections: semi-consolidated Neogene rocks unsuitable for groundwater occurrence on the northern border; a small area comprising Archean consolidated rocks on the extreme south; and lastly unconsolidated alluvial sediments in the plains and foothills comprising major source for occurrence of groundwater. Extending up to northern foothills, lies the piedmont zone covering an area of 8–10 km, followed by younger alluvial floodplain on the south (Groundwater Information Booklet 2013).

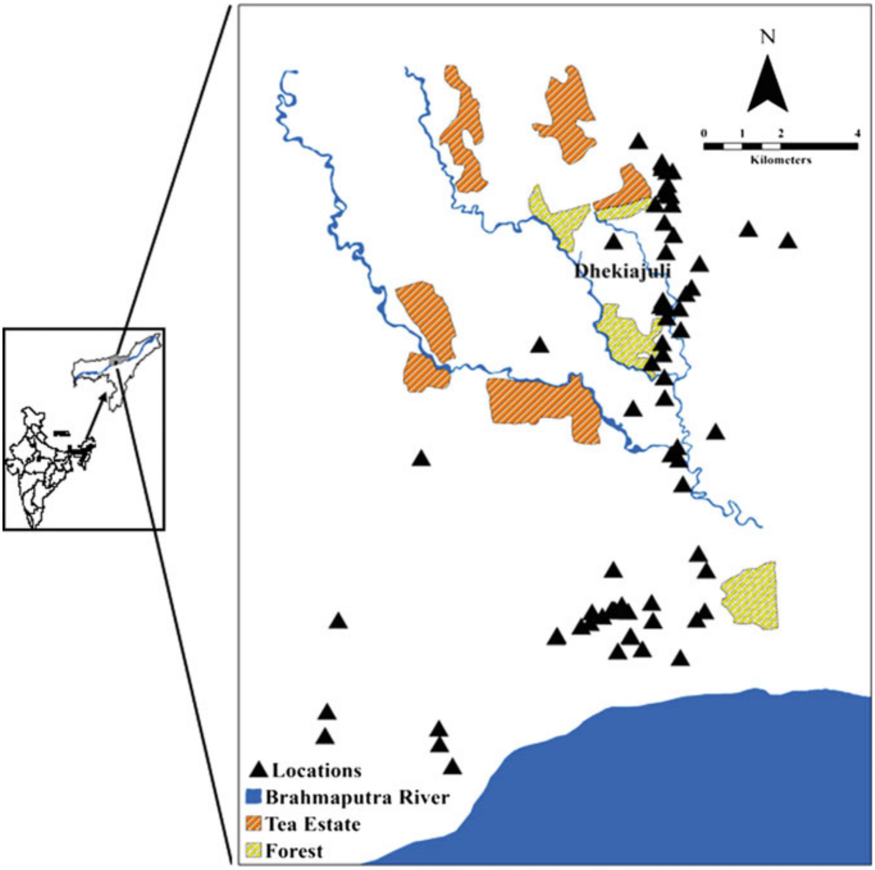

Fig. 8.1 Map showing groundwater sampling locations of the study area

8.4.2 Groundwater Sampling

Groundwater samples (n = 80) were collected from tube wells in poly-propylene bottles from different localities during the period 2010–2017. A GPS device (Garmin GPS Oregon model 650) was used for positioning of each location. Flushing of tubewells was done for 5–10 min before each sampling. Depth of tube wells ranged from 5 to 46 m. Sample preservation was done by storing them at a temperature less than 4 °C prior to analysis. Another set of samples were filtered and preserved using nitric acid for analyzing trace metals. A multiparameter probe (HANNA Model no. HI9828) was used for in situ measurements of pH, Conductivity, ORP and TDS.

8.4.3 Analytical Methods and Instrumentation

Methodologies adopted for analyzing different water quality parameters were taken from APHA (1995). Total Hardness, HCO_3^- and Cl^- were measured by acid titration methods. Anions like SO_4^2, PO_4^{3-} and NO_3^- were measured spectrophotometrically. Flame photometry was used for analyzing cations viz. Na^+ and K^+. ICP-OES (Optima 2100 DV Perkin Elmer) was used for analysis for Fe, Ca^{2+} and Mg^{2+}. Benchtop pH/ISE meter and atomic absorption spectroscopy (AAS) was used for estimation of F^- and As in the samples respectively. Analytical accuracy for As was ensured by obtaining >10% relative standard deviation. Piper diagram (Piper 1944) was prepared using aquachem software. Statistical interpretation for different water quality parameters was done by SPSS version 20.

8.4.4 Biological Sampling

A total of 11 biological samples viz. urine and hair (4 samples each) and nail (3 samples) were analysed for estimating As body burden which were collected in the month of March 2017. Polyethylene containers were used for sample collection which was further preserved using 1:1 HCL and stored at 4 °C until analysis. The collected hair and nail samples were washed with soap and distilled water to remove any external contaminant, followed by micro oven heating in deionized water suspension and again washed with deionized water and acetone, finally dried in hot air oven at 50–60 °C and stored until analysis. ICP-OES hydride system was used for the determination of total As in the samples and the obtained results were in reduced form (As^{3+}).

8.5 Results and Discussion

8.5.1 Groundwater Ion Chemistry

Summary statistics of different water quality parameters are shown in Table 8.2. Both acidic and alkaline pH was observed in the study area with majority of the samples (86%) within acceptable limits. Bicarbonate was found to dominant among the anions followed by Cl^- and SO_4^{2-} while among the cations Na^+ was dominant followed by Mg^{2+}, Ca^{2+} and K^+. Following Piper (Fig. 8.2) classification $MgHCO_3$ water type (42.5%) was found to be dominant followed by NaCl (25%), $NaHCO_3$ (16.25%), CaCl (6.25%), MgCl (5%) and $CaHCO_3$ (5%) water types.

Table 8.2 Descriptive statistics of different water quality parameters

Parameters	Mean ± SD	Range
pH	6.56 ± 0.51	5.60 to 8.03
EC (μS/cm)	286.83 ± 257.03	77 to 1140
ORP (mV)	126.75 ± 177.36	−123 to 576
TDS (mg/L)	141.22 ± 126.55	35 to 565
Depth (m)	10.51 ± 6.73	4.57 to 45.72
TH (mg/L)	110.08 ± 67.40	15 to 240
HCO_3^-(mg/L)	163.74 ± 65.56	68.34 to 346.56
SO_4^{2-} (mg/L)	9.55 ± 13.33	BDL to 47
Cl^- (mg/L)	43.61 ± 32.92	0.34 to 130.67
NO_3^- (mg/L)	3.35 ± 5.48	BDL to 35.60
F^- (mg/L)	0.28 ± 0.41	BDL to 2.68
PO_4^{3-} (mg/L)	0.28 ± 0.27	BDL to 1.48
K^+ (mg/L)	15.36 ± 12.34	1.11 to 49
Na^+ (mg/L)	32.46 ± 24.31	2.68 to 107
Mg^{2+} (mg/L)	15.29 ± 8.64	BDL to 32.65
Ca^{2+} (mg/L)	19.11 ± 11.76	3.20 to 52.10
Fe (mg/L)	8.96 ± 13.11	BDL to 47.32
H_4SiO_4 (mg/L)	18.87 ± 9.31	3.60 to 43.76
As (μg/L)	10.55 ± 11.94	BDL to 44.39

BDL represents "Below Detection Limit"

8.5.2 *Hydrogeochemical Evaluation and Major As Release Mechanism*

Correlation analyses (Table 8.3) of the hydrogeochemical parameters showed that EC has strong positive correlation with TDS (r = 0.97**) implying mineral dissolution contributing to conductivity. The positive correlation of HCO_3^- with TH (r = 0.60**), Ca^{2+} (r = 0.54**), Mg^{2+} (r = 0.75**), K^+ (r = 0.69**) indicates the occurrence of carbonate and silicate weathering processes. HCO_3^- also showed positive correlation with Fe (r = 0.58**) and As (r = 0.56**) indicating alkaline conditions favoring the dissolution of As from Fe(hydr)oxides. Higher values of As (>40 μg/L) has been found to be associated with HCO_3^-water type further indicated by Piper diagram (Fig. 8.2). The positive correlation of H_4SiO_4 with HCO_3^- (r = 0.56**), TH (r = 0.59**), Ca^{2+} (r = 0.54**), Mg^{2+}(r = 0.62**) and K^+ (r = 0.53**) suggested the occurrence of silicate mineral weathering (Das et al. 2015; Patel et al. 2019a).

PCA analysis evaluating the hydrogeochemistry of the study area is shown in Table 8.4. Component 1 (C1) represents 27.42% of total variance and has positive loadings for HCO_3^-, TH, Ca^{2+}, Mg^{2+} and K^+ indicating both silicate and carbonate weathering processes controlling the ion chemistry of the region. This component also has positive loading for Fe and As representing As release from Fe containing

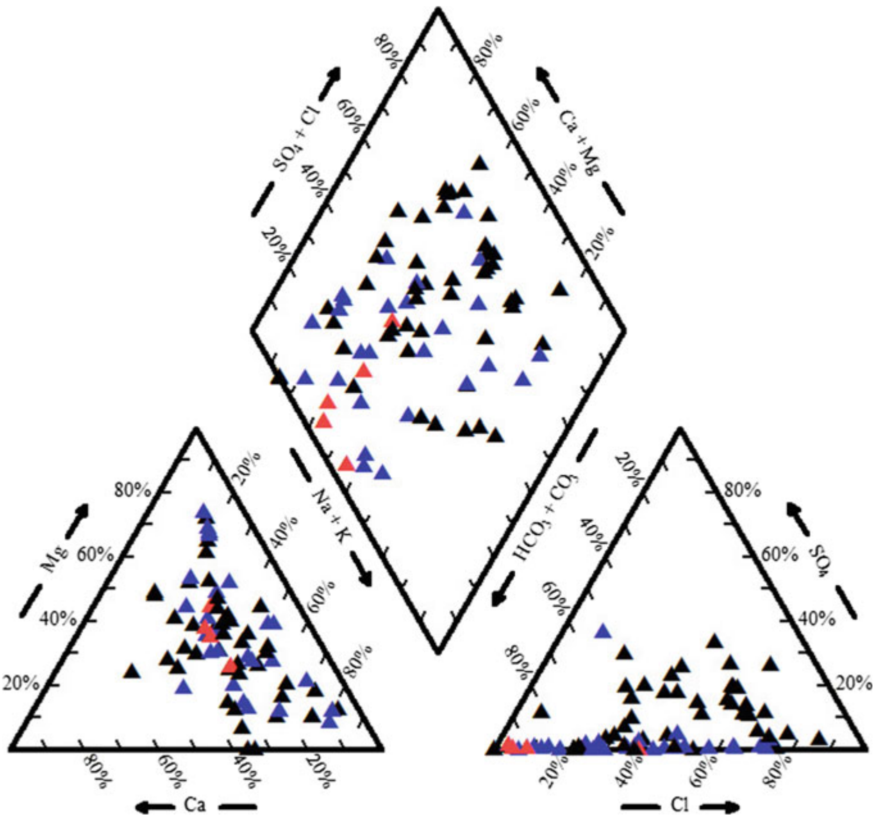

Fig. 8.2 Piper diagram showing the dominant water types. The colours viz. black, blue and red indicates As concentrations <10, 10–40 and >40 μg/L respectively

sources. Component 2 (C2) represents 18.47% of total variance and has positive loadings for ORP, NO_3^- and SO_4^{2-} while negative loadings for As, denying its release from oxidative sources. Component 3 (C3) and component 4 (C4) represents 10.03% and 9.23% of total variance and have positive loadings for EC and TDS, Na^+ and Cl^- respectively, indicating mineral dissolution contributing to TDS and conductivity of groundwater. Component 5 (C5) have positive loadings for pH, Fe and As indicating pH dependent processes governing As release into the groundwater.

Arsenic level in the study area ranged from BDL to 44.39 μg/L. About 41% of the total collected samples has As levels exceeding the safe limit of WHO (2008). Scatter plots between As and ORP (Fig. 8.3a, r = −0.60**) and As and SO_4^{2-} (Fig. 8.3b, r = −0.44**) further strengthen the findings of PCA denying As release from oxidative sources. A strong relationship between As and Fe (Fig. 8.3c, r = 0.79**) observed in the study area indicates As release to be governed by dissolution of Fe(hydr)oxides. Scatter plot between As and pH (Fig. 8.3d, r = 0.34**) further supports the release/desorption of As from Fe(hydr)oxides

Table 8.3 Correlation analysis for different water quality parameters

	pH	EC	ORP	TDS	Depth	TH	HCO_3^-	SO_4^{2-}	Cl^-
pH	1								
EC	−0.15	1							
ORP	−0.18	−0.004	1						
TDS	−0.21	0.97**	0.01	1					
Depth	−0.03	−0.17	0.03	−0.14	1				
TH	−0.18	0.34**	0.15	0.37**	−0.20	1			
HCO_3^-	0.07	0.17	−0.17	0.14	−0.29*	0.60**	1		
SO_4^{2-}	−0.23*	0.35**	0.54**	0.36**	−0.03	0.15	−0.15	1	
Cl^-	−0.07	0.20	0.37**	0.17	−0.18	−0.10	−0.13	0.30**	1
NO_3^-	−0.02	0.13	0.58**	0.17	0.07	0.28*	−0.03	0.36**	0.06
F^-	−0.02	−0.21	0.06	−0.20	−0.04	0.19	0.07	−0.10	−0.19
PO_4^{3-}	0.20	−0.09	−0.13	−0.10	0.32**	−0.41**	−0.29**	−0.20	−0.06
K^+	0.02	0.30**	−0.03	0.29**	−0.27*	0.54**	0.69**	0.09	0.001
Na^+	0.19	0.13	0.29**	0.08	−0.19	−0.12	0.04	0.14	0.80**
Mg^{2+}	−0.14	0.29**	0.01	0.26*	−0.30**	0.73**	0.75**	0.11	0.02
Ca^{2+}	−0.07	0.24*	0.33**	0.28*	−0.28*	0.59**	0.54**	0.28*	0.26*
Fe	0.25*	0.12	−0.42**	0.07	−0.20	0.42**	0.58**	−0.33**	−0.18
H_4SiO_4	−0.17	0.13	−0.02	0.11	−0.03	0.59**	0.56**	−0.05	0.01
As	0.34**	−0.001	−0.60**	−0.04	−0.16	0.30**	0.56**	−0.44**	−0.28*

NO_3^-	F^-	PO_4^{3-}	K^+	Na^+	Mg^{2+}	Ca^{2+}	Fe	H_4SiO_4	As

(continued)

Table 8.3 (continued)

NO_3^-	F^-	PO_4^{3-}	K^+	Na^+	Mg^{2+}	Ca^{2+}	Fe	H_4SiO_4	As
1									
0.03	1								
−0.18	−0.15	1							
0.13	0.04	−0.32**	1						
0.16	−0.14	−0.02	0.01	1					
0.06	0.05	−0.37**	0.64**	−0.10	1				
0.22*	0.07	−0.27*	0.55**	0.09	0.57**	1			
−0.14	0.11	−0.16	0.54**	−0.06	0.40**	0.36**	1		
−0.04	00.14	−0.29*	0.53**	−0.06	0.62**	0.54**	0.44**	1	
−0.26*	0.03	−0.16	0.37**	−0.09	.34**	0.16	0.79**	0.27*	1

*Significant at the 0.05 level (two-tailed)

**Significant at the 0.01 level (two-tailed)

Table 8.4 PCA suggesting the occurrence of weathering processes governing ion chemistry and dissolution of Fe(hydr)oxides in reduced environment favouring As mobilization in the groundwater systems

	C1	C2	C3	C4	C5	C6
pH					0.86	
EC			0.93			
ORP		0.84				
TDS			0.93			
Depth						−0.80
TH	0.78					
HCO_3^-	0.82					
SO_4^{2-}		0.62				
Cl^-				0.92		
NO_3^-		0.86				
F^-						
PO_4^{3-}						−0.70
K^+	0.76					
Na^+				0.88		
Mg^{2+}	0.83					
Ca^{2+}	0.76					
Fe	0.61				0.49	
H_4SiO_4	0.84					
As	0.45	−0.52			0.55	
Eigen values	5.21	3.51	1.91	1.75	1.15	1.05
% of variance	27.42	18.47	10.03	9.23	6.06	5.53
Cumulative %	27.42	45.89	55.92	65.14	71.20	76.73

sources under alkaline conditions. This finding also corroborates the results of PC5 (Table 8.4). Several laboratory experiments lend support to the release of As from sources like Fe(hydr)oxide and clay minerals under alkaline pH, rendering pH to be a dominant factor governing As mobilization (Dzombak and Morel 1990; Kumar et al. 2016b).

8.5.3 Arsenic in Biomarkers

Arsenic levels in urine, hair and nail samples ranged between 25.75 to 29.25 µg/L, 416.79 to 743.15 µg/L and 2175.78 to 3059.52 µg/L respectively (Table 8.5). Similar results have been observed by Samantha et al. (2004) in their work. Arsenic in urine, nail and hair of subjects not exposed to any external As sources, normally ranged between 5 to 50 µg/L, 20 to 500 µg/kg and 20 to 200 µg/kg respectively (NRC 1999). Excess level of As in the biomarkers except urine suggest probable sub-clinical effects of the metalloid amongst the exposed population.

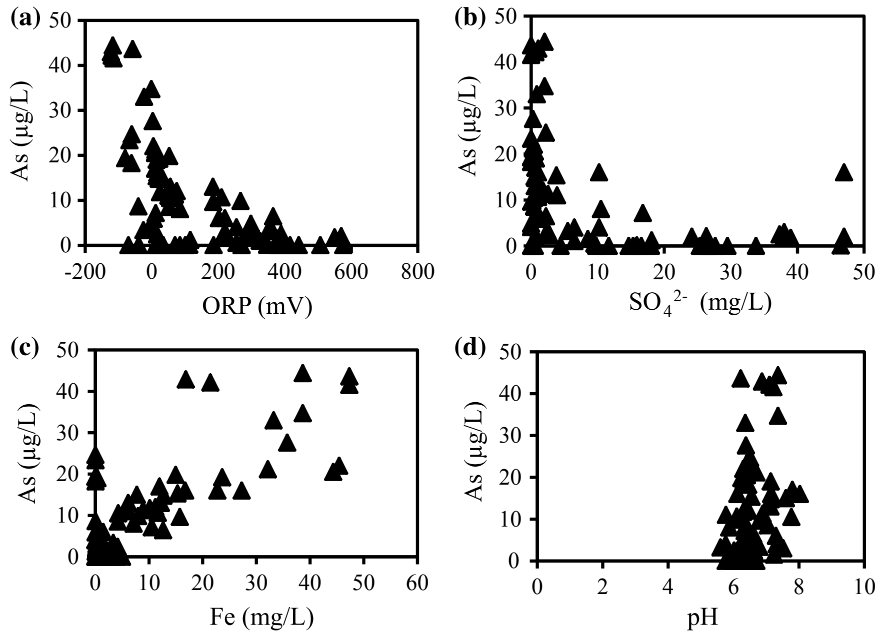

Fig. 8.3 Plots representing relationship between **a** As and ORP **b** As and Fe **c** As and SO_4^{2-} **d** As and pH

Table 8.5 Statistics of As concentration in urine, hair and nail samples

	As (urine)	As (hair)	As (nail)
No. of samples	4	4	3
Mean	27.12	553.00	2617.65
SD	1.87	169.73	624.90
Range	25.75–29.25	416.79–743.15	2175.78–3059.52

Note Arsenic in urine is expressed as µg/L while in hair and nail as (µg/kg)

8.6 Conclusions

Arsenic contamination in the aquifers of the Brahmaputra Floodplain is a sought-after concern owing to the numerous health hazards, the metalloid is competent of. Almost 41% of the samples collected from the study area contain As concentrations more than the WHO maximum permissible limit. Hydrogeochemical evaluation aided by statistical analyses suggested the occurrence of both silicate and carbonate weathering processes in the aquifer domain. A look into the probable As release mechanism revealed that reductive dissolution of Fe(hydr)oxide under alkaline condition has favoured the mobilization of the metalloid in the area. The results of PCA further confirm the findings. Arsenic exposure assessment on the population using biomarkers viz. urine, hair and nail revealed probable sub-clinical effects of the metalloid. This was concluded owing to the excess values of As in nail and hair samples, urinary As however, was within the normal values.

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Chapter 9
Assessment of the Land-Use Pattern Changes and Its Impact on Groundwater Quality in Parts of the National Capital Region (NCR) Delhi, India

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9.1 Introduction

The process of urbanization has significantly impacted the groundwater regime of many parts of the Indo-Gangetic plains, including areas around National Capital Territory (NCT) Delhi (Sarkar et al. 2016). The districts of Sonipat and Rohtak, which are located in the north-west of the capital city, have also been affected by the growing urbanization in the region. These two districts are located in the central-western part of Haryana between latitudes 28.66° to 29.28° North and longitudes 76.21° to 77.21° East (Fig. 9.1). They cover a total area of 4005.53 km^2(CGWB 2007) and are bounded by the river Yamuna in east, NCT Delhi in south-east, Jhajjar district in south, Bhiwani district in west, Hissar district in north-west and Jind and Panipat districts in north (Fig. 9.1).

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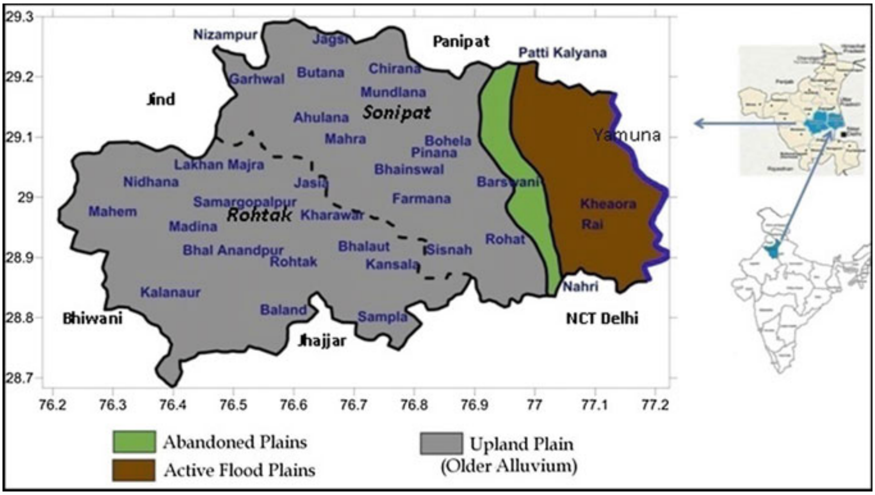

Fig. 9.1 Location map for Sonipat and Rohtak districts of Haryana. *Source* Kaushik 2015

A number of hydrological studies conducted by the Central Ground Water Board (CGWB), have revealed that both these districts have issues pertaining to their groundwater resources. While Sonipat is more water stressed than the Rohtak district, the latter has more areas with groundwater salinity (CGWB 2013a and b).

These districts have witnessed a rise in their combined population from 23, 37,858 (Census of India 2001) to 25,11,205 (Census of India 2011) at a growth rate of 7.41%. A growing population coupled with more concretization of land could impede the natural groundwater rejuvenation processes. This could aggregate the existing groundwater condition in the region. Hence, it was important to understand the linkage between the land-use pattern changes and the groundwater quality. Motivated by this objective, a study was conducted for the two districts using groundwater availability and quality data from annals of CGWB for years 2006, 2010 and 2014. This data was further processed to create water level maps using software Surfer 12 and hydrochemical plots using software AquaChem 5.1. This was supplemented by Landuse Pattern maps created with the help of Arc-GIS 9.3 for the same time-frame using Landsat data (Landsat 8 OLI/TIRS for 2014 and Landsat 7 ETM+ for 2006 and 2010).

9.2 Geology and Climate of the Study Area

Both Sonipat and Rohtak lie in the alluvial plains of Upper Yamuna basin, which are a part of the Indo-Gangetic plains (Sarkar et al 2016).

The climate of both districts is characterized by dry, hot summer. On the other hand, Rohtak is reported to have milder and drier winter than the Sonipat district

(CGWB 2013a, b). The average temperatures in both districts ranges from 7 to 40.5 °C that could reach up to 47 °C in Summer (CGWB 2013a, b).The region doesn't show much topographic variation as the average elevation of the districts is from 215 to 230 m above mean sea level (mamsl). However, it does show a significant physiographic variation as we move from east to west (Fig. 9.1):

1. The active floodplains of river Yamuna lies in the easternmost part of the Sonipat district. The sediments of the active flood plain in NCR are predominantly medium to coarse sandy with silt, clay, and gravel (Shekhar and Prasad 2009; Bawa et al. 2014; Sarkar et al. 2016, 2017; Sarkar 2017).
2. The abandoned floodplains of recent past lie in the central part of the Sonipat district. They mark the end of the active floodplains and are characterized as wider, low lying flat tracts.
3. The rest of the study area (western part of Sonipat district and entire Rohtak district) lies in the upland plains (older alluvial plains), that are almost aligned along the western Yamuna canal. These plains in NCR are reported to have fine to medium sand, silt and clay in different proportions along with "*Kankar*" (calcareous material) present in few places (Sett 1964; Thussu 2006; Shekhar 2007; Shekhar and Prasad 2009; Sarkar et al. 2016, 2017; Sarkar 2017).

The alluvial plains present in Sonipat and Rohtak districts belong to the Quaternary age and are composed mainly of alluvial sand, silt, kankar and gravel, these formations are known to be potential aquifer zones in NCR (CGWB 2006a; Thussu 2006; CGWB 2007; Chatterjee et al. 2009; Sarkar et al. 2016, 2017; Kumar et al 2017a).

The transmissivity and discharge rate of the active floodplains of NCR (younger alluvial plains) has been reported to be more than older alluvium, making them better aquifers (Shekhar et al. 2009, 2016, Kumar et al. 2017a). The hydrogeological characterization of the subsurface was further carried out by the Central Ground Water Board (CGWB) through groundwater exploration in these districts.

9.3 Groundwater Exploration

The CGWB conducted groundwater explorations in 14 locations (Fig. 9.2). Eight of these exploratory wells were located in Sonipat district, while six exploratory wells were located in Rohtak district (Fig. 9.2).

It was seen that in most of these locations, wells were abandoned either due to low yield (LY), lack of granular zone (NG) or low quality (LQ) of water (CGWB 2013a and b).

The results of some of these explored wells are shown in Table 9.1. The deep drilling in these locations was able to establish the potential aquifer horizons. It was seen that the granular zones were found to be as deep as 460 m in some places. The general exploration revealed the occurrence of three aquifer groups.

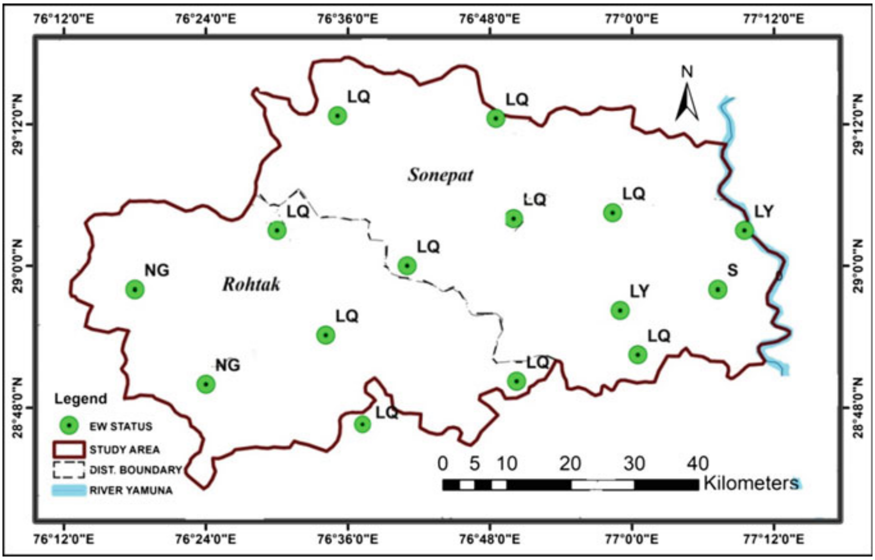

Fig. 9.2 Location of some of the exploratory well drilled by CGWB and its status (LQ: Low Quality, NG: No Granular zone, S: Successful, LY: Low Yield). *Source* CGWB 2013a and b

Table 9.1 Representative Litholog of exploratory well drilled by CGWB in study area. *Source* CGWB 2013a and b

Locations	Granular zone deciphered (mbgl)	Zone tapped	Subsurface material
1. KHEORA (Sonipat) 28.966° N, 77.121° E	21–40; 50–69; 90–100; 108–112; 117.75–123; 124–127; 132.5–135; 43–147.5; 153–163; 184.5–188; 193–195; 214–220; 227–233; 245–247.5; 258–260; 268–274; 282–285	21–26.7 31–41 50–68.1 (Status: Successful)	Sandy clay and Kankar
2. KAMI (Sonipat) 29.05° N, 77.158° E	17–25.5; 29–33.5; 38.25–43.5; 44.5–54.5; 55.75–57.5 (mix); 59–62.5(mix); 65.67 (mix)	19–22.25; 30–33; 39.1–43.1; 45.1–54.1 (Status: Abandoned: Low yield)	Clay mixed with gravel
3. DIGHAL (Rohtak) 28.76° N, 76.62° E	11–52; 56–60; 66–72;82–88;101–124;148–151; 163–186; 190–197; 200–202; 206–210; 224–228; 235–239	(Status: abandoned: bad quality)	Clay mixed with kankar
4. MEHAM (Rohtak) 28.96° N, 76.3° E	41.7–45.7; 100.8–104.8; 188.3–195.3; 231.3–241	(Status: abandoned: lack of granular zone)	Clay mixed with kankar

The shallowest aquifer group was observed at around 70 mbgl. It was unconfined in nature and tapped by majority of the tubewells due to availability of fresh water in it. This first aquifer showed discharge capacity of 4540 L per minute (lpm), and transmissivity of 2340 m^2/day along with the specific yield of 0.2 (CGWB 2013a and b).

The other two aquifer groups were found in the range of 90–200 m and 250–450 m respectively and contained brackish to saline groundwater (CGWB 2013a and b).

It should be noted that the ability of the shallowest aquifer to yield groundwater decreases in the western part (Rohtak district) of the study area as we move from younger alluvial to older alluvial plains. This variation was also observed in groundwater dynamics of the districts, represented by the depth to water level and water table contour maps.

9.4 Groundwater Dynamics

The average depth to water level in the study area was reported to be in the range from 1–23.3 m below ground level (mbgl) in pre-monsoon season for periods May2006 (Fig. 9.3). The post-monsoon (November 2006) depth to water level in the study area, on the other hand, ranged from 1 to 24.5 mbgl (Fig. 9.4).

The shallower water levels are mostly found in Rohtak district, while deeper water levels are mostly found in Sonipat district (Figs. 9.3 and 9.4). In general, the water level has declined in these districts over the past decade. Since the northern

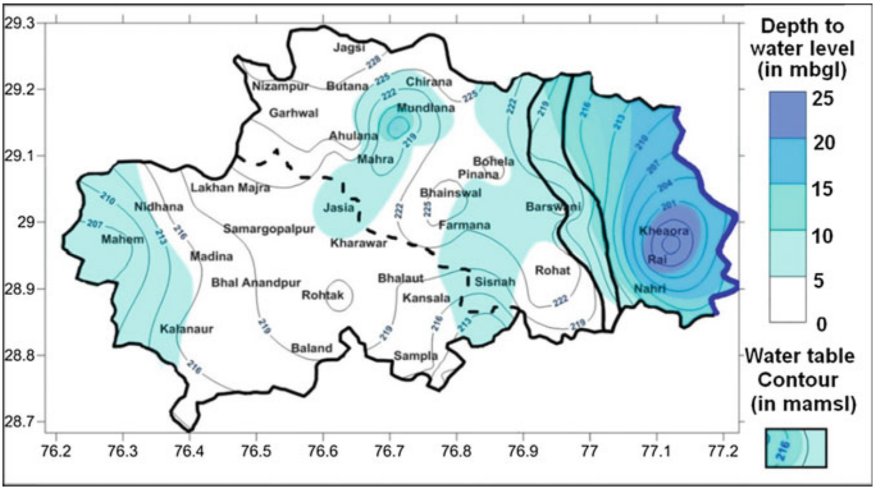

Fig. 9.3 Depth to water level and water table contour map for pre-monsoon 2006 indicating deeper water levels in the eastern parts of the study area

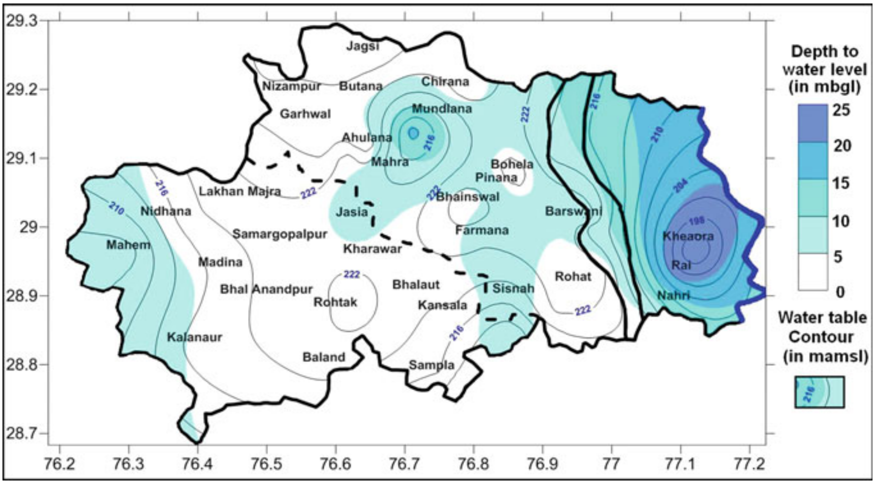

Fig. 9.4 Depth to water level and water table contour map for post-monsoon 2006 indicating deeper water levels in the eastern parts of the study area

part of the area is more elevated and the groundwater gradient in the area is from north to south, thus the general flow direction is from north to south. Exploratory boreholes drilled by the Central Ground Water Board to delineate and determine potential aquifer zones and evaluation of aquifer characteristics reveal that clay group of formations dominate over the sand group in the area. (CGWB 2007; Kaushik 2015).

The depth to water level in the year 2010 shows a general decline for the entire region for both pre-monsoon (Fig. 9.5) as well as the post-monsoon (Fig. 9.6). However, it virtually returned to the similar level in the year 2014 (Figs. 9.7 and 9.8) with respect to the year 2006 (Figs. 9.3 and 9.4).

The depth to water level and water table contour map for pre-monsoon of 2006 (Fig. 9.3) reveal the presence of a regional depression demarcated by 200 mamsl water table contour. The depth to water level is more than 20 mbgl in these areas around Rai and Kheora in Sonipat district. This depression in close proximity to river Yamuna is a clear indicator of anthropogenic interference on the natural groundwater dynamics of the study area. Similar depression in water table could also be observed in other parts of the study area such as areas around Mundlana, Rohtak and Mahem (Fig. 9.3). However, these depressions are much smaller with much shallower depth to water levels. The presence of these water table depressions were also observed in post monsoon of 2006 (Fig. 9.4). It was observed that everywhere except Rohtak, the depth to water level declined further, leading to deepening of these water table depressions (Fig. 9.4).

The trend for these changes continued in 2010 as well with the depth to water level and water table contour map for pre-monsoon of 2010 (Fig. 9.5) showing depth to water level declining further to of more than 25 mbgl in areas around

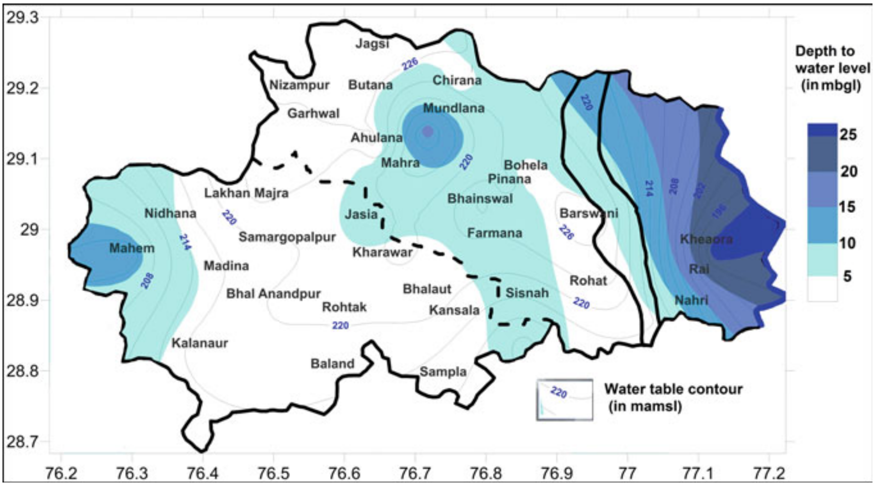

Fig. 9.5 Depth to water level and water table contour map for pre monsoon 2010 indicating decline in water level with respect to pre-monsoon 2006 (Fig. 9.3)

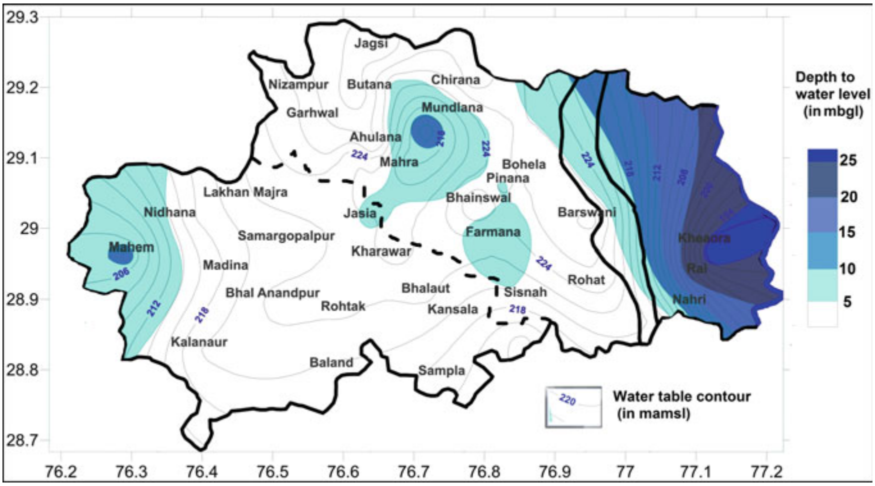

Fig. 9.6 Depth to water level and water table contour map for post-monsoon 2010 indicating decline in water level with respect to post-monsoon 2006 (Fig. 9.4)

Kheora in Sonipat district. Further, decline in water level was also observed in areas around Mundlana and Mahem (Fig. 9.5). This decline could also be seen in post monsoon of 2010 as well (Fig. 9.6). It was observed that general the depth to water level in the study area declined further, leading to deepening of these water table depressions (Fig. 9.6).

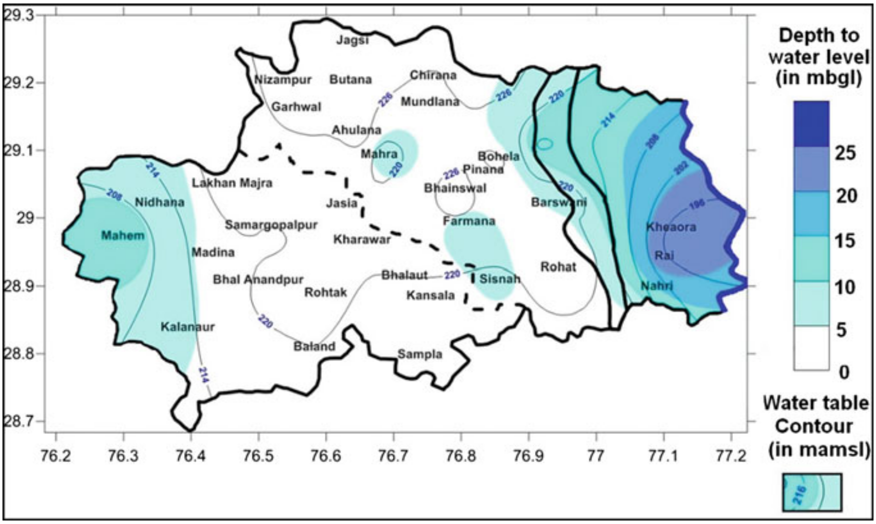

Fig. 9.7 Depth to water level and water table contour map for pre-monsoon 2014 indicating changes in water level with respect to pre-monsoon 2010 (Fig. 9.5)

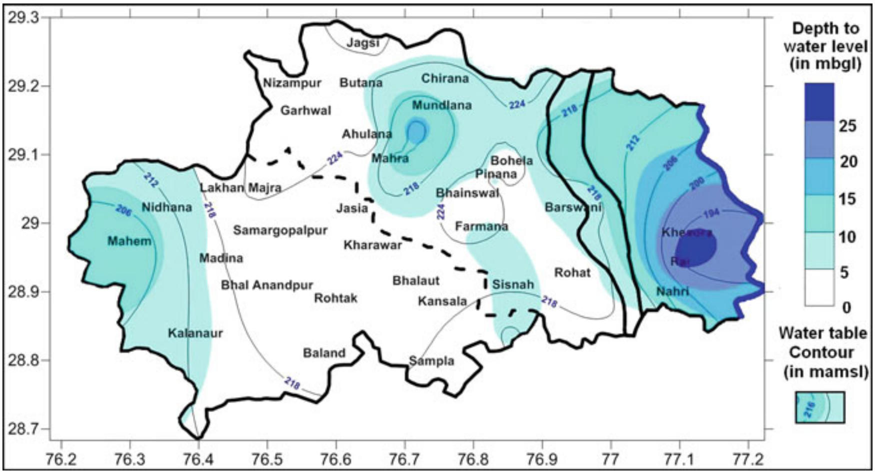

Fig. 9.8 Depth to water level and water table contour map for post monsoon 2014 indicating decline in water level with respect to post-monsoon 2010 (Fig. 9.6)

The depth to water level and water table contour map for pre-monsoon of 2014 (Fig. 9.7) showed significant changes with rise in the regional water table in comparison to previous years. However, the local water table depressions in areas around Kheora, Mundlana, and Mahem were still observed (Fig. 9.7).

The water table did not show any major change in post monsoon period (Fig. 9.8). However the decline in depth to water level around Kheora, Mundlana, and Mahem was observed.

Based on these observations, it could be suggested that in areas around Kheora, Mundlana, and Mahem, heavy groundwater abstraction could be a major cause of changes in the groundwater dynamics.

9.5 Assessment of Groundwater Resource

The region is known to have various sources for the groundwater recharge. The average rainfall in Rohtak usually ranges around 592 mm, occurring in a span of 23 days, while about 567 mm of average rainfall in 30 days was observed for Sonipat district (CGWB 2013a and b). Other sources of groundwater recharge include water seepage from the canal, ponds, irrigation return flow etc. The groundwater in these districts is used mainly for irrigation, domestic and industrial activities (CGWB 2013a and b).

The assessment of groundwater resource has been estimated by CGWB using GEC-1997 method in the study area. Table 9.2 shows the availability of groundwater resources and its utilization for the assessment year 2009.

It was observed that out of 12 assessment units/blocks studied by CGWB in the region 3 were categorized as over-exploited. Further, while 2 were categorized as critical and 2 categorized as semi-critical, only 5 out of 12 were safe in terms of status of groundwater exploitation.

It was also suggested that if this trend continues, 6 out of 12 assessment units/block would become groundwater deficit by the year 2025. However, the recent studies have shown that the status of 2 assessment units/blocks out of these 6 blocks (Lakhan Majra and Gohana) improved to safe and semi-critical categories respectively (CGWB 2017).

CGWB also assessed the temporal variation in the net groundwater availability of the two districts (CGWB 2006b, 2011a, 2014 and 2017) and observed significant changes over the years (Fig. 9.9). The net groundwater availability was calculated using groundwater abstraction (draft) values from different sectors for the assessment years of 2004, 2009, 2011 and 2013 in the study area.

It was observed that while agriculture was observed as the major consumer of the groundwater, there was little contribution of domestic sector in groundwater depletion (in the range of 2–4%) in both the districts (Fig. 9.9). Further, it was also seen that Sonipat district utilized more groundwater in comparison of the Rohtak district. The stage of groundwater development of the study area for the year has been calculated as 96.6, 102, 114 and 95.5% for the assessment year 2004, 2009, 2011, and 2013 respectively (CGWB 2006b, 2011a, 2014 and 2017).

Table 9.2 Block-wise assessment of groundwater resources of study area for the year 2009 (Rohtak and Sonipat district), Haryana. *Source* CGWB 2013a and b

Blocks	Net GW Availability (in Ham)	GW Draft for Irrigation (in Ham)	GW Draft for Domestic & Industrial water supply (in Ham)	s GW Draft for all uses (Ham)	Allocation Domestic industrial upto next 25 years (Ham)	Net GW availability for future irrigation development (Ham)	Stage of GW Development	Category of the Block
Rohtak	12137	10789	775	11564	1183	165	95%	Semi Critical
Kalanaur	8307	4715	403	5118	449	3143	62%	Safe
Lakhan Majra	3223	3357	229	3586	229	-363	111%	Semi Critical
Meham	11451	6053	578	6631	459	4939	58%	Safe
Sampla	9899	3522	312	3844	342	6025	39%	Safe
Ganaur	19778	22384	1327	23711	1327	-3933	120%	Over Exploited
Gohana	7609	10183	99	10282	99	-2673	135%	Critical
Kathura	5344	4187	6	4193	261	896	78%	Safe
Kharkhoda	8067	11420	121	11541	121	-3474	143%	Critical
Mundlana	15751	12566	9	12575	9	3176	80%	Safe
Rai	7902	14472	1054	15526	1054	-7624	196%	Over Exploited
Sonipat	12975	15410	1297	16707	1297	-3732	129%	Over Exploited
Total	122443	119058	6210	125278	6830	-3455	102.315	Over Exploited

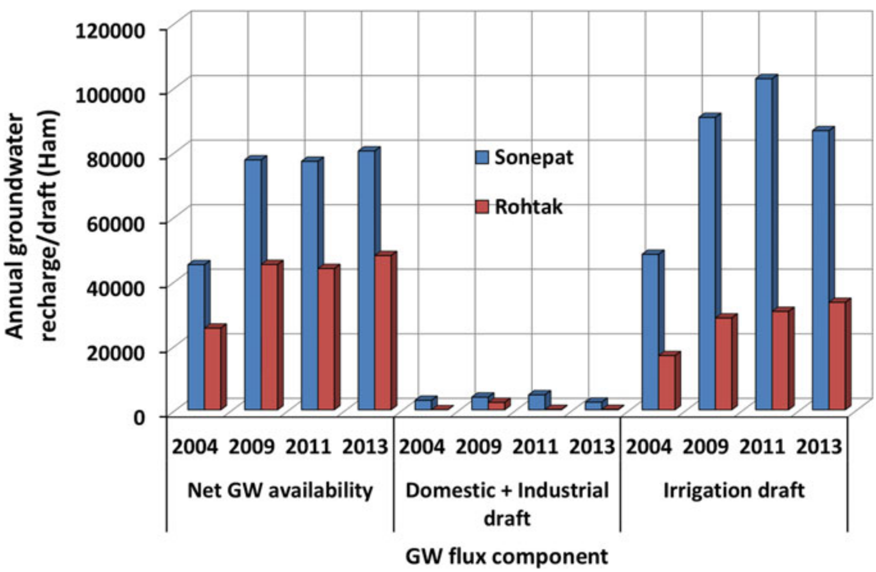

Fig. 9.9 Temporal variation in groundwater resources of the study area for the year (Rohtak and Sonipat districts), Haryana. *Source* CGWB 2006b, 2011a, 2014 and 2017

Based on these observations, it is evident that the condition of the groundwater resources in the region has been restored to the conditions that existed a decade back (2004). This has been possible by adoption of prudent land and water resource management strategies and better conjunctive use of surface and groundwater. Further, it was also believed that the changes in land-use pattern could also be responsible for these changes. Hence, the variations in landuse–land cover patterns for the same time period was also studied.

9.6 Landuse-Land Cover Pattern

The landuse/land cover maps were prepared by unsupervised classification using LANDSAT data. The maps for the years 2006, 2010 and 2014 (Figs. 9.10, 9.11 and 9.12) showed expanding boundaries of large as well as small cities in Sonipat and Rohtak districts. The exponential increase in the urbanized area seems to be localized in the south-west and western parts of the study area. Although a significant increase in clusters is seen in the entire study area, (Figs. 9.10, 9.11 and 9.12), drastic changes could be seen in and around Rohtak, Mahem, Nahri, Mundalana, Samargopalpur, Butana, Farmana and Madina (Figs. 9.10, 9.11 and 9.12). The total change in urban areas show significant increase from 3,56,455 m^2

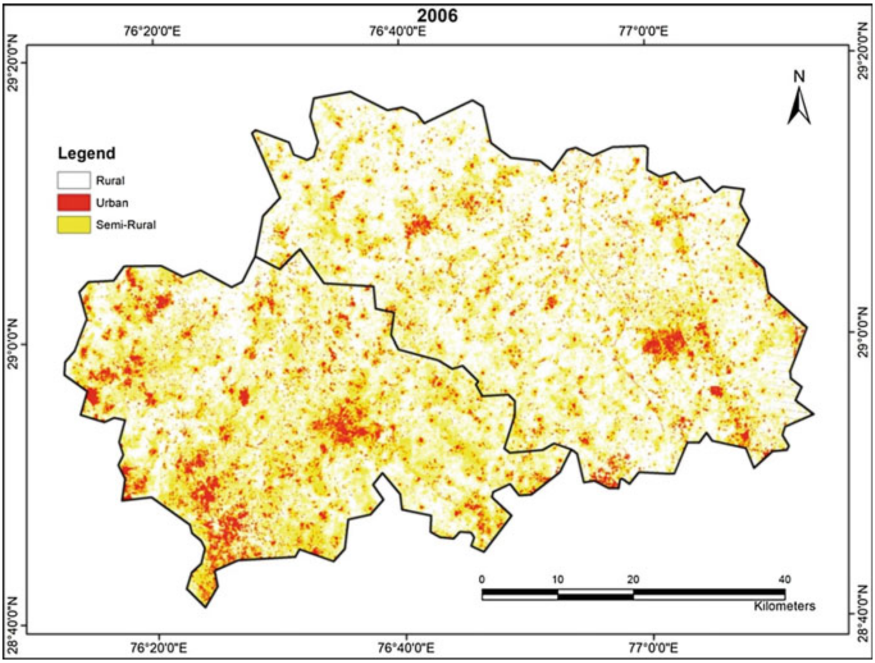

Fig. 9.10 Land use/land cover pattern of the study area in the year 2006

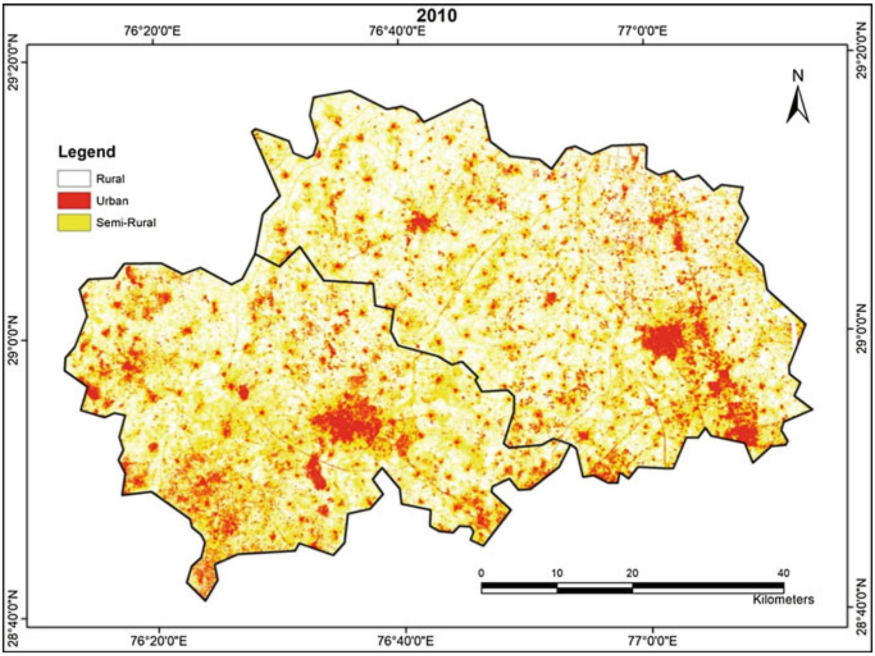

Fig. 9.11 Land use/land cover pattern of the study area in the year 2010

in 2006 to 5,71,401 m^2 in 2010 to 8,35,402 m^2 in 2014. The urbanization reflects an increase of 478 km^2 from 2006 to 2014, more than twice in 8 years (Fig. 9.13). These changes corresponded with the decline in overall semi-urban and rural areas in Sonipat and Rohtak districts (Fig. 9.13).

This rapid urbanization and development in the area has an unavoidable impact on the groundwater quality of the region. However, majority of the land cover is still dominated by rural areas with a marginal decline of 4% between 2006 and 2014 (Fig. 9.13). Hence, it is the agricultural activities that are expected to influence the groundwater quality in the region. This was further examined through the groundwater quality assessment of the two districts.

9.7 Groundwater Quality Assessment

The studies pertaining to the groundwater quality in the study area mainly included assessment of hydrochemical facies variation. There are a number of studies that highlights the importance of hydrochemical facies in understanding the spatial and temporal variations in major ion chemistry in different parts of the Upper Yamuna basin (Kumar et al. 2006, 2009, 2017b; Shekhar and Sarkar 2013; Sarkar and Shekhar 2013, 2015; Sarkar et al 2017; Das et al. 2015).

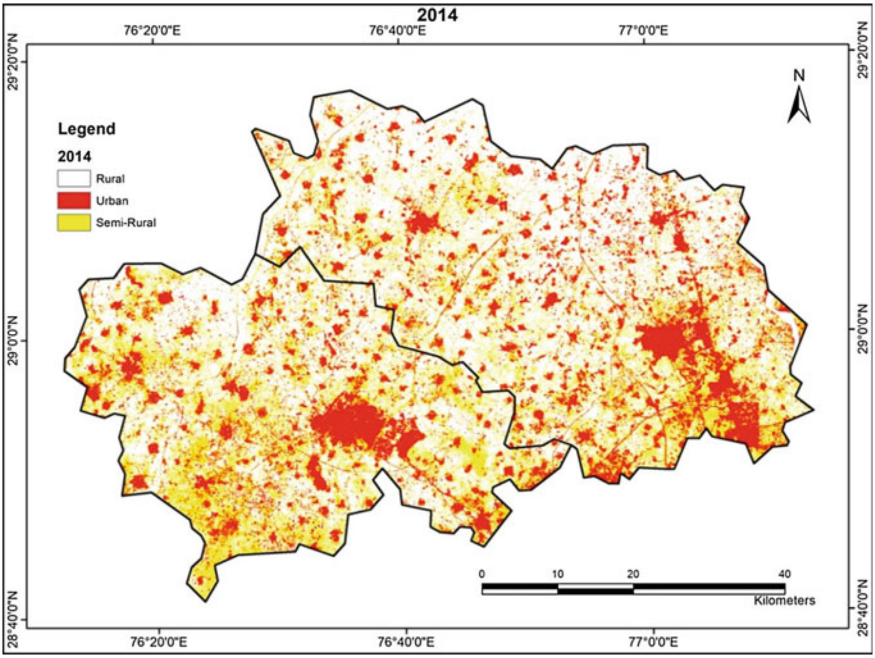

Fig. 9.12 Land use/land cover pattern of the study area in the year 2014

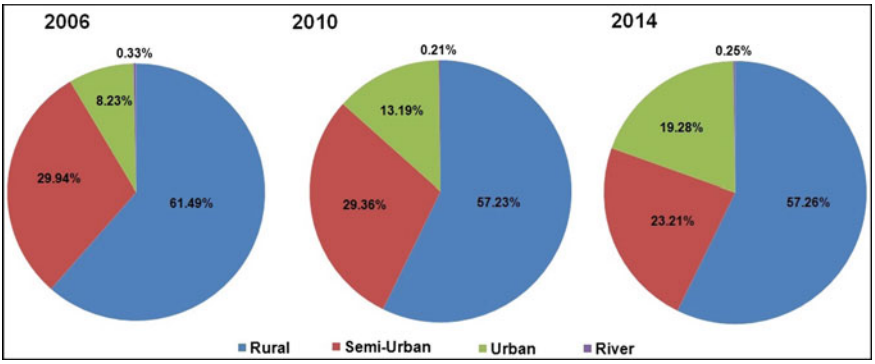

Fig. 9.13 Change in land use pattern from year 2006 to 2014

The ternary plot for cation concentration in the Hill Piper plot for the year 2006, 2010 and 2014 (Fig. 9.14) showed that almost all locations in the study area showed Na-K type facies with no significant change during this period (Das et al. 2017).

However, the part representing anion concentration in the Hill-Piper plot for groundwater samples showed an evolution of groundwater quality from pre

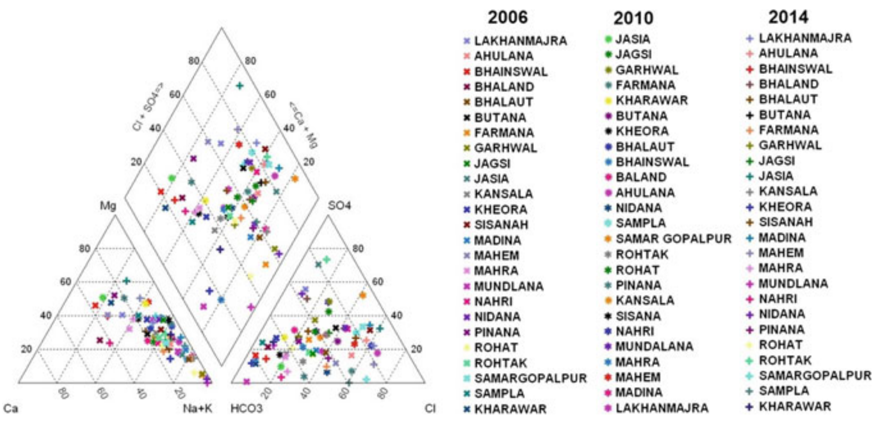

Fig. 9.14 Hydrochemical Facies variation in the study area for the year 2006, 2010 and 2014. *Source* CGWB 2007, 2011b and 2015

dominantly bicarbonate to mixed facies in 2006 to mixed facies in 2010 to mixed to chloride dominant facies in 2014 (Fig. 9.14).

Based on these observations, it is proposed that the general hydrochemical facies in the study area seem to be evolving towards chloride facies between the years 2006 to 2014.

However, on a local level, this trend is not a simple transition from bicarbonate to chloride facies but a highly uneven trend that varies from place to place.

For instance, in certain locations such as Bhainswal, the hydrochemical facies did not show any significant variation (Na-K-HCO_3 in 2006 to Na-K-Ca-HCO_3 in 2014). However, in other locations such as Jasia groundwater evolved from mixed type in 2006 to chloride dominant in 2014. Further, in some locations such as Nahri, facies varied from mixed type in 2006 to bicarbonate dominant in the year 2014. In Rohtak city, the facies varied from mixed to sulphate-chloride type facies from the year 2006 to 2014, while in Rohat (close to Sonipat) the facies moved from bicarbonate type facies in 2006 to mixed facies in 2010 and re-evolving to bicarbonate type facies in the year 2014 (Fig. 9.14).

The facies variation suggests complex localized changes in groundwater quality regime in the region. The suitability for irrigation was further explored with the help of the Wilcox plots (Kumaresan and Riyazuddin 2006; Sarkar and Shekhar 2013) for the years 2006, 2010 and 2014 (Fig. 9.15).

The Wilcox plot revealed that in the year 2006, locations such as Pinana, Samargopalpur and Nidhana showed very high Electrical Conductivity (EC) values for groundwater. Further, six locations showed Sodium Absorption Ratio (SAR) values well above the permissible limit, indicating a serious problem of sodium hazard in these areas. Very high SAR value were seen in Farmana and Garhwal areas (Fig. 9.15). Remaining locations have medium to low SAR values indicating little to no sodium hazard in most locations in the study area. Locations

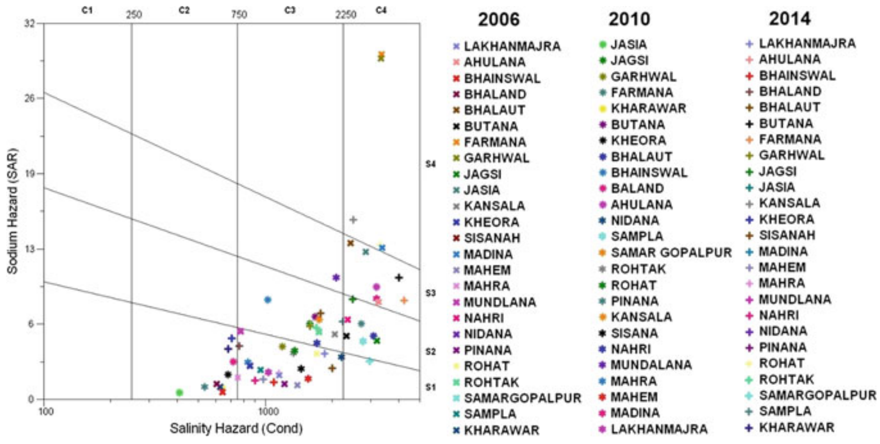

Fig. 9.15 Wilcox plot for the study area for the year 2006, 2010 and 2014. *Source* CGWB 2007, 2011b and 2015

such as Garhwal, Farmana and Madina fell in the class C4S4 of the corresponding Wilcox plot indicating extreme salinity problems in these locations. Bhalaut, Jasia, Baland and Ahulana fall in the class C4S3 of the Wilcox also indicating harmful water with very high EC and high SAR values (Fig. 9.15).

The Wilcox plot for the year 2010 (Fig. 9.15) showed a significant decline in SAR values, indicating a dilution event leading to an improved water quality in the study area (Kaushik 2015). It was observed that no samples fell in class C4S4 of the Wilcox plot plotted for the year. However, in locations such as Madina and Ahulana, groundwater was seen in class C3S3, indicating poor quality (Fig. 9.15).

The Wilcox plot for the year 2014 (Fig. 9.15) showed an increase in the SAR values. It was observed that in locations such as Butana, Ahulana and Kansala, poor groundwater quality was associated with high EC and SAR values (Fig. 9.15).

The observations from the Hill-Piper and Wilcox plots were substantiated with the help of correlation matrices for the year 2006, 2010 and 2014 (Tables 9.3, 9.4 and 9.5).

The matrix for the year 2006 (Table 9.3), showed TDS having a very strong positive correlation with almost all the ions. Further, sodium had a strong correlation with chloride, sulphate and carbonate. Based on this, it could be presumed that sodium in groundwater was most likely from a geogenic source (Kaushik 2015). It was also observed that calcium has a very strong positive correlation with magnesium. Further, both Calcium and Magnesium show a high negative correlation with Carbonate ions, while they show a high correlation with Nitrate. Since, the presence of nitrate in groundwater has been reported to be of anthropogenic origin in many studies in the region (Datta et al. 1997, Kumar et al. 2006, 2009; Lorenzen et al. 2012; Sarkar and Shekhar 2013, Sarkar et al. 2016); it is possible that the calcium and magnesium concentration in the region was augmented through anthropogenic processes (Patel 2019a).

Table 9.3 Correlation matrix for the year 2006

		TDS	pH	T.H.	SAR	Na	K	Ca	Mg	Cl	SO4	HCO3	NO3
TDS	mg/L	1.00	-0.45	0.88	0.41	0.84	0.57	0.73	0.88	0.95	0.88	0.58	0.73
pH			1.00	-0.62	0.32	-0.11	-0.41	-0.77	-0.56	-0.54	-0.31	0.01	-0.43
T.H.	mg/L			1.00	0.01	0.59	0.46	0.89	0.99	0.87	0.72	0.33	0.83
SAR	meq/l				1.00	0.77	-0.05	-0.16	0.05	0.29	0.45	0.64	0.03
Na	mg/L					1.00	0.13	0.36	0.64	0.76	0.81	0.68	0.47
K	mg/L						1.00	0.54	0.42	0.54	0.43	0.25	0.46
Ca	mg/L							1.00	0.82	0.79	0.62	0.04	0.65
Mg	mg/L								1.00	0.85	0.72	0.40	0.84
Cl	mg/L									1.00	0.79	0.45	0.59
SO4	mg/L										1.00	0.36	0.51
HCO3	mg/L											1.00	0.35
NO3	mg/L												1.00

Table 9.4 Correlation matrix for the year 2010

		TDS	pH	T.H.	SAR	Na	K	Ca	Mg	Cl	SO4	HCO3	NO3
TDS	mg/L	1	0.03	0.68	0.43	0.75	0.9	0.42	0.67	0.89	0.92	0.15	0.93
pH			1	-0.42	0.31	0.15	0.17	-0.48	-0.35	-0.17	0.11	0.32	0.08
T.H.	mg/L			1	0.05	0.43	0.39	0.59	0.98	0.84	0.48	0.04	0.5
SAR	meq/l				1	0.88	0.24	0.07	0.04	0.37	0.4	0.52	0.19
Na	mg/L					1	0.49	0.32	0.4	0.72	0.67	0.38	0.5
K	mg/L						1	0.24	0.38	0.65	0.92	0.03	0.98
Ca	mg/L							1	0.41	0.52	0.4	-0.26	0.31
Mg	mg/L								1	0.82	0.43	0.11	0.49
Cl	mg/L									1	0.67	0.12	0.7
SO4	mg/L										1	-0.01	0.93
HCO3	mg/L											1	-0.07
NO3	mg/L												1

Table 9.5 Correlation matrix for the year 2014

		TDS	pH	TH	SAR	Na	K	Ca	Mg	Cl	SO4	HCO3	NO3
TDS	mg/L	1	0	0	0	0	0	0	0	0	0	0	0
pH			1	-0.47	0.37	0.16	0.01	-0.73	-0.36	-0.28	0.01	-0.14	-0.06
TH	mg/L			1	-0.3	0.13	0.3	0.8	0.98	0.83	0.49	-0.03	0.69
SAR	meq/l				1	0.68	-0.09	-0.29	-0.2	-0.13	0.39	0.38	-0.01
Na	mg/L					1	0.27	0.19	0.13	0.46	0.71	0.58	0.21
K	mg/L						1	0.12	0.32	0.57	0.22	0.43	0.53
Ca	mg/L							1	0.67	0.69	0.34	0.23	0.28
Mg	mg/L								1	0.8	0.5	-0.08	0.76
Cl	mg/L									1	0.49	0.23	0.61
SO4	mg/L										1	0.1	0.61
HCO3	mg/L											1	-0.17
NO3	mg/L												1

The correlation matrix for the year 2010 (Table 9.4) showed a strong correlation of potassium with TDS. The anomalous high concentration of potassium at Samargopalpur was attributed to a localized anthropogenic source (Kaushik 2015). Further, the strong correlation of potassium with nitrate and sulphate validates the prominent role of anthropogenic processes in potassium enrichment in the groundwater (Patel 2019b).

The complexity in correlation between major ions is more prominent in 2014 (Table 9.5) with TDS having no correlation with any major ion. Further, correlation of calcium, magnesium and chloride ions with hardness and weaker correlation of sodium ions with all major ions except sulphate indicated the possibility of multiple sources for groundwater contamination.

9.8 Summary and Conclusion

The study establishes spatio-temporal variation in groundwater quality of the Rohtak and Sonipat districts of Haryana. The variations in groundwater dynamics and land-uses have been linked to groundwater quality variation in the region.

The eastern parts of the study area (Sonipat) that include the active Yamuna floodplains, have relatively fresh groundwater. While the western and central parts are prone to problems of high salinity and sodicity. The general trend of water table contours throughout the study period (2006–2014) remained consistent with local water table depressions observed in the western part of the Rohtak district around Mahem and central-western part of the Sonipat district between Mundlana and Mahra (Figs. 9.3, 9.4, 9.5, 9.6, 9.7 and 9.8). Similarly, another major area showing a depression in water table was observed near Kheaora and Rai in the eastern part of the Sonipat district (Figs. 9.3, 9.4, 9.5, 9.6, 9.7 and 9.8). These same locations also showed change in land use pattern for the same time period, indicating a possible link between changes in groundwater dynamics and urbanization.

However, a detailed insight into land use pattern changes showed that the urbanization in the study area was highly uneven. Further, the impact of land use change on groundwater quality was limited to certain locations such as Ahulana, Madina etc.

It has been observed that in the decade (2006–2014) the prudent land and water management strategies helped in improving the groundwater resources of the region.

It was seen that even though of the eastern part of the study area showed evidence of heavy groundwater abstraction and urbanization, water quality has remained good in these areas between the year 2006 and 2014. This could be attributed to regular recharge of groundwater from a less contaminated, River Yamuna (Kaushik 2015).

The western and central parts of the study area, on the other hand, suffered from severe water quality problems, which could be attributed to both geogenic as well as anthropogenic sources. In these areas, the changes in groundwater dynamics coupled with urbanization process could be responsible for the deterioration in groundwater quality. A similar process was observed in the alluvial plains in Delhi, where heavy groundwater abstraction could lead to pumping of saline water in both younger and older alluvial plains (Rao et al. 2006, 2007; Shekhar and Rao 2010; Sarkar and Shekhar 2015). In these parts, however, the high concentration of sodium in groundwater could be linked to the presence of sodium salts in the subsurface that has been reported by many researchers in the parts of Yamuna plains (Thussu 2006; Lorenzen et al. 2012; Kumar et al. 2009). It is possible that the interaction of these naturally occurring evaporite minerals (such as $NaCl$, $CaSO_4$ etc.) present in the subsurface with groundwater could have increased with urbanization and changes in groundwater abstraction (Thussu 2006; Kaushik 2015).

Based on these observations, it could be suggested that the impact of land use pattern change on groundwater quality of Sonipat and Rohtak districts is uneven. For most of the locations, a general source for groundwater contamination was not identified. Hence; the process of land use change between the year 2006 and 2014 seem to have impacted the groundwater quality differently.

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Chapter 10
Assessment of Water Quality Using Multivariate Analysis—A Case Study on the Brahmaputra River, Assam, India

Pallavi Das and Manish Kumar

10.1 Introduction

Rivers are progressively changed in terms of flow and form, and those changes are not only both events of the anthropocene but also worldwide threats to water security (Poff and Matthews 2013) During the past decades the impact of the anthropogenic activities in the surface waters has increased significantly. The impact of humans in river ecologies over the past 250 years has been intense. Freshwater pollution problems are receiving much attention worldwide because of their impacts on social, economic and cultural life of the people (Kannel et al. 2007). Anthropogenic activities and natural processes have lead to serious decline in surface waters impairing their use for agricultural, drinking, recreational, other purposes (Carpenter et al. 1998).

Progressive pollution of the river waters are critical as rivers in floodplain zones recharge ground water; a vital source of drinking water in India. Chemical composition of river water is vital to assessment of water quality for irrigation, agriculture and domestic usage. Chemical attributes of riverine water primarily governed by natural weathering of rocks have become overshadowed by increasing range of anthropogenic activities. Rivers are major part of the worldwide water cycle which plays a vital role in the geochemical cycling of elements. The composition of surface water is subordinate on common components (geographical, meteorological, hydrological and organic) within the drainage basins and shifts with

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regular contrast in runoff volumes, climate conditions and water levels (Sarin 2001; Krishnaswami and Singh 2005). The water chemistry of rivers relies upon contributions from the atmosphere, the geology through which it travels and from anthropogenic activities. Study of chemical composition of river water is of great importance for quantifying the dissolved load and various sources of major ions to rivers and estimation of weathering and CO_2 consumption rate (Gaillardet et al. 1999; Grasby and Hutcheon 2000). Investigation of chemical composition of river water is of incredible significance for evaluating the dissolved load and different sources of major ions to rivers and estimation of weathering and CO_2 consumption rate (Jha et al. 2009; Singh et al. 2005). In addition weathering of rocks contributes majority of ions in the river system. Therefore seasonal variation in major ion composition in the river reflects dominant weathering process.

In India, a few researchers discussed on major ion chemistry within the Himalayan and Peninsular river basins and set up geochemical budget due to catchment weathering in expansive waterway frameworks. (Subramanian 1983; Sarin et al. 1989; Ramesh and Subramanian 1988; Sharma and Subramanian 2008). However, still long term understanding of hydro-geochemical process within the Himalayan River like Brahmaputra River is extremely important. Therefore the main objectives of the present study (1) To understand spatial and temporal variations in major ion chemistry of the Brahmaputra River (BR) (2) To evaluate freshwater quality through multivariate statistical tool.

10.2 Study Area

The Brahmaputra River originates on the Angsi Glacier, situated on the northern side of the Himalayas in Burang Province of Tibet, at an elevation of 5300 m above mean sea level (Sarin et al. 1989). The Brahmaputra River discharges high sediment and is the fifth largest river in the world (Berner et al. 1996) and second with respect to sediment transport per unit area (Milliman and Meade 1983). The River has high regular variety, high sediment load, and is described by continuous changes in channel position. The River has high seasonal variation, high sediment load, and is characterized by frequent changes in channel position (Thorne et al. 1993). The Brahmaputra River has a drainage area of 580,000 km^2 and shared by China (50.5%), India (33.6%), Bangladesh (8.1%), Bhutan (7.8%), (Berner et al. 1996; Subramanian 2004). The width of the river varies from 3 km to 18 km with an average of 10 km in the plains of Assam and Bangladesh. Geologically, the Brahmaputra Basin is divided into Higher and Lesser Himalaya sequences consist of schists, marbles with amphibolites, and quartzites (Sarin et al. 1989). All over the Brahmaputra valley of Assam comprises of consists of older and newer alluvium deposits. Alluvium shaped amid the Pleistocene age (older alluvium) is found in marginally undulating zones on the two sides of the Brahmaputra River and the new alluvium soils close to the river comprise of alluvial materials washed down from the highland areas. On the northern side, alluvial plain of Assam abuts Siwalik ridges of the Himalayas, which are in turn overlain by highly tectonized Paleozoic sediments. On the northern side, alluvial plain of Assam adjoins Siwalik ridges of the Himalayas and overlain by exceptionally tectonized Paleozoic sediment. The alluvial deposits are occurring in the eastern side of Assam valley. The Tertiary rock sequences occur in Patkai and Naga Hills on the southern side of the alluvial plain and comprises of dark grey shales, sandstones and shales with coal seams, clay and conglomerates.

The Brahmaputra Valley is basically a Quaternary fill valley with many separated sedimentary residual hill in Upper Assam and inselbergs and hill of gneissic rocks within the Darrang, Kamrup, and Goalpara area. The Brahmaputra and its tributaries experience frequently changing meandering course due to lateral erosion, periodic, local and sudden changes in the basement levels due to tectonic activity.

10.3 Materials and Method

The water samples (n = 54) were collected from main stream of the Brahmaputra River in pre-monsoon, monsoon and post-monsoon consecutively in three different seasons during 2011–2012 and 2013–2014. Nine sampling locations were selected for this study covering upstream to downstream of the Brahmaputra River namely; Guijan (B1), Roumeria (B2), Dibrugarh (B3), Jorhat (B4), Dhansiri Mukh (B5), Tezpur (B6), Guwahati (B7), Jogighopa (B8), Dhubri (B9) are shown in Fig. 10.1. Water samples were collected in polypropylene bottles. Samples were brought to the laboratory and were filtered using 0.45μm Millipore filter papers and acidified with nitric acid. In- situ measurements included pH, electrical conductivity (EC), total dissolved solid (TDS) which were measured using Multiparameter Water Quality Portable Meter (Hanna model-HI 9828) and bicarbonate (HCO_3^-) was measured by potentiometric titration method in unfiltered samples. For anion analysis, samples were stored below 4 °C until analysis. All chemicals used in the study were obtained from Merck, India and were of analytical grade. All glass-wares and other sample containers were cleaned with milli-Q water. The major ion analyses were carried out as per standard methods given in American Public Health Association (1995), {Calcium (Ca^{2+}) and Magnesium (Mg^{2+}) ICP-OES}; {Sodium (Na^+) and Potassium (K^+), Flame Photometer}; {Phosphate (PO_4^{3-})}, {Dissolved silica (H_4SiO_4), Sulphate (SO_4^{2-}), Nitrate (NO_3^-), UV Spectrophotometer}; {Chloride (Cl^-), titration method}. Statistical analyses (ANOVA and PCA) were performed using SPSS Version 22.0.

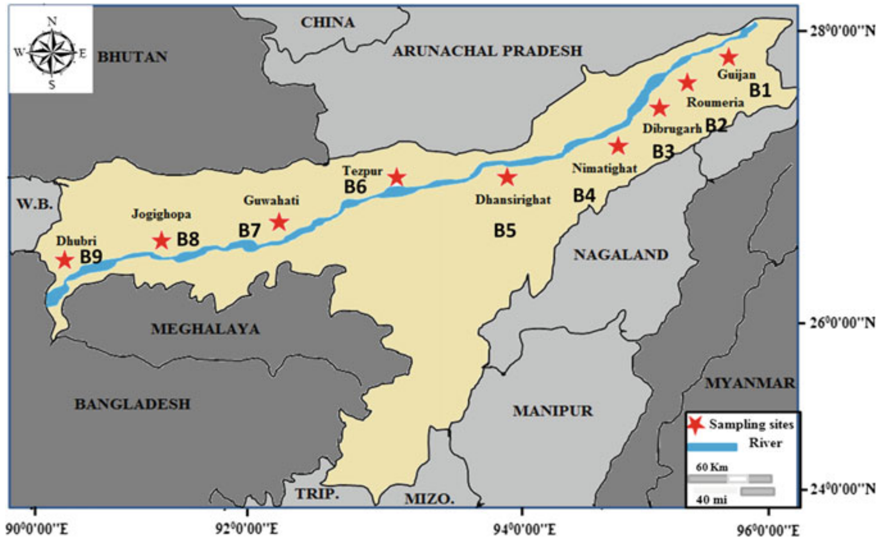

Fig. 10.1 Map of the Brahmaputra River showing sampling locations

10.4 Results and Discussion

10.4.1 Hydro-geochemical status of the Brahmaputra River

Spatio- temporal variations of major ions of the Brahmaputra River are shown in Table 10.1 and Fig. 10.2.

All units are in μM except EC (μS cm^{-1}), TDS (mgL^{-1}) and pH; **SD*-standard deviation.

10.4.2 Spatial variation

pH of river water showed slightly neutral to alkaline in nature and there was no so much in variation. EC and TDS concentration was observed to be high in downstream location (B7 and B9) amid pre-monsoon and post-monsoon seasons which might be because of different anthropogenic activities such as dredging, sand recuperation, transportation of ship, fishing, cremation on the banks and cultivation. High HCO_3^- concentration at S1 and S7 might be because of seasonal and anthropogenic factors. SO_4^{2-} concentration was maximum at B5 and B8; its increase towards downstream of the river showing anthropogenic impact. Cl^- content was found to be highest at B5 and B6. NO_3^- and PO_4^{3-} content found to be highest in upstream locations might be attributed to occurrence of several tea gardens and populated villages with cultivable land along the river bank. H_4SiO_4

Table 10.1 Statistical summary of major ion concentrations of the Brahmaputra River water samples in pre-monsoon, monsoon and post-monsoon season for 2011–2012 and 2013–2014

Variable	Pre-monsoon		Monsoon		Post-monsoon	
	Avg ± SD*	Avg ± SD*	Avg ± SD*	Avg ± SD*	Avg ± SD*	Avg ± SD*
	2011–2012	2013–2014	2011–2012	2013–2014	2011–2012	2013–2014
pH	7.48 ± 0.41	7.36 ± 0.47	7.41 ± 0.22	7.58 ± 0.43	7.85 ± 0.30	7.91 ± 0.21
EC	195 ± 31.2	147 ± 17.2	115 ± 26.0	139 ± 26.6	121 ± 21.9	135 ± 31.2
TDS	138 ± 20.9	98.8 ± 11.6	91.4 ± 41.8	93.4 ± 17.8	58.3 ± 44.3	90.5 ± 20.9
HCO_3^-	2058 ± 385	1657 ± 321	1403 ± 156	1559 ± 334	1281 ± 180	1504 ± 258
Cl^-	145 ± 49.2	119 ± 35.6	180 ± 70.9	162 ± 43.3	178 ± 67.4	134 ± 36.8
NO_3^-	19.0 ± 0.54	18.8 ± 0.53	19.5 ± 0.24	21.3 ± 3.40	19.2 ± 0.66	20.5 ± 3.38
SO_4^{2-}	166 ± 36.1	229 ± 56.0	271 ± 111	396 ± 121	65.9 ± 24.9	216 ± 41.0
PO_4^{3-}	0.64 ± 0.14	1.22 ± 0.57	0.64 ± 0.20	0.80 ± 0.43	0.57 ± 0.07	1.0 ± 0.33
H_4SiO_4	28.4 ± 9.34	62.6 ± 24.8	64.5 ± 29.0	82.7 ± 32.9	13.6 ± 14.0	42.2 ± 15.8
Na^+	308 ± 61.7	329 ± 80.0	359 ± 104	338 ± 78.0	354 ± 95.4	360 ± 64.1
K^+	51.8 ± 6.38	67.2 ± 21.5	55.8 ± 6.88	76.6 ± 15.6	47.5 ± 6.30	69.8 ± 12.3
Ca^{2+}	597 ± 102	494 ± 131	470 ± 73.1	533 ± 113	419 ± 86.1	636 ± 147
Mg^{2+}	277 ± 82.4	247 ± 79.3	254 ± 63.9	212 ± 47.8	186 ± 46.5	166 ± 43.0
TZ^+ (μEq)	2108 ± 349	1882 ± 270	1361 ± 209	1864 ± 141	1612 ± 206	2032 ± 346
TZ^+- (μEq)	2534 ± 416	2174 ± 233	2434 ± 143	2209 ± 216	1779 ± 182	1959 ± 257

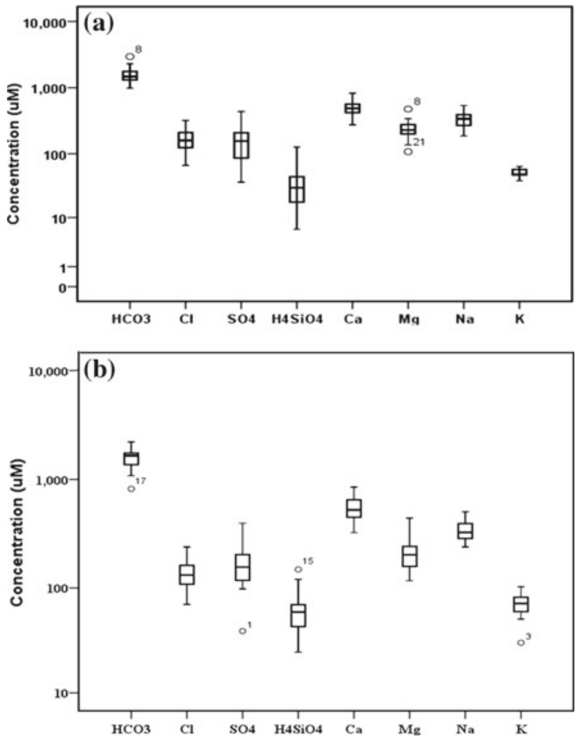

Fig. 10.2 Temporal variation of major ion concentration of the Brahmaputra River during different seasons represents the time of sampling event **a** cycle-I (2011–2012) **b** cycle –II (2013–2014)

content was found to be high at downstream location. B9. Na^+ concentration was found to be high at B2 and B6, K^+ at B1 and B8. The concentration of Ca and Mg show increasing trend from upstream to downstream.

10.4.3 Temporal variation

A comparative statistical summary of the Brahmaputra River water chemistry from different seasons during 2011–2012 and 2013–2014 is showed in Table 10.1. Average pH value of water samples in all year in different seasons varied from 7.48 to 7.91 indicates alkaline in nature. Variation in pH values during various period of the year were ascribed to factors like exclusion of CO_2 by photosynthesis through bicarbonate degradation, dilution of water with fresh water influx, decrease in temperature and decay of natural matter (Rajasegar 2003).

EC is an important water quality parameter shows presence of dissolved ions in the water. The average value of EC was maximum in pre-monsoon season followed by post- monsoon season attributed to high concentrations of dissolved salts and presence of more alluvial-derived soil (entisol, inceptisol, alfisol) and less resistant minerals in the catchment area. Low EC values during monsoon might be owing to dilution effect by rain water. In general, the TDS values are likely to be diluted by surface runoff in monsoon season and for most rivers there is an inverse correlation between discharge rate and TDS (Charkhabi and Sakizadeh 2006). TDS value in post monsoon season was increased which may be due to increase in dissolved minerals.

Temporal change in the major ion concentration of the Brahmaputra River from 2011 to 2014 is shown in Fig. 10.2. Seasonal difference of average anion content in water samples in decreasing order are as follow: $HCO_3^- > SO_4^{2-} > Cl^- > H_4SiO_4^- > NO_3^- > PO_4^{3-}$. Average cations concentrations in all seasons in decreasing order are as follows: $Ca^{2+} > Mg^{2+} > Na^+ > K^+$.

Among dissolved anion, HCO_3^- was present in high concentration in pre–monsoon and monsoon seasons for both year. High bicarbonate concentration in river water samples indicate bicarbonate is formed via mineral weathering and influence of anthropogenic activity. On the contrary decreased HCO_3^- concentration was caused by low pH in post-monsoon season. Average Cl^- content was maximum in monsoon season might be due to mixing of runoff water which bring larger amount of salts from catchment area. Other probable sources of Cl^- are release of domestic and industrial waste to the river. EC is a good marker for the chloride and patterns appear that low Cl^- concentration in 2013–2014 was due to low EC. Average NO_3^- content was highest in monsoon season and PO_4^{3-} content was highest in pre-monsoon season for all the year. Leaching of fertilizers from the agriculture overwhelmed zones; sewage effluents and decay of organic matter are potential source of NO_3^- and PO_4^{3-}.

Average SO_4^{2-} concentration was high in monsoon season for all the year. Oxidation of pyritic sediments and dissolution of gypsum or anhydrites is major donor of sulphate in water (Gansser 1964; Das et al. 2016a; Patel et al. 2019a, b). Other probable anthropogenic sources of SO_4^{2-} are runoff from agricultural land and untreated effluents released within the river system. Average H_4SiO_4 content was found to be high in monsoon season which may be due to high discharge during monsoon season. In addition weathering of igneous and metamorphic rocks contributes higher concentrations of silica in water (Stallard et al. 1981; Das et al. 2016a) and below pH 9 silicon is released by weathering as silicic acid (H_4SiO_4) (Iler 1979). Hence weathering of minerals is the major source of silica in the freshwater system.

Average Na^+ content was highest in pre-monsoon season for 2011–2012 and in monsoon for 2013–2014. Weathering of silicate minerals, halite dissolution and atmospheric precipitation are the probable source of sodium. Average potassium (K^+) concentration was high in monsoon season for both years. It was found that there was not much variation in K^+ concentration during the three seasons. Weathering of rocks and minerals in the catchment are the key contributor of K^+ in water. Other potential sources of K^+ are decomposition of organic matter and springs/groundwater (Krishnaswami and Singh 2005).

Among the cations, Ca^{2+} was the dominant ion concentration and average Ca^{2+} content was highest in pre-monsoon and post-monsoon season. Dissolution of carbonate rocks (limestones, dolomite) is the major source of Ca^{2+} in water (Nikanrov and Brazhnikova 2006). Average Mg^{2+}content were high in pre-monsoon for all the year. The high concentration of Mg in non-monsoon season may be due to anthropogenic impact. It was reported that magnesium in natural water is primarily supply through ferromagnesian minerals (e.g. olivine, pyroxene, amphiboles) which are present in igneous rocks and sedimentary rocks.

In general, results show that ion concentration was high during pre-monsoon followed by monsoon and post-monsoon season. In 2011–2012 concentration of HCO_3^-, Ca^{2+}, Mg^{2+}, Na^+, K^+ was high in pre-monsoon season. In 2013–2014 concentration of Cl^-, SO_4^{2-}, H_4SiO_4, HCO_3^-, Na^+, K^+ was found to be high in monsoon season. For 2011–2012, pre-monsoon was dominant and for 2013–2014 monsoon and post-monsoon were dominant. The high Maximum ion concentration in non-monsoon season credited anthropogenic impact and in monsoon season was because of flow of runoff, influence through cyclic salts. Taking into account the most land use for agriculture, manures and pesticides are vital supply of NO_3^- and PO_4^{3-} (Patel et al. 2019b).

The quality of hydro-geochemical data of the BR is measured using charge balance (μeq) between total dissolved cations ($TZ^+ = Na^+ + K^+ + 2Ca^{2+} + 2Mg^{2+}$) and total dissolved anions ($TZ^- = Cl^- + HCO_3^- + 2CO_3^{2-} + 2SO_4^{2-}$). Water samples from the mainstream show specific charge balance typically higher than 10% which is evaluated using Eq. (10.1) (Friedman and Erdmann 1982):

$$\text{Charge Balance }(\%) = (TZ^+ - TZ^-)/(TZ^+ + TZ^-) \times 100 \tag{10.1}$$

10.5 Identification of Hydrogeo-Chemical Processes

Groundwater chemistry in the study area is regulated by various processes and mechanisms. Thus Gibbs plot is employed in the present study to understand the primary mechanism controlling water chemistry i.e. atmospheric precipitation, mineral/rock weathering and evaporation (Gibbs 1970). Various workers have applied Gibbs plot in tracing major mechanisms that control water chemistry for rivers like Ganga, Cauvery, Krishna, Amazon. In Fig. 10.3 Gibbs plots have been used to show the relationship between TDS and (Na + K)/(Na + K + Ca) or Cl/(Cl + HCO_3^-) ratios, so as to assess the significance of three major natural mechanisms controlling water chemistry. Figure 10.3 illustrates that most of the samples falls in the weathering zone except few samples in the monsoon 2011 and 2013, indicating that the chemical weathering of the rock-forming minerals is the primary mechanism controls the major ion chemistry of the Brahmaputra River. Monsoon season of both cycles seem to have differences in terms of cationic input.

10.5.1 Characterization of chemical facies

Piper diagram is the indicative of overall water type which indicates that Ca is the dominant cation in all samples and the difference among them are due to their anionic compositions. Overall, majority of BR river water samples fall in the

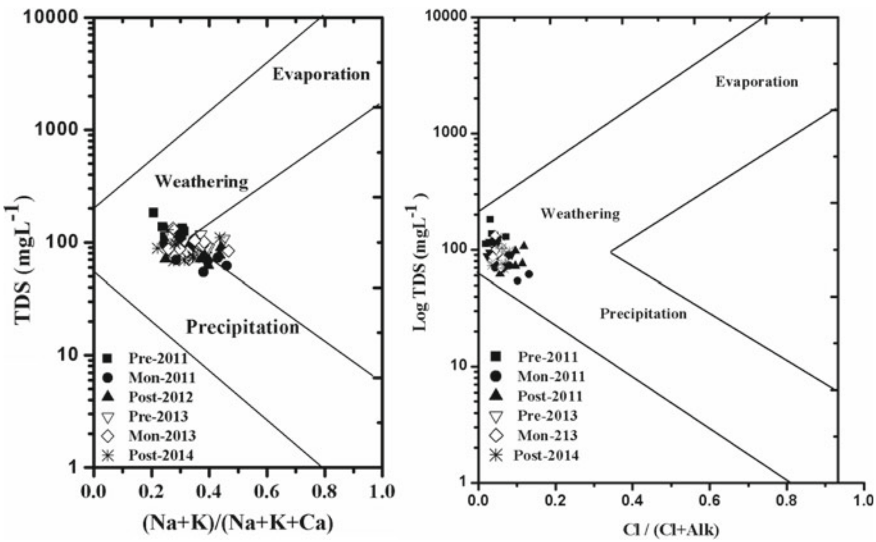

Fig. 10.3 Gibbs plot representing the main processes governing water chemistry in different seasons

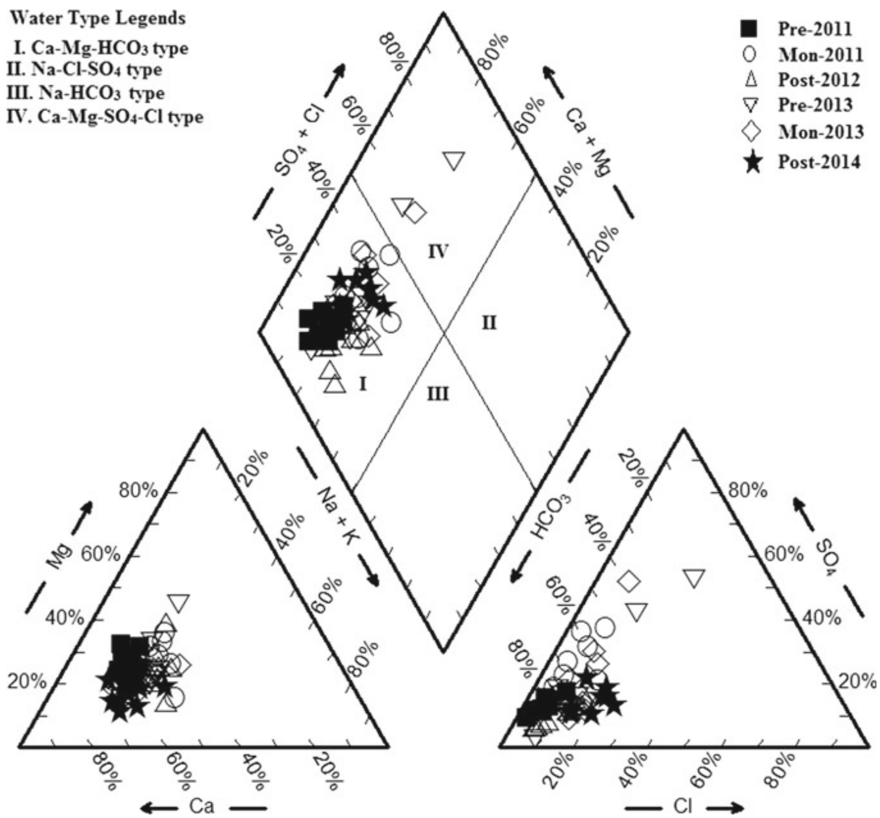

Fig. 10.4 Piper plot showing the water type of the Brahmaputra River

category of Ca–HCO_3 along with Ca–Mg–HCO_3–SO_4 type (Fig. 10.4). Chemical weathering of silicates with carbonic acid seems to be the dominant process here which releases Na, K, Mg, Ca from them to solution along with HCO_3. SO_4 being the second dominant anion attributed to the oxidation of pyrites and organic acids present in the upper layers of sediment, the humic and fulvic acids (Berner and Berner 1996).

10.5.2 Percent of sodium (Na%)

Sodium content expressed in terms of sodium percentage or soluble sodium percentage defined as

Table 10.2 Water quality of the Brahmaputra River for irrigation purposes

	Pre-monsoon		Monsoon		Post-monsoon	
2011						
Parameter	Mean	Range	Mean	Range	Mean	Range
SAR (2011)	0.332 ± 0.07	0.26–0.44	0.43 ± 0.15	0.25–0.71	0.46 ± 0.13	0.24–0.67
Na% (2013)	17.3 ± 3.22	11.7–21.1	22.4 ± 5.88	15.4–34.5	24.9 ± 5.06	15.9–33.5
2013						
SAR (2011)	0.39 ± 0.10	0.27–0.53	0.40 ± 0.11	0.28–0.63	0.41 ± 0.08	0.27–0.54
Na% (2013)	21.3 ± 4.17	16.5–25.8	22.0 ± 4.47	16.3–30.7	21.6 ± 4.67	14.2–30.2

$$\%\,\mathrm{Na} = (\mathrm{Na}^{+} + \mathrm{K}^{+})/(\mathrm{Ca}^{2+} + \mathrm{Mg}^{2+} + \mathrm{Na}^{+} + \mathrm{K}^{+})$$

where, all ionic concentrations are expressed in meq/l

Table 10.2 shows the result of Na% values of the BR ranges in 2011 ranges from 11.7 to 21.1 (mean = 17.3 ± 3.22) in pre-monsoon, 15.4–34.5 (mean = 22.4 ± 5.88) in monsoon, 15.9–33.5 (mean = 24.9 ± 5.06) in post-monsoon. In 2013, % of Na varies from 16.5 to 25.8 in pre-monsoon (mean = 21.3 ± 4.17), 16.3–30.70 (22.0 ± 4.47) in monsoon, 14.2–30.2 (21.6 ± 4.67) in post-monsoon.

High level of percentage of sodium (%Na) in water (>15%) is vital for soil richness, plant development and better condition as it lessens the permeability of the soil (Todd 1980). In the present study it was found that.% of Na in BR is suitable for agriculture purposes and monsoon season is most suitable for irrigation purpose. In Table 10.3 most of the BR water samples in all seasons fall in excellent to good categories indicating their suitability for irrigation. No water sample of the BR is fall in unsuitable category.

10.5.3 Sodium Adsorption Ratio (SAR)

Sodium adsorption ratio, an important determining suitability for irrigation, is a measure of alkali/sodium hazard to crops (Thomas et al. 2014). The excess sodium or limited calcium and magnesium are evaluated by SAR which is expressed as

$$\mathrm{SAR} = \mathrm{Na}^{+}/\surd(\mathrm{Ca}^{2+} + \mathrm{Mg}^{2+})/2$$

All concentrations are in meqL^{-1}

Irrigation waters are classified based on sodium adsorption ratio (WHO 2011). As per Richards (1954), water with SAR ≤ 10 is considered as of excellent quality.

Table 10.3 Classification schemes of irrigation parameters proposed by Richards (1954) and Wilcox (1955), which indicate suitability of the Brahmaputra River waters for irrigation

Parameter	Thresholds	Class	Brahmaputra River water					
			2011			2013		
			Pre	Mon	Post	Pre	Mon	Post
% of sample								
SAR	<10	Excellent	27	27	27	27	27	27
	10–18	Good						
	18–26	Fair						
	>26	Poor						
Na %	<20	Excellent	6	3	1	4	2	3
	20–40	Good	3	6	8	5	7	6
	40–60	Permissible						
	60–80	Doubtful						
	>80	Unsuitable						

In Table 10.3, mean SAR in BR was found to be is 0.332 ± 0.07 (0.26–0.44) in pre-monsoon, 0.43 ± 0.15 (0.25–0.71) in monsoon, 0.46 ± 0.13 (0.24–0.67) in post-monsoon. Based on the Bower (1978) classification, the water samples belong to 'no problem category' of irrigation water quality (i.e., SAR < 6), thus water is suitable for irrigation purpose. According to the SAR classification, 100% of BR water samples in all seasons fall in excellent category which can be used for irrigation on almost all soil.

10.6 Effective CO_2 Pressure

In aquatic system the partial pressure of CO_2 (pCO_2) reveal both internal carbon dynamics and external biogeochemical processes in terrestrial ecosystems (Jones et al. 2003). When carbonate rocks weathers, alkalinity is produced leading to an increase in pH and a decrease in pCO_2. The effective CO_2 pressure (Log pCO_2) for different seasons has been calculated from pH values and HCO_3^- concentration. The average pCO_2 values was found to be $10^{-2.4}$ in pre-monsoon, $10^{-2.9}$ in monsoon and $10^{-3.2}$ in post-monsoon are higher than the atmospheric value, i.e. $10^{-3.5}$. The higher pCO_2 in the river water could be a worldwide drift showing that the river water appears disequilibrium with the atmosphere (Garrels and Mackenzie 1971). This might be because of input of groundwater containing high CO_2 and the slow rate of its re-equilibrium between surface water and the atmosphere by release of excess CO_2 (Subramanian et al. 2006; Sharma and Subramanian 2008).

10.7 Multivariate Analysis

10.7.1 Principal Component Analysis (PCA)

Table 10.4 shows the result of factor analysis, for three seasons i.e. pre-monsoon, monsoon and post-monsoon seasons. In pre-monsoon four factors were identified which controls the river chemistry. Factor 1 accounted for 33.6% variance and dominant variables are pH, EC, TDS, HCO_3^-, Ca^{2+} and Mg^{2+} indicate contribution of ions through carbonate weathering. Factor 2 accounted for 15.2% variance and dominant variables are Cl^- and SO_4^{2-} indicating oxidation of pyretic sediments and gypsum or anhydrites were the source of sulphate in water. Negative loading of PO_4^{3-} indicate less anthropogenic input. Factor 3 accounts for 14.6% variance with high positive loading of Na^+ indicate contribution through weathering process and negative loading of NO_3^- indicate influence of less anthropogenic activities. Factor 4 accounts for 12.4% with high positive loading of K^+ and Mg^{2+} indicate anthropogenic influence.

In the monsoon season, four factors were identified. Factor 1 accounted for 27.3% variance and high positive loading of EC, TDS, K^+ and Ca^{2+} as variables indicate contribution of weathered material in the river system. Negative loading of Cl^- and Na^+ indicate evaporation enrichment. Factor 2 accounted for 14.4% variance and dominant variables were PO_4^3, H_4SiO_4 and K^+ input of anthropogenic runoff. Factor 3 accounted for13.6% variance and dominant variables were HCO_3^- and SO_4^{2-}. Factor 4 accounted for 13.2% and dominant variables were pH and negative loading of Mg^{2+}.

In post-monsoon season, four factors were identified. Factor 1 accounted for 26.0% variance. The variables were HCO_3^-, SO_4^{2-}, PO_4^{3-}, H_4SiO_4 and K^+ indicates contribution of ion through anthropogenic activities. Factor 2 accounted for 22.2% and variables were EC, TDS, Cl^- and Na^+ indicated contribution from atmospheric input. Factor 3 accounted for 13.5% variance and dominant variables were pH and NO_3^- indicated pH regulated the contribution of ion and influence of anthropogenic input. Factor 4 accounted for 11.8% variance and dominant variables were Na^+ and Mg^{2+}.

10.7.2 Cluster analysis

Cluster analysis (CA) has been used to identify similarities and differences between water qualities of different sampling sites. Figure 10.5 illustrates the clustering method of groups of similar locations. In Fig. 10.5 CA is present in the form of dendrogram that classifies locations into three significant clusters: cluster 1 (locations 3, 9, 7) and cluster 2 (locations 1, 2 and 6) and cluster 3 (locations 4, 5 and 6). In cluster 1, sites 7 and 9 are located in downstream of the Brahmaputra River. These sites likely receive pollution from anthropogenic source such as industry

Table 10.4 Factor analysis of the Brahmaputra water samples for pre-monsoon, monsoon, post monsoon

Parameters	Pre-monsoon				Monsoon				Post-monsoon			
	F1	F2	F3	F4	F1	F2	F3	F4	F1	F2	F3	F4
pH	**0.63**	−0.09	0.354	0.294	0.06	−0.24	0.165	**0.713**	−0.17	−0.13	**0.90**	−0.11
EC	**0.83**	0.46	0.057	−0.10	**0.82**	0.208	0.152	0.087	0.272	**0.86**	0.05	0.05
TDS	**0.83**	0.46	0.057	−0.10	**0.82**	0.208	0.152	0.087	0.272	**0.86**	0.05	0.05
HCO_3^-	**0.95**	−0.11	−0.002	0.057	0.27	0.079	**0.834**	−0.30	**0.604**	0.35	0.188	−0.34
Cl^-	0.13	**0.58**	**0.550**	0.203	**−0.82**	0.0074	0.210	0.094	−0.34	0.67	−0.39	0.09
SO_4^{2-}	−0.12	**0.85**	−0.144	0.022	0.16	0.112	**−0.76**	−0.23	**0.617**	0.24	−0.14	0.24
NO_3^-	−0.08	0.07	**−0.801**	−0.047	−0.09	−0.045	0.453	0.090	−0.01	0.23	**0.749**	0.413
PO_4^{3-}	−0.26	**−0.54**	0.218	0.349	0.037	**0.786**	−0.20	−0.19	**0.850**	0.14	−0.10	−0.01
H_4SiO_4	−0.68	−0.13	0.267	0.312	0.052	**0.548**	0.252	0.495	**0.822**	−0.03	−0.17	0.057
Na^+	−0.09	−0.15	**0.81**	−0.35	**−0.83**	0.256	0.189	−0.02	0.046	**0.56**	−0.09	**0.58**
K^+	−0.18	−0.01	−0.104	**0.89**	**0.557**	**0.593**	0.080	0.291	**0.845**	.125	0.141	0.109
Ca^{2+}	**0.86**	−0.20	0.094	−0.095	**0.656**	0.386	0.063	0.089	0.465	.607	0.315	−0.06
Mg^{2+}	**0.56**	0.278	−0.10	**0.563**	−0.07	−0.12	0.17	**−0.81**	−0.12	.018	−0.13	**−0.90**
Eigen value	4.37	1.97	01.90	1.61	3.55	1.87	1.77	1.71	3.39	2.88	1.76	1.53
% of variance	33.6	15.2	14.6	12.4	27.3	14.4	13.6	13.2	26.0	22.2	13.5	11.8
% of CV	33.6	48.8	63.4	75.8	27.3	41.7	55.3	68.5	26.0	48.2	61.7	73.5

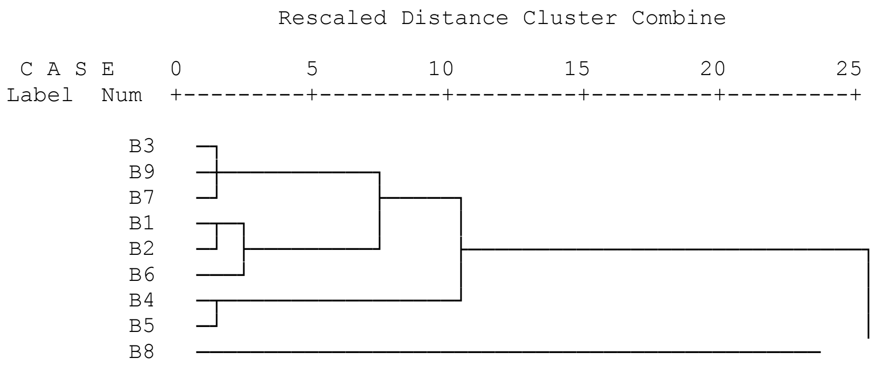

Fig. 10.5 Dendogram using ward method showing the clusters of different monitoring stations

effluents, oil spill etc. In cluster 2, sites 1 and 2 are located in upstream region which are slightly polluted and are less influenced by industrial discharge.

In cluster 3, sites 4 and 5 are closely associated which are located in upstream region and less polluted as compared to downstream sites (Das et al. 2016b).

10.8 Conclusion

The spatial-temporal variation of water quality from 2011 to 2014 was studied from upstream to downstream of the Brahmaputra River. Water quality of the Brahmaputra River was found to be neutral to alkaline in nature. High concentration of EC and TDS values in pre and post-monsoon season implies contribution of runoff water which carries larger amount of salts from catchment region. Concentrations of ions were higher during pre-monsoon followed by monsoon and post-monsoon season. For 2011–2012 pre-monsoon was dominant and for 2013–2014 monsoon and post-monsoon was dominant. The high concentration of ion in non-monsoon season was credited to anthropogenic impact; and in the monsoon season is due to influx of runoff. In the Brahmaputra River, temporal variation of average anion concentration is in order: $HCO_3^- > SO_4^{2-} > Cl^- > H_4SiO_4 > NO_3^- > PO_4^{3-}$ and cation concentration is in the $Ca^{2+} > Mg^{2+} > Na^+ > K^+$ in all the seasons. High average molar ratio of $(Ca^{2+} + Mg^{2+})/(Na^+ + K^+)$ and $(Na^+ + K^{+)}/Tz^+$ suggested contribution of ions through carbonate and silicate minerals. The average precipitation corrected molar ratio of (Ca^{2+}/Na^+), (HCO_3^-/Na^+) and (Mg^{2+}/Na^+) reflected influence of silicate and carbonate weathering. Relatively lower ratio of $(Ca^{2+} + Mg^{2+})/(Na^+ + K^+)$ during monsoon season of 2013–2014 signifies addition of Na^+ and K^+ ions through anthropogenic source, which may be due to high runoff.

Gibbs plot implied weathering as the major mechanism that controls the water chemistry of the Brahmaputra River. Dominant hydro-chemical facies in the BR are

Ca–HCO_3 and Ca–Mg–HCO_3–SO_4. High effective CO_2 pressure (pCO_2) in the river water shows that weathering of rocks that regulate the water chemistry of the River exerts a strong influence on the global climate. The water chemistry of the Brahmaputra River is chiefly governed by weathering of rocks with minor contributions from atmospheric and anthropogenic sources. Therefore regular monitoring of hydro-chemical composition of the river water is essential in the context of climate change.

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Chapter 11
Performance Appraisal of Filter-Based Sanitation System for Onsite Treatment of Domestic Wastewater

M. K. Sharma, V. K. Tyagi and A. A. Kazmi

11.1 Introduction

The on-site sanitation systems have been popularly used in the developing countries like India, particularly in the areas where centralized treatment facilities are not available. These areas are generally the rural areas or the areas around the cities. The majority of the people living in these areas utilize the conventional septic tank (CST) for the management of the domestic wastewater. However, the low treatment efficiency of the CST is a major concern, which needs to be addressed to safeguard the environment and the public health. Several alternatives have been developed for improving the quality of the septic tank effluent, including UASB-septic tank, membrane bioreactors, anaerobic baffled reactor and constructed wetlands (Nakajima et al. 1999; Brix and Arias 2005; Abegglen et al. 2008; Kumar et al. 2019; Gogoi et al. 2018; Shim et al. 2019). However, all these systems require large-size reactors with high cost involvement. The filter-based package systems have become quite popular nowadays for domestic wastewater treatment due to some advantages over the conventional treatment systems (Greaves et al. 1990). The factors behind their popularity are requirement of less masonry work, easy installation and above all the compact size as compared to other systems. Therefore, the present study was focused on the performance evaluation of anaerobic package filter-based sanitation systems for on-site treatment of domestic wastewater to identify their potential as an alternative to the CST. The present system was fabricated by combining a modified septic tank and an upflow anaerobic filter as a single unit and therefore termed as "package system".

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Generally, the on-site systems come across large variations in both quantity and quality of the influent wastewater continuously. A biofilm process was identified as the best option for treatment of the highly fluctuating domestic wastewater (Watanabe et al. 1993). Keeping the suggestions of this study in consideration, the present system was designed to accommodate two bio-reactor (settling tank and anaerobic filter) within a single unit. The idea was to make use of the process of sedimentation and biofilm simultaneously. The settling-tank chamber of the unit was able to do the primary treatment quite effectively by trapping the solid fraction in the domestic wastewater up to a considerable degree. Consequently, the organic load on the anaerobic-filter chamber was reduced substantially. It also provided equalization of the flow. The anaerobic-filter chamber (bio-film process) was used as the secondary treatment unit for the septic tank effluent. It was designed to be able to treat the highly fluctuating wastewater, both in the quantity and the quality. Finally, an anaerobic filter-based sanitation system, which consisted of two bio-reactor chambers, was developed to carry out the present study in the actual field conditions.

It is well known that the efficiency of the treatment unit is significantly affected by the quality of the incoming wastewater. It has been observed at a number of wastewater treatment plants in India that performance of the treatment systems is unsatisfactory due to low organic load in the wastewater (Tay et al. 2004). Thus a field-scale study was carried out to evaluate the performance of a filter-based system for on-site treatment of domestic wastewater to identify whether it could be an appropriate alternative to the conventional septic tank. The system was designed by accommodating a modified septic tank and an upflow anaerobic filter in a single compact unit. The applicability potential of the system was studied for its efficiency to remove the pollutants as well as the desludging interval for a duration of one year.

11.2 Materials and Methods

11.2.1 Experimental Set-up and Installation of Sanitation System

The field-scale study was conducted under the actual conditions using filter-based anaerobic reactor for the treatment of domestic wastewater. The system was single unit divided into two chambers. The first chamber was a septic tank and the second one an anaerobic filter. The study was carried out for family of five members at the Indian Institute of Technology Roorkee (IITR), Roorkee, India. The typical layout as well as the pictorial view of the experimental set-up in actual field conditions are illustrated in Fig. 11.1. The system was directly installed after excavating down to a 2000 mm depth from the ground surface after the formation of 10 cm thick Portland Cement Concrete platform at the base.

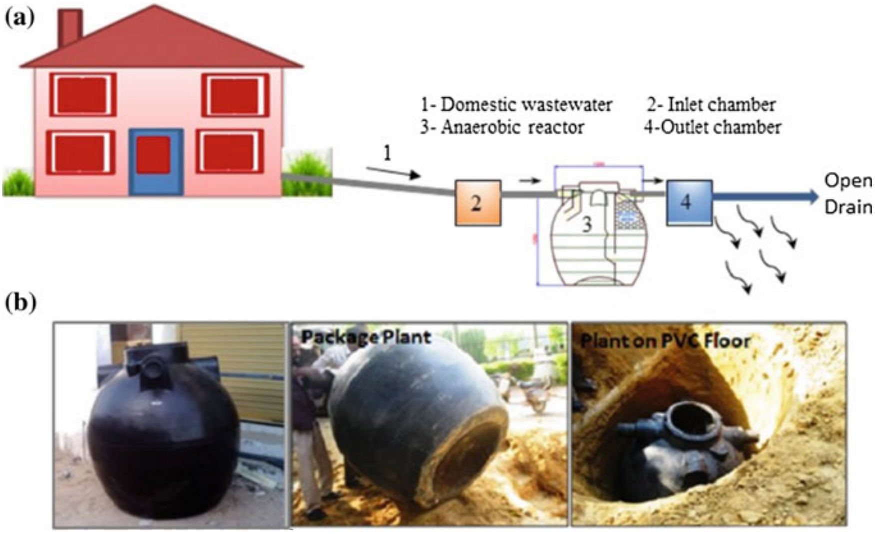

Fig. 11.1 Sanitation system for wastewater treatment **a** typical layout and **b** pictorial view

The field-scale system was brought in operation without inoculum to identify some issues including the variations in the pollutant removal efficiency and requirement of desludging in the long run. During the entire span of the study, all the sludge was retained in the reactor to maintain higher biomass density and greater sludge retention time (SRT). It helped in obtaining a higher treatment efficiency consequently. The wastewater generated by the household was made to flow directly into the treatment plant without any change in its characteristics.

11.2.2 Characterization of 24-h Flow Variation

The on-site systems generally come across large variations in both quantity and quality of the domestic wastewater round the clock. These daily variations in the influent domestic wastewater significantly affect the performance of the system. Therefore, it is necessary to carry out detailed characterization of the domestic wastewater. There is lack of information about the 24-h flow variation in the quantity of domestic wastewater generated by a typical singly Indian household. Therefore, the monitoring of the system was done for 24 h for quantitative analysis. Spot sampling was done at many consumption points and was made to be collected in a tank for characterization point of view. The tank had the facility to measure the volume of wastewater generated at each drain point of the house over a period of 24 h. The collected wastewater was also analysed for flow variation and mass loading rates.

11.2.3 Analytical Procedure

To investigate the performance of the filter-based sanitation system, the samples of influent and effluent wastewater were collected and analysed for the various physicochemical and microbiological parameters, while sludge samples were analysed for the total and volatile fraction of the suspended solids. The physicochemical parameters, such as chemical oxygen demand (COD), biochemical oxygen demand (BOD), total suspended solids (TSS), volatile suspended solids (VSS), total nitrogen (TN), and total phosphorous (TP). Total nitrogen (TN) was measured as sum of all forms of nitrogen (subject to presence) in a sample as N which can be expressed by Eq. (1), where Organic-N was measured as the difference of Total Kjeldahl Nitrogen and ammonia nitrogen (NH_4^+-N).

$$TN = NH_4^+\text{-N} + NO_3^-\text{-N} + NO_2^-\text{-N} + \text{Organic-N} \quad (1)$$

The Standard Methods for the examination of water and wastewater (APHA 2005) were followed for all the analyses barring alkalinity. The concentration of alkalinity was measured according to the titration method suggested by Dilallo and Albertson (1961). The measurements of pH and Oxidation reduction potential (ORP) of the samples were done on-site by HQ Series portable pH/ORP probes (Model 40 D Hach, USA).

The sludge samples were also collected from the primary chamber of the field-scale anaerobic sanitation system and were analysed for the TSS and VSS on monthly basis.

The influent and effluent samples were also assayed for faecal indicators: total coliform (TC), fecal coliforms (FC) and pathogenic microbes (*Salmonella* and *Shigella*). The concentration of TC and FC were enumerated according to the Standard Methods (APHA 2005) while pathogenic bacteria *Shigella* and *Salmonella* were detected according to the procedure reported by Sharma and Kazmi (2015a).

11.2.4 Sludge Activity and Morphology

The characterization of anaerobic sludge is often done on the basis of its specific methanogenic activity (SMA), which represents the methane production capacity of methanogenic bacteria present in the accumulated sludge (Sharma et al. 2014). The SMA is measured in batch which was performed according to the procedure reported by Isa et al. (1993) with the modification in the serum reaction bottle and the liquid displacement gas measurement method. The volatile suspended solids in the sludge sample were determined before and after the start of the activity test. The activity test was performed in the shaking condition at 30 ± 2 °C.

The sludge morphology was examined using scanning electron microscope (SEM). The sample was first fixed with 2.5% (w/v) glutaraldehyde in phosphate buffer for 1-h at 4 °C. It was then dehydrated through a graded series of acetone-water mixtures. The samples of each mixture were subsequently brought to equilibrium for 10 min. and finally dried off by the critical-point drying method. Afterwards the samples were sputter-coated with gold particles (Gopal Krishna et al. 2009; Sharma et al. 2014). At last, the examination of the samples was done using SEM (LEO 435 VP).

11.2.5 Mass Balance

The mass balance is a useful tool to measure the distribution and transformation of the influent COD fed to the treatment unit as it gets transformed into methane and biomass. A partial fraction of COD is also consumed in sulfates reduction. Therefore, the examination of COD mass balance of the whole sanitation system for the entire study period was carried out by using Eq. (2).

$$COD_{inf} = COD_{eff} + COD_{CH_4} + COD_{aqCH_4} + COD_{biomass} + COD_{SO_4} + COD_{unacc} \tag{2}$$

where COD_{inf} and COD_{eff} indicate the total masses of influent and effluent COD respectively in g/d, while the terms COD_{CH_4} and COD_{aqCH_4} represent the COD of methane produced in gaseous and aqueous forms respectively in g/d (Metcalf and Eddy 2003). Here, $COD_{biomass}$ is the COD of the developed sludge within the system and COD_{SO_4} is the fraction of COD consumed in sulphate reduction, in g/d (Arceivala and Asolekar 2010).

The measurement and collection of the generated methane gas was not carried out during the experiment. Therefore, it was determined by means of calculation, which also included the fraction of unaccounted COD, indicating errors in the measurement of gas collection. Comparison of the calculated results of methane gas generation was also done with the results of the methanogenic activity test. The results of the on-site methane production corroborated with the activity test performed on the sludge in the laboratory bioassay.

11.2.6 Hydrodynamic Study

The hydrodynamic study was performed to identify the flow regime within the sanitation system and determine the difference between the theoretical and actual residence time of substrate within the treatment unit. For this purpose, tracer experiment was conducted and a residence time distribution (RTD) curve was generated. This curve was determined on the basis of dimensionless concentration against the dimensionless time, which was further characterized for hydraulic regime. The hydraulic regime of non-ideal plug flow reactors can be modelled on the basis of dispersion (Sharma and Kazmi 2015b). The dispersion coefficient represents a general term, which is used to characterize the axial dispersion. At the steady state, the governing mass balance equation that could be used to establish the axial dispersion model by applying Fick's law in axial direction. Further, to investigate the hydraulic characteristics and flow regime, some theoretical interpretations were used for the analysis of experimental data in Levenspiel (2004), Metcalf and Eddy (2003).

11.3 Results and Discussion

11.3.1 Wastewater Generation and Flow Variation at Household Level

During the flow characterization study at household level, the average amount of generated domestic wastewater, excluding the water used for gardening, was found to be 140 L/cap/d. About 13% of the generated wastewater was used for toilet flushing. As far as the contribution from different consuming was concerned, the maximum share was from the kitchen (about 44%) providing about 37% of the COD loading on the system. The individual contribution in the total wastewater generation by different consuming points with the respective pollutant loading has been illustrated in Fig. 11.2.

The hourly variations in the flow of the generated domestic wastewater by the single household during the study period are presented in Fig. 11.3.

When observed for a typical period of 24 h for hourly fluctuations in the quantity of the influent wastewater, it was noted that the average hourly flow rate was about 13 L/h with the maximum rate of wastewater generation observed between 06:00 A.M. and 02:30 P.M. in the afternoon. It was also noted that there was almost zero flow during the night between 11:00 P.M. and 06:00 A.M. and a particular duration in the evening (07:00 P.M. to 09:00 P.M.) representing a total of nine hours of no-flow condition. The maximum flow was observed to be 119 L/h, which showed more than six turns of average flow. Based on the 24-h flow variation, the daily flow variation in the domestic wastewater was noted to be around 587 L/d, and indicated that the filter-based sanitation system was operated at about 48-h HRT.

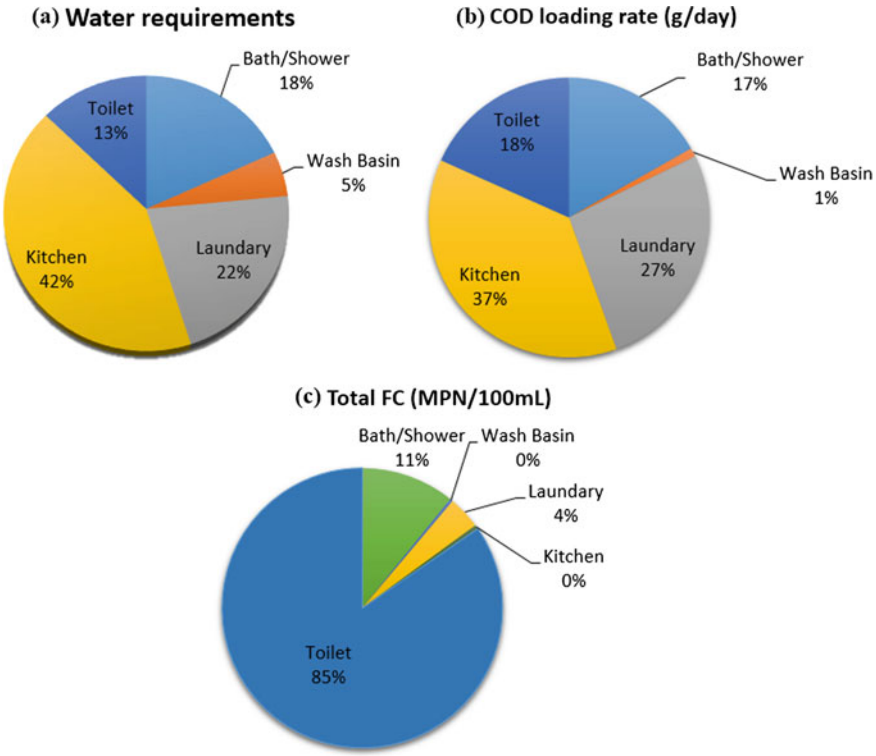

Fig. 11.2 Relative quantity and characteristics of domestic wastewater produced from different generating point **a** Quantity, **b** COD, **c** FC load in the domestic wastewater

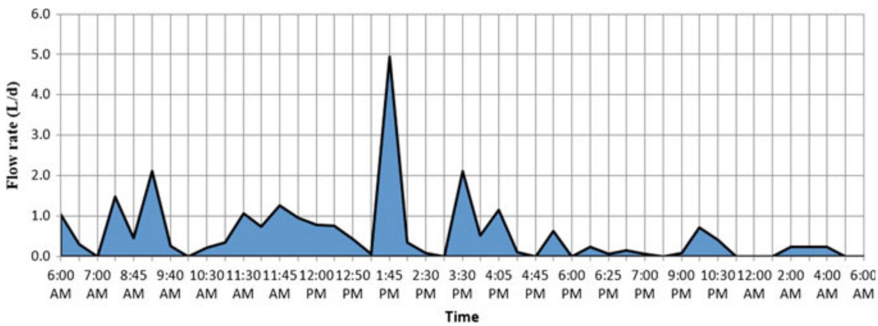

Fig. 11.3 Hourly fluctuations in the generated domestic wastewater

Table 11.1 Concentration of various parameters of wastewater during the study

Parameter	Influent[a]	Effluent[a]
pH	7.30 ± 0.49	7.26 ± 0.31
Alkalinity (mg/L as $CaCO_3$)	342 ± 45	351 ± 38
COD (mg/L)	858 ± 254	208 ± 84
BOD (mg/L)	382 ± 80	123 ± 51
TSS (mg/L)	442 ± 119	85 ± 23
TN (mg/L)	47 ± 12.8	37.5 ± 8.0
TP (mg/L)	10.1 ± 2.6	8.2 ± 2.3
TC (MPN/100 mL)	$1.5 \times 10^7 \pm 7.4 \times 10^6$	$7.8 \times 10^5 \pm 3.3 \times 10^5$
FC (MPN/100 mL)	$6.8 \times 10^5 \pm 2.6 \times 10^5$	$1.3 \times 10^4 \pm 9.4 \times 10^3$
Salmonella (MPN/100 mL)	$2.9 \times 10^3 \pm 5.0 \times 10^2$	$1.3 \times 10^3 \pm 2.1 \times 10^2$
Shigella (CFU/100 mL)	$6.4 \times 10^3 \pm 2.4 \times 10^3$	$1.6 \times 10^3 \pm 4.1 \times 10^2$

[a]Average value ± standard deviation

11.3.2 Domestic Wastewater Characteristics at Single Household

The present study was done using the actual domestic wastewater, which included the toilet-flush water also. The average concentration of the various physico-chemical and microbial constituents in the raw domestic wastewater are illustrated in Table 11.1. The concentrations of COD, BOD and TSS in the wastewater were observed to be of varying degree of characteristics. The estimation of the organic matter, which is a mixture of biodegradable and non-biodegradable contents, can be done by the COD to BOD ratio. If the COD to BOD ratio varies from 1.5 to 2.0, it indicates presence of readily biodegradable organic matter (Metcalf and Eddy 2003). During the study, the average COD to BOD ratio was observed to be 2.31 ± 0.55, which indicated that the domestic wastewater could be effectively treated by means of biological treatment process.

11.3.3 Long-Term Performance Evaluation of the Sanitation System

The anaerobic filter-based sanitation system was started without using inoculums and was operated for a period of approximately one and a half years. The performance of the system was regularly monitored throughout the study. The average performance of the system in terms of influent and effluent characteristics of wastewater, are summarized in Table 11.1.

During the study, it was observed that the ORP values were found to be vary in the range of −198 to −236 mV, which indicated that the sanitation system worked under anaerobic conditions. The pH and alkalinity, which are closely related, are very important factors of anaerobic processes. The pH of the effluent varied in the range of 7.02–8.10 which was an indication that no excessive acidification occurred within the system due to excess production of fatty acids. Further, the anaerobic system had good buffering as the effluent pH never dropped below 6.8. However, the concentration of alkalinity in the effluent was found to be in the range of 296–416 mg/L as $CaCO_3$, which was 4.7–11.9% higher than the influent alkalinity. This increased concentration of alkalinity might be attributed to carbonate and bicarbonate formation.

Much variations were observed in the concentration of COD and BOD due to the use actual domestic wastewater, which are reflected in the standard deviation (Table 11.1). The average concentrations of COD and BOD in the effluent were observed as 208 ± 84 and 123 ± 51 mg/L respectively, which represents about 70.9 and 68.7% average removal efficiency. The data clearly showed that the removal of BOD was lesser than COD. This difference could be attributed to the inclusion of measurement of other compounds, such as metallic cations and inorganic compounds, in the COD analysis. These measurements were excluded from the BOD analysis. Moreover, some of the compounds included in the COD analysis are absorbed by the biofilm. Consequently, there is increased removal and low concentration of COD in the effluent (Perez et al. 2007). The BOD concentration in the effluent varied within the range of 34.5–175 mg/L, which was slightly higher than the prescribed disposal standards for BOD of 30 mg/L as illustrated in Fig. 11.4.

The average concentration of TSS in the effluent was observed as 85 ± 23 mg/L with the average removal efficiency of 78.1%. The concentration of TSS in the effluent varied within the range of 46–125 mg/L. It was found that the effluent quality in terms of TSS concentrations fulfilled the prescribed disposal standards of 100 mg/L, after accumulation of sufficient quantity of sludge in the primary chamber of the sanitation system as illustrated in Fig. 11.5.

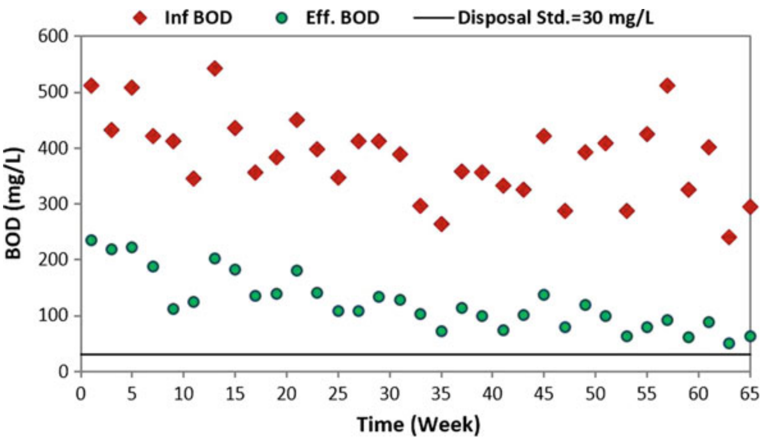

Fig. 11.4 Time series plot of BOD concentrations with reference to disposal standard

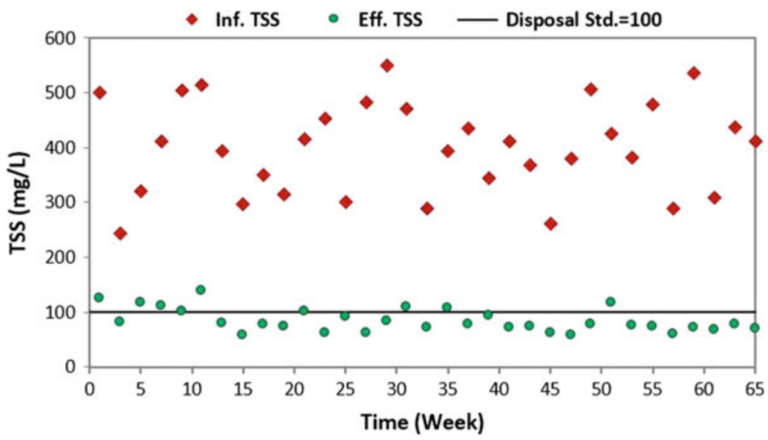

Fig. 11.5 Time series plot of TSS concentrations with reference to disposal standard

The nutrient removal from the domestic wastewater is an important task to protect the water bodies from eutrophication. However, anaerobic sanitation system is not found to be very effective in the removal of nutrients from the domestic wastewater (Mohapatra et al. 2012). During the present study, average removal efficiency of TP was observed as 13.8% with average effluent concentration of 8.2 ± 2.3 mg/L. The phosphorous content is removed on account of its utilization for biomass growth, precipitation and entrapment within the digested sludge (Wanasen 2003). The system could also not remove the TN substantially while obtaining only 20.2% average removal efficiency and the average effluent concentration of 37.5 ± 8.0 mg/L. It was observed that the system was not able to remove the nitrogen efficiently, which could be attributed to the volatilization of ammonia under anaerobic conditions (Chu et al. 2005).

The average effluent concentrations of TC, and FC were observed as 7.8×10^5 and 1.3×10^4 MPN/100 mL respectively (Table 11.1). Average effluent concentration of *Salmonella* and *Shigella* concentrations were found to be as 1.3×10^3 MPN/100 mL and 1.6×10^3 CFU/100 mL respectively. On an average, $\log_{10}$ reductions of faecal indicators and pathogens by the anaerobic sanitation system were represented as 1.30, 1.10, 0.35 and 0.61 for TC, FC, *Salmonella* and *Shigella* respectively. The removal of the pathogens was observed to be insignificant when compared to the removal of faecal indicators. This might be attributed to the fact that removal of pathogens is a result of physico-chemical process coupled with natural die-off and presence of toxicity of the specific pathogens. Yang et al. (2000) had also evidenced the same reason of natural die-off of microbes.

11.3.4 Sludge Bed Development and Sludge Characteristics

Development of the sludge bed plays an important role in the proper functioning of a wastewater treatment system as it regulates the effluent quality as well as the desludging interval. The sludge bed was developed at the bottom of the primary chamber (settling tank) of the anaerobic filter-based sanitation system due to accumulation of the particulate fraction of the influent wastewater and its partial solubilisation. During the study, no sludge was thrown off from the anaerobic package system to maintain higher biomass density and sludge retention time, which subsequently played a vital role in achieving higher treatment efficiency. To calculate the biomass density, evaluation of the solid content of the sludge accumulated at the bottom of the primary chamber was done on a monthly basis after four months from start-up. It was observed that the TSS concentration continuously increased over time, resulting in growth of the sludge bed. The solid concentration within the system continuously increased over time as illustrated in Fig. 11.6.

The VSS/TSS ratio varied from 0.77 to 0.74, which showed hydrolysis and stabilization of the sludge over time. At the end of the study, the system achieved a VSS/TSS ratio of 0.69, which indicated that the sludge still required further treatment for stabilization before its final disposal. After one year of operation, the sludge occupied approximately one third of the reactor-height in the primary chamber indicating that the system still had capacity to hold more sludge.

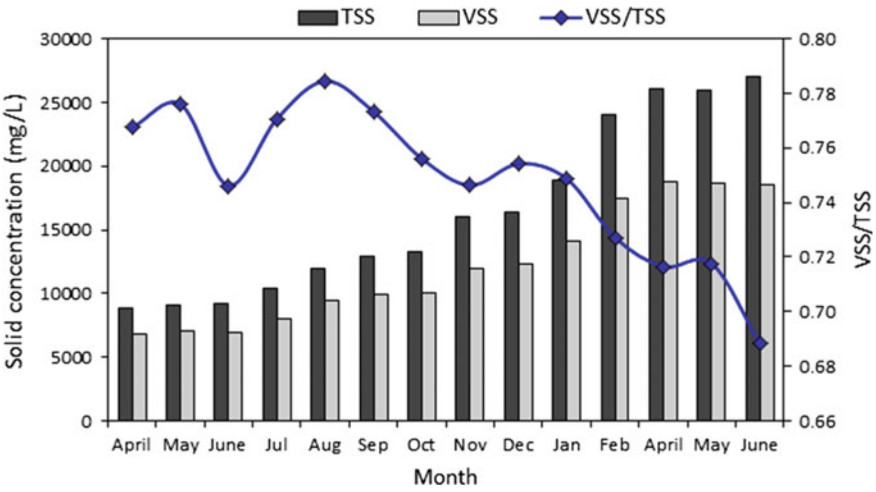

Fig. 11.6 Monthly changes in concentration of solids within the systems

11.3.5 Methanogenic Activity of Anaerobic Sludge

The value of specific methanogenoc activity of the anaerobic sludge was observed as 0.137 g COD-CH_4/gVSS.d. The result revealed that the accumulated sludge was in active state to produce methane gas when the value of SMA in the range of 0.08–0.20 g CH_4-COD/gVSS.d (Kalogo et al. 2001). This active state of anaerobic sludge was evidence that there was a significant amount of methanogens present in the sludge blanket (Jawed and Tare 1996). However, the SMA value of primary sludge without using substrate was found as 2.6 mL CH_4/gVSS.d, which indicated that the sludge still contained degradable organic matter and required more stabilization prior to being disposed off.

11.3.6 COD Mass Balance

During the study period, the COD mass balance was applied to the system with the average input and output concentration of COD being 486.1 and 120.4 g COD/day respectively. The results indicated that 69.4% of the input COD was removed within the reactor and got converted into different forms during the anaerobic treatment. The measurement of the methane gas generated from the reactor was done by calculation. Mass balance analyses indicated that the input COD was mainly converted into useful methane gas. Out of the total removed COD, 12 and 41% were recovered in aqueous and gaseous forms respectively. The sludge accounted for 17% of COD consumed within the system. COD consumed in sulfate reduction was quite low at 2.3% only. Additionally, the calculated results of methane gas generation were compared with the results of the methanogenic activity test, which revealed that the results of the on-site methane production were in agreement with the activity test performed on the sludge in the laboratory bioassay.

11.3.7 Bacterial Morphology

During the study, no sludge was disposed of from the sanitation systems, and the developed sludge was characterized by SEM examination. The SEM analysis was performed to examine the morphology of microbes on the surface of the anaerobic sludge. SEM images of the sludge withdrawn from the bottom of the primary chamber of the filter-based sanitation system are illustrated in Fig. 11.7. The SEM morphology revealed the presence of various *Methanococcus* and *Methanosaeta* bacterial species together with inert material in the flocs.

The morphotypes, as illustrated in Fig. 11.7a, were typically characteristic of the *Acetoclastic methanogen* and *Methanosaeta*. The other morphotypes resembling the cocci shaped bacteria were also observed with some quantity of inert material

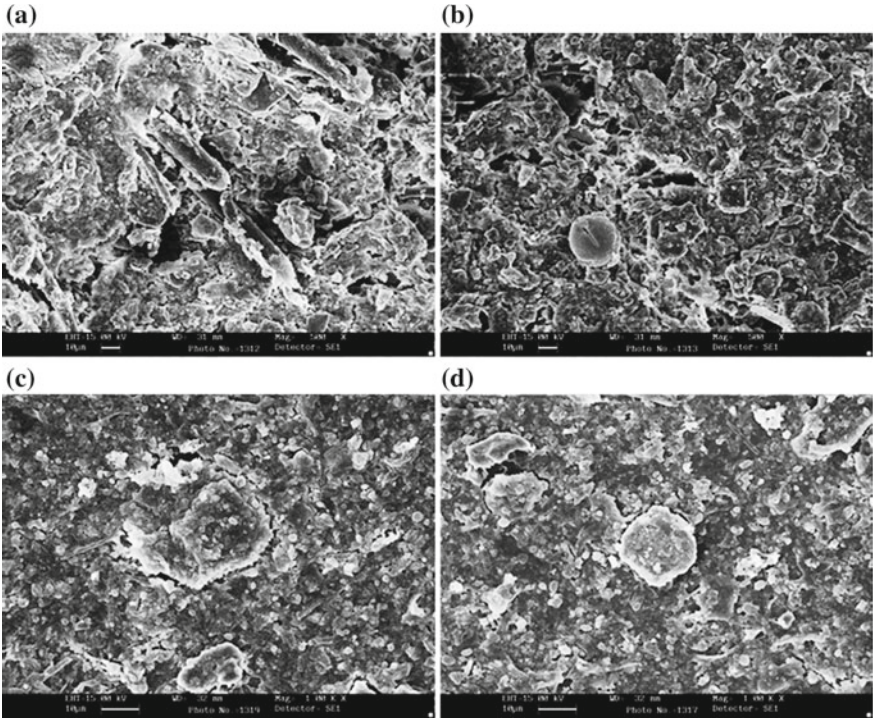

Fig. 11.7 SEM images of sludge sample

(Fig. 11.7b–d). These cocci resembled species of the *Methanococcus* genus, which plays an important role in methanogenesis, which is the final stage of anaerobic digestion process.

11.3.8 Hydrodynamic Characteristics

The results of the tracer study indicated that the mean HRT of the filter-based sanitation system was observed as 28.8-h, which indicated the actual exposure time and retention of substrate within the system. The presence of dead space affects the mean HRT and effective volume of the system. The system showed only 19.8% dead volume, which indicated a uniform distribution of wastewater and an increased contact with the active biomass. In addition, the low percentage of the dead space considerably reduced the possibility of short-circuiting and also helped in maintaining the desired retention time within the system. The calculated dispersion number 0.087 indicated that the flow pattern within the system could be considered to have a plug-flow regime (Levenspiel 2004; Tandukar et al. 2006). Similarly, the calculated value of Morrill Dispersion Index (MDI), obtained as 3.86, also showed the presence of low dispersion. However, the MDI was more than 2.0, which indicated that the system was outside the range of "effective plug flow regime" (Metcalf and Eddy 2003).

The tracer study provided significant evidence that a non-ideal flow regime occurred within the system, which partially explained the performance of the anaerobic packaged system. Therefore, after one year of continuous operating the system, less than 50% volume of the system was filled with the accumulated sludge indicating that the system did not require frequent desludging.

11.4 Summary

Based on the comparative performance analysis between the filter-based package-type system and the CST, the present system has a good potential to be an alternative to the CST. The filter-based system provided lower pollutant concentrations in the effluent and delivered substantially higher removal efficiency than the CST. Although, the filter-based system could not fulfil the Indian Disposal Standards, it delivered appreciable treatment efficiency as compared to the CST under actual onsite conditions. Thus, the present filter-based system, having simple operation and design with no power supply required, has a significant potential to be an alternate to the CST for the treatment of domestic wastewater in the non-sewered areas of the developing countries, including India.

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Chapter 12
Lake Eutrophication: Causes, Concerns and Remedial Measures

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12.1 Introduction

Eutrophication of water bodies is becoming one of the major environmental challenges all over the world in last few decades. The problems associated with lake eutrophication is increasing day by day and it has been brought to attention of researchers all over the world in recent times. The word 'eutrophic' is derived from a Greek word "eutrophos" which means rich or well nourished. Rast and Thornton (1996), have defined eutrophication as an evolution process of an waterbody, wherein a water body is progressively enriched with essential nutrients like nitrogen (N) and phosphorus (P), as a result primary productivity of the waterbody gets increased (Qin et al. 2013). From the beginning of a waterbody, it passes through different stages during development; e.g., oligotrophic, mesotrophic, eutrophic and hypereutrophic, i.e. aging and death to form a swamp. Eutrophication in lakes and rivers generally involve heavy algal or Cyanobacterial blooms and fish kills, the consequences of eutrophication, although profound, are often not as noticeable to the casual observer. In general, eutrophication of waterbodies can be categorised into two types, namely, natural eutrophication and cultural or anthropogenic eutrophication. Natural eutrophication refers to the gradual degradation of aquatic ecosystem in due course of time. It is a slow and gradual process, generally taking a period of centuries to occur as nutrient-rich soil washes into lakes. But this process can be greatly accelerated by anthropogenic activities which is generally referred to as man-made or cultural eutrophication (Rast and Thornton 1996; Khan and Ansari 2005; Serrano et al. 2017). Cultural eutrophication is triggered by unabated human activities like improper sewage disposal, use of agrochemicals, industrial by-products etc. which elevates the nutrient inputs on the water body beyond the

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required level. It is generally accepted that nutrient pollution mainly with nitrogen (N) and phosphorus (P), is one of the major factor responsible for cultural eutrophication of water bodies (Vollenweider 1968; Hecky and Kilham 1988; Lowery 1998; Smith 1998; Gurkan et al. 2006; Patel et al. 2019a; Das et al. 2016; Kumar et al. 2019; Gogoi et al. 2018). From 1940s onwards lake eutrophication cases became widespread all over the world at faster rate due to several factors such as increase in population, application of agrochemicals to crops rich in nutrient concentration, use of laundry detergents having high phosphate content and environmental pollution from different sources (Chloupek et al. 2004). Because nutrients can come from many sources, from natural to anthropogenic, comprehensive strategies are required to mitigate eutrophication. Various watershed programs have been successfully used to encounter the problem but these are not sufficient because the number of eutrophicated lakes and rivers are increasing day by day.

This review deals with the lake eutrophication case studies all around the world with special emphasis on the conditions of water bodies in Asiatic regions. An attempt has been made to cover the mechanism and impact of water eutrophication as well as various mitigation strategies to encounter the problem.

12.2 Major Sources and Causes of Lake Eutrophication

It is well known fact that N, P etc. are the key nutrients essential for growth and sustainability of different microorganisms and aquatic lives that constitute the surface water ecosystem. But higher inflow of these nutrients to the waterbody, may result in rapid growth of different kind of algae or phytoplankton groups, and consequently may deteriorate the water quality and degrade the ecosystem balance. Domestic and industrial waste water effluents, solid waste dumping, run off from agricultural areas carrying fertilizers, pesticides etc. to the water body are the major sources of nutrient enrichment which accelerates eutrophication process. Under conducive condition of temperature, light and high nutrient concentration, rapid algal or cyanobacterial bloom may occur in the waterbody which may result in breakdown of aquatic ecosystem balance (Smith et al. 1999). Sunlight or temperature is also an important factor governing the eutrophication process. For instance, during summer season, cyanobacteria are the major phytoplankton in eutrophic water. But during winter time as the turbulence increases and lack of sunlight causes their replacement by the diatoms. But in tropical regions, seasonal variations in the environment are often not great enough for replacement of the cyanobacteria by other phytoplankton species.

The general process of eutrophication of water bodies can be illustrated with Fig. 12.1.

Smith et al. (1999), have mentioned two types of sources for nutrient loading; point source and nonpoint sources. Point sources are those which can be easily monitored and localized whereas nonpoint sources are difficult to monitor and

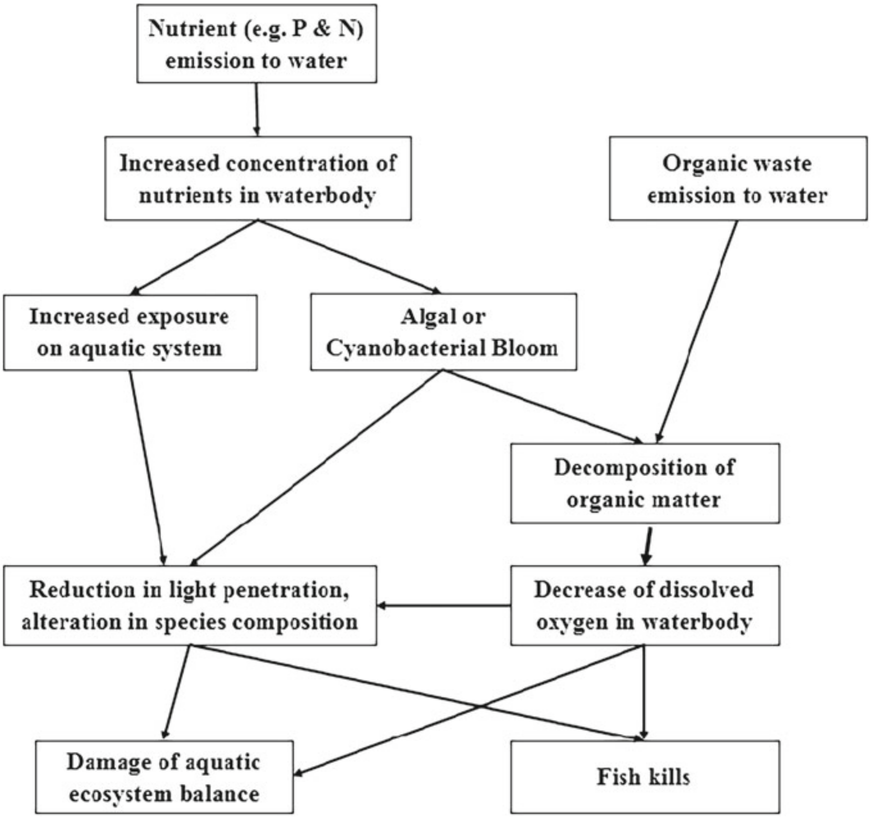

Fig. 12.1 Schematic diagram showing eutrophication process

regulate. Relative contribution of the two types of sources on eutrophication will vary from region to region and also depends on the population density and land use pattern. Table 12.1 illustrate different types of sources of nutrient loading on water bodies (Carpenter et al. 1998, Smith et al. 1999). Till recent times it was considered that nutrient enrichment with nitrogen and phosphorus were the only factors resulting water eutrophication, however it is seen that they are essential factors but not the sufficient ones to outbreak eutrophication. Eutrophication may not occur if only nitrogen and phosphorus concentrations are very high but other factors such as sunlight, water current speed is not optimal. According to Li and Liao (2002), optimal concentration of nutrients, adequate temperature and favorable environmental conditions, water current velocity and microbial activity and biodiversity in the aquatic ecosystem etc. are quite necessary to outbreak eutrophication.

Table 12.1 Sources of Nutrient pollution of water bodies (after Carpenter et al. 1998, Smith et al. 1999)

Point sources	Non-point sources
• Municipal and industrial wastewater effluent • Runoff and leachate from waste disposal sites • Runoff and infiltration from animal feedlots • Runoff from mines, oil fields, and unsewered industrial sites • Storm sewer outfalls from cities with populations >100,000 • Overflows of combined storm and sanitary sewers • Runoff from construction sites with an area >2 ha	• Agricultural runoff • Runoff from pastures and rangelands • Urban runoff from unsewered areas and sewered areas with populations <100,000 • Septic tank leachate and runoff from failed septic systems • Runoff from construction sites with an area <2 ha • Runoff from abandoned mines • Atmospheric deposition over a water surface • Activities on land that generate contaminants

12.3 Consequences

As discussed in preceding sections eutrophication of waterbodies have serious negative impact on health, economy and ecological aspects which are complex and interrelated. The heavy algal bloom as a result of high nutrient enrichment lowers the dissolved oxygen required for other aquatic lives and reduces water transparency. In extreme cases anoxic conditions prevail in lower part of the waterbody which encourages growth of bacteria that may secrete toxins harmful for other aquatic species. Such a condition results in adverse impact that may vary from mortality of fish and other aquatic species, poisonous seafood, economic aspects, loss of ecosystem balance and health hazards to humans as well as other animals. In general, due to eutrophication whole intrinsic equilibrium of the ecosystem gets destroyed.

Health Impacts: Harmful algal blooms due to eutrophication have been reported increasingly all around the world. It was reported that around 60,000 intoxication cases per year around the world are due to algal toxins or cyanotoxins (Hallegraeff 1993; Van Dolah 2000). Although cyanobacteria toxin poisoning is mainly marine origin but may occur in fresh waters like lake, pond, reservoirs etc. The genera such as *Anabaena, Aphanizomenon, Cylindrospermopsis, Lyngbya, Microcystis, Nostoc,* and *Oscillatoria* etc. are listed as major toxin producing cyanobacteria (Carmichael 2001). These cyanobacteria may secrete cyanotoxins and biotoxins which may result in acute, lethal, chronic and sub-chronic poisoning of human and animals. Moreover algae outbreaks caused by eutrophication can impart unpleasant odors to drinking water. Drinking water collected from such a source having high nitrogen concentration have threat of *blue baby* syndrome in infants. Odours from waterbody contaminated with decaying algae may also lead to serious health effect to people getting continuous exposure.

Ecological Impacts: Eutrophication has severe impact on the structure and composition of aquatic ecosystem. As a result of heavy algal bloom, some zooplankton species also grow at faster rate which rely on phytoplankton as their food source. As algae die, bacteria uses dissolved oxygen during decomposition process and as a result hypoxic conditions prevail in lower parts of the waterbody. This results in fish kills and changes in fish composition have direct impact on the aquatic ecosystem. Moreover algal bloom reduces water transparency and lower penetration of light may inhibit growth of aquatic plants. In general, eutrophication leads to competition for light and available nutrients in the aquatic system and this leads to changes in species composition and only the tolerant species can sustain.

Economic impacts: All the impacts discussed in the preceding section has direct or indirect impact on the economy of a society. Once eutrophication has taken place in a waterbody, the management and corrective measures can be quite expensive. The cost of water treatment also increases significantly if water has to be used for drinking purpose. Health hazards of human and animal due to cyanotoxins have direct economic impacts. The poor water quality and degradation in aesthetic view of the waterbody as a result of eutrophication restricts its use for recreational and tourism purposes.

12.4 Case Studies

At present lake eutrophication cases have been reported throughout all around of the world. High rate of population growth, rapid urbanisation and industrialisation in last few decades have made this issue a global concern (Wassmann and Olli 2005). Around 54% of lakes in Asia Pacific region, 53% of European lakes, 28% of African lakes, 48% of North American lakes and 41% of South American lakes are facing the problem of eutrophication (ILEC 1988–1993), causes of most of the cases being anthropogenic activities. Lake eutrophication studies conducted for major waterbodies in different parts of the world reveal that for almost every case, it is the human induced factors that needs utmost attention to mitigate this ever increasing water quality challenge (Bhagowati and Ahamad 2018; Patel et al. 2019b; Das et al. 2017; Kumar et al. 2017). In Asia pacific region developing countries like China, India, Pakistan etc. are facing serious water quality and eutrophication related problems. For brevity of work, lake eutrophication cases mainly in India and a few from other parts of the world addressed in the succeeding section.

In India, lakes are spread over an area of about 7.2 lakh hectares. Severe water quality degradation and cultural eutrophication cases have been reported to the lakes in India. However, owing to the huge water resources available in the country, detailed investigations available are very limited. India has grown tremendously in terms of industry, agriculture and urbanization in the last couple of decades and large population density make the water bodies vulnerable to eutrophication. It is reflected in the fact that the number of lakes are reducing tremendously due to man-made causes in last one or two decades in famous cities like Bangalore and

Ahmadabad (Excreta Matters, 2012). From the study conducted to examine lake water quality and floral ecology by Garg et al. (2002), on three major lakes of Bhopal, it was found that highest level of eutrophication was observed in Mansarovar Lake. The world famous Udaisagar Lake in Udaipur, India is also facing the problem of eutrophication. From the research of R. P. Vijayvergia (2008), it was seen that untreated sewage of nearby areas, agricultural runoffs and industrial wastewater are the major causes of Cyanobacterial bloom in the lake. Lake Bellandur is one of the main lakes in Banglore city facing the problem of eutrophication mainly due to addition of effluents from the urbanized city (Chandrashekar et al 2003). Presently the lake is in hyper eutrophic state and is like an artificial dump yard for domestic and industrial wastewater. Heavy nutrient concentrations and poor water quality were reported for Lake Mirik in Darjeeling (Jha and Borat 2003). Deepor Bil, a RAMSAR site in Guwahati city is getting polluted in recent times with severe municipal solid waste dumping in nearby areas. Continuous flow of city sewage and traces of fertilizers and pesticides from agricultural fields have degraded water quality, leaving the Bil prone to eutrophication. In fact, eutrophication is gradually taking place in the waterbody (Churing Still Water 2012). Garjan Bil, in Hajo, Assam (having gross area of about 678 ha) is also facing the problem of water quality deterioration, heavy weed production which is severely affecting its fish fauna (Baishya and Bordoloi 2007). Similarly, water quality deterioration and anthropogenic eutrophication cases have been observed for Fateh Sagar lake in Udaipur (Dave 2011), Sagar lake in Madhya Pradesh (Pathak and Pathak 2012), Dal lake in Kashmir (Ahmed and Bhat 2007), Lake Budha Pushkar in Rajasthan (Sarma and Chauhan 2007) etc.

In China, cases of water quality deterioration and eutrophication of the lakes are increasing, making it a major concern. In eastern China, there are more than 90 numbers of shallow lakes, which are facing the threat of heavy nutrient discharges into these waterbody since 1990s and presently most of them are in mesotrophic to eutrophic stage (Huang et al. 2014; Jørgensen and Vollenweider 1989). Dianchi lake in Yunnan province of China (Yang et al. 2008) and Taihu lake, one of the largest lakes in China (Liu and Qiu 2007) are another examples of cultural eutrophication. Lake eutrophication cases have been reported to some major Japanese lakes in last few decades. Lake Biwa, the largest lake in Japan, had faced the problem of eutrophication and water quality deterioration due to urbanization and industrialization till 1980s (Yamashiki et al. 2003). It is reported that gradual eutrophication process initiated in 1949 for lake Suwa in Honshu, and by the year 1977 the lake was in hypereutrophic stage (Okino 1987). Komatsu et al. (2007) have reported that the trophic stage is changing from mesotrophic to eutrophic for Shimajigawa reservoir in western Japan due to the organic pollutants and nutrients flowing from the nearby areas and wastewater effluents. The second largest lake in Japan, Lake Kasumigaura, is also currently eutrophic due to high nutrient load (Oyama et al. 2009).

Eutrophication cases has been reported to many European lakes also (Sondergaard et al. 2007). Pamvotis Lake in Northern Greece which has undergone cultural eutrophication over the past 40 years and is currently eutrophic (Romero et al 2002). In a study carried out by Pelechaty et al. (1997) in Jaroslawieckie Lake, in Poland, it was found that most habitats of this lake were eutrophic. Analysis of the phytoplankton samples and bottom sediment of the lake showed a succession of algae, corresponding to the increasing trophic levels. In Netherlands, most of the lakes in are very shallow and they vary in area from a few hectares to a few thousand hectares. Gulati and van Donk (2002), reported that the input of phosphorus and nitrogen and of polluted waters from the rivers and canals have been the major cause of eutrophication in these lakes. The majority of lakes in Denmark are highly eutrophic due to high nutrient input from domestic sources and agricultural activities. Several factors reduced nutrient retention, more rapid removal in catchments, and channelization of streams also play a role in eutrophication (Jeppesen et al. 1999). Surface runoff rich in agricultural wastes and underground seepage from urban and rural areas enriched the Lake Kastoria in Greece with nutrients and resulted into eutrophication (Koussouris et al. 1991). Barbieri and Simona (2001), reported eutrophication in lake Lugano, between Italy and Switzerland. Eutrophication was observed at a faster rate due to increase human activity around the lake. Water eutrophication cases have been reported in USA for Lake Erie (Reutter 1989), Washington Lake (Welch and Crooke 1987), Okeechobee Lake (Schelske 1989), City Park Lake (Ruley and Rusch 2002), etc.

12.5 Eutrophication Control and Mitigation

From the discussion above it is evident that in the last 50 years eutrophication has evolved as the major threat to lake water bodies around the world. According to Walmsley, (2000), restoration or management of eutrophied waterbody is generally based on the nutrient limiting concept which is one of the major cause of eutrophication. The concentration and ratios of different nutrients present in waterbody governs the growth of aquatic plants. So identification and minimisation of the key nutrients input (mainly N and P) to the waterbody directly hinders the unwanted rapid growth of algae and other aquatic plants. In many European and North American countries lake restoration has been done in recent times by limiting external input of phosphorus (Jeppesen et al. 2005a, b, Søndergaard et al. 2005), however nitrogen limitation may be effective in other cases. Lake Erie, one of the most investigated eutrophied waterbody in North America was successfully restored by limiting external loading of domestic and industrial wastes in a joint venture between government of Canada and USA in 1972. The reduction in P-loadings have resulted in decrease in phytoplankton growth to about half of peak value observed in 1968 within ten years after implementation (Makarewicz and Bertram 1991). Lake Suwa which was in hypereutrophic stage till 1977 as mentioned earlier, was restored in similar way by reducing external load of nutrients. With the introduction of sewage treatment plant and increase in public awareness, nutrient concentration reduced significantly in the lake water in the mid-1980s (Okino 1987). However restoration success of external nutrient limiting require sufficient time and even after sufficient reduction of external load, resistance to restoration may occur due to chemical and biological factors (Sas 1989). Chemical resistance is mainly due to the release of nutrients from sediments which is generally accumulated in the sediment during high loading. Some planktivorous and benthivorous fish particularly provide biological resistance which affects internal nutrient loading and physio-chemical environment the aquatic ecosystem (Scheffer et al. 1993). In recent times few biological and physio-chemical restoration measures have been developed, a brief overview of these have been presented in the next section.

Biological Control: Various biological control measures such as fish manipulation, control of aquatic plant growth etc. to overcome biological resistance in general is termed as "biomanipulation". Planktivorous and benthivorous fish removal from the waterbody is referred to as fish manipulation. Meijer et al. (1999) have recommended that by removal of 75% of plankti-benthivorous fish in 1 to 2 year, restoration and growth of piscivorous fish in the waterbody can be expected. In comparison with the physio-chemical methods, fish manipulation technique is generally cheap however long term restoration efficiency is uncertain (Jeppesen and Sammalkorpi 2002). Fish manipulation generally results in decreased phytoplankton biomass, increase in bigger sized zooplankton species and improved transparency of water (Jeppesen et al. 2009). Improved light conditions favors the growth of microbenthic algae on sediment surface. Overall increase in benthic algae, less sedimentation of phytoplankton, increase in benthic animals results in a higher redox potential at sediment surface which in turn reduces the sediment release of nutrients (Søndergaard et al. 2005).

In addition with fish manipulation, construction of enclosures to protect macrophytes may be beneficial for successful colonization (Søndergaard et al. 1996). Billore et al. (1998), have reported that aquatic weed *water hyacinth* root is beneficial in removing nitrogen and particulate matter, subsequent removal of the weed from the water body will hinder eutrophication and can be used for production of compost. Eutrophication control by nutrient reduction may be done through other weed species such as *Typha, Phragmites*, and *Glyceria spp*. etc. (Beltman et al. 1990).

Physio-chemical Control: Several physio-chemical methods have been developed in recent times to minimize internal nutrient load from sediments. Removal of sediment by dredging is one of the methods to reduce internal loading. Treatment of sediment with chemicals such as aluminium, calcium or iron may result in reduction of internal release of nutrients (Beklioglu et al. 2011).

Prior to implementation of any lake restoration or eutrophication control program, a proper strategy must be considered with proper understanding and through investigation. Such a procedure may be executed in the following way (Jeppesen et al. 2005a, b).

- Define the target or degree of restoration.
- Determine the major nutrients responsible for eutrophication and its loading by direct measurements or by using ecological models.

- Based on total nutrient concentration, reduce the external loading.
- If the lake still contains nutrients more than critical value, internal loading may be high. Then apply biological or physio-chemical methods based on site specific condition.
- Monitor the results periodically.

12.6 Conclusion

From the above discussion it is evident that human activities have turned many freshwater lakes into highly eutrophied waterbody by completely destroying its natural ecosystem in last few decades. Eutrophication have serious impact on the whole ecosystem, drinking water, agriculture, fisheries, and affects the economy of a country. As the sources and causes of lake eutrophication vary for different conditions, identification of causes of eutrophication and lake specific detailing are very much essential for proper selection and implementation of restoration methods. In recent times, mathematical modelling has come out to be an effective tool for better management and restoration of eutrophic lakes. Ecological modelling now a days are quite advanced and can be very useful for finding solutions to problems such as prediction of time required to regain original trophic stage, sedimentation rate, sediment removal rate etc. The predictive capacity of such models are quite high and as such modelling approach can gives better restoration results of the eutrophication control measures discussed earlier. Moreover proper government policy making and strict legislative measures are very essential for protection and restoration of waterbody. There should be strict law against waste water and solid waste dumping in waterbody, permissible levels of phosphate content in the laundry detergents etc. Finally, public awareness about protection and conservation of natural water resources is of utmost importance for sustainable development of the society.

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Chapter 13
Role of Phytoremediation Strategies in Removal of Heavy Metals

Leela Kaur

13.1 Introduction

Heavy metal pollution is a matter of great concern in recent times. Toxic heavy metals have mutagenic ability which will going to cause damage to DNA and produces carcinogenic effects in animals and humans (Knasmuller et al. 1998; Baudouin et al. 2002). Heavy metals get into the soil by anthropogenic activities or through natural sources. Heavy metal pollution is mainly due to mining and smelting of metalliferous ores, fossil fuels burning, municipal wastes, downwash from power lines, sewage and use of fertilizers and pesticides. Removal of heavy metals at the source is the best practice; however, it is not always possible. Metals can not be degraded they are only transformed from one oxidation state or organic complex to another. There may be four possibilities after the modification of the oxidation state such as (i) the metal is naturally less toxic, or (ii) if the metal is more water soluble then it is taken out by leaching, or (iii) if the metal is less water soluble then precipitation occurs and afterward the metal is either taken out from contaminated site or becomes less bio accessible, or (iv) if the metal is volatile in nature then it is volatilized and removed from the polluted area (Garbisu and Alkorta 1997).

Metal-contaminants from soil and water can be remediated by chemical, physical or biological techniques. Chemical and physical treatments have several disadvantages like toxic sludge and effluent generation, which again needs disposal as well as high cost. Hence, scientists and researchers are trying on biological techniques as they are sustainable techniques.

Phytoremediation is an example of one such biological technique. It is made up of the Greek word "Phyton" (plant) with Latin word "Remediare" (to remedy)

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(Cunningham et al. 1997). Phytoremediation is a miscellaneous set of plant-based expertise to clean contaminated areas by using naturally occurring or genetically engineered plants (Flathman and Lanza 1998). The technology was first applied on waste water discharge for the past 300 years (Chaney et al. 2000). Though this technique has been used for three centuries, only recently it started picking up. This paper provides a review on the phytoremediation strategies for heavy metal removal and its current status.

13.2 Role of Phytoremediation Strategies in Removal of Heavy Metals

Various phytoremediation techniques are being used in the treatment of contaminants such as phytodegradation, phytovolatilization, phytostabilization, phytoextraction and rhizofiltration. Phytoremediation techniques applied in the inorganics (heavy metal and radionuclide) treatment are phytostabilization, phytovolatilization, phytofiltration, and phytoextraction.

13.2.1 Phytostabilization

Phytostabilization is the stabilization of heavy metals in soil by decreasing heavy metals movement. Figure 13.1 shows schematic diagram of phytostabilization mechanism. Metal immobilization process facilitates the protection of the contaminated site from wind erosion, water erosion and limit transfer of metals from contaminated sites to the biotic trophic levels of ecosystems. Phytostabilization can be controlled by pH, redox potential and evapotranspiration by plants, etc. Phytostabilization of metal contaminated soils by different amendments such as organic materials, phosphorus compounds or liming agents decrease metal transportation and bioavailability in soils and it emerges most promising technique for sites contaminated with high contents of various metals.

Phytostabilization is more effective than traditional heavy metal treatment methods for remediating large-scale areas having low contamination. However phytostabilization is more difficult to apply at sites containing higher metals concentration that affect plant growth. Therefore, the most suitable-plants should tolerate high levels of contaminants, and produce an extensive root biomass with the ability to hold contaminants in the roots (Miller 1996). Yoon et al. (2006) found that those plants which have a high bio-concentration factor (BCF) and low translocation factor (TF) are potentially suitable for phytostabilization.

Table 13.1 lists plant species that are potentially useful for phytostabilization and plants listed are native species documented in the cited papers to accumulate metal in above-ground biomass at concentrations that do not exceed domestic

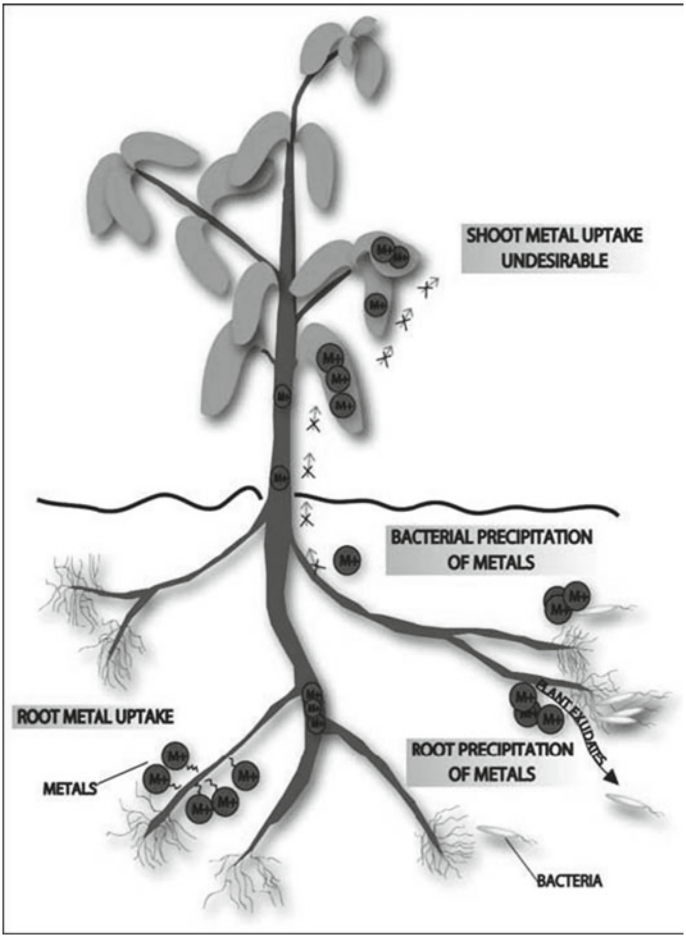


Fig. 13.1 Phytostabilization mechanisms (Mendez and Maier 2008)

animal toxicity limits which are 10, 30, 40, 100, 100, 500 and 2000 mg kg^{-1} for Cd, As, Cu, Pb, Ni, Zn and Mn respectively (NRC (National Research Council) 2005).

In a field trial, Schnoor (1997) was able to stabilize the metals from the leachate and decreased their migration to groundwater. Jadia and Fulekar (2008) conducted a greenhouse phytostabilization experiment using sorghum to remediate soil contaminated by heavy metals. The order of heavy metals uptake was as follows: Zn > Cu > Cd > Ni > Pb. Marques et al. (2009) examined *Rubus ulmifolius* as a potential candidate for phytostabilization of As, Pb and Ni polluted soil.

Remediation of mine tailings by phytostabilization is a favourable technology. However, understanding of mine tailings chemistry and selection of efficient stabilizing plant species should be investigated for its enduring attainment.

Table 13.1 Plant families of potential phytostabilization candidates (Mendez and Maier 2008)

Plant[a]	Metal contaminants
Anacardiaceae	
Pistacia terebinthus Bieberstein *Schinus molle L.*	Cu Cd, Cu, Mn, Pb, Zn
Asteraceae	
Baccharis neglecta Britt. *Bidens humilis H.B.K.* *Isocoma veneta (Kunth) Greene* *Viguiera linearis (Cav.) Sch.*	As As Ag, As, Cd, Cu, Pb, Zn Cd, Cu, Mn, Pb, Zn
Chenopodiaceae	
Teloxys graveolens (Willd.) W.A. Weber *Atriplex lentiformis (Torr.) S. Wats.* *Atriplex canescens (Pursh) Nutt.*	Cd, Cu, Mn, Pb, Zn As, Cu, Mn, Pb, Zn As, Hg, Mn, Pb
Euphorbiaceae	
Euphorbia sp.	Cd, Cu, Mn, Pb, Zn
Fabaceae	
Dalea bicolor Humb. and *Bonpl. Ex Wild.*	Cd, Cu, Mn, Pb, Zn
Plumbaginaceae	
Lygeum spartum L.	Cu, Pb, Zn
Poaceae	
Piptatherum miliaceum (L.) Coss.	Cu, Pb, Zn

[a]Plants metal accumulation is not above domestic animal toxicity limits (NRC 2005)

Phytostabilization as a revegetation strategy has also been studied (Maier 2004) in arid and semi-arid mine tailings by finding metal uptake in native metal tolerant and drought tolerant plant species. This research brought out that high transpirating plants are beneficial for phytostabilization due to reducing the movement of contaminant from the carrying contaminant site like reeds, grasses, forage plants and sedges (Suresh and Ravishankar 2004). These plants along with strong, evergreen, dense or deep rooted trees (poplar, cottonwoods) can be an efficient amalgamation (Berti and Cunningham 2000).

13.2.2 Phytofiltration/Rhizofiltration

Ground water and industrial waste water containing metals are generally treated by precipitation or flocculation method, followed by sedimentation and ultimately sludge removal (Ensley 2000). A promising substitute is rhizofiltration which is aimed to remove metals from water bodies. Here, plants are grown in hydroponics and further transplanted into metal-laden water. Plants absorb and concentrate the metals in their biomass (Flathman and Lanza 1998; Dushenkov et al. 1995; Salt et al. 1995; Zhu et al. 1999a). Root exudates and variations in pH in the rhizosphere may also cause metals to precipitate onto root surfaces. As the plants saturated with the metal contaminants, roots or whole plants are harvested for disposal (Flathman and Lanza 1998; Zhu et al. 1999a). Rhizofiltration is particularly effective in the applications where low concentrations and large volumes of water are involved and is subjected to low (stringent) standards (Miller 1996).

Phytofiltration plants with characteristics of high accumulation and tolerance of metal combining easy to handle, low maintenance cost and least waste generation are good candidates. While, plants with high translocation factor of metals should not be applied in rhizofiltration as plant residue is more contaminated (Salt et al. 1995).

Phytofiltration plants are required to have substantial amount of root biomass or root surface area (Dushenkov and Kapulnik 2000). Elless et al. (2005) demonstrated a solar-powered hydroponic technique that enables the efficient cleanup of arsenic-contaminated drinking water in a cost-effective manner and its basis is provided by phytofiltration technology. Karkhanis et al. (2005) observed that *Pistia* has high potential uptake capacity of Zn, Cr, and Cu and duckweed showed good heavy metal uptake potential next to *Pistia*. This research showed that pistia/duckweed/water hyacinth can be good accumulators of heavy metals in aquatic environment contaminated by coal ash (0–40%) containing heavy metals. A study by Seenivasan et al. (2008) demonstrated that *Pteris vittata* is effective in remediating As-contaminated groundwater to meet recommended standards. Phytofiltration using aquatic plants including species of *Azolla*, *Eichhornia*, *Cabomba*, *Lemna*, *Ludwigina*, *Mentha*, *Myriophyllum*, *Nelumbo*, *Nymphaea*, *Pistia*, *Potamogeton*, *Salvinia* and *Scapania* have high potential for the treatment of heavy metals containing water and industrial wastewaters based on the choice of a suitable plant species (Anawar et al. 2008). Radioactive contaminants in low amount can also be eliminated from liquid streams (EPA (Environmental Protection Agency) 1998).

However, aquatic plants have limited potential for rhizofiltration, because they are not efficient at metal removal due to their small, slow-growing roots (Dushenkov et al. 1995). Dushenkov et al. (1995) have pointed out that the high water content of aquatic plants impedes the drying, composting, or incineration process. Terrestrial plants have long and significant fibrous root system as well as large root surface area for which makes them more appropriate candidate for rhizofiltration which enhance metal sorption. Indian mustard (*Brassica juncea Czern.*) efficiently removes Cd, Cr, Cu, Ni, Pb, and Zn (Dushenkov et al. 1995), and sunflower (*Helianthus annuus L.*) removes Pb (Dushenkov et al. 1995), U (Dushenkov et al. 1997a), Cs^{137}, and Sr^{90} (Dushenkov et al. 1997b) from hydroponic solutions.

Rhizofiltration is more reasonable and effective technology than similar technolgies. A cost estimate of \$2 and \$6 per thousand gallons of radionulide water remediated using sunflower shows that it is a low-cost technology (Cooney 1996).

13.2.3 Phytovolatilization

Phytovolatilization involves plant's uptake and transpiration of contaminants. Mainly organic compounds are remediated by phytovolatilization. These contaminants are taken up the plant and further either pass through the plant or get modified and finally they are evaporized or vaporized into the atmosphere.

Some metal pollutants such as As, Hg, and Se may exist as gaseous species in the environment. In recent years, researchers have sought naturally-occurring or genetically-modified plants capable of absorbing elemental forms of these metals from the soil, biologically converting them to gaseous species within the plant, and releasing them into the atmosphere. This makes phytoremediation more debateable. There is an uncertainity of safe byproducts in the atmosphere from volatilization of Hg and Se as both elements are toxic (Suszcynsky and Shann 1995; Watanabe 1997).

Terry et al. (1992) reported that members of the Brassicaceae are capable of releasing up to 40 g ha^{-1} day^{-1} Se in gaseous form. Cattail (*Typha latifolia L.*), an aquatic plant is a good candidate for Se phytoremediation (Pilon-Smits et al. 1999a). As volatilization is very well known in natural environments (Frankenberger and Arshad 2002), but for soil it suggests that volatile compounds account only for small proportions of total As in the absence of plant roots (Turpeinem et al. 1999).

Phytovolatilization have advantages of no requirement to dump contaminated plant, less erosion and least disturbance to site (Heaton et al. 1998). Heaton et al. (1998) suggest that the transfer of elemental mercury to the atmosphere would not contribute significantly to the atmospheric pool because the contaminants are likely to be subjected to more effective natural degradation processes such as photodegradation (Azaizeh et al. 1997). However, it is advised to avoid phytovolatilization for sites near population centers and at places where fast settlement of volatile compounds occur due to meteorological conditions (Heaton et al. 1998; Rugh et al. 2000).

13.2.4 Phytoextraction

In phytoextraction, metal contaminants are removed from a soil matrix with the help of plants (Kumar et al. 1995). Plants are incinerated after harvesting. The incinerated ash is disposed off in a landfill. Alternatively, metal are extracted from harvested plants which is known as phytomining. Even, precious metals can be recovered after going through harvesting, drying and smelting processes.

Hyperaccumulators are those plants which are able to accumulate and tolerate unusually large amounts of metals in comparison with other plants. Baker and Brooks (1989) defined hyperaccumulator for different metals based on their dry weight shoot metal concentrations such as 0.001% for mercury, 0.01% for Cd and Se, 0.1% for Al, Co, Cr, Cu, Pb and Ni, and 1% for Mn and Zn. Examples of some metal hyperaccumulators are listed in Table 13.2.

Table 13.2 Common metal hyperaccumulators with accumulation characteristics

Plant species	Metal	Accumulation characteristics
Pistia stratiotes	Ag, Cd, Cr, Cu, Hg, Ni, Pb and Zn	All elements accumulated mainly in the root system (Odjegba and Fasidi 2004)
Spartina plants	Hg	Organic Hg was absorbed and transformed into an inorganic form (Hg^{+}, Hg^{2+}) and accumulated in roots (Tian et al. 2004)
Helianthus annuus	Pb	Pb concentrated in the leaf and stem indicating the prerequisites of a hyperaccumulator plant (Boonyapookana et al. 2005)
H. indicus	Pb	Heavy metal mainly accumulated in roots and shoots (Chandra Sekhar et al. 2005)
Sesbania drummondii	Pb	Pb accumulated as lead acetate in roots and leaves, although lead sulfate and sulfide were also detected in leaves, whereas lead sulfide was detected in root samples. Lead nitrate in the nutrient solution biotransformed to lead acetate and sulfate in its tissues. Complexation with acetate and sulfate may be a lead detoxification strategy in this plant species (Sharma et al. 2004)
Lemna gibba	As	A preliminary bioindicator for As transfer from substrate to plants. Used for As phytoremediation of mine tailing waters because of its high accumulation capacity (Mkandawire and Dudel 2005)
Pteris vittata, *P. cretica*, *P. longifolia* and *P. umbrosa*	As	All species are suitable for phytoremediation in the moderately contaminated soils (Caille et al. 2004). *P. vittata* showed 27,000 mg/kg As bioaccumulation potential (Wang et al. 2002). *P. umbrosa* showed 7600 mg/kg bioaccumulation potential while *P. cretica* showed 3030 mg/kg bioaccumulation potential (Zhao et al. 2002; Wei et al. 2002). Efficiency of arsenic removal can be greatly elevated by the P addition at high rates (Chen et al. 2002)
Alyssum	Ni	Majority of Ni is stored either in the leaf epidermal cell vacuoles, or in the basal portions of the numerous stellate trichomes. The metal concentration in the trichome basal compartment was the highest ever reported for healthy vascular plant tissue, approximately 15–20% dry weight (Broadhurst et al. 2004)

(continued)

Table 13.2 (continued)

Plant species	Metal	Accumulation characteristics
Solanum nigrum and *C. canadensis*	Cd	High concentration of Cd accumulated. Tolerant to combined action of Cd, Pb, Cu and Zn (Wei et al. 2004)
T. caerulescens	Cd and Zn	High Cd-accumulating capability, acquiring Cd from the same soil pools as non-accumulating species (Schwartz et al. 2003). 1800 mg/kg Cd content (Baker and Walker 1989). 39,600 mg/kg of Zn bioaccumulation potential in shoots (Reeves and Brooks 1983)
Arabis gemmifera	Cd and Zn	Hyperaccumulator of Cd and Zn, with phytoextraction capacities almost equal to *T. caerulescens* (Kubota and Takenaka 2003)
Sedum alfredii Hance	Cd	Mined ecotypes had a greater ability to tolerate, transport, and accumulate Cd, compared to non-mined ecotype (Xiong et al. 2004)
	Cd, Zn	Accumulated maximum of approximately 9000 and 6500 mg/kg DW in the leaves and stem respectively at 400 µmol/L Cd (Yang et al. 2002, 2004)
Stanleya pinnata	Se	Adapted to semi-arid western U. S. soils and environments (Parker et al. 2003). Uptake, metabolism and volatilization of Se
Austromyrtus bidwillii. P. acinosa Roxb	Mn	Australian native hyperaccumulator of Mn, grows rapidly, has substantial biomass, wide distribution and broad ecological amplitude (Bidwell et al. 2002; Xue et al. 2004)
Ipomea alpine	Cu	12,300 mg/kg bioaccumulation potential (Baker and Walker 1989)
Sebertia acuminate	Ni	25% by wt. dried sap (mg/kg) bioaccumulation potential (Jaffré et al. 1976)
Haumaniastrum robertii	Co	10,200 mg/kg bioaccumulation potential (Brooks 1998)
A. racemosus	Se	14,900 mg/kg bioaccumulation potential (Beath et al. 1937)
Berkheya coddii	Ni	5500 mg/kg bioaccumulation potential (Robinson et al. 1997)
Iberis intermedia	Ti	3070 mg/kg bioaccumulation potential (Leblanc et al. 1999)

(continued)

Table 13.2 (continued)

Plant species	Metal	Accumulation characteristics
Arabis paniculata F.	Cd	Accumulated 1662 and 8670 mg/kg DW Cd at 178 μM Cd treatment in shoots and roots respectively (Qiu et al. 2008)
Pityrogramma calomelanos	As	8350 mg/kg bioaccumulation potential (Francesconi et al. 2002)
Bidens pilosa L	Cd	Useful for phytoremediation of soils co-contaminated by As and Cd (Sun et al. 2009)
Rorippa globosa	Cd	Extraction efficiency of Cd in shoots increased 42.8% by two phase planting compared to that of at its single maturity (Wei and Zhou 2006)
Arabidopsis halleri	Cd, Zn	Zn and Cd concentrations in leaves were >20,000 and >100 mg/kg, respectively (Dahmani-Muller et al. 2000)
Viola baoshanensis	Cd	Cd concentration varied from 456 to 2310 and 233 to 1846 mg/kg in the shoots and in the roots, respectively (Liu et al. 2004)
Sedum jinianum	Cd	Field survey, hydroponic culture, and pot experiments showed *S. jinianum* as Cd hyperaccumulator. It also has high capability to accumulate Zn in the shoots (Xu et al. 2009)
Arabis paniculata F.	Cd, Pb, Zn	Hyperaccumulates Pb, Zn and Cd (Tang et al. 2005). Cd concentrations reached a maximum of 162 and 8670 mg/kg Cd DW in shoots and roots respectively at 178 μM Cd treatments (Zhang et al. 2007)
Leersia hexandra Swartz	Cr	The highest bioaccumulation coefficients of the leaves for Cr(III) and Cr(VI) were 486.8 and 72.1, respectively (Shu et al. 2001)
Commelina communis	Cu	Cu concentration in leaves reached 1000 mg/kg (Nie et al. 2004)
Amaranthus tricolor L., *Sophora japonica*, *Bidens maximowicziana*	Pb	Total lead translocation can be increased by regulating the soil N, P, K level (Shao et al. 2006)
Thlaspi arvense L.	Se	Se in its leaf is >1000 mg/kg DW (Huang et al. 1998)
Brassica chinensis L., *Brassica juncea* (*L.*) *Czern.*, *Brassica narinosa L.*	U	Induced U hyperaccumulation by plants with the addition of citric acid to soil (Xue et al. 2004)
Phytolacca acinosa Roxb	Mn	Maximum Mn concentration in the leaf was 19,300 and 36,380 mg/kg DW (at 12,000 μmol/L Mn supply) on Mn tailings wastelands and under nutrient solution culture conditions respectively (Xue et al. 2004)

Jambhulkar and Juwarkar (2009) conducted a field experiment at Khaperkheda Thermal Power Plant, Nagpur (India) on fly ash dump where *Pongamia pinnata*, *Tectona grandis*, *Delbergia sisoo*, *Cassia siamea*, *Eucalyptus hybrida*, and *Dendrocalamus strictus* were planted using bioremediation technology. Nitrogen-fixing strains of *Bradyrhizobium* and *Azotobacter* species and nutrient-mobilizing vesicular arbuscular mycorrhizal spores of *Glomus* and *Gigaspora* species in combination with organic amendments were applied. The lush growth of plant species was found after three years of plantation. This study revealed that *C. siamea* could be used as a hyper-accumulator plant for bioremediation of fly ash dump.

Phytoextraction remediates metal contaminants within 1–20 years time frame. Since remediation time is governed by many factors such as type of metal contamination, level of metal contamination, metal accumulation capacity of plants and period of growing season. Therefore, low to medium range of metal contamination at surface of vast areas can be significantly remediated by phytoextraction technology (Kumar et al. 1995; Jambhulkar and Juwarkar 2009).

13.2.5 Types of Phytoextraction

Two methods have currently been used to reduce the concentration of heavy metals to controlling ranges in contaminated soils with proper time durations. (1) Natural phytoextraction using hyperaccumulators, and (2) induced phytoextraction utilizing high-biomass crop plants, such as corn, barley, peas, oats, rice, and Indian mustard with the help of chelants (Huang et al. 1997; Salt et al. 1998; Lombi et al. 2001; Chen et al. 2004). Figure 13.2 shows process of natural and induced phytoextraction. Plants used for phytoextraction should be efficient in translocation of metals from root to shoot with abundant root system and capable to grow in any conditions. These plants should show high biomass production, rapid development, high metal tolerance, higher numerous metal accumulations, defense against illnesses and insects, repulsion to animals, and lessen the threat of transporting metals to upper trophic levels of the terrestrial food chain (Thangavel and Subhuram 2004).

New transgenic plants with upgraded remediation traits can be designed by enhancing the indepth knowledge of hyperaccumulation mechanisms especially rhizosphere interaction, metal uptake, metal transport and metal sequestration in hyperaccumulators (Eapen and D'Souza 2005). Furthermore, the rate of phytoremediation can be enhanced by selecting and testing various hyperaccumulators (Suresh and Ravishankar 2004).

The biomass produced by phytoremediation can be utilized as an energy source through thermo-chemical conversion practices like combustion, gasification and pyrolysis. Application of phytoextraction in biomass production, energy generation and metal recovery at large scale can make profit too. Profit could be additional for Cu, Ni, Zn, etc. metals reclamation (Chaney et al. 1997; Watanabe 1997; Thangavel and Subhuram 2004).

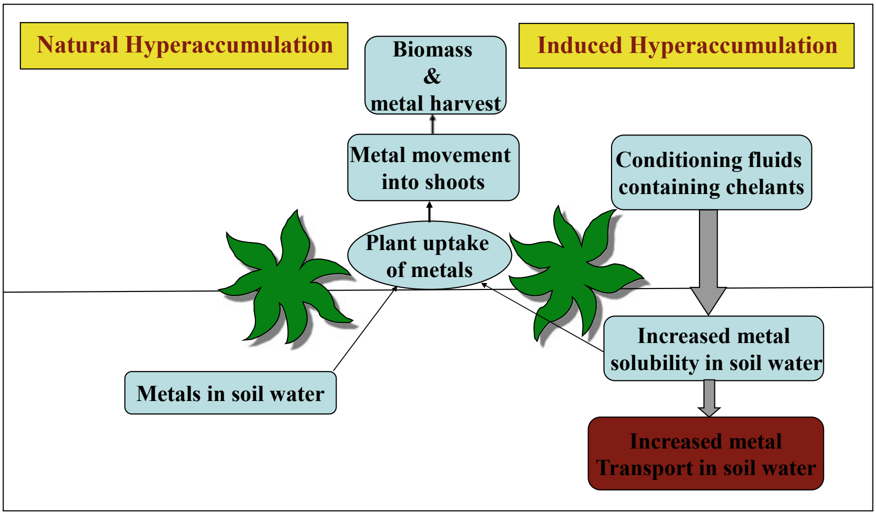


Fig. 13.2 Mechanisms of natural and induced phytoextraction

Remediation potential of plants can be further enhanced by optimization of agronomic practices. Investigation of the use of chemical amendments to induce metal bioavailability is important as in many instances metal adsorption in roots is limited by low solubility in soil solution. Synthetic chelators, e.g. ethylenediamine tetraacetate (EDTA), have been used to artificially enhance heavy metals solubility in soil and thus to increase heavy metals phytoavailability. The addition of chelators into the soil induces phytoextraction and translocation of heavy metals from the roots to harvestable, above-ground parts of several crops with high biomass production (Huang et al. 1997). Research in induced phytoextraction have achieved substantial results too. Though, more research is required in identification of remediating plant species with potential to bear various metals accumulation. Chelant search is essential to obtain an efficient metal chelant that is an environment-friendly and of low cost. Further information on optimization of harvesting time is also required. When rate of metal accumulation in plants decreases then plant biomass should be harvested as it will decrease the growth cycle duration and it will enhance number of harvesting plants in a growing season.

13.3 Applications of Genetically Modified Plants (Transgenic) in Heavy Metal Phytoremediation

Genetic engineering has already been used successfully in phytoremediation of heavy metals (Kramer 2005; Pilon-Smits 2005; Cherian and Oliveira 2005; Hooda 2007; Doty 2008; Macek et al. 2008; Memon and Schroder 2009; Dickinson et al.

2009). This was achieved either by citrate type overproducing metal chelating molecules (De la Fuente et al. 1997), metallothioneins (Evans et al. 1992; Hasegawa et al. 1997), phytochelatins (Zhu et al. 1999a, b), ferritin (Goto et al. 1999), or by overexpression of metal transporter proteins (Samuelsen et al. 1998; Arazi et al. 1999; Van der Zaal et al. 1999; Curie et al. 2000; Hirschi et al. 2000). Also, mercury volatilization and tolerance was accomplished by introduction of a bacterial pathway (Rugh et al. 1996; Bizily et al. 1999, 2000). The increase in metal accumulation as the result of these genetic engineering approaches is typically two to threefold more metal per plant, which potentially enhances phytoremediation efficiency by the same factor (Bennett et al. 2003). Since, no field studies have been reported to clear the applicability of genetic engineering for environmental clean up. Some examples of heavy metal detoxification mechanism by transgenic plants are as follows:

13.3.1 Mercury (Hg)

Chemical, paper, mining and defense industries uses mercury in a variety of applications which causes mercury toxicity. In 1960s Hg toxicity led to two epidemics of human poisoning in Japan (Bizily et al. 2000), so that methyl mercury contamination of aquatic sediments is now considered as one of the most serious global environmental evil.

According to Bizily et al. (2000), transgenic *Arabidopsis thaliana* plants were produced using two bacterial genes, namely merA and mer B, for mercury detoxification pathway. The gene merA for mercury reductase was artificially synthesized applying codon usage, so that such a synthesized gene merApe9 proved effective in releasing free mercury, which was considered to be less toxic (relative to Hg^{2+} ions) volatile. The transgenic plants produced thus were also tolerant to gold (Au^{3+}) contamination.

$$R - CH_2 - Hg + H^+ \overset{merB}{\rightarrow} R - CH_3 + Hg(II)$$

$$Hg(II) + NADPH + H^+ \overset{merA}{\rightarrow} Hg(0) + NADP + H_2$$

The above two genes containing transgenic plants could grow on 50-fold higher methyl mercury concentration than wild type plants, and on up to 10-fold higher concentration than plants that carry the gene merB alone. These genes have been transferred to many plant species like Arabidopsis, chlorella, eastern cottonwood, peanut, poplar, rice, salt marsh grass and tobacco (Ruiz and Daniell 2009). Transgenic plants raised exceptionally well in soil contaminated with organic ($\sim$400 mM phenyl mercuric acetate) or inorganic mercury ($\sim$500 mM $HgCl_2$), accumulating Hg in roots surpassing the concentration in soil ($\sim$2000 mg g^{-1}). Our recent ability to express membrane proteins opens the possibility of transforming the chloroplast genome with mer transporters to enhance Hg accumulation (Singh et al. 2008). Chloroplast genetic engineering is especially advantageous for the development of transgenic plants when multiple genes are required for effective phytoremediation (Quesada et al. 2005). In a single transformation event without the need for backcrosses of independent lines or re-transformation the multigenetic pathways can be developed by using chloroplast transformation. Because plastids have reserved the genetic machinery from bacterial ancestor, their genomes can transcribe and translate operons (Quesada et al. 2005). Instead, transgenic plants with Hg accumulation could be developed by insertion of coupling genes merC and chelator gene like metallothionein (MT) or polyphosphate kinase (ppk) (Ruiz and Daniell 2009). Plant expression of modified mercury transport genes (*merP* and *merT*) may also provide a means of improving mercury uptake with organelle and tissue specific targeting (Eapen and D'Souza 2005). Advances in transgenic systems for Hg phytoremediation are summarized in Table 13.3.

The second approach used in plants to remove Hg from soils is based on the use of nontoxic thio-containing solutions to induce Hg accumulation in above-ground tissues of high biomass (nontransgenic) plant species. In one such study, application of ammonium thiosulfate to substrates increased, up to 6 times, the Hg concentration in the shoots and roots of Indian mustard, relative to controls (Moreno et al. 2005). Similarly, in a previous study, ammonium thiosulfate has been used to induce Indian mustard to accumulate 40 mg kg^{-1} Hg of shoot tissue from a lead-copper-zinc metal mine contaminated with Hg (Moreno et al. 2004).

13.3.2 Arsenic (As)

Arsenic also contaminates thousands of sites world-over and adversely affects human health. It causes various health effects like skin lesions and lung/kidney/liver cancers and nervous system damage (Patel et al. 2019a, b; Kumar et al. 2017; Das et al. 2015). Arsenic contaminated sites are often not cleaned due to high cost involved. *Pteris Vittata* was discovered in 2001 (Ma et al. 2001) but since then, additional ferns have been found to have similar capabilities of As phytoremediation. About 400 taxa of hyperaccumulating plant species have been reported, but only a few species belong to a collection of As hyperaccumulators which include: *Pityrogramma calomelanos* (Visoottiviseth et al. 2002), *Pteris longifolia*, *P. umbrosa* (Zhao et al. 2002) plus several varieties of *Pteris cretica* (Zhao et al. 2002; Srivastava et al. 2006). The mechanism for this uptake relies on the plant's vascular systems to translocate arsenic up the plant along with phosphate (Meharg and Macnair 1992).

Dhanker et al. (2002) has obtained arsenic tolerant and hyperaccumulating transgenic *Arabidopsis thaliana* plants. The modified plants accumulated three times more arsenic than the wild plant. Two bacterial genes (arsC, γ-ECS) were transferred, one for arsenate reductase (ArsC) and the other for g-glutamylcysteine

Table 13.3 Advances in transgenic systems for Hg phytoremediation (Moreno et al. 2004)

Species	Gene	Expression compartment	Level of resistance	Mode of resistance	Special feature
A. thaliana	mer*A*	Cytoplasm	100 μM $HgCl_2$	Hg(II) to Hg(0)	First report of mer*A* in plants
Yellow poplar (*L. tulipifera*)	mer*A*	Cytoplasm	50 μM $HgCl_2$	Hg(II) to Hg(0)	mer*A* transformed into a tree species
A. thaliana	mer*B*	Cytoplasm	2 μM $HgCl_2$	PMA to Hg(0)	First report of mer*B* in plants
A. thaliana	mer*A*/*B*	Cytoplasm	5–10 μM organic-Hg	PMA to Hg(II) to Hg(0)	First report of mer*A* and mer*B* in plants
Tobacco (*N. tabacum*)	mer*A*	Cytoplasm	50 μM $HgCl_2$	PMA to Hg(II) to Hg(0)	mer*A* transformed into tobacco
Tobacco	mer*A*/*B*	Plastid	400 μM PMA	Hg(II) to Hg(0)	First chloroplast phytoremediation system
Tobacco	mer*B*	Endoplasmic reticulum (ER)	5 μM PMA	Hg(II) to Hg(0)	mer*B* targeted to the ER
Rice (*O. sativa*)	mer*A*	Cytoplasm	250 μM $HgCl_2$	Hg(II) to Hg(0)	First monocot for Hg phytoremediation
Eastern cottonwood (*P. deltoides*)	mer*A*	Cytoplasm	25 μM $HgCl_2$	Hg(II) to Hg(0)	mer*A* transformed into a forest tree
Peanut (*A. hypogaea*)	mer*A*	Cytoplasm	100 μM $HgCl_2$	Hg(II) to Hg(0)	mer*A* transformed into peanut
A. thaliana	mer*A*	Cytoplasm of root cells	80 μM $HgCl_2$	Hg(II) to Hg(0)	Root-specific expression of mer*A*
Salt marsh cordgrass (*S. alterniflora*)	mer*A*	Cytoplasm	500 μM $HgCl_2$	Hg(II) to Hg(0)	First wetland grass for Hg phytoremediation
Chlorella	mer*A*	Cytoplasm	40 μM $HgCl_2$	Hg(II) to Hg(0)	First transgenic alga for Hg bioremediation
A. thaliana	mer*C*	Cell membrane	10 μM $HgCl_2$	Hypersensitivity to Hg(II)	First use of Hg membrane transporter
Tobacco	*ppk*	Cytoplasm	10 μM $HgCl_2$	Hg chelation	First use of a Hg-scavenging agent
Eastern cottonwood	mer*A*/*B*	Cytoplasm	10 μM PMA	PMA to Hg(II) to Hg(0)	mer*A* and mer*B* transformed into a forest tree

(continued)

Table 13.3 (continued)

Species	Gene	Expression compartment	Level of resistance	Mode of resistance	Special feature
Tobacco	mer*A*/*B*	Plastid	300 µM PMA/ $HgCl_2$	PMA to Hg(II) to Hg(0)	100-fold increase in Hg translocation and accumulation
A. thaliana	mer*P*	Cell membrane	10 µM $HgCl_2$	Possible Hg(II) chelation	Localization to the cell membrane

PMA: phenylmercuric acetate; mer*A*/*B*: expression of mer*A* and mer*B* genes; organic-Hg: PMA and methyl mercury

synthetase (γ-ECS), both under the influence of specific regulatory sequences. While ArsC converts arsenate (AsO_4^{3-}) to arsenite (AsO_3^{3-}), γ-ECS converts amino acids, glutamine and cysteine into g-glutamylcysteine, which in turn is used for the synthesis of organic thiols (RS) including glutathione (GSH) and phytochelatins (PCs), to which arsenite (but not arsenate) binds. This led to an increase tolerance toward As allowing its hyperaccumulation.

$$AsO_4^{3-} + 2\,GSH \xrightarrow{ArsC} GS - SG + AsO_3^{3-}\ RS$$

$$Glu+Cys \xrightarrow{\gamma\text{-ECS}} \gamma\text{-Glu-Cys} \longrightarrow \longrightarrow \longrightarrow AS$$

Arsenate reductase genes have been cloned and characterized in *A. thaliana* and *P. vittata* (Bleeker et al. 2006; Dhankher et al. 2006; Ellis et al. 2006; Rathinasabapathi et al. 2006) to maximize arsenic uptake and increase translocation from root to shoot.

There exist some concerns regarding the disposal of arsenic loaded plants. Francesconi et al. (2002) suggested disposal to a marine environment where any anionic arsenic would rapidly be altered to non-toxic organic arsenic compounds such as arsenobetaine $Me_3As(+)CH_2CO_2$. As phytoremediation is still in development stages and many possibilities are being explored but common methods used in phytoremediation disposal such as incineration cannot be used with arsenic because the metal remains among the ash.

13.3.3 Cadmium (Cd)

Cadmium kinesis in soils and plants is greater as compared to other heavy metals which results in its easy uptake by plants (Lehoczky et al. 2000). But, Cd does not contribute in plants' essential functions till date. Cd can accumulate in some plants without causing any toxicity symptoms (Lehoczky et al. 1998). Antioxidative enzymes play an important role in heavy metal tolerance (Boominathan and Doran 2003a, b). This was validated on the roots of *T. caerulescens* plants grown in high

Cd concentration and the results indicated presence of oxidative stress in plants with no side effects on plants growth due to Cd uptake.

Role of catalase enzyme as an antioxidant defense system have been studied in the hyperaccumulator phenotype of *T. caerulescens* (Boominathan and Doran 2003b). *Phragmites australis* plants had shown the highest accumulation in roots and then in leaves when it was treated with high concentration of Cd (Iannelli et al. 2002). In the roots of Cd-treated plants, Cd detoxification process inducted due to high Cd concentration leads to increased activity of glutathione and glutathione-S-transferase.

An increase in the concentrations of antioxidative enzymes of plants like catalase, ascorbate peroxidase, glutathione reductase, and superoxide dismutase is found due to Cd stress. These enzymes have potential to tolerate Cd stress up to 1000 times of Cd concentration due to formation of phytochelatin complex with Cd (Kneer and Zenk 1992). Phytochelatins (PC) have an unexpected sequestration potential such as reactivation of metal stressed nitrate reductase enzyme up to 1000 times better than chelators such as glutathione (GSH) or citrate (Fig. 13.3).

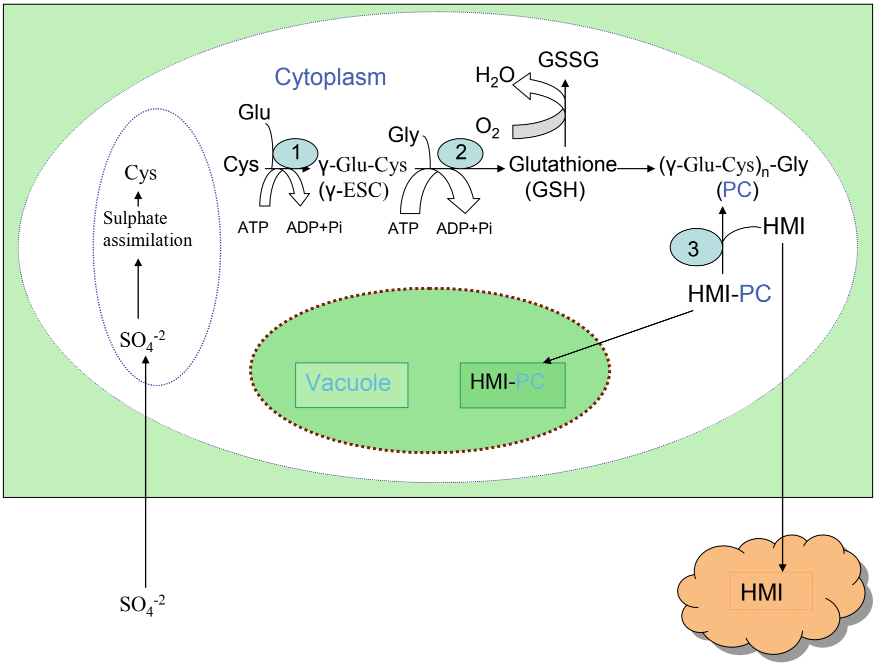


Fig. 13.3 Detoxification and plant sequestration of heavy metal ions in plant cells by phytochelatins. Cys, cysteine; γ-Glu-Cys, γ-L-glutamyl-L-cysteine; γ-ECS, γ-glutamylcysteine synthetase; GSH, glutathione; GSSG, oxidized glutathione; PC, phytochelatine; HMI, heavy metal ion; HMI-PC, heavy metal–phytochelatine complex; toxin, xenobiotics; toxin–SG, toxin–GSH conjugate. (1) γ-Glutamylcysteine synthetase; (2) glutathione synthetase; (3) phytochelatine synthase; (4) glutathione S-transferase (GST)

PC-metal-complexes of Ag, As, Cd, and Cu are being known (Shah and Nongkynrih 2007). An enhanced metal accumulation and metal tolerance for Cd, Cu, Mg, Ni, Pb and Zn heavy metals in transformed tomato plants have been observed when bacterial gene 1-aminocyclopropane-1-carboxylic acid (ACC) deaminase was expressed in these plants (Grichko et al. 2000).

The application of yeast protein YCF1 in Cd and Pb phytoremediation have been done by Song et al. (2003). They showed that transgenic *A. thaliana* plants over-expressing YCF1 was more tolerant and accumulated large amounts of Cd and Pb than wild type plants. YCF1 catalyzes the transport of bis(glutathionato) cadmium ($Cd\text{-}GS_2$) into vacuoles (Li et al. 1997), as well as $As\text{-}GS_3$ (Ghosh et al. 1999) and $Hg\text{-}GS_2$ (Gueldry et al. 2003).

Cd tolerance in native plants of mining areas is controlled by a single gene or two/three genes. However, Cd detoxification mechanism is possibly controlled by multiple genes which makes this process a multifaceted one (Sanitàdi Toppi and Gabbrielli 1999). Hence, the future Cd phytoremediation research will be governed by coupling of various detoxification mechanisms to enhance Cd accumulation and tolerance and additionally, combining several homeostatic processes as per detoxification mechanism.

13.3.4 Lead (Pb)

Lead, one of the most toxic heavy metal, is hazardous to the environment especially to children (EPA (Environmental Protection Agency) 2005). The most common sources of Pb poisoning are lead paint, lead dust, lead contaminated soil, lead contaminated water, and lead contaminated food (Xintaras 1992). The high concentrations of Pb is also found in lead mining, lead smelting ($PbSO_4$, $PbO{\cdot}PbSO_4$, and PbS), disposal sites for lead wastes and shooting ranges. Generally, plants shows two strategy for lead phytoremediation. Few plants shows lead exclusion strategy like *Thlaspi praecox*, which excludes Pb but hyperaccumulates Cd and Zn (Vogel-Mikus et al. 2005). The other group of plants have lead hyperaccumulation strategy such as many species of *Brassica* and *Sesbania drummondii* (a leguminous shrub) accumulate substantial amounts of Pb in their roots (Blaylock et al. 1997; Wong et al. 2001; Sahi et al. 2002). A grass, *Piptathertan miliacetall*, accumulates Pb in correlation with soil concentrations without toxicity symptoms for long time (Garcia et al. 2004). Sahi et al. (2002) noted that up to 1500 mg l^{-1} Pb levels can be tolerated by *S. drummondii* and it accumulate $\sim$40 g kg^{-1} shoot dry weight. *Brassica juncea* plants showed reduced growth in soil containing 645 mg kg^{-1} Pb, and they accumulated 0.0345 mg kg^{-1} shoot dry weight. Though, substantial Pb accumulation in shoot was only observed when roots were get saturated to Pb. The accumulation of Pb in leaves were lower than stems out of total shoot accumulation which could be due to low solubility of Pb (Suresh and Ravishankar 2004). Scanning electron microscopy of *S. drummondii* roots showed the lowest concentration of Pb in central axis of root, and transmission electron microscopy and X-ray microanalysis electron microscopy of *S. drummondii* roots revealed the deposition of Pb in the cell membrane and cell wall (Sahi et al. 2002).

The biggest challenge to effective phytoremediation of Pb is its extremely low solubility, as only ~0.1% of soil Pb is available for extraction (Huang et al. 1997). Efforts at phytoremediation of Pb have concentrated on using soil amendments like EDTA to increase the available Pb uptake (Huang et al. 1997, 1998; Blaylock et al. 1997; Wu et al. 1999). Addition of chelators does increase the solubility and uptake, but the amount Pb transferred to shoots is still low in comparison to the amount of Pb in the soil, and thus increases the likelihood of mobilized Pb-EDTA to leach out of the soil and contaminate groundwater (Wu et al. 1999). A slight increase of Pb accumulation and tolerance in transgenic *Arabidopsis* has been observed by the effect of the glutathione-Cd vacuolar transporter YCF-1 (Song et al. 2003). Hence, the future research on Pb phytoremediation will be decided by mainly two factors; (i) the process of Pb solubilization, and (ii) the mechanism of maximum Pb transportation to leaves.

13.3.5 Aluminium (Al)

Aluminium also causes toxicity in the soil. Normally, lime is used to amend these Al-contaminated soils (Caires et al. 2006). However, number of transgenic plants have been produced, which can tolerate aluminium toxicity by secreting organic acids into the soil around the root tip. These organic acids (malate and citrate) have the ability to chelate (bind up, sequester) the Al that is in the soil solution right around the root tip. After binding with one of these organic acids, Al cannot enter the plant root and cause damage (Matsumoto 2006). Sasaki et al. (2004) cloned a wheat Al-activated malate transporter gene (*ALMT1*) from wheat. Heterologous expression of *ALMT1* led to higher malate exudation that is associated with enhanced Al tolerance in transgenic plants.

To date, a number of Al-induced genes have been identified and isolated from roots of wheat (Snowden and Gardner 1993; Cruz-Ortega and Ownby 1993), rye (Milla et al. 2002), and *Arabidopsis* (Sivaguru et al. 2003), cells of tobacco (*Nicotiana tabacum*) (Ezaki et al. 1995), seedlings of *Arabidopsis* (Richards et al. 1998), shoots of *Arabidopsis* (Sivaguru et al. 2003), and leaves of rice (Ming et al. 2002).

13.3.6 Nickel (Ni)

Nickel is a vital element that can be poisonous and possibly carcinogenic in high concentrations (ATSDR (Agency for Toxic Substances and Disease Registry) 2005). The continual Ni exposure at work place causes asthma, dermatitis, or headaches in humans (Akesson and Skerfving 1985; Davies 1986). However, Ni contamination of soils is primarily constrained to regions surrounding Ni smelting operations such as Sudbury, Ontario, and Harare, Zimbabwe (Johnson and Hale 2004; Lupankwa et al. 2004). The wastes from Ni mining and smelting contain As, Cd, and Pb. These metals contaminate soil and water system with values greater than the permissible limits set by the government (Lupankwa et al. 2004).

The regions having serpentine and ultramafic soils contain high Ni concentrations with superior nickel tolerant flora. The common Ni hyperaccumulators are found in these soils such as species of *Alyssum* and *Thlaspi* from Brassicaceae family (Persans et al. 1999). In the genus *Alyssum* alone, 48 different species have been discovered containing between 1000 and 30,000 mg kg^{-1} Ni in leaf dry biomass (Baker and Brooks 1989; Kerkeb and Kramer 2003). The reports shows nickel accumulation as 9490 mg kg^{-1} Ni dry weight in *Thlaspi goesingense* (Reeves and Brooks 1983; Krämer et al. 1997; Freeman et al. 2004). Ni phytoextraction using hyperaccumulators has been patented (Chaney et al. 1999).

A study by Vacchina et al. (2003) suggested that nicotianamine is linked with Ni detoxification in *T. caerulescens*. Further, the constitutive expression of Nicotianamine synthase (NAS) in both *T. caerulescens* and *A. halleri* at great level strongly advocates nicotianamine's role in hyperaccumulation of Ni (Becher et al. 2004; Weber et al. 2004). In another study, it was found that intracellular nickel had association with citrate in *T. goesingense*, and vacuolar association was expected between both (Krämer et al. 2000). Free histidine also makes a good chelate for Ni at cytoplasmic pH and the concentration of free histidine in roots of certain *Alyssum* species strongly correlates with Ni hyperaccumulation ability (Ingle et al. 2005). Further, overexpression of ATP-PRT1, a gene involved in histidine biosynthesis, appears to drive this histidine overaccumulation (Ingle et al. 2005).

Mine sites have been phytoremediated by using various *Alyssum* species to grade their hyperaccumulation capacity (McGrath and Zhao 2003). Further, Ni phytomining have been done with *Alyssum* hybrids of feasible traits (Chaney et al. 1999; Li et al. 2003a), and phytomining technology has been commercialized (Li et al. 2003b). Exploration of new metal hyperaccumulators for phytomining of gold, nickel, and thallium are being done (Sheoran et al. 2009; Boominathan et al. 2004).

The first field study by Farwell et al. (2007) documented the increase in Ni tolerance of transgenic canola plants (*Brassica napus*) amended with plant growth-promoting bacteria (PGPR) exposed to multiple stressors at a Nil-contaminated field. One way PGPR stimulate plant growth is through the activity of the enzyme 1-aminocyclopropane-1-carboxylate (ACC) deaminase, which causes a lowering of plant ethylene levels resulting in longer roots of canola.

Phytomining and phytoremediation of Ni may be elevated by increasing metal accumulation and metal tolerance of nickel hyperaccumultors. Plants metal accumulation and tolerance could be increased by coupling of genes like metal-tolerance proteins (MTPs) with metal tolerance gene serine acetyl transferase (SAT). The shoot nickel accumulation in various hyperaccumulators could be enhanced by MTP genes (Peer et al. 2006).

13.3.7 Zinc (Zn)

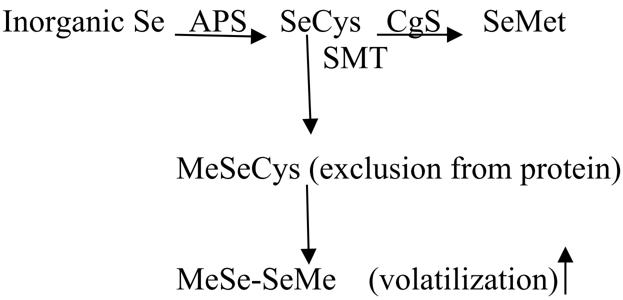
A. halleri naturally accumulates and tolerates concentrations in leafs that exceed 2.2% Zn and 0.28% Cd of their dry mass (Talke et al. 2006). Moreover *A. halleri* has undergone natural selection for Zn tolerance (Roosens et al. 2008a). Genes associated with metal accumulation and tolerance features of plants could be searched with transfer of the quantitative trait loci (QTL) (Roosens et al. 2008b). Recent studies showed the common QTL for Zn and Cd tolerance in *A. halleri* (Courbot et al. 2007; Willems et al. 2007). In *A. thaliana*, the QTL common to Zn and Cd tolerance covers a region comprising 739 genes and, among them, 11 genes are differentially expressed in *A. halleri* and *A. thaliana* (Roosens et al. 2008b). From these 11 genes, only one has been depicted as heavy metal-transporting ATPase4 (HMA4) and belongs to a P-type ATPase family involved in the transport of transition metals (Talke et al. 2006; Chiang et al. 2006). Hanikenne et al. (2008) showed that RNA interference of HMA4 in *A. halleri* down regulated its expression and reduced the hyperaccumulation of Zn and full tolerance to Cd and Zn in the plants. In another approach, increasing glutathione peroxidase activity in the transgenic poplars increased its tolerance to zinc stress (Bittsanszky et al. 2005).

13.3.8 Copper (Cu)

To improve higher plant metal sequestration, the yeast metallothionein Cup1 was introduced into tobacco plants, and the Cup1 gene expression and Cu and Cd phytoextraction were determined (Thomas et al. 2003). Over-expression of copper inducible MT cup1 gene also enhanced Cu tolerance in plants (Hamer 1986). Memon et al. (2006) found a *Brassica nigra* ecotype from a Diyarbakir site contained a very high amount of Cu in their shoots. When this ecotype plants were regenerated from callus culture and grown in soil culture containing 200 mg l^{-1} Cu, the shoots accumulated three times more Cu (700 mg kg^{-1} dry weight) than roots. The γ-EC expression in the shoots of Cu-treated plants was around 3.5 times that of control plants (Memon et al. 2008). This ecotype could be considered a good candidate for Cu phytoremediation. A study by Martinez and colleagues observed that transgenic tobacco (*Nicotiana glauca*) grown in mine soil accumulated Cu, Cd, Pb, Zn, Ni and B metals than nontransgenic plants with less metals. This transgenic plant contained a gene to encode a phytochelatin synthase from wheat (*Triticum aestivum*) (Martinez et al. 2006).

13.3.9 Selenium (Se)

A study on Se removal in wetland system using single plant species or group of species have been done (Gao et al. 2003) which concluded that Se uptake by plants depends on plant species. Wetland plant species like cattail, iris-leaved rush (*Juncus xiphioides*), parrot's feather (*Myriophyllum aquaticum*), and sturdy bulrush have been obtained high Se accumulation (Gao et al. 2003). Volatilization of Se involves assimilation of inorganic Se into the organic selenoamino acids selenocysteine (SeCys) and selenomethionine (SeMet). Selenomehtionine can be methylated to dimethylselenide and is volatile (Terry et al. 2000).



The first enzyme mediating selenate to selenite conversion, ATP sulfurylase (APS) from *A. thaliana* was constitutively expressed in *Brassica juncea* (Indian mustard) (Pilon-Smits et al. 1999b). In another study, Indian mustard plants overexpressing cystathionine-γ-synthase (CgS) were established. A comparative study of wild type and the CgS Indian mustard found that the CgS Indian mustard had less Se accumulation in roots and shoots but it had increased selenite tolerance and 2–3 times faster Se volatilization (Van Huysen et al. 2003). Transgenic *A. thaliana* plants expressing a selenocysteine methyltransferase (SMT) isolated from the Se hyperaccumulator *Astragalus bisulcatus* accumulated methylselenocysteine (MeSeCys) and contained up to eight fold higher Se concentrations than wild-type plants, when grown on a soil supplemented with selenite (Ellis et al. 2004). In *B. juncea* seedlings expressing the same SMT protein, LeDuc et al. (2004) observed slight selenate tolerance and an approximately five fold increase in Se accumulation when plants were exposed to selenate. They reported slightly enhanced dimethyl diselenide (MeSe-SeMe) volatilization from mature transgenic *B. juncea* plants exposed to selenite or selenate. Coupling of two genes to form double transgenic plants was done lately (LeDuc et al. 2006). Double transgenic Indian mustard plant with co-expression of both APS and SMT genes had shown up to 9 times more Se accumulation than their wild-type plants. Here, SMT gene was taken from Se hyperaccumulator *A. bisulcatus*. Lab and field trials with various transgenic plants have yielded encouraging results, showing up to nine-fold higher levels of selenium accumulation and up to threefold faster volatilization rates (Pilon-Smits and LeDuc 2009). Se accumulation in leaves of transgenic Indian mustard plant had increased in the field trial too (Bañuelos et al. 2005). Advances in transgenic systems for Se phytoremediation are summarized in Table 13.4.

Risk-assessment studies performed recently on Se and Hg volatilization specified that, in phytoremediation, these elements do not cause any serious threat due to their good amount of dispersion and dilution in the environment (Moreno et al. 2005; Lin et al. 2000; Meagher et al. 2000).

The genome structure of *A. thaliana* (The Arabidopsis Genome Initiative 2000) have been thoroughly marked. This plant is not a metal tolerant but it is used as a base for comparison of gene mapping within the Brassicaceae family. For example, to identify the potential genes intricated in metal hyperaccumulation and/or metal tolerance, a comparative study of gene expression levels between *A. halleri* (metal hyperaccumulator and metal tolerant) and *A. thaliana* (non-metal tolerant) have been done newly (Bechsgaard et al. 2006; Weber et al. 2006). Comaprison of genome sequence of *A. thaliana* with *Arabidopsis lyrata*, *A. petraea* and *Capsella rubella* have been done (Schat et al. 2002) but *A. halleri* remains yet (Boivin et al. 2004; Kuittinen et al. 2004; Koch and Kiefer 2005; Yogeeswaran et al. 2005).

These phytoremediation processes can be maximized by either plant may be selected or engineered that have higher levels of transporters involved in uptake of an inorganic pollutant from the xylem into the leaf symplast. Better understanding of the transporters involved in the process would be helpful because this is still a largely unexplored area. Similarly, plants with high transporter activities from cytosol to vacuole can be more efficient at storing toxic inorganics (Van der Zaal et al. 1999; Hirschi et al. 2000; Song et al. 2003).

Still many gaps are to be filled about the fundamental mechanisms that control movement and accumulation of heavy metals in plants. A genetic approach may assist in understanding the mechanism of metal tolerance. Genetic engineering of the chloroplast genome offers a novel way to obtain high expression without the risk of spreading the transgene via pollen (Ruiz et al. 2003). Critical investigation is required for the cellular and molecular basis of thermoprotection of heavy metals and heat stock protein induced by heavy metals. An enhanced knowledge in these crucial areas will help to interpret the molecular mechanisms that lie beyond plant metal tolerance and homeostasis (Hasan et al. 2009).

Bell et al. (2014) reviewed the omics tools to enhance the efficiency of phytoremediation. Omics-based approaches can be used for assay of biological responses to soil contaminants at single-organism omics to multiple-organism omics such as (i) Cultured microorganisms, (ii) Isolated single cells of uncultivated microorganisms, (iii) Plant omic analyses, (iv) Mixed microbial communities, (v) Large-insert functional screening, and (vi) Metaorganism omics.

Table 13.4 Advances in transgenic systems for Se phytoremediation

Gene	Product	Source	Target plant	Performance
APS	ATP sulfurylase	*A. thaliana*	*B. juncea*	2–3 fold higher Se accumulation than wild type (WT) plants (Pilon-Smits and LeDuc 2009)
CGS	Cystathionine-γ-synthase	*A. thaliana*	*B. juncea*	2–3 fold higher Se volatilization but accumulated 40% less Se than WT plants (Bañuelos et al. 2005)
SMT	Selenocysteine methyltransferase	*A. bisulcatus*	*A. thaliana*	Transgenic plants have ability to volatilize 1.5 times more Se than WT plants when supplied with SeCys (Bañuelos et al. 2007)
SMT	Selenocysteine methyltransferase	*A. bisulcatus*	*B. juncea*	Transgenic plants have ability to volatilize 2.5 times more Se than WT plants when supplied with selenate (Bañuelos et al. 2007)
SMT	Selenocysteine methyltransferase	*A. bisulcatus*	*A. thaliana*	Transgenic plant accumulated up to $\sim$1000 mg/kg DW Se (Van Hoewyk et al. 2008)
APS and SMT	ATP sulfurylase and selenocysteine methyltransferase	*A. thaliana* and *A. bisulcatus*	*B. juncea*	9 times higher Se concentration than WT when treated with selenate (200–500 μM) (Agalou et al. 2005)
CpSL (CpNifS)	Chloroplast SeCys lyase	Mouse	*A. thaliana*	CpNifS overexpression significantly enhanced 1.9 fold selenate tolerance and 2.2 fold Se accumulation by significantly reduced Se incorporation into protein (Lin et al. 2000)
APS	ATP sulfurylase	*A. thaliana*	*B. juncea*	A field study in USA (Se-contaminated sediment in the San Joaquin Valley, CA) showed 4 fold higher Se accumulation in transgenics than WT plants (Tamaoki et al. 2008)
CpSL and SMT	Chloroplast SeCys lyase and selenocysteine methyltransferase	Mouse and *A. bisulcatus*	*B. juncea*	2 fold higher Se accumulation in transgenics than WT plants in the same Se-polluted sediment (Meagher et al. 2000)
SBP1-SBP3	Se-binding protein	*A. thaliana*	*A. thaliana*	SBP1 transgenic plants showed enhanced tolerance to selenite (Bechsgaard et al. 2006)
SBP1	Se-binding protein1	*A. thaliana*	*A. thaliana*	Detoxified Cd potentially through direct binding (Weber et al. 2006)
Biosynthesis and inducible genes of ethylene and jasmonic acid	Jasmonic acid and ethylene	*A. thaliana*	*A. thaliana*	Increased Se tolerance (Schat et al. 2002)

13.4 Status of Phytoremediation

An American company, (D. Glass Associates 2001) specialised in market studies of phytoremediation, estimated market growth in the USA for the last years:

- 1998: an estimated USA market revenue of 16.6–29.5 million dollars
- 1999: an estimated USA marked revenue of 30–49 million dollars
- 2002: an estimated USA marked revenue of 50–86 million dollars
- 2005: an estimated USA marked revenue of 235–400 million dollars.

Phytoremediation is usually the cheapest cleanup option when it is applied to a site with its favourable conditions. For example, the estimated cost of phytoextraction of lead contaminated site was $200,000 while it was $12 million for excavation and disposal and $6.3 million for soil washing (Cunningham 1996). Though, the estimated cost of phytoextraction of a sandy loam site was $60,000–$100,000 (Salt et al. 1995). The estimated cost of removing radionuclides from water with sunflowers in a rhizofiltration system was $2.00–$6.00 per thousand gallons (Cooney 1996). For phytostabilization, cropping system costs have been estimated at $200–$10,000 per hectare, equivalent to $0.02–$1.00 per cubic meter of soil, assuming a one-meter root depth (Cunningham et al. 1995). Estimated costs for hydraulic control and remediation of an unspecified contaminant in a 20-foot deep aquifer at a one acre site were $660,000 for conventional pump-and-treat, and $250,000 for phytoremediation using trees (Gatliff 1994). A recent study estimated the economic value of the phytoremediation function to farmers as assessed by the substitution cost and hedonic price analysis to about 14,600 and 14,850 € per hectare, respectively, over a period of 20 years (Lewandowski et al. 2006).

Phytoremediation costs include preliminary treatability studies to select the proper plant and to assess its accumulation capacity; preparation of soil; plantation; maintenance (like fertilization and irrigation); monitoring (like status of plant nutrients, contaminant concentrations in plant, soil or water, and monitoring of air in phytovolatilization process); and disposal of contaminated biomass. Cost recovery, and the appropriateness of including it as a plant selection criterion, is a subject of matter which will get maturity with more research outcomes in the field of phytoremediation and making its application more accepted and widespread.

Phytoremediation is also the inexpensive and undoubtedly the only solution to resolve the recovering of large contaminated areas. This open up the great deal of research and governmental interest all over the world. In near future the biomass of phytoremediators will be used for bioenergy production (Schröder et al. 2008; Gogoi et al. 2018).

Recently, Pandey et al. (2015) described a strategy to achieve sustainable phytoremediation along with challenges of heavy metal phytoremediation of contaminated sites. Lugli and Mahler (2016) applied numerical modelling to a phytoremediation application in heavy metals (Cd, Pb, Ni, Zn) contaminated soil using Vetiver grass (*Chrysopogon zizanioides L Roberty*).

13.5 Conclusion

Phytoremediation can get advantages from various methods due to its interdisciplinary area. Several results have proved metal hyperaccumulation capacity of some plants. However, detailed investigation is required about the factors affecting biochemical mechanisms such as availability of metal, uptake of metal, translocation of metal, metal chelation, degradation and volatilization.

This enhanced understanding of biochemical mechanisms may lead to: (i) Identification of innovative genes to enhace metal accumulation in plants and following designing of transgenic plants with greater remediation capacities; (ii) Better interpretation of the ecological interactions involved (e.g. plant-microbe interactions); (iii) Appreciation of the effect of the remediation process on ecological interactions; and (iv) Information of the entry and movement of the pollutant in the ecosystem. Optimization of plant genetic abilities and agronomic practices is required for commercial utilization of phytoremediation technique. To increase the efficiency of the phytoremediation processes suitable agronomic practices, i.e., irrigation, fertilization, planting and harvest time and the timing of amendment application are applied (Ensley et al. 1997).

Future research could be pursued in modelling of phytostabilization systems, development of new plant and microbial species through genetic engineering, development of microbe-plant combination systems and monitoring of existing field experiments to acquire systematic understanding. Newly discovered genes and mechanisms played a role in metals tolerance and their hyperaccumulation. However, there is still a requirement for better understanding of the mechanisms such as the characterization of promoters of genes controlling metal tolerance and hyperaccumulation. This new acquaintance would significantly enhance perception of the regulation and expression of different genes in hyperaccumulators. This regulation and expression of genes in high biomass and non-hyperaccumulators is critical to imitate in order to obtain the hyperaccumulator phenotype. Biofuel crops can be used for remediation of the contaminated sites as they can produce valuable biomass.

Commercialization of phytoremediation technology began in the last few years. Phytoremediation is already well used in tertiary treatment of sewage, destruction of hydrocarbons and explosives, nuclear industry and immobilisation and extraction of heavy metals at abandoned mining sites. Numerous companies are gradually investing in phytoremediation research as the significance of this approach is realized. Such companies are Phytotech Inc., Phytokinetics Inc., Ecolotree, Inc., Applied Natural Sciences and Phytoworks Inc. But phytoremediation has not been fully commercialized. Henceforth phytoremediation can be a vital tool in sustainable management of contaminated media due to conservation of media and prevention of pollution. Research with time will make it successful.

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Chapter 14
Phytoremediation of Heavy Metals/Metalloids by Native Herbaceous Macrophytes of Wetlands: Current Research and Perspectives

Monashree Sarma Bora and Kali Prasad Sarma

14.1 Introduction

Heavy metal pollution in different subsystems (water, soil) of the environment has become a global concern. Besides natural sources, anthropogenic inputs such as rapid industrialization and imbalance in natural biogeochemical cycles have led to release of the metals/metalloids to the environment. Heavy metals/metalloids are accumulated in the environment as well as in biological system due to their non-biodegradable nature (Ali et al. 2013). Based on the biological significance of the heavy metals/metalloids they can be classified as essential and non-essential. Essential heavy metals such as manganese (Mn), zinc (Zn), iron (Fe), copper (Cu), cobalt (Co) are needed for proper physiological and biochemical functioning of organisms whereas, non-essential heavy metals/metalloids such as cadmium (Cd), lead (Pb), arsenic (As), antimony (Sb), mercury (Hg) have no role in any biochemical or physiological functioning of organisms (Cobbett 2003; Dabonne et al. 2010).

As stated earlier, sources of heavy metals/metalloids in the environment can be both natural and anthropogenic. Volcanic activities, weathering of minerals, erosion are significant known natural sources, while industrial sources such as metal refineries, mining activities and smelters have been considered as major anthropogenic sources of metal/metalloid in the environment (Fulekar et al. 2009; Sabiha-Javied et al. 2009). Most of the heavy metals/metalloids are reported as carcinogens having deleterious effects on human health as well as the environment (Memon and Schroder 2009). Regarding toxicities, Pb, Cd, Hg, As, Cr, Sn, Zn and

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Cu are the most problematic heavy metals/metalloids in the environment (Ghosh 2010; Patel et al. 2019). The availability of the metals/metalloids depends on the forms in what they exist. Metals which are easily soluble and exchangeable, are the most available metals, whereas metals that can precipitate as inorganic compounds and also able to form complexes with high molecular weight humic materials are considered as potentially available metals. On the other hand, metals that are bound in the crystalline lattice of minerals and precipitated as insoluble sulfide, are reported as essentially unavailable (Gambrell 1994).

14.2 Phytoremediation: A Green Technology

Phytoremediation is an environmentally friendly, cost effective and in situ applicable strategy which generally refers to the use of plant species with associated soil microbes for remediation of contaminants in different spheres of the environment (Greipsson 2011; Singh and Prasad 2011). Phytoremediation concept (as phytoextraction) was proposed by Chaney (1983) and subsequently, it has gained good acceptance due to its practical suitability of large scale field application. Compared to other chemical and physical remediation techniques, phytoremediation is a low cost option in both the terms of installation and maintenance (Van Aken 2009). Plant species ideal for phytoremediation should have some characteristics such as rapid growth rate, high biomass production, profuse root system, tolerance capacity to the adverse effects of the target heavy metal/metalloid, adaptation to the prevailing environment and capacity to translocate pollutants to the harvestable parts (Shabani and Sayadi 2012; Valipour and Ahn 2016). Phytoremediation techniques can be implemented in a variety of contaminated water such as industrial wastewater, sewage and municipal wastewater, agricultural runoff, landfill leachate, coal pile runoff, metallurgic plant wastewater, tannery wastewater and groundwater plumes (Olguín and Galván 2010).

14.2.1 Phytoremediation Mechanisms and Techniques

The term 'phytoremediation' comprises a set of techniques based on the use of plant species and target contaminant. Heavy metal/metalloid uptake mechanisms include accumulation, exclusion, translocation, osmoregulation and distribution. The mechanism of metal/metalloid uptake can be different from species to species. The plants used for phytoremediation generally accumulate metals/metalloids in their biomass. Hyperaccumulator plants, which accumulate metals/metalloids mostly in above ground parts (shoot) in comparison to roots, are preferred for phytoremediation.

Phytoremediation can be broadly classified as direct phytoremediation and explanta phytoremediation. In the direct phytoremediation plants uptake contaminants through roots and translocate to the aerial parts whereas contaminants are retained in the rhizosphere in case of explanta phytoremediation (Gerhardt et al. 2009). Depending on the mode of action to remediate contaminants from soil, sediment and water, following subfields of phytoremediation are identified: phytostabilization, phytoextraction, rhizofiltration, phytovolatilization, phytodegradation, hydraulic control and rhizodegradation (Fig. 14.1). Rhizofiltration, phytoextraction, and phytostabilization are commercially preferred methods of phytoremediation (Thakur et al. 2016). Rhizofiltration (phytofiltration) is the main phytoremediation technology used for different wastewater purification (Rezania et al. 2016). Aquatic macrophytes follow this method for heavy metals/metalloids removal from wastewater.

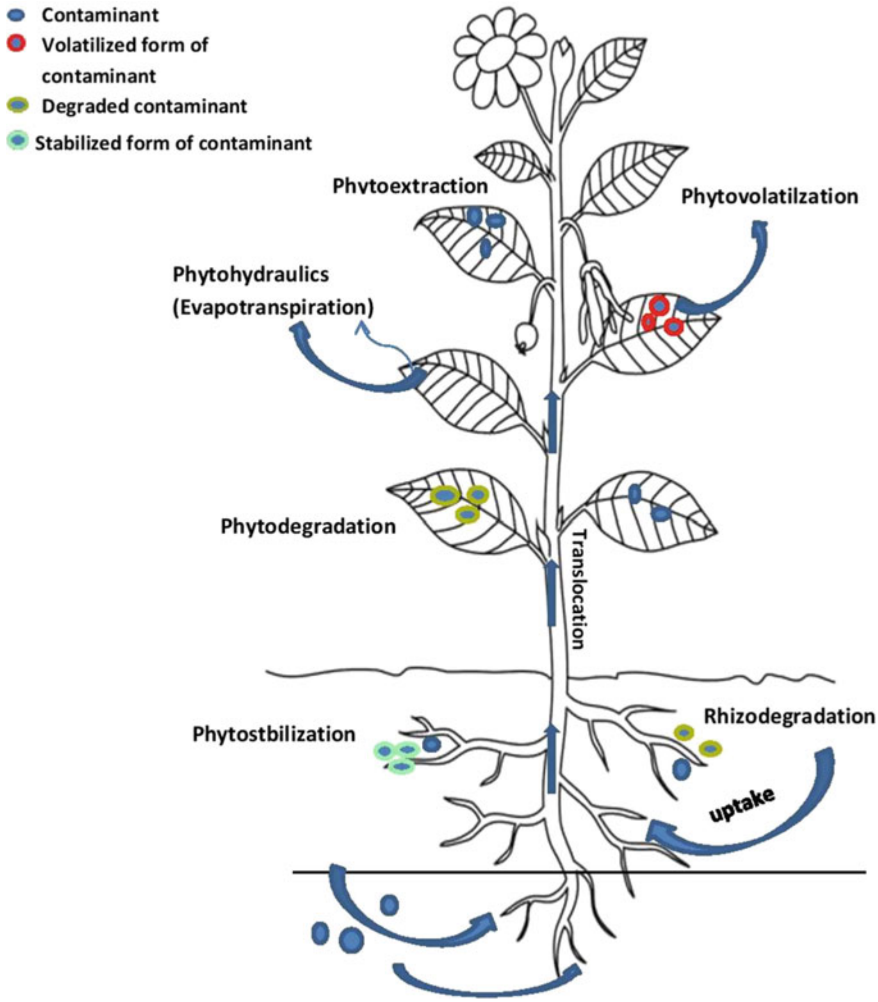

Fig. 14.1 Schematic diagram of different subfields of phytoremediation

14.2.1.1 Phytoextraction

In phytoextraction process plants are utilized to accumulate contaminants and translocate them to the aerial parts (Milic et al. 2012). As mentioned earlier, plants suitable for this process should have ability to tolerate trace metal concentration accumulated and also should be a good translocator with high biomass. For phytoextraction of trace element three strategies have been identified: (i) natural phytoextraction of contaminants by hyperaccumulators, (ii) natural phytoextraction using fast-growing non-hyperaccumulator plants for trace element removal; (iii) induced phytoextraction with the application of soil amendments (e.g., chelators) for mobility of trace element in soil or sediment. But the efficiency of these strategies mainly depends on the amount of the accumulated trace elements in the aerial harvestable parts as well as biomass yield of the plant species under metal/ metalloid stressed environment (Vangronsveld et al. 2009). The suitability of the plant species for this process also depends on the depth of contaminated soil or sediment. Around 500 species are reported that hyperaccumulate at least one heavy metal/metalloid among which 450 species for Ni, 32 species for Cu, 30 species for Co, 20 species for Se, 14 species for Pb, 12 species for Mn, 12 species for Zn, 5 species for As and 2 species for Cd have been identified (Van der Ent et al. 2013). Majority of the metal/metalloid hyperaccumulator species are reported to belong to the families Asteraceae, Brassicaceae, Caryophyllaceae, Cunoniaceae, Cyperaceae, Euphorbiaceae, Fabaceae, Flacourtiaceae, Lamiaceae, Poaceae and Violaceae (Van der Ent et al. 2013). Deep rooted plants such as *Salix* sp., *Populus* sp. are suitable for soil or sediment deeply (20–30 cm depth) contaminated with trace elements. Ma et al. (2001) reported *Pteris vittata* as As hyperaccumulator and it was found to bioaccumulate up to 7500 mg/kg of As in As contaminated soil. The main advantage of this technique is the cost-effectiveness compared to other available conventional remediation options. Cost-effectiveness of this technique was reported by Wan et al. (2016) using As and Pb hyperaccumulator *Pteris vittata* (Ma et al. 2001) and Cd hyperaccumulator *Sedum alfredii* Hance (Long et al. 2009) in contaminated soil for two years. In this cost-benefit analysis, total cost was \$US75,375.2/hm^2 or US\$37.7/m^3 based on the market rates of China, which was lower than most of the conventional technologies (Wan et al. 2016). On contrary to this, time duration for decontamination is considered as major constraint for phytoextraction of trace elements (Vangronsveld et al. 2009). Limited biomass in some hyperaccumulator species is also considered as a limitation (McGrath and Zhao 2003).

14.2.1.2 Phytostabilization

Phytostabilization refers to conversion of the pollutant to a stable complex in the rhizosphere of plants by limiting the mobility and bioavailability of the pollutant. The microbes present in the root zone form static complexes by releasing chelating agents which eventually binds metals/metalloids and inhibits the entry of the pollutants to the plant. This process of chemical alteration of the contaminants can be achieved by modifying the soil properties (e.g., pH, redox potential) around plant roots with the help of microbes. Arbuscular mycorrhizal symbiosis is reported to be beneficial in heavy metal immobilization (Audet and Charest 2007). The plant used for phytostabilization should be a poor translocator with profuse root system to quickly cover the contaminated site (Yang et al. 2014). *Brachiaria decumbens* and *Festuca rubra* L. are reported as suitable grass species for phytostabilization of heavy metals/metalloids in soil (Andreazza et al. 2013; Touceda-Gonzalez et al. 2017). Phytostabilization technique is reported to apply in the fields mainly for soils contaminated with trace elements, and soil amendments such as lime, biosolid composts, iron oxides, cyclonic ashes, zeolites, phosphates, clays also have been reported to use for stabilization of trace elements in the soils of industrial area, agricultural land and landfill site (Vangronsveld et al. 2009).

14.2.1.3 Phytodegradation and Rhizodegradation

Phytodegradation or phytotransformation refers to the uptake of pollutants (organics) from media (soil, sediment, sludge) by plant, and their subsequent breakdown and metabolization through various enzymatic reactions and metabolic processes inside the plant body (Ali et al. 2013). This technique is used to remediate organic xenobiotics in soil. Some plants are reported to produce nitroreductases enzymes which are responsible for reduction and catalysis of harmful organic contaminants such as trinitrotoluene (TNT), 1,3,5,7-tetranitro-1,3,5,7-tetrazocane (HMX) and 1,3,5-trinitroperhydro-1,3,5-triazine (RDX) (ITRC 2009). Main limitation of this approach is that difficulty in determination of contaminants destruction or degradation (Adams et al. 2000). On the other hand, rhizodegradation process can be defined as the process of degradation of toxic organic contaminants in rhizosphere with the help of microbial activities (Mukhopadhyay and Maiti 2010). This process of degradation of contaminants is induced by plants by releasing nutrient-rich root exudates.

14.2.1.4 Phytovolatilization

Phytovolatilization is the use of plant to extract contaminant from media (groundwater, soil, sediment, sludge) and release of the contaminant to atmosphere by transpiration in its original form or metabolically modified form. Phytovolatilization has been reported for selected heavy metals/metalloids (Hg, As, Se) and organic compounds (Terry and Bañuelos 2000). Organic compounds such as chlorobenzene, carbon tetrachloride (CCl_4), 1,2-dichloroethane (DCA), ethylene dibromide (EDB), methyl tert-butyl ether (MTBE), *m*-xylene, trichloroethylene (TCE) and trichloroethene can be remediated from soil by phytovolatilization (Burken and Schnoor 1999; Ma and Burken 2003). Several plant species of the genus *Astragalus* accumulate and volatilize Se (White 2016). However, the release of volatile pollutants to the atmosphere through leaves also raise questions on the merits of this technique (Ma and Burken 2003). To overcome this limitation engineered endophytic bacteria could be used to decrease evapotranspiration of the pollutants in the plant (Weyens et al. 2009).

14.2.1.5 Phytohydraulics

Phytohydraulics or hydraulic control is the potential of the plants to uptake and evapotranspire sources of surface water and ground water (ITRC 2009). This technology can be applied to remediate contaminated groundwater under suitable hydrogeological conditions such as contaminated sites with shallow groundwater depth. Phytohydraulics also restricts migration of leachate towards groundwater (Prasad 2004). Use of phreatophytes in phytohydraulics technique has been studied. Phreatophytes are deep rooted, high-transpiring plants which can survive in temporary saturation condition (Gatliff 1994). These plants hinder the downward migration of surface water by water interception capacity of their aerial canopy cover and its resultant evapotranspiration. Typical phreatophytes such as polars, willows and cottonwoods from the Salicaceae family are suggested candidates having potential for phytohydraulics (ITRC 2009). Advantage of this technique is that no engineered system is necessary because the roots of phreatophytes are in contact with a large portion of soil (Adams et al. 2000).

14.2.1.6 Rhizofiltration: The Sole Method of Phytoremediation by Macrophytes

Rhizofiltration or phytofiltration can be defined as the uptake, accumulation and precipitation of heavy metals/metalloids by plant roots from contaminated effluents (Raskin et al. 1994). Plant should have dense root system for the maximum uptake of pollutant by this technique. The efficiency of rhizofiltration also depends on the physicochemical parameters of the plants (Olguín and Galván 2012). Alteration of rhizosphere pH and the root exudates may cause metals/metalloids to concentrate on root surfaces and, after saturation of accumulating metals plants are harvested. Rhizofiltration is believed to have benefits of low cost as well as minimal environmental disruption. It is an economically profitable wastewater treatment technique in which plants are able to uptake around 60% of their dry weight biomass as heavy metals/metalloids (Rai 2009a). However, uptake of metals/metalloids by macrophyte also depends on physicochemical parameters of the aquatic system such as pH, salinity, light, temperature, and presence of other cations and anions (Rai 2009a). An increase in pH with negatively correlated toxic metal concentrations was reported for utilization of wetland plants for remediation of acid mine drainage in sulfate-reducing conditions (MoEF 2011). This phytoremediation technique is considered as effective as well as the most economically feasible technique for remediation of lower to medium concentrations of pollutants in large volume of effluents, which also makes it suitable to use for radionuclide contamination (MoEF 2011).

Based on rhizofiltration technique constructed wetlands (CW) have been utilized for wastewater treatment from a long time which mimics the structure of a natural wetland. Different varieties of wastewaters such as municipal, agricultural and industrial effluents have been reported to be remediated in CWs. The main mechanism of CWs in wastewater treatment is uptake of heavy metal/metalloid by plant and microbes (Rezania et al. 2016). CW treatments are categorized into three classes: free water subsurface CWs (FWS CW), subsurface flow CWs (SSF CW), and hybrid CWs. On the basis of effluent flow direction SSF CWs can be classified into another two types: vertical subsurface flow (VSSF) and horizontal subsurface flow (HSSF) systems (Vymazal 2007). Selection of CW system depends on targeted contaminants, availability of the treatment area, geographical location and treatment goals (Horner et al. 2012). For wastewater treatment aquatic macrophytes are reported to be more preferred option than other plants because of their significant faster growth rate with high biomass yield, and higher potential of removal of pollutants directly from contaminated water (Sood et al. 2012). Horizontal subsurface flow (HSSF) system has been used to treat municipal sludge in a pilot plant of Mother Dairy in India with the application of *Phragmites australis* (Ahmed et al. 2008). According to MoEF report (2011), India generates nearly 90 million tonne of fly ash per annum and land occupied by the ash ponds is around 65,000 acres. Application of CWs with aquatic macrophyte is a suitable solution for treatment of fly ash. CWs have been successfully used in NALCOs Angul plant in Odisha, India with macrophyte for fly ash slurry generated from captive coal power plant (MoEF 2011). Though use of CW is spreading rapidly in developed countries, it has not achieved desired importance in tropical countries because of water scarcity issues and higher rate of surface evapotranspiration (MoEF 2011).

14.3 Role of Wetland Macrophytes in Heavy Metals/Metalloids Remediation

The term 'macrophyte' refers to the plants emerging in or near water in the form of submerged, emergent and free floating plants (Rai 2009a). Aquatic plants are mainly represented by the members of Cyperaceae, Haloragaceae, Hydrocharitaceae, Juncaceae, Lemnaceae, Najadaceae, Pontederiaceae, Potamogetonaceae, Ranunculaceae, Typhaceae and Zosterophyllaceae (Prasad 2007). Many common weeds are included in aquatic macrophytes that also enable this phytotechnology using macrophytes as a cost-effective method for treatment of wastewaters polluted with inorganic or organic contaminants and heavy metals/metalloids (Prasad 2003). Macrophytes are considered as biological filters which have significant contribution in the maintenance of the aquatic ecosystem (Rai 2009a). Potential aquatic macrophytes such as water hyacinth (*Eichhornia crassipes*), duckweeds (*Lemna minor*, *Lemna gibba*, *Spirodela polyrhiza*), water velvet (*Azolla pinnata*) are prevalent in fresh water bodies all over the world. Therefore, wastewater treatment by the use of these macrophytes is practiced all over the globe due to its abundancy and cheap cost (Rai 2009a).

Aquatic macrophytes possess significant characteristics like high biomass in the aerial parts and high ability to uptake and accumulate heavy metal/metalloid, thus making them suitable candidates for phytoremediation (Vymazal 2016). As roots are the initial sites for metal uptake, the heavy metal concentrations are usually found much higher in root parts than in shoots. However, this limitation of accumulation of metal/metalloid in roots is also considered as a protective action of plant against toxicological damages in the photosynthetic apparatus in their aboveground part (Drazkiewicz and Baszynski 2005). Metal-rich rhizoconcretions are also found on the roots of some wetland macrophytes (Vale et al. 1990). Mostly iron hydroxides along with other metals (e.g. manganese) are reported in these rhizoconcretions or plaques. These metals are mobilized from the anoxic reduced environment of wetland sediments and precipitated in the oxidized environment in the rhizosphere (Weis and Weis 2004).

Aquatic macrophytes such as *Cyperus malaccensis*, *Phragmites australis*, *Typha latifolia*, are reported as potential bioaccumulator of different heavy metals (Yadav and Chandra 2011). Some of native wetland macrophyte species of Assam, which are reported to have phytoremediation potential of heavy metal/metalloid removal, are presented in Table 14.1. Widely distributed macrophyte, *E. crassipes* is reported to have great phytoremediation potential for the removal and accumulation of metals/metalloids such as As, Cd, Cr, Cu, Ni, Se (Zhu et al. 1999; Shim et al. 2019). Similarly, *Lemna* sp. are reported to be capable of phytoremediation of As, Pb, Cd, Co, Cu, Cr, Fe, Hg, Mn, Ni, Zn (Miranda et al. 2014; Parra et al. 2012). Other species such as *Azolla pinnata*, *Bacopa monnieri*, *Ceratophyllum demersum*, *Ceratopteris thalictroides*, *Colocasia esculenta*, *Cyperus rotundus*, *Hydrilla verticillata*, *Phragmites australis*, *Pistia stratiotes*, *Polygonum* sp., *Salvinia* sp., *Spirodela polyrhiza*, *Trapa natans* are also reported as potential accumulators of different metals/metalloids (Table 14.1).

Wetlands may act as a source as well as a sink for persistent pollutants and heavy metals/metalloids. Senescent plant tissues are reported as the possible source of elements which are released by mineralization and leaching processes, and on contrary to this it also can be acted as a sink through the processes of element adsorption in litter and microbe induced elements immobilization. Toxic Cr(VI) reduction to the comparatively less toxic form, Cr(III) was also evident in marsh sediments (Pardue and Patrick 1995).

14.3.1 Metal Speciation in Aquatic Macrophyte

Studies have been carried out by researchers on plant altered metal/metalloid speciation. Active methylation of mercury has been reported in the roots of

Table 14.1 Mode of action of remediation of different heavy metals/metalloids by some of the native wetland macrophytes of Assam, India

Plant species	Heavy metal/metalloid	Mode of action	References
Azolla pinnata	Zn, Ni, Mn, Fe, Cr	Rhizofiltration; bioaccumulator of Zn, Ni, Mn, Fe; reported as Cr hyperaccumulator	Rai (2009b), Kumari et al. (2016a)
Bacopa monnieri	Cd, Cr	Rhizofiltration; bioaccumulator of Cd, Cr	Shukla et al. (2007)
Cyperus rotundus	Pb, Sn	Phytoextractor of Pb; Sn hyperaccumulator	Ashraf et al. (2011), Bordoloi and Basumatary (2016)
Ceratophyllum demersum	Pb, Cr, Al, Cd	Rhizofiltration; bioaccumulator of Pb, Cr, Cd, Al	Abdallah (2012), Dogan et al. (2018), Poklonov (2016)
Ceratopteris thalictroides	Fe, Cd, Ni, Al	Rhizofiltration; bioaccumulator of Fe, Ni, Al; hyperaccumulator of Cd	Kumari et al. (2016a)
Colocasia esculenta	Mg, Fe, Zn	Rhizofiltration; phytoextractor of Mg, Fe and Zn	Skinner et al. (2007), Mazumdar and Das (2015)
Commelina benghalensis	Cu, Mn, Pb, Cd, Zn	Good candidate for phytostabilisation of Mn, Zn, Pb, Cd and, suitable for phytoextraction of Cu in urban drainage system	Sekabira et al. (2011)
Cynodon dactylon	Pb	Rhizofiltration; phytoextractor of Pb	Mazumdar and Das (2015), Sekabira et al. (2011)
Eichhornia crassipes	Al, Fe, Pb, Cu, Cr, Cd, As, Zn, Mn, Se, Ni	Rhizofiltration; Cd, Cr, Cu, Ni, As mostly accumulated in root, Se accumulated in shoot	Aurangzeb et al. (2014), Hazra et al. (2015)
Hydrilla verticillata	Cu, Pb, Cr	Rhizofiltration; suitable for phytostabilization of Pb and Cr	Ahmad et al. (2011)
Hygroryza aristata	Cr, Cd, Hg	Rhizofiltration; Cr, Cd, Hg accumulated mostly in the roots	Ahmad et al. (2011)
Ipomoea aquatica	Pb, Zn, Cr	Rhizofiltration; Cr bioaccumulator and good translocator of Pb, Zn	Chen et al. (2010), Mazumdar and Das (2015)
Lemna minor	Fe, Al, Co, Cr, Cd, Pb, Ni, Cu, Mn, Hg, Zn	Rhizofiltration; bioaccumulator of Zn, Hg, As, Cr, Zn, Pb and Al at diluted concentrations	Miranda et al. (2014), Parra et al. (2012), Radić et al. (2010)
Lemna purpusilla	Cd, Fe, Mn, Zn	Rhizofiltration; bioaccumulator of Cd, Fe, Mn and Zn	Clark et al. (1981)
Marsalia quadrifolia	Pb, As, Cu, Cr, Hg, Cd	Good candidate for phytoextraction and phytostabilization; good translocator of Cr and Pb	Ahmad et al. (2011)

(continued)

Table 14.1 (continued)

Plant species	Heavy metal/metalloid	Mode of action	References
Monochoria hastata	Cd	Rhizofiltration; Cd mostly accumulated in roots	Baruah et al. (2017), Hazra et al. (2015)
Monochoria vaginalis	Cd, Pb	Rhizofiltration; bioaccumulator of Cd and Pb	Liu et al. (2007)
Pistia stratiotes	Fe, Cu, Mn, Ni, Pb, Cr, Zn	Rhizofiltration; reported as hyperaccumulator for Fe, Cu, Mn, Ni, Pb, Cr and Zn	Lima et al. (2013), Lu et al. (2011)
Polygonum amphibium	Cu, Cr, Fe, Mn, Pb, Cd	Rhizofiltration; Cu, Pb, Cr, Fe, Mn and Cd mostly accumulated in roots	Rai (2009b)
Polygonum hydropiper	Pb, Cd, Zn	Rhizofiltration; bioaccumulator of Zn, Pb, and Cd	Liu et al. (2007)
Phragmites australis	Cd, Cr, Pb, Cu, Mn, Ni, Fe, Zn	Phytoextractor of Fe, Cr, Pb, Mn, Ni and bioaccumulator of Cd and Cu in roots	Klink (2017), Chandra and Yadav 2011
Salvinia molesta	Cr, Cu, Pb, Ni, Zn	Rhizofiltration; bioaccumulator of Cr, Cu, Pb, Ni, Zn	Kumari et al. (2016b)
Salvinia natans	Cr, Fe, Ni, Cu, Cd, Co, Zn, Mn	Rhizofiltration; bioaccumulator of Ni, Cu, Co, Pb, Fe, Zn and Cr; Cr, Ni and Pb mostly accumulated in roots	Dhir et al. 2009, 2011
Spirodela polyrhiza	As, Cd	Rhizofiltration; bioaccumulator of As; Cd accumulator at lower concentration	Chaudhury et al. (2014), Rahman et al. (2007)
Trapa natans	Cd, Cr, Fe, Cu, Mn, Pb, Zn	Good translocator of Cd, Fe, Cu, Zn and Mn; Cr and Pb accumulated mostly in the roots	Kumar and Chopra (2018)
Typha latifolia	Ni, Zn, Fe, Cu, Cd, Cr, Pb	Phytoextractor of Ni, Fe, Cu, Cr; hyperaccumulator of Zn, Pb and Cd	Hazra et al. (2015), Klink (2017), Kumari et al. (2016a)
Utricularia gibba	Cr	Rhizofiltration; Cr accumulator and efficient for removal of chromate over a short term period	Augustynowicz et al. (2015)

E. crassipes which can be attributed to the microbe induced methylation in the rhizosphere of aquatic plants (Mauro et al. 1999; Guimaraes et al. 2000). The root exudates serve as the carbon source to induce microbial activity in the root zone. Lytle et al. (1998) reported conversion of Cr(VI) to Cr(III) in lateral roots of *E. crassipes*, and subsequent translocation of Cr(III) to aerial tissues. Alteration in sediment properties (e.g. Eh and pH) also can induce speciation of metals/metalloids. This can lead to influx of metals/metalloids of sediment to porewater and eventually to the overlying water. Alteration in salinity of sediments may also play significant role in metal/metalloid speciation (Weis and Weis 2004).

14.3.2 Role of Halophyte in Phytoremediation

Another phytoremediation approach 'phytodesalination' also have been evolved to reclaim salt affected area where halophytes are applied to accumulate and tolerate salt stress. Halophytes are the plants which can inhabit in high nutrient containing saline environment. These are reported as tolerant under abiotic stress conditions like xerothermic environment with high salinity, and severe seasonal temperature fall (Flowers et al. 2010). Use of halophytes has been paid attention in the phytoremediation technology as they are probably the only candidate for the reclamation of saline soils and sediments polluted with heavy metals/metalloids (Ghnaya et al. 2005). These plants may be represented by annual or perennial species, monocot or dicot species, and selected trees. Halophytes possess morphological, physiological as well as biochemical adaptation mechanisms which vary with plant species and degree of salt stress. The adaptation mechanisms present in the halophytes overlap the mechanisms for heavy metal tolerance which makes them promising solution for remediation of heavy metals/metalloids. As a part of adaptation mechanisms some salt excretion organs such as salt bladders and salt glands are developed the leaves of some tolerant halophytes for maintaining ion concentration in plant tissue. Members of Poaceae, Chenopodiaceae, Frankenaciaceae and Tamaricaceae, are generally found to have salt accumulating glands in their leaves. It has been documented that some members of *Spartina* genus possess such salt glands through which they excrete toxic metal ions in salt crystals (Redondo-Gómez 2013). Synthesis of osmoprotectant such as proline, glycinebetaine also plays role in tolerance mechanism for maintaining suitable water potential gradient to protect cellular ultrastructures of halophytes under metal stress condition (Manousaki and Kalogerakis 2011). These osmoprotectants are also reported to have beneficial effects on metals/metalloid binding and antioxidant defense. As metal/metalloid stress also induce water stress as well as antioxidant stress in plant, halophytes are considered to be compatible to cope metal/metalloid with the synthesis of these osmoprotectants (Manousaki and Kalogerakis 2011). Halophytes such as *Nerium oleander* L., *Atriplex nummularia*, *Tamarix smyrnensis* Bunge are reported to have potential for phytoremediation of heavy metals/metalloids (Manousaki et al. 2008; Manousaki and Kalogerakis 2011). A number of species from Poaceae such as *Spartina argentinensis*, *Spartina maritima*, *Spartina densiflora* have been proved their ability for phytostabilization and accumulation of heavy metals/metalloids such as Fe, Cu, As, Pb, Mn and Zn (Cambrollé et al. 2008; Redondo-Gómez 2013).

14.3.3 Physiological and Biochemical Changes of Plant Induced by Heavy Metal/Metalloid Exposure

Heavy metals/metalloids induce deleterious physiological and biochemical effects in aquatic plants by affecting essential plant metabolic processes (Prasad et al. 2001; Vaillant et al. 2005; Zhou et al. 2009; Jayasri and Suthindhiran 2017). Heavy metals/metalloids affect photosynthetic pigments by three ways: first, heavy metals/metalloids may enter to the chloroplast and accumulate there causing oxidative stress which eventually cause peroxidative damages to the chloroplast membranes; second, inhibition of uptake and transportation of essential metals like manganese and iron by heavy metal/metalloid ions; third, heavy metal/metalloid induced activation of different pigment enzyme responsible for decomposition of pigment (Sandalio et al. 2001; Das et al. 1997; Wenhua et al. 2007). The cause of chlorophyll content reduction in plants under metal/metalloid exposure could be due to the inhibition of two necessary enzymes of chlorophyll biosynthesis, δ-aminolevulinic acid dehydratase (δ-ALAD) and ferredoxin $NADP^+$ reductase (Cenkci et al. 2010; Gupta et al. 2009). Increase in chlorophyllase activity also can inhibit photosynthetic activities of plant under stress conditions (Liu et al. 2008).

Heavy metal/metalloid exposure develops oxidative stress in plants with the formation of ROS such as singlet oxygen ($^1O_2$), superoxide radical ($\cdot O_2^-$), hydrogen peroxide (H_2O_2) and hydroxyl radical (·OH). ROS can lead to the peroxidase damages of cellular metabolites such as nucleic acids, fatty acids, proteins and photosynthetic pigments (Gallego et al. 2002). However, a complex antioxidant system is present in plant cell which is capable of scavenging such ROS by redox homeostasis. Antioxidant enzymes such as catalase (CAT), peroxidase (POX), superoxide dismutase (SOD) and ascorbate peroxidase (APX) play major roles in scavenging ROS. The enzymatic reaction of SOD, which is a major ROS scavenger, results in decomposition of superoxide anion into H_2O_2 and O_2. On the other hand, CAT, POX and APX involve in scavenging H_2O_2 resulted from SOD reaction. Enhanced activities of these enzymes for complementing ROS production under metal/metalloid stressed environment eventually affects lipid-protein structure of cell membrane, synthesis of photosynthetic pigment and nucleic acid (Zhang et al. 2007). As a toxic byproduct of lipid peroxidation, malondialdehyde (MDA) plays the role of an indicator for ROS production in stressed cells (Li et al. 2013).

14.3.4 Cellular Mechanisms for Heavy Metal/Metalloid Detoxification and Tolerance

Accumulation of toxic heavy metals/metalloids in plant cells deactivates cellular enzymes responsible for various metabolic processes in the cell due to which normal metabolic activities and growth of the plant are inhibited. Therefore, plants adapt some detoxification mechanisms for normal functioning of the cellular metabolic activities under metal/metalloid stress conditions. One of such mechanisms is storage of toxic metal/metalloid complexes in the less metabolically active cellular compartments such as vacuole (Bidwell et al. 2004). Sub-cellular localization study is an essential step to understand the mechanisms behind the metal/metalloid tolerance, detoxification and bioaccumulation in plant cell. Different techniques such as electron energy loss spectroscopy (EELS) (Liu and Kottke 2004), nuclear micro-probe technique (NMP) (Ager et al. 2003), particle-induced X-ray emission (micro-PIXE) (Vogel-Mikus et al. 2008), and transmission electron microscopy (TEM) (Sridhar et al. 2005; Baruah et al. 2017) are applied to investigate distribution of metals/metalloids in cellular and subcellular level. Hall (2002) reported some cellular mechanisms responsible for metal detoxification as well as tolerance under heavy metal stress. Some morphological structures act as primary defense mechanisms in plant body under metal/metalloid stress. Such defensive structures of plant body include cell wall, trichomes, cuticle and also mycorrhizal symbiosis (Harada et al. 2010). Other potential mechanisms reported to be involved in heavy metal/metalloid tolerance in plant cell are efflux of metal/metalloid cations in plasma membrane and deposition of metal/metalloid cations in the vacuole to decrease concentration of these toxic metal/metalloid in the cytoplasm. Detoxification mechanisms in ultrastructural level are shown in TEM micrographs of *Monochoria hastata* plant under Cd exposure (Figs. 14.2 and 14.3). In Fig. 14.2, deposition of metal was observed along the cell wall in the Cd treated root cell compared to control plants. Similarly, metal deposition in vacuoles of root cell was observed in Fig. 14.3 in comparison to control root cell. This metal/metalloid stress causes alteration in calcium level in plant cell and also causes changes in kinase activity which eventually affects gene expression (Dal Corso et al. 2010). Plants

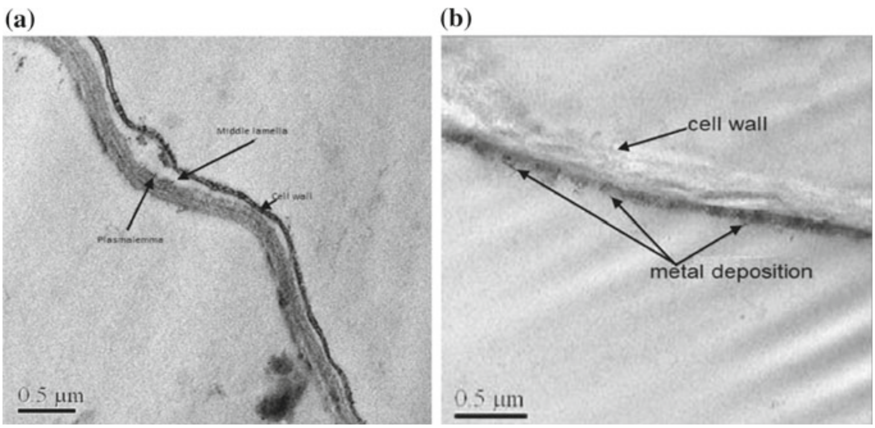

Fig. 14.2 Cd detoxification mechanism in root cells of *Monochoria hastata* **a** control cell showing no metal deposition along cell wall **b** Cd treated cell showing metal deposition along the cell wall. Reprinted from Baruah et al. (2017) courtesy of Springer Nature

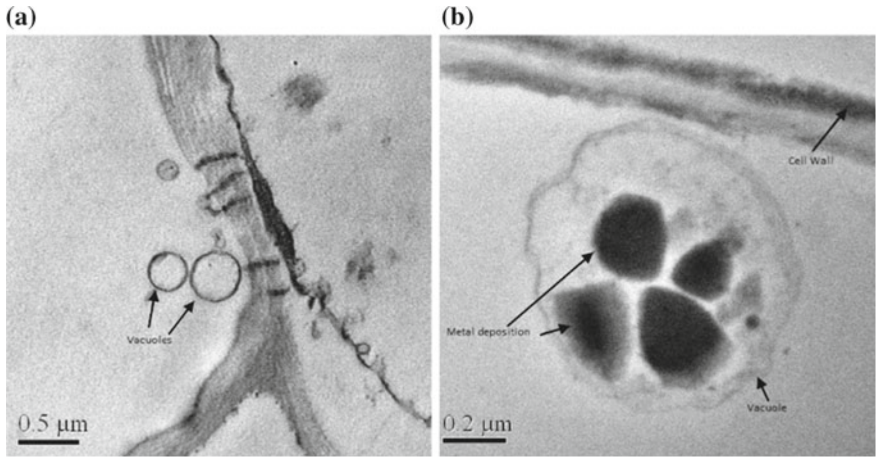

Fig. 14.3 Cd detoxification mechanism in root cells of *Monochoria hastata* **a** control cell showing no deposition in vacuole **b** Cd treated cell showing metal deposition in the vacuole. Reprinted from Baruah et al. (2017) courtesy of Springer Nature

produce a wide range of cellular biomolecules in order to tolerate metal/metalloid toxicity. Such biomolecules are mainly represented by low-molecular weight proteins, metallochaperones such as mugineic acids, nicotianamine, putrescine, organic acids spermine, glutathione (GSH), metallothioneins (MTs), phytochelatins (PCs). Heat shock proteins, protons, flavonoid, phenolic compounds, some specific amino acids, such as proline and histidine, and hormones such as ethylene, jasmonic acid and salicylic acid are also reported to be involved in metal/metalloid tolerance mechanisms (Dalvi and Bhalerao 2013; Sharma and Dietz 2006).

14.4 Post-harvest Management of Plant Biomass

Use of phytoremediation technique for removal of pollutant has also escalated due to its additional benefits such as carbon sequestration and improvement of soil quality (Abhilash and Yunus 2011). But, the most asked question on phytoremediation is 'What is the fate of the metal/metalloid containing biomass?' As a part of post-harvest management different techniques have been reported for volume reduction of the contaminated by products of phytoremediation. These techniques include composting, compaction, gasification and combustion of the harvested biomass (Mohanty 2016). After harvesting, the metal loaded biomass also can be disposed in specified dumps with hazardous waste safety or proceed to the 'phytomining' process.

14.4.1 Phytomining

Phytomining is the process of biomass combustion in order to get energy and extraction of the metal/metalloid from the remaining 'bio-ore' (Ali et al. 2013). Processing of the bio-ore to metal/metalloid recovery causes less SO_x emissions which make this option of harvested biomass treatment more environmentally friendly compared to the conventional ore mining process. Advantages of phytomining over other mining techniques include higher metal containing bio-ore production with less SO_x emission, energy production from biomass combustion and soil remediation (Anderson et al. 1999). Hyperaccumulators are preferred for phytomining process as the efficiency of this process depends on sufficient biomass production and higher metal accumulation in the aboveground parts of the plant. Besides phytoextraction efficiency, the commercial feasibility of this technique also depends on current market value of the targeted metals (Ali et al. 2013). This process is considered as potential, cost effective and environmentally sustainable method of metal extraction from low-grade ores, mill tailings, and also from mineralized soil. India is endowed with significant resources of various metallic and non-metallic minerals. Therefore, application of this economically feasible technique is suggested to be effective over conventional mining in India. However, proper management of the metal containing biomass is essential to restrict its entry to the ecosystem. This process has been used for Ni at commercial basis and found it cheaper than the conventional one. From the practical applicability this bio-based mining process of Ni has been proved as a profitable agricultural technology (Chaney et al. 2007).

14.5 Biotechnological Approaches in Phytoremediation

Advancement of genetic tools and unravelling of structures and functions of plant gene have accelerated the application of biotechnological approaches in the phytoremediation technology. Kotrba et al. (2009) reported three main biotechnological approaches to modify plants to be useful for heavy metals/metalloids phytoremediation: (i) manipulation of transporter genes responsible for metal/metal uptake (ii) enhancing production of metal/metalloid binding ligand; (iii) speciation of metals/metalloids to less toxic and volatile forms. These biotechnological approaches are reported to be applied for phytoremediation As, Cu, Hg, Cd, Pb, and Se (Mosa et al. 2016).

Manipulation of metal/metalloid transporter genes in plants holds great potential in phytoremediation technology for enhancement of heavy metal/metalloid tolerance and accumulation. Overexpressing of yeast gene named yeast YCF1 (Yeast Cadmium Factor1) which involves in Cd transport to the vacuole in plant cell, enhanced Pb and Cd accumulation and tolerance capacity in *Arabidopsis thaliana* (Song et al. 2003). In addition, de novo transcriptome sequencing approach has also been applied by researchers to identify Cu tolerant genes in *Paeonia ostii* (Wang et al. 2016).

Several reports have been published by researchers in related to the enhancement of heavy metal/metalloid tolerance in different plant species by overexpressing genes responsible for production of metal/metalloid binding ligands. Enhanced accumulation and tolerance to Cd was resulted in Indian mustard (*Brassica juncea*) when *E. coli* glutathione synthetase gene (gshII) encoding GSH synthetase (GS) was overexpressed in the cytosol of the plant (Liang Zhu et al. 1999). Similarly, enhanced tolerance for Pb and Cd was reported in tobacco after overexpression of wheat phytochelatin synthase gene (TaPCS1). Similarly, co-expression of two bacterial genes namely, *E. coli* arsenate reductase (arsC) and g-glutamylcysteine synthetase (g-ECS), in *Arabidopsis thaliana* resulted in three fold more As accumulation in harvestable biomass and 17 fold more biomass than wild type plants when grown in an exposure of 125 μM As solution (Dhankher et al. 2002). Furthermore, Xu et al. (2015) has documented use of de novo sequencing to identify a number of candidate genes responsible for Cd accumulation and detoxification. These are the genes encoding for GSHs, MTs, PCs and, genes responsible for synthesis of ATP-binding cassette transporters (ABC transporters) and zinc iron permease (ZIPs) under Cd induced stress conditions.

Biotechnological approaches have been reported by researchers for phytoremediation of Hg and Se by converting them into less toxic volatile forms. Bacterial genes such as mercury(II) reductase (merA) and organomercurial lyase (merB) have been overexpressed in different plant species that are responsible for conversion of mercury into less toxic forms (Dhankher et al. 2011). Poplar (Rugh et al. 1998), Rice (Heaton et al. 2003) and tobacco (Heaton et al. 2005) were reported to exhibit significant Hg(0) volatilization when overexpressed with merA gene, whereas transgenic *Arabidopsis* (overexpressed with merB) was reported to enhance tolerance capacity of the plant for higher concentrations of monomethylmercuric chloride and phenylmercuric acetate (Bizily et al. 2000). Plants such as *Arabidopsis* with little Se tolerance do not possess genes encoding functional selenocysteine methyltransferase gene (SMT). Therefore, Se volatilization has been enhanced in *A. thaliana* and *B. juncea* after overexpressing with SMT gene of Se hyperaccumulator *Astragalus bisulcatus* (LeDuc et al. 2004).

In aquatic macrophyte *Azolla filiculoides*, a cDNA responsible for synthesis of type 2 metallothionein (named as AzMT2) was isolated and found that addition of Cu, Cd, Zn had induced AzMT2 RNA expression (Fumbarov et al. 2005). Nandakumar et al. (2005) has documented *Agrobacterium tumefaciens*-mediated model transformation system to introduce responsible genes for phytoremediation in wetland macrophyte *Typha latifolia*. However, there are still some social as well as legal objections in the field application of transgenic organisms. It is expected that spectacular development of genetic engineering with increased efficiency of transgenic plants to remediate contaminated soil, sediment and water may change the adverse public opinion.

14.6 Limitations of Using Aquatic Macrophyte in Phytoremediation

On contrary to the all advantages of using aquatic plants for phytoremediation, some limitations or constraints are also reported. Longer time duration for remediation of contaminated site is considered as a limitation of this process. Seasonal growth of various macrophytes is one of the constraints of using these plants for phytoremediation which gives a limited phytoremediation interval (Jain et al. 1990). Another constraint is maintaining the physicochemical parameters of the medium, for example, pH of the medium, because they affect the metal/metalloid uptake capacity of the plant. Disposal of biomass is also considered as constraint by some researcher but phytomining is one of the options to deal with this constraint (Rai 2009a). Another limitation of this technology is the risk of entry of contaminant into the food chain due to lack of proper care or mismanagement (Ali et al. 2013).

14.7 Conclusion and Future Perspectives

This review outlined the current research on the phytoremediation potential as well as cellular mechanism of uptake, detoxification of some of the potential native wetland macrophytes of Assam, India. Many of these plant species have worldwide distribution which indicates their global interest in the research area of phytoremediation. Though submerged and emergent macrophytes have the ability to uptake metals/metalloids from different wastewaters, free floating macrophytes are considered as more suitable for this purpose due to their specific morphology. It is also reported that biological invasions into an ecosystem can affect the structure and function of the ecosystem (Pimentel et al. 2001). Use of native macrophytes in the purpose of metal/metalloid containing wastewater remediation maintains the ecological balance. So, more research is needed understand the wetland vegetation and their role in phytoremediation. As this research area is multidisciplinary, an integrated scientific knowledge will enable this phytotechnology more suitable for field applicability.

Some researchers have suggested the application of genetically modified aquatic plants for metal/metalloid phytoremediation in future (Parmar and Singh 2015; Rahman et al. 2016). Further biotechnological research on this approach is on progress to identify genes for metal/metalloid hyperaccumulation. In the future research, further advancement this biotechnological approach of identifying hyperaccumulating genes and combining the desirable traits will enable this technology as a new frontier in this scientific research area to combat environmental pollution.

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Chapter 15
Mitigating the Risk of Arsenic and Fluoride Contamination of Groundwater Through a Multi-model Framework of Statistical Assessment and Natural Remediation Techniques

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15.1 Introduction

Arsenic, believed to be released in the groundwater through oxidation of pyrite enriched with Arsenic under fluctuating oxicgroundwater levels, has been a significant problem in the Ganga Brahmaputra Plains (GBP) (Nickson et al. 1998; Chowdhury et al. 1999). While extensive studies have been done focussing on Arsenic contamination of GBP, the inability to link it with a single recurrent phenomenon makes its occurrence and removal a challenge to deal at a global scale under different aquifer conditions (Polya and Charlet 2009; Thakur et al. 2011; Kumar et al. 2010; Das et al. 2015; Kumar et al. 2016; Patel et al. 2019a, b). Under such situation the process of remediation becomes bit easier to tackle as compared to prediction of Arsenic, as evident by the high proportion of published scientific literature and the problem becomes region specific with no two hypotheses supporting each other (Winkel et al. 2011; Neumann et al. 2010; Burgess et al. 2010; Johnston et al. 2010; Langner et al. 2012). Few outlying kinds of literature like Goswami et al. (2015) have speculated Arsenic to be brought closer to human contact in suspended form through volcanic eruptions. Nagarnaika et al. (2012) observed that Inorganic Arsenic in Arsenite form is more toxic owing to its ability to form compounds with a sulfhydryl group, which increases the total time of stay of Arsenic in the suspended form. The WHO has recommended the Arsenic concentration to not reach beyond 10 ppb, however, Assam (India) has places where

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Arsenic reaches beyond 300 ppb (The North Eastern Regional Institute of Water and Land Management 2007). In districts such as Jorhat, Golaghat, and Lakhimpur the Arsenic concentration has reached beyond 490 ppb (Chakraborti et al. 2004).

Although Arsenic poisoning is dangerous, its spread is mostly restricted to Himalayan River basins. However, Fluoride with less comparative carcinogenic impacts is a widespread problem in India (Raj and Shaji 2016; Whitford 1996). The co-occurrence of Arsenic and Fluoride is another challenge that has attracted interest among the research community of late. As compared to Arsenic, the causes of Fluoride occurrence are relatively few. The characteristics of Fluoride are highly influenced by Fluorine which is the lightest and most electronegative member of the halogen family (Hodge and Smith 1965). The strong electronegative character of fluorine makes it extremely vulnerable to react with other elements to form fluoride compounds. Minerals like fluorite, fluorapatite, micas, amphiboles, topaz, and rock phosphates exist as fluoride compounds in groundwater (Hussain et al. 2004). According to Kateja and Joshi (2017) the bedrock containing fluoride in the form of cryolite and fluoroapatite extends from Gujarat to Haryana.

To predict the concentration of Arsenic and Fluoride generally, two types of modeling techniques are applied by the researchers. One technique is based on spatial interpolating and predicting values within the ensemble of study boundary and thereby introducing slight dilution to the result accuracy. The other technique involves using machine learning algorithms based on the input of predictor variables which often achieves higher accuracy during validation (Podgorski et al. 2018; Ayotte et al. 2009). The advantage of using such models is to be able to do a global assessment of contamination with the help of known influencing variables in a short time (Amini et al. 2008; Winkel et al. 2011; Rodríguez-Lado et al. 2013; Podgorski et al. 2017; Jha et al. 2010; Ayotte et al. 2017). A spatial prediction of Arsenic and Fluoride will enable zoning of regions based on concentration values, and hence we can suggest suitable remediation technique for different spatial concentration zones. Remediation of Arsenic and Fluoride through a cost effective, sustainable method without inducing toxicity is another challenge (Tsai et al. 2009; Wang and Mulligan 2006; Ma et al. 2001; Mench et al. 2006). Substances such as biochar, iron oxide nano-particles, fly ash, micro-organisms, alumina, activated carbon etc. have been extensively used for effectively adsorbing Arsenic and Fluoride across the globe (Madejón and Lepp 2007; Sharma and Sohn 2009; Saunders et al. 2008). Few remediation studies involve using ores like siderite and haematite in removing elements like Arsenic (Guo et al. 2007). Many literatures have pointed that removal of elements like Arsenic are highly dependent on pH. pH again is a function of aquifer characteristics, and therefore no same technique applied to two different geographically distanced groundwater samples can earn the same results (Baek et al. 2009; Mondal et al. 2006). Therefore assessment of contamination and it's environment based on statistical models should be the first step before proceeding with the process of removal using low cost adsorbent materials.

15.2 Prevalence of Fluoride Occurrence Across the Globe and Its Identified Causes

Fluorosis has been a significant health risk throughout China. In 2010 there were 41.76 million reported cases of fluorosis. 58.2% of the cases included exposure to extremely high concentration of fluoride (Ministry of Health of China). Fluoride concentration in Southwest China exceeds 4 mg/L which according to China's standard is classified as dangerously high (Chen et al. 2012). Concerns of fluoride contamination also exist in Russia. In Russia, a detailed study by the Russian Academy of Sciences has concluded that high fluoride concentration in drinking water may induce endoplasmic reticulum stress. This plays a role in making the body insulin resistant and aiding diabetes mellitus of type II. The secondary effects include obesity in the patient (Agalakova and Gusev 2012; Balasubramanyam et al. 2012). The concentration of fluoride in European countries is less compared to Asian countries. According to The Scientific Committee on Health and Environmental Risks (SCHER) Ireland, Spain, Germany, and the UK have fluoride in the range of 0.2–1.2 mg/L. In Finland however, the level of fluoride concentration reaches to 3 mg/L. In America, around 41% of the children have symptoms of various degree of dental fluorosis, with fluoride concentration reaching to an average of 1 mg/L (Peckham and Awofeso 2014). Till 1950, America followed a policy of artificially adding a dose of 1 mg/L of fluoride in drinking water with an understanding that this concentration of fluoride will help in the development of teeth and bones. However, this methodology was criticized and was made redundant after 1950 (Sutton 1959). In Africa, high fluoride concentration in the range of 2–9 mg/L is observed in drinking waters of Tanzania, Kenya, and Ethiopia. Fluoride concentration in South Africa at places reaches beyond 40 mg/L. Similarly, Malawi has places where fluoride has reached to 10 mg/L. Algeria, Sudan, Ghana, and Nigeria have fluoride concentration in the range of 1–2 mg/L (Malago et al. 2017; Das et al. 2016, 2017). Before adopting the WHO's standard of fluoride in drinking water as 1.5 mg/L, many African countries like Tanzania had a standard of 8 mg/L for fluoride (Ministry of Water and Power, Tanzania 1974). The concentration of fluoride in waters of Tokyo Bay has been found in the range of 0.15–1.07 mg/L (Kitano and Furukawa 1972). Studies have found fluoride to be in the range of 0.8–1.4 mg/L in the drinking water of Japan and the prevalence of dental fluorosis in the Japanese children between 10 and 12 years of age (Akihito et al. 2007).

Within India, about 15 states have fluoride concentration above 1.5 mg/L. According to Susheela (2001) around 62 million Indians suffer from fluorosis of some kind. Rajasthan, Gujarat and Andhra Pradesh are worst affected by fluoride contamination of groundwater. In Tamil Nadu about 121 blocks in 19 districts have fluoride concentration exceeding the permissible limit (National Institute of Hydrology, Roorkee). However high population density states like Uttar Pradesh and Bihar have low risks of fluoride contamination.

The occurrence of fluoride is due to the presence of certain rocks like cryolite (Na_3AlF_6), hornblende ($(Ca, Na)_2(Mg, F, Al)_5(Si, Al)_8O_{22}(OH)_2$), apatite ($(Ca_5PO_4)_3F$), fluorspar ($CaF_2$), etc. in the groundwater system. The fluoride concentration in the igneous rocks of mafic origin has been observed to be reaching a maximum value of 100 ppm while rocks of alkaline origin have reported fluoride concentration to be around 1000 ppm (Fawell et al. 2006). The high concentration of fluoride is because of the process of magmatic differentiation that happens in the case of igneous rocks (Perel'man and Levinson 1977; Frencken 1992). Fluoride has been reported to be 200 ppm in limestone formation and 1000 ppm in the shale formation. One of the main factor responsible for fluoride concentration in groundwater is carbon dioxide (CO_2). The CO_2 enriched air when it comes in contact with rainwater leads to the formation of acidic conditions. This acidified water when it reaches the groundwater system aids in the release of hydrogen ions. The hydrogen ions are responsible for bringing the weathering of the silicate rocks.

$$2NaAlSi_3O_8 + 2H^+ + 9H_2O \rightarrow Al_2Si_2O_5(OH)_4 + 4H_4SiO_4 + 2Na^+ \qquad (15.1)$$

During the natural course of chemical weathering, the fluoride concentration in groundwater is controlled by Ca^{2+} ion activity. Low precipitation coupled with insignificant recharge, followed by high evapotranspiration makes the groundwater condition to be alkaline thereby affecting the solubility and activity of Ca^{2+} ions. An increase in Na^+/Ca^{2+} ratio triggers excessive fluoride concentration in groundwater system (Ramasesha et al. 2002).

$$CaCO_3 + 2F^- + H^+ \rightarrow CaF_2 + \text{Bi-carbonate}. \qquad (15.2)$$

$$CaF_2 + H_2O \rightarrow Ca^{2+} + 2F^- \qquad (15.3)$$

More than the fluoride containing mineral rock, the concentration of fluoride in groundwater depends on the dissolution activity of fluoride. Factors such as precipitation, dissolution, rock-water interactions, temperature, and pressure play a very significant role (Saxena and Ahmed 2003). If the conditions are acidic, adsorption of fluoride on the surface of clay or silicates take place and when the conditions become alkaline fluoride becomes available for mixing with groundwater. Also, more residence time of water in the groundwater system enables more time for rock-water interactions and hence more chances for fluoride exposure. Presence of bicarbonates or carbonates of sodium also aids in dissociation of fluoride from fluoride-containing mineral compounds in groundwater.

$$CaF_2 + 2NaHCO_3 \rightarrow CaCO_3 + 2Na^+ + 2F^- + H_2O + CO_2 \qquad (15.4)$$

$$CaF_2 + Na_2CO_3 \rightarrow CaCO_3 + 2Na^+ + 2F^- \qquad (15.5)$$

15.3 Prevalence of Arsenic Occurrence Across the Globe and Its Identified Causes

According to WHO, 2011 Arsenic (As) in the atmosphere of rural regions of the world range from 0.02 to 4 ng/m^3. While the air in the urban areas has a concentration of As ranging between 3 and 200 ng/m^3. According to Ball et al. (1983) concentration of Arsenic near industries reaches beyond 1000 ng/m^3. The concentration of As in water usually ranges between 1 and 2 µg/L. According to USNRC, 1999 concentration of As in sediments usually ranges between 5 and 3000 mg/kg. According to Health and Welfare, Canada, 1983 marine fish has As concentration ranging between 0.4 and 118 mg/kg. The mean daily intake of As in an adult is ranging between 16.7 and 129 µg (Hazell 1985).

Across the globe, Bangladesh is perhaps the worst affected country by Arsenic contamination. Around 50% of the population that depends on hand pumps for drinking needs in Bangladesh have reported an As the concentration of more than 50 µg/L which is above the maximum permissible limit suggested by WHO (Josephson 2002). In China it has been estimated that around 5.6 million people are affected by an As the concentration of more than 50 µg/L and around 14.7 million people are exposed to As concentration of more than 10 µg/L (Sun et al. 2001). In Greece, arsenic concentration varies between 30 and 4500 µg/L in areas having geothermal water. However when geological conditions change to alluvium the As concentration varies between 15 and 100 µg/L. Areas which are affected by industrial activities have reported an As concentration of 20–60 µg/L (Katsoyiannis et al. 2014). In Cambodia, the maximum As concentration found is 1300 µg/L. While in Argentina, the maximum concentration level (MCL) has been observed to be 10,000 µg/L. In Chile, the MCL is 1000 µg/L (Nordstrom 2002; Jakaria and Deeble 2008). Countries like Germany, Finland, Hungary and Spain have MCL of 150, 1040, 800 and 615 µg/L respectively much above the maximum prescribed limit of 50 µg/L (Schwenzer et al. 2001; Varsanyi and Kovacs 2006; Svensson et al. 2010). In India, West Bengal and Assam are the two most affected districts concerning As contamination of groundwater (Kumar et al. 2017). In West Bengal, the MCL has been observed to be 3200 µg/L and around 6 million people are at potential risk of As poisoning (Jakaria and Deeble 2008; Nordstrom 2002).

There exist various mechanisms that can trigger a release of Arsenic from sediment form to become an active component in groundwater. The exact reasons for arsenic mobility are still less researched, however many researchers have proposed various theories through which introduction of Arsenic in groundwater can be explained. One such theory proposes that the Arsenic which has been reduced by bacteria in delta regions may get oxidized by an electron accepting species like dissolved oxygen or nitrate under acidic conditions (Mallick and Rajagopal 1996; Mandal et al. 1998; Chowdhury et al. 1999). Few studies have tried to establish manganese ion as the electron accepting species under alkaline hydro-chemical conditions. The second theory suggests that phosphate present in fertilizer when seeps into the groundwater system can remove Arsenic from sediment state through the competitive exchange (Dowling et al. 2002). Another theory suggests that Iron Oxy hydroxides (FeOOH) adsorbs Arsenic on its surface and finally gets deposited along the basins (Moi and Wai 1994; Nickson et al. 1998; Cummings et al 1999; McArthur et al 2001). The possible source of FeOOH being released into the groundwater could be bacteria led dissolution (McArthur et al 2001; Cummings et al 1999).

$$\begin{aligned} FeAsS + 13Fe^{3+} + 8H_2O \rightarrow 14Fe^{2+} + SO_4^{2-} + 13H^+ \\ + H_3AsO_4 \quad (\text{oxidation of Pyrite}) \end{aligned} \tag{15.6}$$

$$8FeOOH - As + CH_3COOH + 14H_2CO_3 \rightarrow 8Fe^{2+} + As + 16HCO_3^- + 12H_2O \tag{15.7}$$

15.4 Arsenic Speciation and Its Toxicity

As already discussed Arsenite (As^{3+}) is more toxic than Arsenate (As^{5+}) because of its higher residence time in the human environment. Penrose (1974) has given an order of Arsenic species in descending order of toxicity $R_3As > As_2O_3$(**As III**) $> (RAsO)_n > As_2O_5$(**As V**)$> (R_nAsO(OH)_{3-n})$ $(n = 1, 2) > R_4As^+$(**As 0**), where R = H, Methyl group, Cl etc. The reduction of As (V) to As (III) is carried out by bacteria *Pseudomonas fluorescens* under aerobic conditions in the aquatic environment. The bacteria Anabaena oscillaroides have also reported the reduction of Arsenate to Arsenite in the Waikato river of New Zealand (Freeman 1985). The bacteria *Scopulariopsis brevicaulis* transforms Arsenic from oxide form to methyl form (Challenger 1945). It is believed that phosphate may suppress Me_3As (Me = methyl group) evolution by hindering the methylation process (Cox and Alexander 1973). As (III) and As (V) differ in their ability to move in pore water due to the difference in their adsorption characteristics. Pierce and Moore (1982) determined the adsorption isotherms on iron hydroxides and concluded that though adsorption of both species increases with concentration As (V) adsorbs more as compared to As (III) under pH range of 4–10. Gulen's et al. (1979) studied the mobility of Arsenic species in groundwater in a confined aquifer system. It was concluded that the adsorption of Arsenic species in groundwater is dependent on the oxidation state of Arsenic, redox environment and the pH of the groundwater system. Also, it was found that As (III) adsorbs on the surface of the sand system more faster than As (V) (about 5–6 times). Even the quantity adsorbed on the sand surface is more of As (III) than As (V) (about eight times) under oxidizing conditions. However, under reducing condition, the adsorption rate of both species become similar. This may happen because of weaker interaction between As (III) and Fe (III) under reducing conditions. It was also observed that with an increase in pH the mobility of As (V) increases. Cherry et al. (1979) used this mechanism to predict the redox state of the groundwater system.

15.5 Fluoride Metabolism in Aquatic Ecosystem and Its Toxicity

The two forms of Fluoride viz., NaF (Sodium fluoride) and Na_2PO_3F (Disodium mono fluoro-phosphate) are considered critical concerning their effect on humans (Whitford et al. 1983). For aquatic ecosystems to Fluoride toxicity carries severe implications (Camargo 2003). According to Smith and Woodson (1965) there is 58–82% inhibition in the population of *Chlorella pyrenoidosa* when Fluoride concentration reaches to 190 mg/L while the population of *Ankistrodesmus braunii* remains unaffected till the concentration of Fluoride reaches 50 mg/L (Hekman et al. 1984). Interestingly the population of *Chaetoceros gracilis* gets enhanced by 70% when the Fluoride concentration goes to 200 mg/L (Antia and Klut 1981). The threat of bio-accumulation of Fluoride exists in all the invertebrates aquatic life. Fishes carry all the possibility of collecting Fluoride in their body in a concentration above the permissible levels (Neuhold and Sigler 1960). Several studies have speculated that the accumulation of Fluoride in the hard tissues is a defense mechanism put into the play by the living organisms (Kessabi 1984).

15.6 Role of Fossil Fuels in Aiding the Concentration of Arsenic

Arsenic is found naturally in bituminous coal having a mean concentration of 150 ppm (Filby et al. 1981). Coal produces a considerable amount of fly ash upon combustion. Arsenic has been found to enrich on the surface of fly ash particles due to condensation of volatile Arsenic species. Breslin and Duedall (1983) found that Arsenite and Arsenate leach from a different variety of fly ash. Shale oil, which is widely used as a fossil fuel has a mean Arsenic concentration of 20 ppm. The As concentration is shale oil is mostly due to the presence of pyrite (Schraufnagle 1983). Therefore the rainwater that comes as a result of mixing with combustion products of coal and shale oil is a leading cause of concern to environmentalists.

15.7 Other Anthropogenic Contaminants of Groundwater Impacting Arsenic and Fluoride Chemistry

In northern China, the nitrate concentration has reached beyond 50 mg/l due to excessive usage of fertilizers. In vegetable producing regions the concentration of nitrate has reached 300 mg/L. In all these places nitrogen-based fertilizers were used in excessive dosages of 500–1900 kg/ha (Zhang et al. 1996). In Denmark, the drinking water supply is sourced from groundwater. Around 15% of the total area of the country has been classified as vulnerable for nitrate abstraction in groundwater (Hansen and Thorling 2008). Application of water high in Residual Soluble Carbonate (RSC) and Sodium Absorption Ratio (SAR) leads to a loss in productivity of soil (Goyal and Sharma 2015). A study by Joshi and Dhir 1989 concluded that application of water with high RSC of 15 MeL^{-1} for 8–10 years could make the soil completely barren. Morss (1927) concluded that temperature, nature of the soil and groundwater table has a profound impact in making a soil alkaline or saline. According to FAO (1973), in arid and semi-arid regions, the potential risk of sodium ion accumulation in the soil system is very high. Sometimes anaerobic bacteria, bring about a change in the soil system to make them alkaline (Richard 1954). When chemical fertilizers, used for increasing the productivity of agriculture, leaches into the groundwater system it degrades the quality of groundwater. Nitrate contamination is a direct indicator of this kind of pollution. Not only to the humans, but increased nitrate concentration also pose a direct threat to livestock (Munoth et al. 2015). It is a very well known fact that the economy of people living in rural regions depend heavily on livestock. Due to nitrate poisoning poor production of milk in lactating cows has been observed (Munoth et al 2015).

15.8 Impact on Health Due to Groundwater Contamination in India

In India, the chronic exposure of Arsenic in the people of Assam could have devastating long term effects. Immediate symptoms of Arsenic poisoning include abdominal pain and vomiting. The problem with identifying the effect of Arsenic in humans is that it varies with the individual and with age. Therefore there is no universally accepted definition of diseases caused by Arsenic (Bordoloi 2012). Also, there exists no method to differentiate a case of cancer caused by Arsenic or by some other factor. However, there exists a strong correlation between skin cancer and skin thickening (hyperkeratosis) concerning Arsenic concentration in drinking water. The human body directly absorbs soluble fluorides. According to WHO the concentration of soluble fluorides can reach up to 0.4 mg/L in 30 min. The human body, depending upon the health may take few hours to years to excrete this amount of fluoride. A single dosage of 5–10 mg/kg of body weight can cause acute toxic effects while a dose of 16 mg/kg can cause death (WHO 1984). In Rajasthan alone around 16,560 villages have fluoride concentration above 1.5 ppm, much above the suggested limit of 1.5 ppm by BIS 10500. Also there are 5,461 villages in Rajasthan with fluoride exceeding 3 ppm (Hussain et al. 2012; Public Health Engineering Department, Rajasthan 1991). A concentration of fluoride above 3 ppm can cause Osteoporosis (Hussain et al. 2004) (Tables 15.1, 15.2 and 15.3).

Table 15.1 Fluoride concentration across various states in India

State	Min. fluoride (mg/L)	Max. fluoride (mg/L)	Number of districts affected/total number of districts
Andhra Pradesh	0.4	29	16/23
Assam	1.6	23.4	02/23
Bihar	0.2	8.32	06/41
Chhattisgarh	**N.A.**	**N.A.**	**N.A.**
Delhi	0.2	32	04/09
Gujarat	1.5	18	18/19
Haryana	0.2	48.32	12/19
Jammu & Kashmir	0.5	4.21	01/14
Jharkhand	0.5	14.32	N.A.
Kerala	0.2	5.4	03/14
Madhya Pradesh	1.5	4.2	16/48
Maharashtra	0.11	10	10/32
Orissa	0.6	9.2	18/32
Punjab	0.4	42.0	14/17
Uttar Pradesh	0.2	25.0	18/83
West Bengal	1.1	14.7	04/18
Tamil Nadu	0.1	7.0	08/29

Source Arfin and Waghmare (2015)

Table 15.2 Effect of fluoride concentration on the human body

Serial no.	The concentration of fluoride in drinking water	Effect
1	About 1 mg/L	Dental carriers reduce in size
2	Between 1 and 3 mg/L	Discoloration of teeth (dental fluorosis)
3	Between 3 and 4 mg/L	Brittle bones
4	Between 4 and 6 mg/L	Crippling of knees and hip bones
5	8 mg/L	10% osteoporosis
6	100 mg/L	Growth retardation
7	2.5–5 g direct dose	Death

15.9 Regulation and Management of Groundwater in India

In 2005, the Ministry of Water Resources of India with the help of various agencies prepared a “Model Bill,” that could be enacted by various states for managing and protecting their groundwater resources. It argued in favour of setting up a state level

Table 15.3 Arsenic removal technologies for As contaminated groundwater

Device	Principal	Filter	Performance
Alcans—AAFS 50	Adsorption	Activated alumina + AAFS 50	The performance of the device has not been rated high despite the device being user-friendly
BOR (bucket of resins)—water system	Ion exchange	Resins	Inconsistent and performance below the standards
GFH (granular ferric hydroxide)—water system	Adsorption	GFH	Better performance than other devices. Operational cost is also cheap
Water purification plant, Durgapur	Adsorption	Activated alumina (AS-37)	Satisfactory performance

Source Central Groundwater Board of India

groundwater authority. One of the primary function of this state-level authority would be to grant a permit to a person or community for digging a well for groundwater extraction for personal or community use. It would be mandatory and binding on the citizen of that state to have acquired a permit before using the groundwater resource. Permit will be issued by the authority considering the type of usage, groundwater quality and availability at that place etc. The bill called for a state wide registration of existing groundwater users. For registration, it would be made mandatory for the existing groundwater users to furnish the details of well's location, type of extraction machine installed, the duration for which water was extracted and purpose for which it was used. It even called for the registration of well-digging groups and their machinery. The bill, if enacted by any state, would give the power to the state authority to carry out the inspection of groundwater well of any private user and apply the Code of Criminal Procedure, 1973 (2 of 1974), Section 93 to penalize the user with a trial of six months. The provisions of the bill dictate that no affected person can demand any compensation of any kind from the state government. Obviously, for a country like India, the provisions look a bit harsh, but at the same time, there exists no other way of preventing millions of people from consuming the fluoride or arsenic-contaminated water.

15.10 Statistical Models that Could Be Used for Assessing the Arsenic and Fluoride Concentration

A Random Forest (RS), based model of classification, has been a conventional technique that is being used by researchers in accurately predicting the concentration of Fluoride throughout India (Podgorski et al. 2018). Earlier techniques like logistic regression to have been used for classifying samples based on binary class outputs (Ayotte et al. 2009). The application of machine learning based algorithms have increased in zoning and classifying groundwater quality. Therefore a review is required about what all methods can be used in the field of Arsenic and Fluoride prediction. More importantly, it should be understood about what all methods have already been applied in the field of hydro-chemistry. Artificial Neural Network (ANN) helps in fitting an accurate model for prediction of groundwater quality parameters. Kheradpishehet al. (2014) applied ANN modeling in predicting four parameters namely NO_3^{2-}, E_C, Cl, and SO_4^{2-} using four different training algorithms. Sarkar and Pandey (2015) used ANN based modeling to predict dissolved oxygen (DO) in the Yamuna river near Mathura region. In their study, the level of dissolved oxygen in the river acted as an indirect indicator of contamination due to humans. Waghet al. (2016) studied the suitability of groundwater for irrigation purpose through an ANN-based prediction modeling system with data being collected from fifty locations. Nasr and Zahran (2014) predicted groundwater salinity using a feedforward propagation method in ANN with pH as an input. Gholami et al. (2015) used ANN in studying the impact of five different parameters namely transmissivity, water table depth, elevation, distance from contamination centers and population on the overall quality of groundwater. Similarly Kuo et al. (2004) studied three different ANN models based on backward propagation method in order to evaluate their respective learning performance. One key finding of their research was that the number of hidden layers in the architecture of ANN does not play any significant role in the performance of the model if only calibration and testing are concerned. Lohani and Krishan (2015) adopted a feed-forward neural network and tried different combinations of training algorithms to predict groundwater level for their study area in Punjab, India. Isazadeh et al. (2017) used ANN as one of the tools to estimate E_c, SO_4^{2-} and Na^+ ion concentration using different parameters. The study suggested that both Artificial Neural Network (ANN) as well as the Support Vector Machine (SVM) based model yield excellent results. The study also tried establishing the importance of various auxiliary parameters considered as an input for the model. Similarly Krishna et al. (2007) used ANN as a tool to predict the level of groundwater for their study area in coastal India. Rao and Swarnalatha (2013) applied backward feed propagation algorithm to train their ANN model in order to predict water pollution and concluded that this algorithm gave good results. Similarly Zaheerand Bai (2003) concluded that backward feed propagation algorithm though complex and time consuming could achieve promising accuracy. Lallahem and Hani (2017) used the same training algorithm to establish a relationship between groundwater abstraction and water quality determinants in the lower Seybouse river and got a coefficient of correlation of more than 95%. Dawood et al. (2016) used the backward propagation method to model river water quality in Shatt Al Arab basin and got good results in prediction. In choosing a hidden layer architecture network trial and error were performed with different combinations of the layer system. Therefore all these techniques could also be studied for useful mapping and predicting Arsenic and Fluoride concentration values.

15.11 Remediation Techniques Used for Sustainable Removal of Arsenic and Fluoride

Studies have indicated that Natural Attenuation can be an active process of removal of Arsenic from the contaminated soil (Wang and Mulligan 2006). Similarly a study by Ma et al. (2001) shows that *Brake ferns* growing in wood preservation sites have the potential to remove Arsenic from chromate copper Arsenate. According to Cundy et al. (2008) iron-based technologies have proved to be another effective method for removal of Arsenic from groundwater. Mohapatra et al. (2010) have used the same concept of using nano-particles as adsorbents, to remove fluoride using goethite powder. However Palahouane et al. (2015) argue that a low-cost electro-coagulation technique could be a better way to remove Fluoride photo-voltaic wastewater. While Turner et al. (2008) found reactive calcite barrier to be an effective method of Fluoride removal. Solangi et al. (2009) studied the behavior of amberlite resin in removing fluoride and found that when it is modified using thiourea binding sites the adsorption capacity reached is 3.286 mmol/g. Cherukumilli et al. (2017) studied the efficiency of bauxite in removing fluoride from the groundwater. Rehman et al. (2015) have already studied the use of magnetically doped ferrites in removing Fluoride. The adsorbent material could be anything that has high surface area or with pores to facilitate the entrapping of contaminants like Arsenic and Fluoride.

15.12 Conclusion

Remediation of groundwater is more difficult compared to a surface water source, and therefore the impacts are long term. As, the medical cost to deal with a challenge like skin or urinary bladder cancer could be unaffordable by the population which has the highest risks of exposure. Therefore any study with regards to finding the risk and exposure of arsenic and fluoride contamination should also include social parameters impacting the local society at large. The process of Health Risk Assessment as suggested by the 1998 guidelines of United States Environmental Protection Agency (USEPA) can help us in identifying the adverse health risks due to these types of contaminants. Through this, not only the identification and assessment of risk can be done, but also the characterization of risk could also be understood. While people in arid regions of India like Rajasthan run the risk of developing bone deformities due to excessive fluoride in drinking water, the people in Assam are at high risks of developing skin cancers and other diseases due to chronic exposure to Arsenic. For India, a death due to fluoride contamination in Rajasthan or because of lung impairment or skin cancer in Assam carry equal magnitude of loss.

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Chapter 16
Water Management: Effects on Human Health and Nutrition

G. Jacks and D. S. C. Thambi

16.1 Introduction

A major portion of human water use is for food production. The use of water in households is around 50–200 L/day/person, while the water for food production varies from 2000 to 5500 L/day/person. Thus approximately 75% of total water use is for food production. In India more than 80% of total water is used for irrigation and 92% of the groundwater portion. Water management has implications for groundwater chemistry as well as for crop yield and crop quality. There may even be health implications involved. The objective of this review is to illustrate these aspects.

India was a net importer of food grains at independence in 1947. The so called "green revolution" in the 1960s and onwards has made the country self-sufficient in food. The factors behind this are irrigation, more high yielding seeds and access and affordability to inorganic fertilizers. Out of these factors irrigation was the most important initially. The first Prime Minister of India, Jawaharlal Nehru said that dams for irrigation are our new temples. In South and South East Asia a major part of food production is produced by irrigation. Globally, 40% of food is produced on 260 million ha irrigated land while 60% is produced on 1200 million ha rain-fed land. In India, about half of the net sown land is irrigated. The yield of cereals from irrigated land in developing countries is about 3 tons/ha or double that of the yield in rain-fed land. The effects of irrigation on the yield and quality of groundwater and crops are mediated via soil conditions. Irrigation has caused salinization mostly

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Table 16.1 Annual requirement of water in India from 2000 to 2050 in Billion m^3. Data from Central Water Commission (2014), Singh and Singh (2002)

Water use	2000	2025	2050
Irrigation	541	910	1072
Domestic	42	73	102
Industrial	8	22	63
Thermal power	2	15	130
Misc. uses	41	72	80
Total	634	1092	1447

Table 16.2 A comparison of relative water use by different sectors in India with water use globally, in China and the USA (FAO Aquastat 2018)

Water use	India (%)	Global (%)	China (%)	USA (%)
Agriculture	89	53	65	36
Industry	3	30	22	51
Domestic	8	17	13	13

in canal irrigated areas while alkalinisation is a more common problem in groundwater irrigated areas. The alkalinisation of soils is a major problem in semi-arid and arid areas in S and SE Asian countries, especially in India and Pakistan.

Water availability in India is facing a great challenge in the coming years. The total available water resources are 1869 km^3. Irrigation accounts for a large portion of that (Table 16.1).

Even though the total water need is projected to be below the available water resources it must be taken into account that the latter are not totally available as they may in part be present where they are not utilizable (Suhag 2016) (Table 16.2).

The comparison is difficult to interpret as it depends on many factors e.g. temperature and precipitation climate. India stands out with a large portion of water for food production. India is self-sufficient in food production while industrialised countries indirectly import large amounts water with their food import.

16.2 Main Health Effects

The introduction of irrigation and more use of groundwater have meant changes in water quality. There are two main parameters standing behind the major threats, fluoride and arsenic. There is a famous saying that goes as follows; “Too much and too little destroys everything”. This is highly true for fluoride which protects against caries at levels around 1 mg/L in drinking water but causes dental fluorosis at slightly higher levels. Fluorosis was first reported in 1937 from Nellore district in South India (Shortt et al. 1937). The presence of arsenic in groundwater came to light in the 1960s a couple of decades after the more intense use of groundwater was initiated (Chakraborti et al. 2016; Kumar et al. 2017). While too much is valid for fluoride and arsenic the opposite is true for zinc in the food produced, mirroring zinc deficiency in about half of the Indian agricultural soils (Cakmak 2009). This has weakened the immune response to infections notably in children.

The introduction of irrigation has greatly improved yields and removed a large part of the total crop-failure risk due to unexpected drought etc. This has been very important for farmers and the nutrition of the overall population. However, the groundwater situation is under stress and irrigation needs to be more efficient.

16.3 Effects of Irrigation on Water and Soil and Associated Health Threats

Canal irrigation covers 22.5 mha while groundwater irrigation is practised on 39.4 mha making India the foremost groundwater irrigating country in the world. A problem with canal irrigation is that poor drainage can cause rising groundwater levels and excess evaporation and salinization. This is seen in Uttar Pradesh, Gujarat, West Bengal and Punjab coming to about 7 mha in total. In groundwater irrigated land alkalinisation is a rather common effect. One of the effects of alkalinisation on groundwater is increasing levels of fluoride exceeding the permissible limit causing dental and skeletal fluorosis. Dental fluorosis is manifested in the malformation of tooth enamel, while skeletal fluorosis causes an imbalance between the bone degrading cells and the bone building ones resulting in excess bone accumulation in joints and the vertebra and calcification of ligaments (Kurdi 2016). Approximately 62 million people are exposed o excess fluoride in their drinking water (Susheela 1999; Arlappa et al. 2013). There is a good correlation between soil pH and fluoride concentration in groundwater (Das and Kumar 2015; Das et al. 2015, 2016) (Fig. 16.1).

Excess fluoride in groundwater is present in 20 out of the 29 states in India (Jacks 2016; Chakraborti et al. 2016; Mukherjee and Singh 2018) and is common

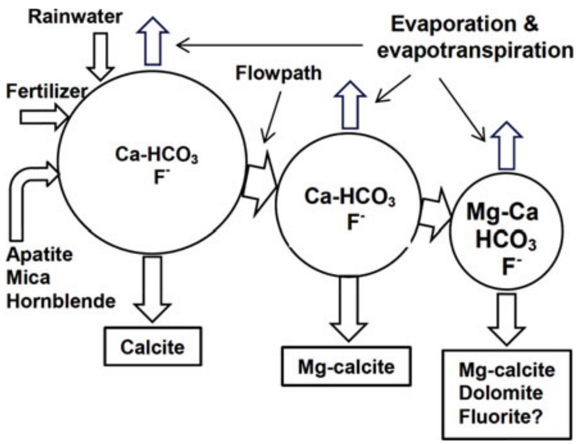

Fig. 16.1 Fluoride in groundwater and associated changes in groundwater chemistry along a slope in Tamil Nadu, South India (Jacks 2016)

also in Pakistan (Naseem et al. 2010) and Sri Lanka (Young et al. 2011). Sodic soils that often host high fluoride groundwater cover about 7 mha in India (CSSRI 2018). Fluorosis, possibly combined with molybdenosis (Agarwal 1975), secondary copper deficiency due to excess molybdenum intake, have been found in areas downstream of three large dam projects in southern India, the Nagarjuna Sagar dam in Andhra Pradesh, the Parambikulam-Aliyar dam on the border between Kerala and Tamil Nadu and the Hospet dam in Karnataka (Padaria et al. 2000; Singh 2002). Molybdenosis in cattle have been described from Punjab (Dhillon et al. 2009) were the soils are often alkaline promoting the mobilization of molybdenum.

Fluoride can be removed by filters. However, the handling of filters is a matter for women but they are often too burdened by other activities (Singh et al. 2005). Other measures to decrease the fluoride in groundwater are water harvesting and the treatment of soil alkalinity. The most common method for the latter is the application of gypsum. This has the advantage that it increases the intake of calcium deceasing the risk for dental fluorosis (Das 2017). Application of gypsum decreased the fluoride content in wells from 5 to 2–3 mg/L (Alveteg and Jönsson 1991). An extensive review of methods to decrease alkalinity of soils is given by Minhas and Sharma (2003). Water harvesting has been used in Andhra Pradesh to dilute the groundwater (Reddy and Raj 1997; Muralidharan et al. 2011). The incidence of fluorosis depends on the intake of calcium and vitamin D (Teotia et al. 1998; Patel et al. 2017).

A serious problem with arsenic poisoning was detected in India and Bangladesh in the 1960s (Chakraborti et al. 2016). Arsenic in groundwater is a global problem that has emerged in S and SE Asia during the last few decades due to an increased use of groundwater for drinking water. Arsenic is a carcinogenic, manifesting itself as skin pigmentation changes and skin lesions (WHO 2017). In Bangladesh the incidence of child mortality decreased rapidly after switching from ponds and surface water to groundwater wells but a backlash came about 10–15 years after in the form of arsenic poisoning. The groundwater has been extracted from sediments where ferric reduction conditions occurs (Bhattacharya et al. 1997). It turns out that sediments of Holocene Age, formed just after the Last Glacial Maximum (LGM) approximately 18,000 years ago when the rapidly-rising sea water levels caused wetlands to form, are organically rich and form reducing conditions with a reduction of ferric oxyhydroxides releasing adsorbed arsenic. Older, Pleistocene sediments formed before LGM when the sea water level sank, are oxidizing as they were exposed to erosion and re-sedimentation giving less possibility of organic matter accumulation (Jacks and Thambi 2017). It has been found that it is possible to identify low arsenic sediments by means of their color.

Hossain et al. (2014). Reddish, yellowish and whitish sediments have low arsenic groundwater while blackish, greyish sediments rich in organic matter carry groundwater with elevated arsenic concentrations (Fig. 16.2). The color tool was developed by the use of Munsell Color Chart and aimed to be used by well drillers (Hossain et al. 2014) supporting their decision where to site the well screen.

The risk for arsenic polluted groundwater is found in many river deltas in S and SE Asia. The problem has been seen in the Mekong and Red River deltas and is

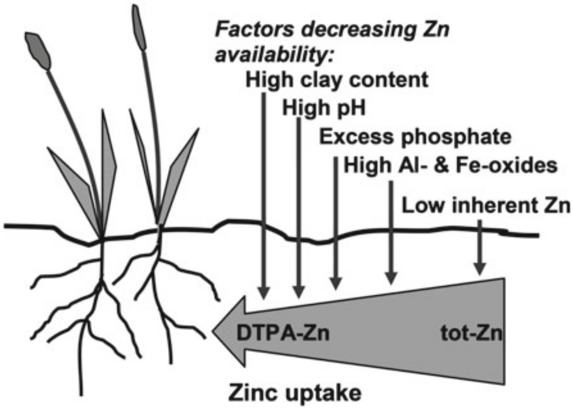

Fig. 16.2 Simplified four color assessment for the risk of arsenic in groundwater related to color of the sediments

likely to exist in the Irrawaddy delta although no data exists from there (Winkel et al. 2008). The existence of the problem is due to the sedimentological history. Only in part of the Red River Delta there is an anthropogenic component in the form of the use of sewage water for irrigation (Norrman et al. 2008). Most of the arsenic pollution in S and SE Asia is found in reducing aquifers. However, in Pakistan both excessive arsenic and fluoride levels may be found in the same aquifer under oxidizing conditions (Farooqi 2015; Patel 2019a, b).

Filters work but the use of filters is hampered by social reasons, women do not find time to handle them (Singh et al. 2005). Cross contamination does not seem to be a risk as long as the water extraction is for a community water supply. The horizontal hydraulic conductivity is several tenfolds higher than the vertical one (von Brömssen et al. 2008; Hoque et al. 2018). However, groundwater irrigation, common in Bangladesh is more of a risk as the large amounts of water withdrawn create strong local head differences in groundwater levels, which can promote vertical flow from reduced arseniferous sediments into more oxidized ones.

16.4 Effects on Yields and Quality of Crops

Zinc deficiency in soils and crops depends on a number of factors (Alloway 2009) but a majority of these factors are due to a high pH and alkalinisation that renders the zinc less plant available (Fig. 16.3). Zinc deficiency is common in many countries, in South Asia, about 50% of the soils in India and 70% of the soils in Pakistan are zinc deficient (Katyal and Sharma 1991; Gupta 2005; Alloway 2009; Cakmak 2009). In Iran and Turkey zinc deficient soils cover more than 50% of the cultivated areas (Alloway 2009). Micronutrient deficiency is a memory of the Green Revolution. When irrigation, high yielding grains and commercial fertilizers were introduced the micronutrients became gradually exhausted in soils (Gupta 2005). Especially wheat is sensitive to zinc deficiency (Kalayci et al. 1999; Kumar and

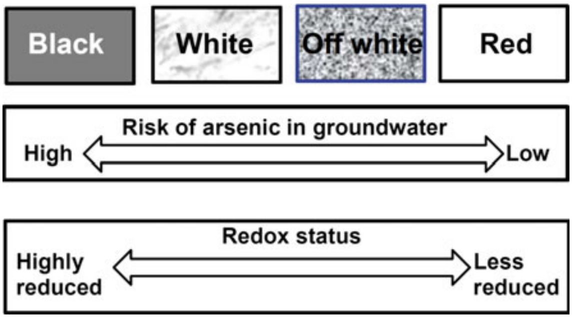

Fig. 16.3 Zinc availability in soil related to soil factors

Qureshi 2012) but also maize has suffered from soil sodicity derived zinc deficiency (Mehotra et al. 1986) Wheat is often grown on soils with a low plant availability of zinc. Zinc is an essential element and the main health effect of deficiency is on children and their immune response. Diarrhea is the most common affection and is responsible for elevated child mortality in many countries (Gårdestedt et al. 2009). Around 40% of the population in India and Pakistan are considered to have zinc deficiency (Akhtar 2013). Zinc deficiency in children below the age of 5 years is considered to be especially threatening. Kapil and Jain (2011) found that the serum zinc levels were below the deficiency limit in 36 to 51% of children in five studied states (Table 16.3). Infants, young children, pregnant and lactating women are considered to be vulnerable groups (Ray 2016). It is estimated that zinc deficiency accounts for 31.5% of child mortality due to diarrhea, malaria and pneumonia in Latin America, Africa and Asia (Walker et al. 2009). The investigation was carried out in a population which had a cereal based nutrient intake. The uptake of zinc in humans is less efficient from plant food than from food of animal origin (Brown et al. 2004).

Zinc deficiency in adults have been investigated in a rural area in Haryana and the result is similar to that found in children in Table 16.3 i.e. 45% were below RDA (Recommended Daily Allowance) (Pathak et al. 2003). Another investigation from Maharashtra revealed a considerable difference between rural and tribal women (Menon et al. 2011). In tribal women 58% were below RDA while the figure was only 39% for rural women.

Table 16.3 Serum zinc levels in children below the age of 5 years in five Indian states (Kapil and Jain 2011)

State	Serum zinc levels		
	<55 mg/dl	<60 mg/dl	<65 mg/dl
Gujarat	25.8	34.0	44.2
Karnataka	19.1	26.4	36.2
Madhya Pradesh	14.7	22.8	38.9
Orisa	34.2	43.2	51.3
Uttar Pradesh	29.4	40.2	48.1

Although low zinc in crops may be due to a low total zinc content in soils, the plant availability of zinc may also be affected by several other factors such as the pH/alkalinity of the soil, high clay content, excess phosphate and high concentrations of ferric oxyhydroxides, a strong adsorbent of zinc (Fig. 16.3) (Katyal and Sharma 1991; Sharma et al. 2006; Kumar and Babel 2011; Mahendra Kumar 2017). Since long back DTPA has been an extractant for assessing the availability of zinc in soils (Lindsay and Norwell 1978). The cited references all show a negative correlation to soil pH which mirrors the alkalinisation of soils. The Deccan trap area in Maharashtra and neighboring states form a zinc deficiency area which depends on the formation of phyllosilicates during weathering which makes zinc less available (Suhr et al. 2018) (Fig. 16.3).

The alkalinisation of soils in India comprises approximately 7 mha (CSSRI 2018). To increase the intake of zinc in the population food fortification or bio-fortification could be used. However, food fortification does not reach everybody, notably not those living mainly on their own products like farmers (Stein et al. 2007). Bio-fortification, by comparison, could be made in different ways, by introducing new seed varieties that are zinc efficient, adding zinc to fertilizers or by foliar application on the crops. Cakmak (2009) advocates for the enrichment of fertilizers with zinc as that might increase the yields.

Besides water, another exposure to arsenic is via rice, the main staple food in S and SE Asia. In the Bengal Delta, there are places where the intake via rice is of the same magnitude as via drinking water (Kippler et al. 2016; Sandhi et al. 2017). A new way of irrigation, intermittent irrigation, has been shown to lower the arsenic content in rice (Mukherjee et al. 2017). Intermittent irrigation (allowing the field to dry up between irrigations) saves about 40% of the water and the yield is often higher due to a better nitrogen economy with less denitrification. The reason for cultivating rice in permanently flooded fields is probably due to the fact that weeds become a lesser problem.

16.5 Soil Erosion and Water Management

A serious effect on the yields in agriculture, threatening the nutrition as a whole is soil erosion. In hilly regions, soil loss could amount to >20 ton/ha/year (Bhattacharya et al. 2015). The mean soil loss due to erosion is in the order of 16.4 ton/ha yearly equal to 1 mm of top soil (The Hindu 2010). Soil erosion is closely related to water management and agricultural practices. There are a number of measures that could prevent soil loss and accompanied loss of nutrients, such as contour farming, vegetative barriers and reduced tillage, the latter especially important in vertisols common in central India (Bhattacharya et al. 2015). The CSWCRTI (2011) advocates an increase of agroforestry to maintain the organic carbon stores in soil for a better nutrient retention and soil structure. Many of the measures taken to avoid excess surface runoff and soil erosion also lead to better water availability for crops and are also improving groundwater recharge.

16.6 Overexploitation of Groundwater

The common use of groundwater irrigation has caused a lowering of the groundwater table especially in Punjab (Kumar et al. 2007; Sarkar 2012) and in several states in peninsular India like Tamil Nadu (Chinnasamy and Agoramorthy 2015). Overexploitation in Punjab has led to a deterioration of the groundwater quality (Kumar et al. 2007), this in turn has increased tensions in the society with decreased equity in the society depending on the individual farmer´s access to, or lack, of groundwater (Sarkar 2012). The same author notes that interest in maintaining the canal system has decreased, which has further accelerated the lowering of the groundwater level.

Until recently, the assessment of recharge has been based on water table fluctuations. However, Sing and Singh (2002) have pointed out considerable discrepancies between different estimates. Satellite-based estimates with gravity measurements indicate a lowering of the groundwater storage by about 0.25 m over the period from 2002 to 2008 in Punjab, Haryana and Rajasthan (Rodell et al. 2009). It should be said that the estimates and the reasons for the changes, like climatic variations are still under debate e.g. Long et al. (2016). A summary of the groundwater situation is found in Suhag (2016) (Table 16.4).

To ensure the food production for a growing population water savings within agriculture are a must. However, there are several complicated issues involved in this fact. One covers is the energy subsidies used for pumping groundwater. Politicians are hesitant to use price as a factor to decrease groundwater pumping, as a major portion of the vote bank are farmers or people depending on agriculture. However, price as a measure to optimize the use of groundwater may be less effective in the coming years as solar pumps become more affordable for farmers. Another problem in this connection is the competition for water in drainage basins. Older irrigation schemes situated higher up in the drainage areas often have a priority to the water and are unwilling to release water to downstream farmers.

While a negative trend in groundwater levels has been observed for several decades (CGWB 2018) there are also positive indications due to active policy implementations seen in Andhra Pradesh from 2002 and onwards, for instance, where farmers have learned to irrigate “just enough” (Bhanja et al. 2017). Another

Table 16.4 Comparative status of the level of water development in India during the past 26 years (Suhag 2016)

Water development (%)	Status	% of districts 1995	% of districts 2004	% of districts 2009	% of districts 2011
0–70	Safe	92	79	72	71
70–90	Semi-critical	4	9	10	10
90–100	Critical	1	4	4	4
>100	Overexploited	3	14	14	15

Data derived from Central Ground Water Board of India of Andhra Pradesh's initiatives to decrease groundwater utilization that has shown some early results is described by Garduño et al. (2009).

Drip irrigation is being gradually introduced saving water and giving a better nutrient economy in agriculture. Indigenous drip irrigation equipment has now been produced that is affordable to farmers. As fertilizer could be added to the irrigation water, the roots will find both nutrients and water in the same environment, facilitating growth and increasing yields.

The practice of intermittent irrigation which is also called System for Rice Intensification (SRI) has already been touched upon. During a drought on Madagascar the Catholic priest Henri de Laulanie recorded the yields when the rice fields could not be kept flooded and he found that the yields were often better. He published his findings in 1983 and this was picked up by Norman Up hoff at Cornell University in USA. There have been quite a lot of controversies about the practice but today it is an established way of cultivating rice to produce "more rice with less water" (Thakur et al. 2009). The increases in yield are in the order of 20–40% (Sinha and Talati 2007) but yields up to 17–18 tons/ha have been recorded in India. The practice in India started early in Tamil Nadu where today approximately 50% of the rice planted area is under SRI. There is an updated homepage on the practice and results in India (SRI 2018).

The water foot prints for cultivating crops vary considerably (Table 16.5). It is evident that India uses considerably more water than other countries. This means that there is a considerable possibility to produce more with less water. Making irrigation more efficient is a challenge but the figures in the table show the potential for improvement.

The measures to decrease soil erosion mentioned above will often also increase the groundwater recharge. In peninsular India small dams, so-called tanks, have been a common way of arresting the surface runoff during the monsoon season. When deeper well became commonly used for groundwater irrigation there was a loss of interest in maintaining the tanks. This was observed in Karnataka, where a negative trend in tank irrigation was seen from 1915 to 1987 while groundwater irrigation has increased over the same period (Chandrakanth and Romm 1990). One of the reasons for the deterioration of the tanks was that the removal of the nutrient-rich sediments implies more work than the now affordable commercial fertilizers. In recent years there has been a renewed interest in restoring the tanks.

Table 16.5 Water use for crops in different countries in m^3/ton product (Chapagain and Hoekstra 2004; Mekonnen and Hoekstra 2011)

Country	Wheat	Rice	Barley	Maize
India	1654	2950	1966	1937
China	690	1275	848	801
Australia	1588	1022	1425	744
Egypt	930	1553	2208	1031
Russia	2378	2401	2359	1397
Brazil	1616	3032	1373	1180
USA	848	1275	702	489

The need for planning and monitoring is well described by Reddy (2015). However, organizing the restoration and the social implications regarding it has not been so straight forward (Aubriot and Prabhakar 2011). It is not uncommon that new institutions for the water management of the tanks have failed due to a lack of interest.

In urban areas rainwater harvesting has been made mandatory in many cities. It was first implemented in 2001 in Chennai, a megacity with a stressed water situation (CSE 2010).

16.7 Water Management and Vector Borne Diseases

This is in itself a very large subject which cannot be dealt with here. However, a few words could be said about it. The construction of dams and canals has promoted the spread of vector-borne diseases like malaria, dengue-fever and chikungunya-fever to mention a few. All major water projects e.g. construction of dams have implied an increased spread of vector borne diseases (Dhiman et al. 2010). After adaptation to the new environmental changes there has been a decrease in vector borne diseases, albeit it has taken time. In the case of canals and dams constructed in Punjab during the British colonial rule, it took several decades to come back the preconstruction levels of malaria (Baeza et al. 2013). Today we should be better prepared with a "tool box" of measures. One of the measures is to shift habitations away from breeding sites, in the case of malaria spread by *Anopheles culicifacies* the distance should be 3 km or more (Anushrita et al. 2015, 2017). The large variety of measures that are needed to decrease the frequency of vector borne diseases are illustrated by the vectors of dengue fever, *Aedes aegypti* and *Aedes albopictus,* who find breeding sites close to where people are living in water contained in coconut shells and similar vessels (Simard et al. 2005). A new challenge in this connection are the plans for interlinking rivers to the peninsular region Mirza et al (2008). It should be mentioned that Guinea worm has been eradicated by the construction of proper wells (Sharma 2000).

16.8 Summary

A major part of water use in S and SE Asia is for food production. Out of this water a major portion is applied by irrigation. The management of irrigation is important for groundwater chemistry as well for crop yields and quality. These facts are important for the health and nutrition of the population. Zinc deficiency is a common reason for child mortality due to an impaired immune response in cases of infections. Major problems are excess fluoride and arsenic in groundwater. Water use in relation to yield is crucial, especially in parts of India and Pakistan where groundwater levels are decreasing. While there is a great challenge to save water and increase production to feed a growing population there are some encouraging reports of policy changes that have given positive results. The intermittent irrigation of rice, a major staple food in S and SE Asia, saves approximately 40% of the water and often increases the yield. In addition, intermittent irrigation decreases the arsenic content in rice grain in areas with arsenic problems. Such areas are found in several river deltas in S and SE Asia. More efficient irrigation methods like drip irrigation are gradually being employed. Cultivation practices like contour farming, vegetative barriers, reduced tillage and agroforestry serves several purposes such a reducing soil erosion and increasing groundwater recharge.

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Chapter 17
Water Scarcity and Land Degradation Nexus in the Anthropocene: Reformations for Advanced Water Management as Per the Sustainable Development Goals

Santanu Mukherjee, Arbind Kumar Patel and Manish Kumar

17.1 Introduction

The geochronological time span of Holocene which had been existing since past eight to ten thousand years had experienced different anthropogenic activities involving geological and morphological changes. After observing significant contribution of a human being in changing the current global environment, the term "Anthropocene" was coined by Crutzen and Stoermer (2000) for explaining the human-induced changes in the current geological era. Steffen et al. (2011a, b) described the influences of humans, whom he designated as the driver of "sixth major extinction event" in altering the hydrological, biogeochemical and nutrient cycle through significant changes on land use management, flow paths of river and water vapor cycle. The several environmental changes like the global rise of temperature, ice cap melting, rising level of sea, biosphere, and lithosphere changes distinguish Anthropocene era from the stable era of Holocene. The challenges of Anthropocene were incubated from the inception of Industrial Revolution since when the boundaries of the earth system had started to gain their fast changes in land, air and water bodies which have now expanded from rural to urban sector, including the changes that have been made among water catchment systems. There are manifold human activities through which negative changes have incurred in the 20th and 21st century which include deforestation activities, modifications of tile and open drainage systems, greenhouse gas emissions, lakes and groundwater pollution through mishandling of chemicals etc. (Miller et al 2013). Therefore, there are a number of water-related issues emerging from non-sustainable water man-

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agement practices like decrease of the level of groundwater, disappearances of wetlands, non-availability of clean water and overexploitation of freshwater that is available to meet the societal need (Heise 2008; Mitchell et al. 2013). A balance between a sustainable ecosystem and human requirements should be connected with new knowledge and new technologies.

Nevertheless, many of the human developments in the Anthropocene era have been approached in an unpredictable and unplanned way which become a barrier for the society and the economic growth of the country. The paradigm shift of human civilization put a remarkable question on the non-judicial uses of the natural resources. Ecologist, biologist, and hydro-engineers are trying to address the possible changes with the state-of-the-art organization, biophysical manipulation and water resource development. The successful existence of any civilization depends largely on its sustainable water use efficiencies, on the contrary misuse of water management can lead to complete destruction of it like Mesopotamian civilizations. The logical and methodological approaches need to be adopted on an urgent basis to prevent the collapses merged with excessive uses of natural resources and associated challenges met by the society. In this context, the methods evolved by local communities (Boran Pastoralists) in Kenya and Ethiopian sub-continent are playing a pioneering role in constructing awareness and technological advancements to stop unprecedented developments which in turn make progress of "Sustainable Development (SDG)" (Samways 1999). There is a famous statement given by Nicholson and Jinnah (2016) in which they have described the presence of "human signatures" as significant drivers of global challenges.

The famous saying of 'nature talks back' can be realized if human interventions exceed certain limits which create different challenges for the society and environment at large in the era of "Anthropocene" (Norton et al. 2010). In the present epoch, the disturbances of natural water cycles are induced by imbalances between events of precipitation, freshwater availability and the unpredictable level of groundwater. It is estimated that by 2050 more than 5 billion people will be affected due to the unavailability of clean fresh water (Rockström et al. 2009). Radical and methodical changes in the urban planning and management, functioning, and roadmap of urban cities, establishing relationships between the social and environmental aspects direct to the extensive research on the new patterns of hydrometeorological aspects of water scarcity. Therefore, currently, the researchers have focused on the water security challenges with socio-economic, socio-cultural and ecosystem services in the context of international relations (Mitchell et al. 2013) and diverse "ecological footprint" to understand their complex properties that have changed the basic support systems of natural ecosystem. Accordingly, in an attempt to present a comprehensive and coordinated view on the subject, this chapter highlights the water security and scarcity challenges of the Anthropocene era and their connections with land degradation and other environmental maladies. This current chapter will also focus on the interaction between sustainable development goals and land degradation factors that significantly contributes to the global challenges of water resource management systems.

17.2 Challenges of Integrated Water Resource Management (IWRM)

There is a dire necessity of adopting Integrated Water Resources Management (IWRM), a holistic concept officially approved at the International Conference on Water and Environment, Dublin in 1992 (Schoeman et al. 2014). IWRM differs from the conventional water management strategies in the aspects of socio-economic progress, economic independence, social equality and ecological sustainability. A truly comparable approach called as "Adaptive Water Management (AWM)" also has evolved to consider uncertainty and policies to reform water ecosystem as a central object in institutional success. However, there are manifold complexities, costs, action-oriented limitations, and institutional ordinances to set up the global water partnership with systemic approaches as mentioned by Pflieger (2016). He critically analyzed the interconnections among different natural resources and explained how the role of politicians, civic groups, and social-reformers are important in the documentation and accumulation of diverse regulations for governing the issues of water resources (water uses, water resources and water rules).

Sometimes, the integrated approaches at national/global/regional levels are not proven fruitful and set aside by some conflicts of interest, promoting non-coherent water management policies and set the foundation goals which restrict the targets of a virtuous cycle of water and economic prosperity which are considered to be the essence of human life. The problems are generally emerging from gradual up and downstream movement/flow of rivers which are connected to nearby cities and therefore become the hubs of pollution due to industrial and anthropogenic activities (Nijman 2011). A big question can be put forward on the progressive development of the modern urban cities and growing population, in which consumptive uses of water greatly relies on the socio-cultural, spatiotemporal and geomorphological aspects, exceeding the borders of planetary boundaries as described by Bouteligier (2014) and Wichelns (2015).

The proper mitigation and adaptation strategies of the smart cities need to be highlighted to increase their resilience to natural hazards, which may be treated as short-term solutions for the global challenges of Anthropocene. Bridging the gap among scientists, environmentalists, and policymakers, a public awareness level can be built up to make the most possible uses of water in different ways and can lead the watersheds development programme under the leadership of South East Asia Pacific network. The efficiency and decision-making power of such network will be helpful to curb the global crisis on water resources and can address the core messages of UN-Water (2013) security goals in the present scenario of transforming the world (Chan and Dan 2016). These challenges in turn potentially uphold the international relations and bring the new environmental challenges that can deal with the significance and purpose of living in the Anthropocene merged with the supply-demand chains of essential goods in various demographic factors/analysis.

17.2.1 Water Management Strategies and Relevant Problems in the Asian Context

Urban sector being the harbinger of modern civilizations will be at the pivotal point of the global economic crisis and the establishment of increasing trend towards climate change-water scarcity-socio-economic nexus will create an ecological chaos. Local governments, regional and international agencies must come up altogether to fulfill the ecological concerns of both the mother earth and human beings. Involvement of local people and their growing consciousness will start up the paradigm shift to move forward for the "global sustainable development governance system" which will add value to the moral ethics and ethos of transforming global scenarios. The great speech delivered in the year of 1968 during the inaugural address at IUCN by Baba Dioum—a famous South African forest engineer and constitutional member of International Union for Conservation of Nature and Natural Resources (IUCN), presented a clear vision about the conservation of earth system sciences through participatory approaches by clearly mentioning the individual role of stakeholders, hydrologists, government bodies and other local societies including academic organizations to alter the translation research into international relation power.

Although there are many articles available regarding the changes that happened in North America and Western Europe during the period of Anthropocene, very scanty information is available regarding Asia and Arctic regions. The direct impact of climate change can be crucial to observe in the daily lives of Indigenous habitats of those arctic regions where the impact of the developments of modern societies might not be given much importance like the other parts of the world. Many people have the concept that Anthropocene is European centric which has not got popularity yet in the Asiatic region. In the historical contexts, although Asia was considered as a higher/medium developed continent compared to North America and Western Europe the modern scenario has changed the picture totally. The critical explanation by Diamond (2005) and Ian Morris (2010) justified the gradual decrease of Asian perspectives and tunes of development from "Winner to loser" approach. The developing Asian countries like China, India, and Brazil are paying high costs in terms of environmental ethics for long-term and intensive uses of fossil fuel based industries (Chakrabarty 2009). Ian Morris (2010) compared the present scenario with "locked-in" situation in Anthropocene, where he has mentioned the non-progressive ideas of Asiatic cultures. It is generally accepted that Asia has a great relationship with nature through its tradition and culture and therefore it is difficult to follow a "sustainable economy" through "closer to nature" and "balance and harmony" concept as showed by Krupnik (1993), Harkin and Lewis (2007), Berkes (2008). The entry of Asia in the Anthropocene was well documented by Adam Smith (1776), where the development of China had been presented as a genesis of "ecological linkage" between "pre-Anthropocene" and "Anthropocene". The outbursts of such developing countries had put the onus on environmental sustainability as clearly depicted by Morton (2010) where he compared the situation with the socio-economic modernization of England where the shortcomings of Anthropocene embedded in time and regional space started around dates back in 1800.

The initial development of Asian civilization with the uses of Coal has been well described by Elvin (1973) and Thomas (1991). They have put light on the fact that how rapid transformation from farming system to industrial set up had changed the socio-cultural phenomenon at inter/intra/trans-sectoral level which was marked by the development of rapid industry resulting in some grave Anthropocene artifacts like massive deforestation, increasing use of natural resources, groundwater level depletion as supported by arising of water scarcity problems, dangers associated with toxic metal/chemicals contaminated water, occurrence of toxic air pollutants etc.

17.2.2 Human Interventions and Socio-economic Aspects of Water Management

The previous researchers (Crosby 2004; Mann 2011) have demonstrated the importance of Landscape management to deal with the sustainable future of Anthropocene. It is well known that Man has modified the existing ecosystem as per his need since the process of mass extinction events happened around 50,000 years ago which has resulted in the rapid loss of biodiversity merged with "early modern colonization effect" as determined by Norton et al. (2010). There were many "ecocultural" relations that led the transformations of Anthropocene which were induced by the Southeast Asian agricultural revolutions including intensive rice farming, erosion of agricultural land, Carbon-dioxide and Methane emissions from livestock and farming activities that consequently had begun the new journey to Anthropocene. With the rise and fall of Mongol, Ming and Mughal dynasties, there was a huge impact on "Paleoanthropocene" which in turn wrote the epic chapters of global and fast alteration of stratigraphic and ethnographic pictures of "Anthropocene epoch" as suggested by Pongratz et al. (2011). They have explained that the natural landscape changes due to overpopulation and growing environmental pressure on the human population are positively connected with modern vulnerabilities of the Anthropocene.

It is difficult to exactly describe the positive role of the human in the era of Anthropocene and to give a rank to Asia according to environmental resilience impacts. Furthermore, the study of water balances in Anthropocene is considered as a complex association of growth, resilience and traditional knowledge. The negative effects of climate change and industrial growth will pose environmental risks to the existing population and the socio-economic factors will largely reduce the industrial developments (Alcorn et al. 2003; Hudson 2014). Therefore a good governance system in Asia by combining the socio-ecological risks should be in the developing stage along with the significant globalization impacts which should include the challenges of “Holocene”, “Pre-Anthropocene” and “Anthropocene” over South East Asia as a sign of progress to ecosystem services with proper improvement strategies for human society which are not in turn “sedimentary” in nature (McMichael 2014).

The emerging economy of India, China, Brazil, and Russia has led the nations towards economic and socio-cultural development but simultaneously degraded the overall scenario of environmental sustainability in a broader sense. For an example, in China the current situation of land, water and air pollution with the outbursts of population is so worse that the Chinese government itself declared the potential threats of growing food crops in contaminated lands which comprise nearly 3 percent of cultivable land as documented in the current review on environmental reports of developing countries by Watts (2010) and Larson (2014). Although the overall carbon footprints of the emerging countries are lower than North America and Europe still the growing number of budding industries, cultural activities and political actions compel the non-judicious uses of natural resources (Kaiman 2014).

The major problems usually lie with the South East Asian overexploitation of natural sources. For example, in case of China, Japan, and Korea excessive fishing activities through special designed fleets can create disturbances among aquatic biodiversities and the consumption of a potentially huge amount of energy can be as harmful as deforestation activities for environmental growth (Chew 2001). Apart from such anti-nature activities the problem also arises with the facing of sustainable food security which involves political corruption, land grabbing issues, export-import dilemma and long-term corporate benefits as reported by Hudson (2014) and Klare (2012). The largest problems can be seen in terms of land degradation and associated issues for agricultural production which are stemming from illegal mining activities for rare earth and natural minerals in Africa and other underdeveloped countries. This is particularly a problem for China and other South East Asian countries where land degradation becomes the primary villain of the period of Anthropocene. The problems of such land degradation are complex and their conjugate effects are lying beyond the socio-economic vulnerabilities of environmental deterioration as summarized by Sponsel (1998) and Chen et al. (2014).

17.3 Land Degradation as a Driver of Water Scarcity

Land degradation refers to a declination in the general soil quality mainly introduced by anthropogenic activities (Vlek et al. 2004). Hereby, land degradation can have different causes (Zhang et al. 2015) including direct pollution of soils from agricultural and industrial practices. These impacts on soil cause changes in the biological (e.g., reduction of soil biota), chemical (e.g., changes in pH-value, nutrient, and carbon content), as well as soil physical (e.g., bulk density, porosity) properties. These indirectly impact the surface and groundwater quality and quantity, as well as vegetation growth especially crop yields.

Land degradation is a global problem, largely related to agricultural practices, whereby the scenarios causing land and environmental degradation are manifold (Vlek et al. 2004). Recent analyses have reported that even small changes in soil properties due to anthropogenic practices critically affect crop yields (Miteva et al. 2015). Additionally, the authors stated that the monitoring of key biogeochemical parameters like bioavailable soil carbon and the integrated fertilizer management is crucial for the risk assessment of land degradation. Soil fertility and nutrient indices are the governing parameters for sustainable maintenance of soil water holding capacity, water quality, soil ecological biodiversity, soil carbon quality and crop yield. Soil compaction due to the operation of heavy machines as well as salinization due to inappropriate irrigation schemes may lead to the development of the degraded ecosystem. Zhang et al. (2015) have documented that more than 30% of the soil organic carbon stock is going to deplete after several decades of intensive agriculture/cropping. As an example, the global soya market of Argentina got popularity in the 1990s because of market surplus prices of soya due to its overproduction during that time to balance the demand-supply chains of competitive global agricultural markets (Toledo and Burlingame 2006). Because more and more farmlands were needed to satisfy the global soya demand, native woodlands were deforested and converted into agricultural lands, whereby some functions of the soil were already altered. There was a huge shift/reduction in soil organic carbon stocks and microbiological communities due to the introduction of soybean cultivation on existing agricultural land through the changes in agricultural management and practices. As a consequence, soil degradation within Argentina's Carcaraña River basin reduced the agricultural productivity by 60 percent of the farmland compared to the state in the 1990s (Toledo and Burlingame 2006).

As mentioned, land degradation can be caused by several natural and anthropogenic impacts. Among all forms, chemical degradation of the soil can cover the loss of nutrients and soil organic matter, salinization, acidification, and pollution. Additionally, land degradation can exert negative effects on water/soil environment through lateral entry of noxious chemicals or changes in the ecological balance. Soil/water contamination is caused by the non-judicious application of chemical inputs from agricultural activities along with improper waste management practices with the rapid advancement of industrialization and urbanization. In general, contamination is positively correlated with the rates of industrialization and chemical usages (Akhtar-Schuster et al. 2016).

17.3.1 Land Degradation in the Aquatic Ecosystem

Although most of the targets of SDG 6 have some relation to LD, the most pertinent one is Target 6.6: '*by 2020, protect and restore water-related ecosystems, including mountains, forests, wetlands, rivers, aquifers and lakes*'. SDG 6 has a good interlinking with SDG 15—in the context of consequences and causes of LD. The recent methodical approaches, where water and land have been considered collectively as independent natural entities, have not proven valid until the scenario of global sustainability has come into the picture (UNEP 2012). An integrated land-water nexus approach has been explained by Bhaduri et al. (2016), where a paradigm shift in the eco-hydrology has been considered as a holistic approach to describe the water security in the light of environmental ethics.

With the rapid growth of population, crop improvement, land use planning and agricultural sectors in the 21st century, an enormous pressure has been exerted on water quality and management issues. Water scarcity is a grave concern for maintaining socio-economic and environmental sustainability which in turn threatens the survival of ecological entities. It is estimated that land degradation and water scarcity undermine the water availability and can relocate up to 700 million people in some arid and semi-arid places by 2030 (WWAP 2012). A great part of Africa is going to face a potential water shortage and water conflicts soon in future since all of the 50 river basins in Africa are at their frontier lines (De Wit and Jacek 2006).

It is a well-known fact that freshwater reservoirs serve as the origin of prime natural resources since its inception (Gordon 2002), and it is already documented that rivers and lakes play a pivotal role in the epic establishment of the historic civilizations. At present, nearly 320 million people (in South East Asian context) depend directly on freshwaters, such as lakes, rivers floodplains, and wetlands, for the provision of food and employment (aquaculture) opportunities (Tockner et al. 2008). It is a matter of great concern that among one of the precious natural resources the quality of water has dramatically deteriorated at a faster rate since the 1990s (UNEP 2016). Ritter et al. (2002) have conceptually demonstrated a hydrological pathway in which the mode of contamination of the surface and groundwater bodies by large quantities of industrial and agricultural effluents have been discussed.

17.3.2 Imbalanced Ecosystems as a Potential Threat for Water Availability

The carbon sequestration potential of Mangroves has been investigated by several researchers and they have concluded that with a unique morphological feature Mangroves can lock up atmospheric CO_2 approx. up to one-third of its dry weight (Barbier et al. 2011; Herr et al. 2015). It is certainly a grave issue that nowadays the rapid loss of aquatic/wetland (tidal marshes, seagrasses, Mangrove) biodiversities seems to be a perfect example of environmental degradation due to the lack of consensus between national and international communities, bio-geo physical losses of ecological diversity and uncontrolled political slugfest. Herr et al. (2015) have analyzed the vulnerability of coastal deltas on a more comprehensive level and discussed the statistical viewpoints about the threats related to biodiversity at global, regional or local scale with the gross estimation of annual losses of 1.9% of mangroves which can cause nearly 220 million tons of CO_2 emissions—these are equivalent to higher values of Carbon dioxide emission indices (>2.19) which correspond to combustion of >500 million barrels of oil from >30 million passenger vehicles.

Tropical peatlands, wetland ecosystems storing 191 Gt or one-third of all carbon globally are really under threat because of unsustainable practices of conversion of agricultural land to oil palm plantation and loss of genetic biodiversity. For example, Petrenko et al. (2016) have discussed the oil palm production scenario of Indonesia, Malaysia, and Thailand which are the world's leading producers of palm oil, meeting approximately 70% palm oil demand of European nations. Such huge profit making industries of Malaysia, Indonesia have an annual average growth rate of >8% which is a prima facie evidence of pandemic impairment of ecosystems influenced by political motivation. Conversion of peatlands which is directly linked to the land conversion strategies will continue to predominate over the Anthropocene era. The organic reach peat land once disturbed, tend to dry up and become susceptible to fire and release carbon. The natural carbon and water balances have been disturbed by anthropogenic activities in different parts of the continents for instances in Canada, the mining activities of oil-sands were originally in marshy swamp areas and the total loss of >10,000 ha of peatlands has led to >2500 t of annual carbon sequestration potential (Rooney et al. 2012).

Saltwater intrusion (SI) into the freshwater bodies is a universal issue, which heavily affects the aquatic ecosystems and lives present within them. The downfall of the local scale management system of natural water resource jeopardizes the sustainable supply of water towards local habitats in coastal areas and their gross socio-economic development. The presence of freshwater in coastal aquifers has undergone severe challenges due to its (i) proximal distance to saltwater, (ii) the increasing trend of the demand of fresh water along with the progressive extension of the coastal areas and the use of those aquifers as the prime source of drinking water. Therefore, the continuous deterioration of the water quality has emerged as an inter-sectoral developing environmental stress issue in low, middle and high-economic countries. In several developed and developing nations, like Cyprus, Srilanka, Malaysia, Italy, Indonesia, Bangladesh hundreds of wells situated in the coastal border areas need to be managed properly because of SI. In the west coast area of USA, merging of Los Angeles Basin coastal aquifer and the incoming saltwater from the Pacific Ocean have replaced freshwater required for millions of inhabitants and industries (Thebo et al. 2014). In current time, several numerical models have been validated to elucidate the overall geochemical processes involved in the detailed explanation of SI. The illustrations of the horizontal accumulative zone between fresh and salt water, as well as the spatial and temporal evolution of the intrusion, were analyzed using geophysical measurement technologies along with numerical modeling (e.g., Vandergeten et al. 2016). Additionally, modern analytical solutions of the intrusion phenomena can deliver a rapid insight into the proper geophysical processes involved, and due to this, a bunch of studies has been conducted in this area (Berry et al. 2006; Nguyen et al. 2011).

17.3.3 The Global Importance of Water Management System

World Water and Development Report (WWAP) has critically analyzed that globally around 1.4 billion (42% of total global workforce) and 1.2 billion (36% of global workforce) jobs depend largely on heavily and moderately water-based technologies respectively (WWAP 2012) as shown in Fig. 17.1. In the perspectives of Central Asia, where climate-smart agriculture is practiced with integrated water management systems, thereby >10% reduction in water supply will lead to >8% of rural unemployment and crop production activities. Such disturbances on agroecosystems will result in gross economic losses up to more than USD 450 million (Bekchanov and Lamers 2016). Therefore, water connects with different sections of SDGs (SDG-1, 6, 8 and 10) by adaptive and reflective methodological approaches providing a future goal for water footprint balance cycle in the global perspective of water economy.

Implementation of Integrated Water Resources Management (IWRM) explains the critical importance of global water resources to living entities, the application of multi-level governance of global water system and links different integrated world water systems. A state-of-the-art coordinated framework has utmost importance in the explanation of successful synergies between different target groups of SDG-6 and LD, without which the potential conflicts of individual targets will not be addressed along with the potential consideration of water's central role in linking

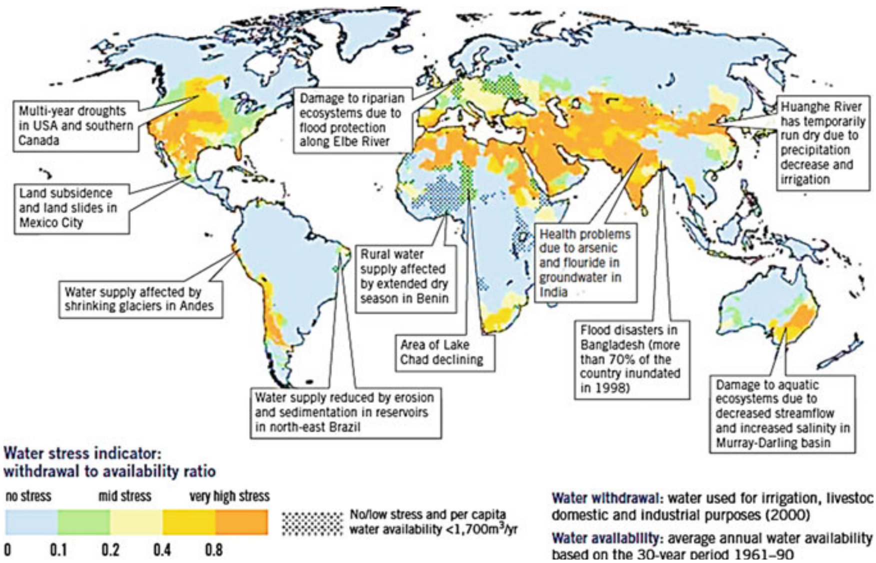

Fig. 17.1 Examples of universal freshwater resource risks in the context of water stress indicator (withdrawal to availability ratio). The figure is reproduced with permission from Kundzewicz et al. (2007); the water stress map is based on Alcamo et al. (2003)

those conceptual domains and describing the mechanics of earth system sciences (UN-Water 2016). The modern cities will also get benefitted by linking water and food security under the theme of water resource development and institutional planning with proper educational envisage.

17.4 Water Pollution, Soil Degradation, and Sustainable Development Goals Nexus

The target group of SDGs-3 describes the theme of "Ensure healthy lives and promote well-being for all at all ages" under which target 3.9 depicts through "a substantial reduction in the number of deaths and illnesses from hazardous chemicals and air, water and soil pollution and contamination by 2030". Water pollution in connection with the land and soil degradation results from poor land management, surface runoff and leaching of toxic contaminants into the vadose zone of groundwater. A conceptual framework is shown in Fig. 17.2, where an interconnected link to different goals of SDG with land degradation has been presented to address global challenges. The pollution at hydro geosphere is caused by indiscriminate usages of chemicals, improper waste handling, and unregulated

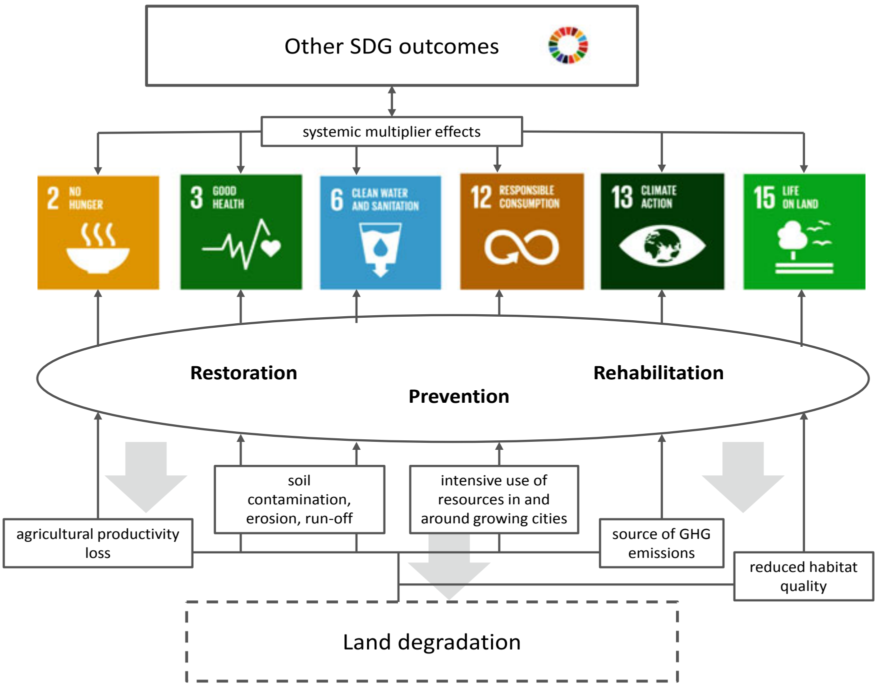

Fig. 17.2 Functional link of different SDGs with multifactor of land degradation. The figure is reproduced with permission from Vlek et al. (2017)

usages of emerging contaminants or by unwanted signatures of heavy metals, radionuclides, and xenobiotic/microbial pollutants at geological scales. Huber and Prokop (2012) have established the positive correlation between the degree of pollution and the rates of chemical dosages applied in the system. There is a direct health-related risk associated with the contamination of water bodies which can estimate the diffuse nature of chemical pollution and can calculate the cost of man-made pollution in a broader sense. Nitrogen and phosphorus are significant sources of nutrient pollution lead by intensive agricultural operations (WWAP 2012). This results in eutrophication of the fresh and marine water bodies which is marked by the rapid growth of algal blooms that in turn deteriorates the quality of marine ecosystems and estuaries (WWAP 2012). The excessive usage of chemicals and fertilizers have aggravated the agro-ecological conditions exerting negative effects on soil physic-chemical and biological properties. Excessive exposure and inappropriate use of toxic chemicals can exert many harmful effects on soil carbon stocks, water and nutrient cycling and lead mass extinction of macro and micro faunas such as birds, bees, small mammals and fishes (Giller et al. 1997).

The negative consequences of air and water pollution have been well described by Chen (2007), where the ill effects of the atmospheric deposition and simultaneous long-distance transportation of SO_X and NO_x particles (micron-sub micron ranges) from industrial sources have included some of the global natural endangerments like ocean acidifications, rising of sea level, deterioration of environmental performance indices followed by huge expenses incurred for cleaning up of large water resource system. Such hazardous chemical effects on vegetation and water bodies disturb the natural water balance and hydrological cycle which can have an indirect effect on natural forest system. The perfect example of such malfunctioning of the natural system is Sudbury region of Canada, where weathering and release of minerals have resulted from soil acidification process caused by SO_X emissions over the past centuries due to ore smelting and illegal mining activities. The more devastating examples are led by copper mining activities of Zambia and the Democratic Republic of Congo. Such kind of environmental mining led to bio-, hydro- and atmospheric pollution and put the above countries within the top ten priority polluted areas of the world (Banza et al. 2009). Additionally, the problems are getting more aggravated with the production of bioenergy crops and the subsequent development of bioenergy industries. Therefore, IWRM was constituted for not only taking care of proper water management scenarios but also to look after the "water-energy nexus" strategies and to augment the implementation of proper trade policies which would be executed in connection with agricultural policies to solve the problems of water supply and other associated challenges (Chew 2001). The trans-boundary concepts of water management systems have also gained popularity in Tanzania and another Western part of Africa as described by McMichael (2014).

Heavy metals/metalloids are mostly associated with the contamination of soil and water (both ground and surface water). In the United States, more than 40, 25 and 30% of lakes, rivers, and estuaries are suffering from potential heavy metal(loid)s contamination (USEPA 2002). Among all the heavy metal(loid)s, the most common and noxious ones are Chromium (Cr), Arsenic (As), Lead (Pb), Nickel (Ni) and Cadmium (Cd) (Kumar et al. 2009). They have received much wider attention in the past because of their non-degradable, persistent and toxic nature. Once the heavy metals pollute the water bodies, they enter the food chain leading to bioaccumulation and their long-term exposure may lead to various adverse health effects on human beings (Das et al. 2016, Patel et al. 2019a, b). Conversely, according to an estimation by World Bank report (2015) on urban population growth particularly in Africa and Asia, it is estimated that by 2030 there will be an increase in the number of the urban population nearly by 5 billion (Kumar et al. 2013).

17.5 Human Health Perspectives of Environmental Degradation

However, the problem of metal contamination is not only confined to the urban areas as groundwater contaminants, where the prevalence of arsenic, fluoride, uranium are considered as geogenic in nature. The widespread use of groundwater for drinking purpose has resulted in metal poisoning in a huge number of people in the developing world, due to the consumption of various toxic elements. In particular, the presence of higher level of As, Cd, Zn, Cu, and Cr in the groundwater has been reported by many countries of the world (Luther et al. 2012). Such toxic metals and metalloids present in the Earth's crust, classified as class I human carcinogen (I.A.R.C 2004), is ranked as the second most significant global health hazard associated with potable water next to contamination by pathogenic microbes (Sanders et al. 2014). A community-level risk assessment approach must be adopted for long-term environmental assessment at a socio-economic level on a global scale to address food, water and sustainable securities resulting from a vicious cycle of LD.

The significance of pollution study greatly relies on the critical analysis of health associated problems which have evolved from primary or secondary contamination pathways via direct or indirect routes of exposure. The developed nations like North America, Western Europe have already prepared some repositories of contaminated lands and their remedial strategies through implementation of legal protocols (Brevik et al. 2015). The problem is much more serious in the developing countries like India, Russia, Brazil, and China were with the advancement of industrial technologies the stringent environmental regulations are yet to be established (Scherr et al. 2015). Therefore, to deal with the environmental maladies of Anthropocene combined ecosystem services need to be built up among policymakers, researchers, socio-economic workers, public, and governments. Above all, rapid and effective earth system management at global and local time scale will provide modern human ethics, transdisciplinary actions and alter cacophony into harmony through improvised global governance, these will restrict further catastrophic changes of planetary boundaries (pivotal point of Anthropocene) at the macro scale.

The detrimental health effects resulting from direct or indirect exposure to chemicals largely depend on the types of pollutants, mode of actions and susceptibility of the target organisms (Luther et al. 2012). Chronic and acute exposures to a suite of heavy metals and metalloids, xenobiotic can make the situation much worse and become responsible for the neurodegenerative disorder, congenital heart diseases, and blockage of the blood-brain barrier system, Teratogenic, and carcinogenic effects. Nitrate, phosphate, and ammonia emanating from agricultural, horticultural and veterinary operations are considered to be one of the major sources of health hazards connected with anthropogenic pollutions (Das et al. 2015, 2017; Kumar et al. 2017).

The health costs due to long-term exposure to air/water/soil pollutants can rise more than 5% in any major cities' (like Beijing, New Delhi, San Francisco, New York etc.) GDP which is equivalent to gross expenses of >USD 2.0 billion annually as reported by Zeng et al. (2007). As per the global scenario around USD 100–400 billion are spent every year to prevent the health impacts and consequent economic costs due to environmental pollution (Lewis et al. 2009). The costs of reclamation of the land and water resources to convert it into more valuable forms range from USD 40–80 billion as explained by Post and Kwon (2000). A summary table (Table 17.1) has been provided in the present scenario to focus on the worldwide contamination sources and associated input costs as described by different national or international researchers and/or agencies.

The potential negative effects of water, soil and air pollution, stemming from indiscriminate uses of chemicals can be a crucial issue for developing countries

Table 17.1 Global distribution of environmental pollution and related costs of treatments (modified after Vlek et al. 2017)

Country/region/cities	Sources of contamination	Approximate costs of treatment (in US $)	References
Japan and Korea	Fertilizers and pesticides, wastes from mining, electroplating and chemical industries	20 billion	UNEP (2002)
Caucasus and Central Asia	Cd, pesticides, As, radionuclides (uranium and metal ore), Cr	14 billion	EEA (2007a, b)
Australia and New Zealand	Hydrocarbons, Cr^{+6}, Pb, As, tri and tetrachloroethylene, pesticides, Cd	100 million	UNEP (2002)
	Saltwater intrusion, illegal/improper application of radioactive wastes and pesticides, acid-mine drainage	30 billion	Coles (2008)
North America	Dioxins, furans, Hg, Pb, As, PCBs, benzene, Cd, PAHs etc.	15 billion	USEPA (2010)
Parts of South and South-east Asia	As, Pb, Cr, abandoned chemical weapons, asbestos, fluorides, Hg, cyanides	15 billion	Ericson (2011)
North-western and Eastern Europe	Heavy metals (37%), mineral oil (33%), PAHs, phenols, cyanides, chlorinated hydrocarbons	32 billion	EEA (2007a, b)
Latin America	Oil spills, wastes from metal and chemical industries, landfills	230 million	Marker et al. (2007)

with limited infrastructure and poor economic growth in maintaining clean water and sanitation (SDG-6) goal, which is the core part of the 2030 agenda for Sustainable Development knowledge platform. In many parts of underdeveloped countries like Central African Republic, Ethiopia, Guinea, Angola, Gambia etc. land users even cannot afford the high price of fertilizers needed for soil as inorganic nutrient supplements for plants. Varis (2006) reported a mismatch between fertilizer inputs and harvest index through statistical analysis report after taking an intensive land survey of more than 50 marginal holding farmers in the suburb of Kenya. On the other hand, due to unavailability of trained personnel/farmers resulting from sociological problems related to urban-rural migration and prevalence of diseases like HIV/AIDS the indigenous rural technology like in-house composting with local raw materials is becoming obsolete with respect to time. Dougill et al. (2002) explained the catastrophic events of remote parts of South Africa where the continuous application of nitrogenous and sulfur fertilization to the poor organic depleted sandy soil results into extreme acidity of soil and nitrate pollution to nearby waterbodies. As a result, the cropping system pattern is also significantly altered and affected (20% reduction in Maize yield) due to overdoses of nitrate caused by poor nutrient management and unbalanced agricultural system backed by fertilizer industries.

17.6 Conclusion and Outlook

Currently, more than 20% of the global ecosystems are under threat due to over and impractical uses of environmental assets. Socio-economic development at local/regional/intergovernmental level must be coupled with the proper functioning of gross economic growth which will indirectly improve the social livelihood and sustainable uses of the terrestrial ecosystem (UNEP 2016). On the other hand, unsustainable land use pattern and improper freshwater use can develop a variety of environmental issues and mark a drastic change in the hydrological cycle at both local and regional scale. A group of ecological indicators for the multiple SDGs has been advocated, which connects with the goals of a healthier environment for the deprived section of the society, better ecological management, and the advanced global services as directed by United Nations (UNCCD 2013). Altogether these diverse indicators directly or indirectly are influenced by land degradation and soil management. Indicators, which have more proximity related to agro-ecological conditions are comprised of different factors like water consumption per capita, the types of soil and water degradation (including salt intrusion, water, soil and wind erosion), agro-ecological biodiversity, soil carbon and nutrient inventory, sustainable natural resource management, and arid land status (UNCCD 2013). Additionally, sustainable farming practices involving the judicious uses of environmental assets are the principal components of action to address land degradation.

Global climate data and soil management inventories are interlinked with each other in regard to GHG mitigation and climate change adaptation strategies.

According to the life cycle assessment of global climate-mining and manufacturing processes, production and transportation of mineral fertilizers are reported to contribute significantly to GHG emissions. Agricultural practices at small scale, without undergoing food processing and transportation, are calculated to be responsible for more than 6% of global energy use (FAO 2011), and therefore, fertilizer production and distribution are the prime factors of determining GHG emissions. Over a long period, global climate change will provide abrupt changes in global ecosystem services, therefore it will exert direct or indirect influences on the welfare of a human being, whereby these changes in a broader sense will influence local to global water cycles (IPCC 2014). Climate change adaptation strategies in farming systems are globally centered on maintaining proper water resource management services as regulated by agro-ecosystems. Judicious use of natural resources is one of the pivotal options for the mitigation of climate change induced inundation of flood-plains (e.g., regulating flooding). Sustainable agricultural practices combined with community ecosystem services are considered as a driver of adaptive socio-ecological management which consider all the essential components of the environment (biodiversity, water, land, climate, and nutrients) (Rockström et al. 2009).

Therefore it is noteworthy that human-induced changes are obvious in Anthropocene on the global and regional scale. The effects of such changes are quite a long-term and they are designed to destabilize socio-ecological connections which interlink all the associated costs for a global transition to ecosystem services to introduce ethics values of Anthropocene era although it is extremely hard to calculate the actual potential budgets. Science and policymakers' approaches are utmost important to establish good governance which has been also necessary to deal with the critical analysis of forest and urban ecosystem nexus since 1997, to give a wider attention to the world's most valuable natural assets as shown by Fazal (2001) and Tal (2015). The social values of conservation of biodiversity at different time scales need not only include active participation from global leaders but also need social awareness among people getting affected by these as suggested by Steffen et al. (2011a, b). The possible solutions for combating the socio-economic changes resulting from disasters caused by Anthropocene events need to be cross-examined by geoengineering techniques based on social, ecological and economic costs rather than valued by only traditional and institutional approaches. We need to know how to give the real value to our environmental assets instead of giving attention only to natural capital assets, which in turn prevents environmental degradation and construct the foundation stone of human growth as a success pillar of our inheritance.

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Chapter 18
Groundwater Contamination Issues in the Shallow Aquifer, Ramganga Sub-basin, India

N. Rajmohan

18.1 Introduction

Groundwater quality monitoring is an important task in sustainable groundwater management especially in the shallow aquifer. Recent days, shallow aquifers are under stress due to high abstraction for irrigation and domestic need as well as quality degradation. Water quality degradation in the shallow aquifers are widely reported worldwide especially South Asian countries due to porous and permeable soil, shallow water table and vadose zone thickness (Nolan et al. 2002; Davraz et al. 2009; Jiang et al. 2009; Rajmohan and Prathapar 2013, 2014). Groundwater quality in the shallow aquifers is governed by various factors and processes that can be broadly classified into natural and man-made activities. Climate variability, rock water interaction, adsorption/desorption, dissolution/precipitation, etc. are natural processes that affect water quality (Matthess 1982; Rajmohan and Elango 2004; Das et al. 2016; Patel 2019a, b). Dumping sites, landfills, industrial and domestic wastewater, irrigation return flow, excess fertilizers and pesticide usage are some of the man-made activities degrade water quality through vertical infiltration. In the Ganges basin and sub basins, groundwater quality deterioration by arsenic, selenium and iron is extensively reported (Saha et al. 2009; CGWB 2014; Rajmohan and Prathapar 2013, 2014; Shah 2014). Besides, nitrate, chloride, phosphate and heavy metals contaminations in groundwater are also documented in this region (Raju et al. 2009; Khan et al. 2015; Rajmohan and Amarasinghe 2016).

In the Ganges basin, Ramganga Sub-basin is a high runoff and water yield basin (Surinaidu et al. 2016; Amarasinghe et al. 2016). In this basin, groundwater is a soul source to balance the domestic and irrigation water requirements due to surface water scarcity (CPCB 2013; Amarasinghe et al. 2016; Khan et al. 2016). Thus, this study was performed to understand the overall groundwater quality status in this

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region using published literature as well as to identify the geochemical processes and pollution sources through groundwater sampling and analysis. Besides, this study provided the recommendations to manage the shallow aquifer efficiently.

18.2 Study Area

Ramganga Sub-basin (RSB) existed in the Central Ganga Alluvial Plain (78° 14′ to 80° 8′ and 27° 7′ to 30° 6′) in India (Fig. 18.1). In this region, groundwater requirement is increased tremendously due to the agricultural development, rapid urbanization and industrialization as well as inadequate surface water resources (CGWB 2009). River Ramganga is one of the important tributaries in the Ganga River and formed from lower Himalayas (about 3110 m above mean sea level) and flows in the states of Uttarakhand and Uttar Pradesh (UP). Length of the Ramganga river is 596 km and it covers 30,839 km^2 (Fig. 18.1) (Rajmohan and Amarasinghe 2016). RSB experiences subtropical monsoon climate and the temperature varies from 40.5 to 8.6 °C during May and January, respectively. The annual average rainfall is 923 mm and 90% of the rainfall occurs from July to September. RSB is sloped from north to south and almost plain. This study region is classified into Lower piedmont plain of Tarai, Older alluvial plain/upland, Younger alluvial plain/low land and Meander flood plain based on geomorphology. In this region, soil is classified into Tarai soils (locally known as "Mar"), Khadar or low-land soils (silty loamy sand or sandy) and Upland or Bangar soils (existed at upland tract of older alluvial plain).

Hydrogeologically, the RSB is covered by the older alluvium (Clay with Kankar and sand), younger alluvium (Fine sand, silty clay with gravel) and Tarai formations (Clay-sandy, sand, gravel and clay). The main water bearing formations are alluvial sediments which formed by the alternate beds of clay and granular material. Based on groundwater exploration work, CGWB (2014) identified the multi-layer aquifer (up to 750 m) in this basin. During premonsoon, the groundwater level ranges from 2.45 to 14.88 mbgl whereas during postmonsoon, it varies from 1.95 to 14.65 mbgl (CGWB 2009).

18.3 Materials and Methods

The groundwater sampling was carried out randomly in the Bareilly, Rampur and Shajahanpur districts in the study region (Fig. 18.1). Survey was carried out to select the wells for water sampling. Groundwater samples were stored in the pre-cleaned two HDPE bottles (1000 and 250 ml) from shallow (n = 37) and deep (n = 7) wells. Water samples were obtained after removing the stagnate water in the borewell casing. In the field, pH and EC were determined by portable meters and water samples were stored in the icebox (4 °C) until analysis. Collected samples

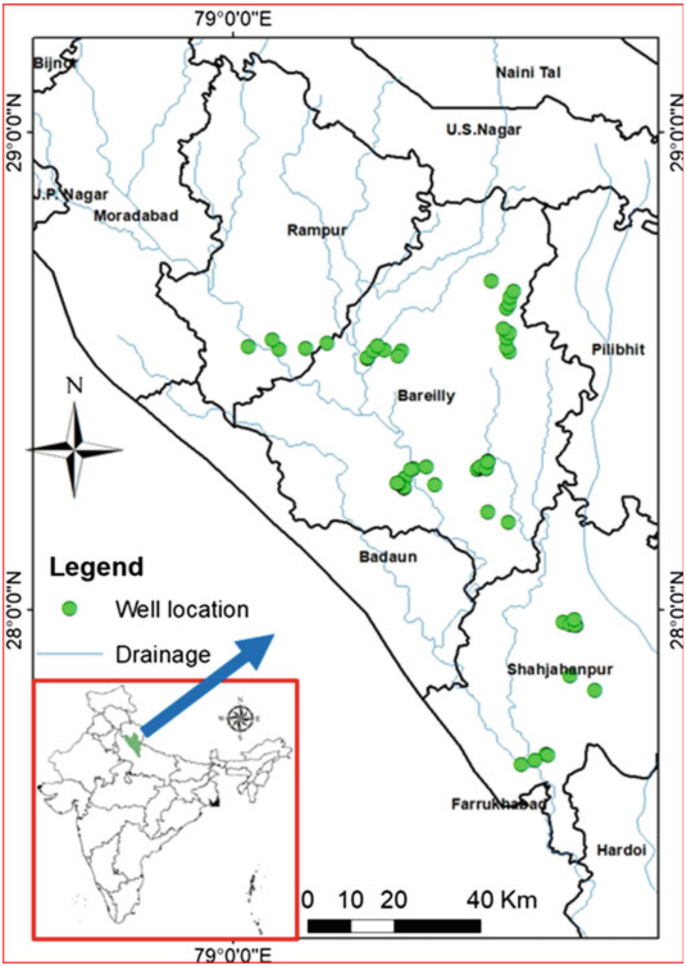

Fig. 18.1 Groundwater sampling wells and other features in the RSB

were filtered using 0.45 µm Millipore filter. For metal analysis, filtered samples (250 ml) were acidified (pH < 2) with ultra-pure HNO_3.

Well depth details were obtained from well owners. Major and minor ions and trace metals were analysed using standard methods (APHA 2012). Trace metals namely As, Cr, Cu, Fe, Mn, Ni and Zn were analysed using Atomic Absorption Spectrophotometer (AAS4141, ECIL). All the analyses were performed at Water Technology Center, Indian Agricultural Research Institute (IARI), New Delhi, India. Analysis accuracy was tested using the ion balance error, which is within ±5%.

SPSS (v 16.0) was used for Pearson correlation analysis. Saturation indices of mineral phases, aqueous species, ion activities and ionic strength were calculated using PHREEQC software (Parkhurst and Appelo 1999). The detailed procedure is given in Parkhurst and Appelo (1999). Ion activities were used to identify the thermodynamic stability of the reaction phases in the groundwater. Further, published literatures was also used to discuss the pollution status of shallow aquifer in the RSB.

18.4 General Groundwater Quality in the RSB

In the RSB, groundwater quality is influenced by the various elements especially salinity, fluoride, arsenic, nitrate and trace metals. Rajmohan and Amarasinghe (2016) carried out a detailed study in all 15 districts in the RSB using secondary data and published literatures. They reported high salinity (Bareilly > Hardoi > Bijnor > Budaun > Shahjahanpur; TDS > 500 mg/l), chloride (Bareilly > J.P. Nagar > Pilibhit > Budaun > Shahjahanpur; Cl^{-} > 250), sulphate (Bareilly > Budaun; SO_4^{2-} > 200), nitrate (Pilibhit > Shahjahanpur > Hardoi; NO_3^{-} > 45), arsenic (Pilibhit; As > 0.05 mg/l) iron (Bareilly > Pilibhit > Bijnor > Hardoi > Shahjahanpur; Fe > 0.3 mg/l) and fluoride (Pilibhit > Shahjahanpur; F > 1.5 mg/l) content in groundwater in the RSB districts. Figure 18.2 indicates the groundwater contamination status in the RSB districts. Groundwater contamination by the Iron and nitrate are widely identified in these districts. Among these districts, groundwater in the Pilibhit is contaminated by the arsenic, nitrate, salinity, iron, fluoride and total hardness. Based on groundwater contamination status (Fig. 18.2), RSB districts can be classified in the order as Pillibhit > Hardoi = Shahjahanpur = J.P. Nagar = Bijnor > Budaun = Bareilly = Moradabad > US Nagar = Chamoli > Almora = Farrukhabad > Nainital = Garhwal = Rampur. In the RSB, groundwater in the upstream districts has low TDS and chloride compared to downstream districts (Rajmohan and Amarasinghe 2016).

Besides, other studies are also performed in the RSB to assess the groundwater contamination status. In the RSB, high salinity is reported in the Bareilly, Chamoil and U.S. Nagar districts (CGWB 2009). High salinity is also reported in the Ganges basin states (i.e. Bihar, Haryana, Rajasthan and Uttar Pradesh) due to irrigation return flow and excess groundwater usage (Chakraborti et al. 2011). Groundwater with high TDS (>500 mg/l) is reported in the Moradabad city.

Like salinity, nitrate contamination in the groundwater is extensively reported in the RSB. CGWB (2009) noted nitrate contamination (NO_3 > 45 mg/l) in Moradabad and Bareilly districts due to improper waste disposal and fertilizer uses for irrigation. Raju et al. (2009) and Khan et al. (2015) also reported nitrate contamination in the lower Kali watershed and Varuna River basin. Uttar Pradesh. Shallow aquifer is highly affected by nitrate compared to deep aquifer and it is documented in the Varanasi city (Nandimandalam 2012).

Apart from nitrate and salinity, iron, arsenic and fluoride contaminations are also reported in the RSB. Iron contamination in groundwater is encountered in most of

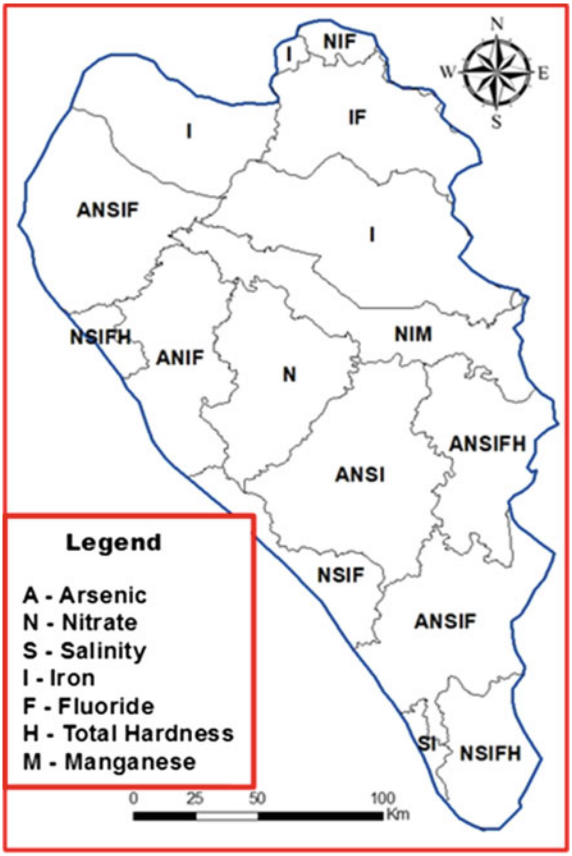

Fig. 18.2 Groundwater pollution status in the RSB districts (i.e. N—Nitrate contamination (NO_3 > 45 mg/l)) (after Rajmohan and Amarasinghe 2016)

these districts. Iron contamination is reported in the Moradabad city (Kumar and Sinha 2008), Bareilly district (Rastogi and Sinha 2008; Singh et al. 2009) and Hasanpur in JP district (Sinha and Saxena 2006). Groundwater in the Bareilly and Moradabad districts is polluted by the arsenic as well (CGWB 2009). According to Agarwal (2014), high arsenic in groundwater is identified in the 19 villages (Bareilly district) during Jal Nigam survey. In the RSB, iron and arsenic are mostly derived from geogenic sources (Rajmohan and prathapar 2013, 2014). Several processes are responsible of metal releases to groundwater such as pH, natural weathering, adsorption/desorption, oxidation/reduction, organic matter, soil texture, etc. (Rajmohan et al. 2014). Reducing environment in the anoxic condition will enhance reduction of oxides/hydroxides/sulphides/carbonates, which results metals enrichment in the groundwater (Kumar et al. 2017; Das and Kumar 2015; Das et al 2015). In the RSB, Sinha and Saxena (2006) and Singh et al. (2009) documented that iron, manganese and zinc have strong interrelationship as well as positive correlation. Likewise, arsenic also released to groundwater from young alluvial deposits in the RSB (Pandey et al. 2009; MDWS 2011; Rajmohan and Prathapar 2014).

Fluoride contamination is documented in the study region as well as Ganges basin. In the Ganges basin, high fluoride in groundwater is identified in the states of Bihar, Chhattisgarh, Delhi, Haryana Jharkhand, Madhya Pradesh, Rajasthan, Uttar Pradesh and West Bengal (CWC/NRSC 2014; Rajmohan and Prathapar 2014). In the RSB, high fluoride is noted in the Shahzad Nagar block, Rampur district (Kumar and Yadav 2011), Bareilly district (Singh et al. 2009) and Hasanpur, J. P. Nagar district (Sinha and Saxena 2006). Besides, Rastogi and Sinha (2008) recorded high manganese concentration in the groundwater in the Moradabad city. Sinha and Saxena (2006) mentioned that shallow hand pumps have high concentration of major ions and low dissolved oxygen compared to deeper hand pumps in the Hasanpur (J.P. Nagar district). Kamal et al. (2014) suggested that anthropogenic sources are responsible for high nitrate, sulphate and phosphate in groundwater in the J.P. Nagar district.

18.5 Groundwater Quality in the Shallow Wells

Previous studies implied that groundwater in the shallow unconfined aquifer is polluted by the various elements. Hence, in order to assess the sources of contamination and detailed geochemical processes, groundwater samples were obtained from 37 shallow and 7 deep wells in the RSB and analysed for major and minor ions and metals. Results suggest that groundwater quality is potable in the study region (TDS < 1000 mg/l; Freeze and Cherry 1979). In the shallow wells (n = 37), the depth ranges from 6 to 26 m (Table 18.1). The average EC, TDS and pH are 896 µS/cm, 573 mg/l and 7.4, respectively and the groundwater is alkaline in nature (Table 18.1). $CaMgHCO_3$ (n = 17) > CaMgCl (n = 15) > $NaHCO_3$ (n = 4) > NaCl (n = 1) are dominant water types in the shallow wells, which justify that the water quality is influenced by the minerals dissolution, recharge, mixing and ion exchange reactions.

Figure 18.3 illustrates that groundwater in the shallow wells are more mineralized (Deep wells are plotted in the Figs. 18.3, 18.4, 18.5 and 18.6) just for comparison only). This variation is significant in the major ions, nitrate, phosphate and metals. Figure 18.3 justify that the water quality in the shallow wells is not governed by the natural processes alone. But, anthropogenic sources are also affected the water quality. Metal distributions (i.e. Mn, Cu and Cr) indicate that these elements are partially/totally derived from the non-lithological sources (Fig. 18.3). In addition, high standard deviations (Table 18.1) also justify that these metals are derived from multiple sources. In the case of Mn, it is widely used in various products such as varnish, batteries, cleaning, fireworks, bleaching, fungicides, fertilizers, livestock food supplements, etc. (ATSDR 2000; HSDB 2001; WHO 2011). Likewise, Cu compounds are used in the pipes, valves electrical wiring, building materials, cooking utensils, algicides, fungicides, insecticides, fertilizers, wood preservatives and animal feeds (Landner and Lindestrom 1999; ATSDR 2002; WHO 2004). Dye, wood preservatives, paint pigments, metal coatings, paints

Table 18.1 Descriptive statistics of parameters analysed in the groundwater, Ramganga sub-basin

	Unit	Range	Mean ± STD	Kurtosis	Skewness
Depth	m	6–26	12 ± 4	1.5	1.1
EC	µS/cm	270–2000	896 ± 392	1	1
pH		7–7.7	7.4 ± 0.2	−0.9	−0.1
TDS	mg/l	173–1280	573 ± 251	1	1
Na		12–233	63 ± 45	5	1.8
K		1.3–173	28 ± 42	4	2.2
Ca		21–86	52 ± 15	−1	0
Mg		14–84	33 ± 16	3	1.6
Cl		25–355	113 ± 61	5.8	2
HCO_3		97–678	295 ± 129	0.95	0.93
SO_4		17–147	72 ± 37	−0.83	0.26
NO_3		BDL-38	6.9 ± 11	2.1	1.7
PO_4		BDL-1.3	0.1 ± 0.23	22	4.4
F		0.05–0.41	0.13 ± 0.08	4.8	2.1
Si		2.9–6.1	3.98 ± 0.96	−0.61	0.65
Cu	µg/l	39–299	122 ± 81	−0.6	0.8
Mn		55–3592	676 ± 762	5	2.1
Fe		BDL-2436	603 ± 614	1.4	1.3
Zn		BDL-1188	193 ± 244	7.7	2.4
Cr		BDL-860	63 ± 152	22	4.3

STD standard deviation; *BDL* below detection limit

pigments, paper, cement and rubber contain Cr compounds. These elements are entered into the aquifer through irrigation return flow and sewage water.

Pearson's correlation analysis was performed to understand the possible sources, processes and elements association in the aquifer. pH, Ca, PO_4, H_4SiO_4, Fe, Mn, Zn, Cu and Cr do not show correlation with other variables; hence, excluded in Table 18.2.

Table 18.2 indicates that bicarbonate shows significant positive correlation with EC, TDS and major ions. Major ions show strong positive correlation with each other. Fluoride and nitrate have positive correlation but not correlating with other variables. Chloride shows positive correlation with major ions. Variables correlating with chloride suggest that the water quality is highly affected by surface contamination sources.

Processes regulating water quality

In the RSB, groundwater quality is regulated by the mineral weathering (carbonates and silicates), ion exchange reactions and surface sources. Ionic ratios are informative tool to assess geochemical processes in the aquifer. In this study, Na/Cl ratio ranges from 0.41 to 2.11 with a mean value of 0.85. Higher ratios (Na/Cl >1) shows silicate weathering/cation exchange whereas lower ratio (<1) expresses reverse ion

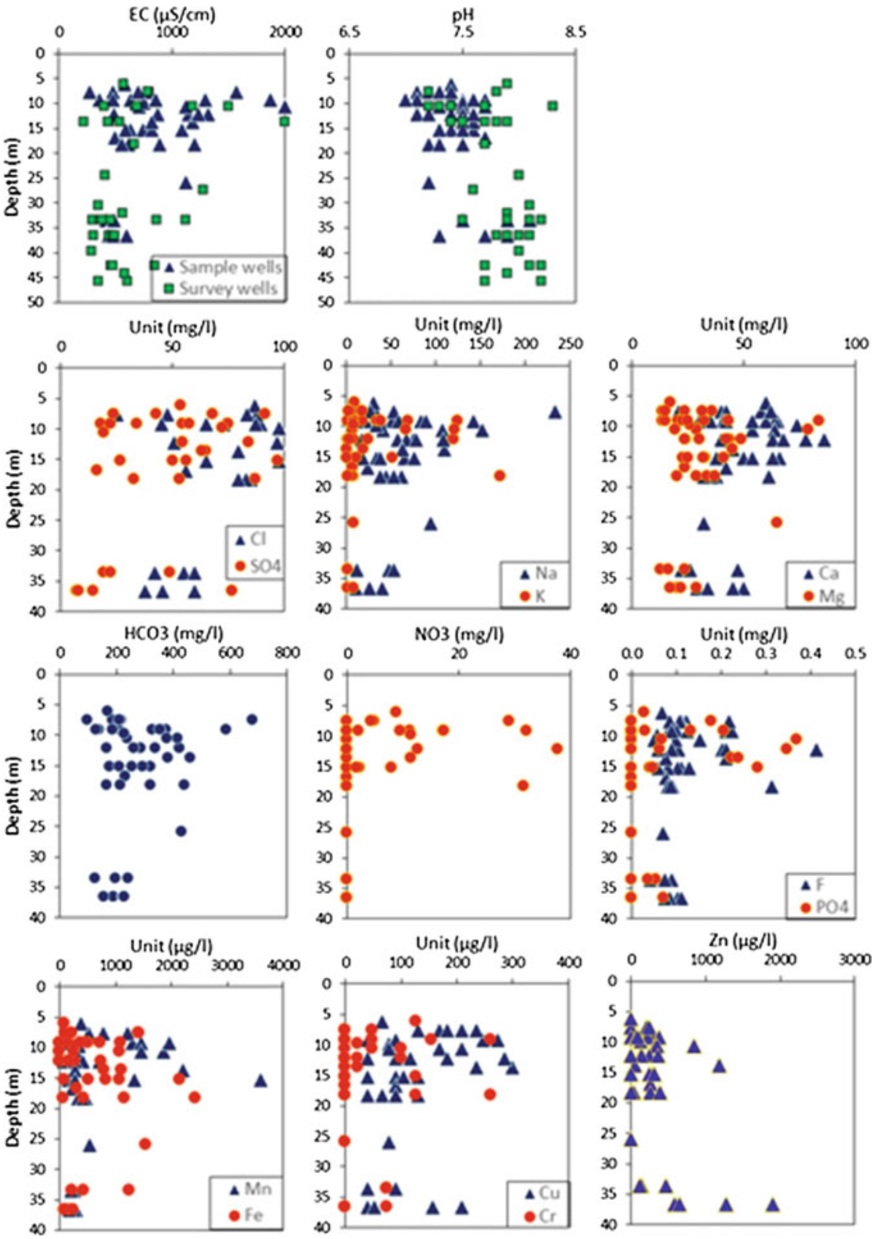

Fig. 18.3 Vertical distribution of EC, pH, major and minor ions and trace metals in the groundwater

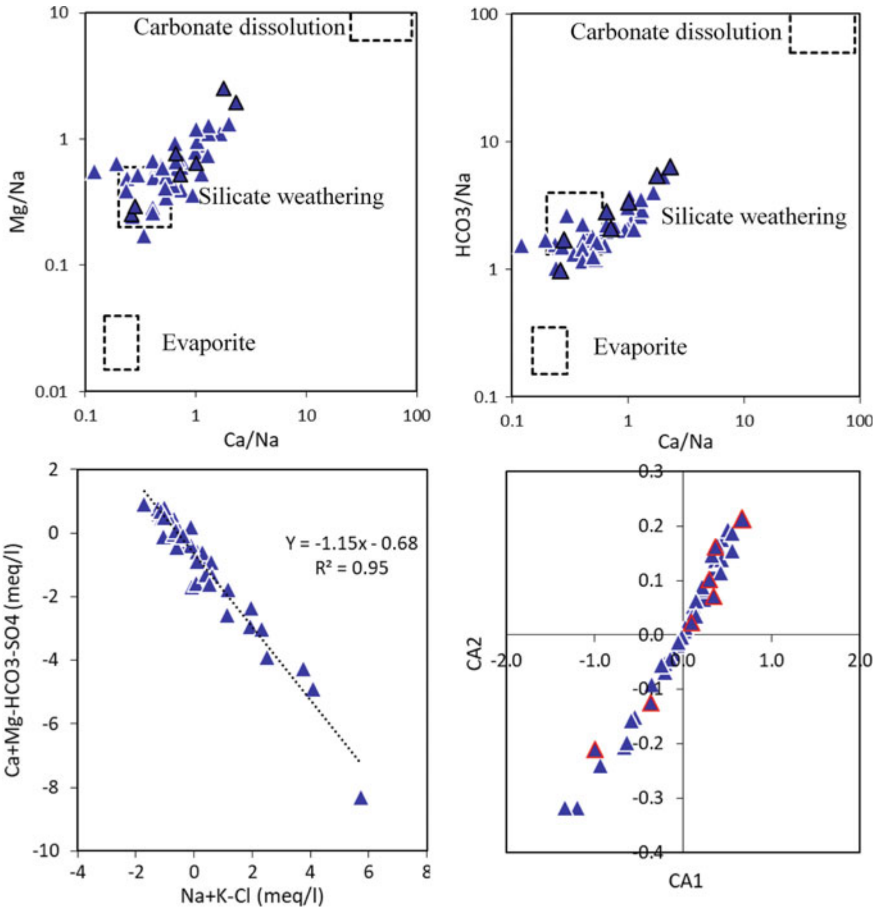

Fig. 18.4 Role of silicates and carbonates minerals weathering and ion exchange reactions on water chemistry

exchange reactions. Likewise, Na/Cl = 1 shows halite dissolution or surface input. As halite is highly undersatured in this region (SI <−6), chloride is derived from anthropogenic sources. To explain the impact of mineral weathering process on groundwater quality, Na normalized molar ratios of Ca/Na, Mg/Na and HCO_3/Na are employed (Gaillardet et al. 1999).

Figure 18.4 depicts that most of the samples plotted between silicate and carbonate weathering zones, which suggests that the water quality is predominantly controlled by the carbonate dissolution. In fact, weathering rate of carbonates is faster (12 times) than silicates (Meybeck 1987). In addition, $mHCO_3$/mNa + K ratio is higher than one in most of the samples. Molar Ca/Mg ratio is generally used to distinguish the impact of dolomite (mCa/Mg = 1), calcite (2 > mCa/Mg > 1) and silicate (mCa/Mg > 2) weathering processes on water quality (Mayo and

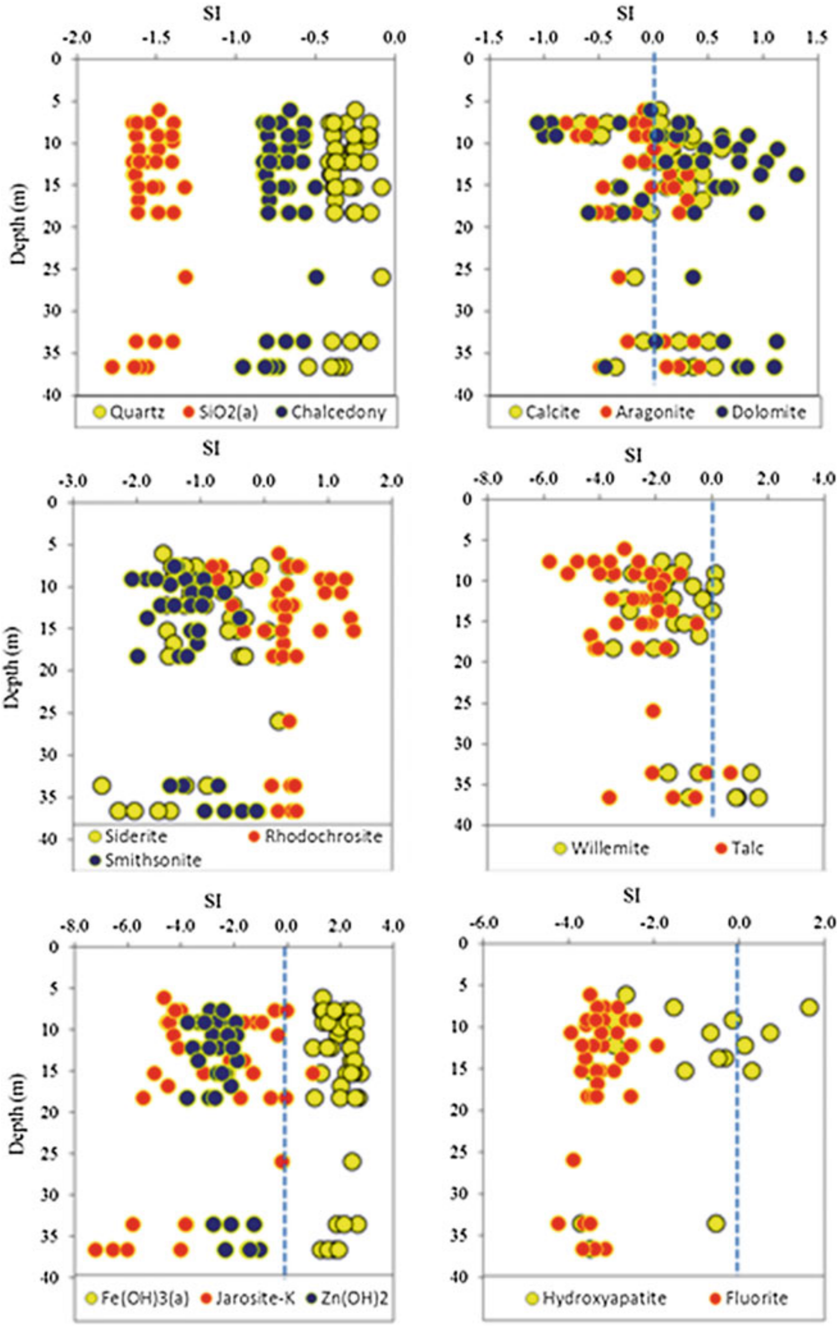

Fig. 18.5 Saturation state of selected phases in the groundwater

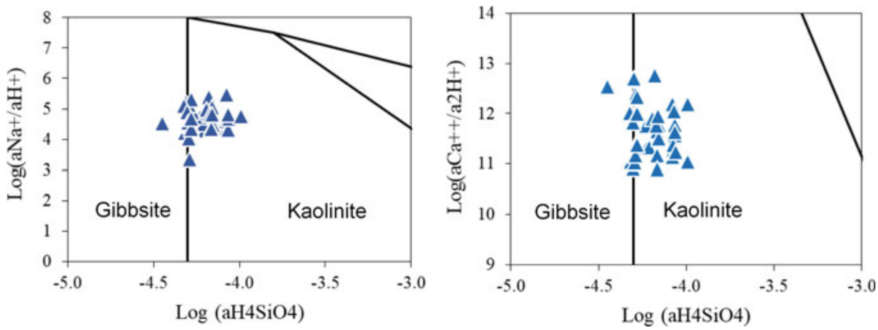

Fig. 18.6 Stability diagram of the partial system $Na_2O–Al_2O_3–H_2O–SiO_2$ and $CaO–Al_2O_3–H_2O–SiO_2$

Table 18.2 Pearson correlation analysis results obtained from groundwater quality data

n = 37	EC	TDS	Na	K	Mg	Cl	HCO_3	SO_4	NO_3	F
EC	1									
TDS	**1**	1								
Na	**0.9**	**0.9**	1							
K	**0.7**	**0.7**	0.4	1						
Mg	**0.8**	**0.8**	**0.6**	**0.5**	1					
Cl	**0.9**	**0.9**	**0.7**	**0.6**	**0.7**	1				
HCO_3	**0.9**	**0.9**	**0.9**	**0.5**	**0.7**	**0.6**	1			
SO_4	**0.8**	**0.8**	**0.6**	**0.6**	**0.6**	**0.6**	**0.6**	1		
NO_3	0.1	0.1	0	0.3	−0.1	0.1	0.1	0	1	
F	0.1	0.1	0.1	0.1	−0.2	−0.1	0.1	0	**0.6**	1

$P < 0.05$

Loucks 1995; Rajmohan and Elango 2004). In this study, this ratio is generally less than two, which justify that carbonate dissolution is a major process that regulates water quality in the RSB.

In order to explain the mineral water interaction, silicate weathering products and carbonate minerals dissolution in details, aqueous geochemical modelling (PHREEQC code) is employed. Saturation indices (SI) and ion activities were calculated using PHREEQC. Dissolution and precipitation of particular mineral phases are identified using SI values. Figure 18.5 illustrates the saturation state of SiO_2, carbonate, silicates, hydroxides and fluorite phases. The dissolved CO_2 in the shallow wells ranges from −2.5 to −1.3 with an average value of −1.9, which is higher than atmospheric CO_2 (−3.5). This observation indicates that system is opened to atmosphere and dissolved CO_2 is likely derived from organic matter degradation/root respiration (Appelo and Postma 2005) or vertical leakage of wastewater (Sinha and Saxena 2006). In the study region, carbonate phases (calcite, aragonite and dolomite) show saturation and over saturation in the groundwater in most of the samples. Hence, dissolution and precipitation of carbonate minerals largely governed the groundwater quality in the study region. In contrast, sulphate phases (anhydrite, gypsum, melanterite; SI: −10.3 to −1.6) fluorite (SI < −1.9) and halite (SI < −5.9) are undersaturated. SI of silicates indicate that phases such as sepiolite (−7 to −2.7), chrysotile (−7.9 to −1.7), amorphous silica (−1.8 to −1.3) and chalcedony (−0.5 to −1.0) are undersaturated while quartz (−0.5 to −0.1), willemite (−3.6 to 1.7) and talc (−5.8 to 0.7) are saturated or near saturation in the groundwater.

In the case of iron, groundwater shows saturation/oversaturation with hydroxides ($Fe(OH)_3$(amorphous), Goethite), oxides (Hematite) and carbonates [Siderite ($FeCO_3$)]. In contrast, manganese oxides (Hausmannite, Pyrolusite) and hydroxides (Manganite, Pyrochroite) show undersaturation but manganese carbonate [rhodochrosite ($MnCO_3$)] expresses saturation/oversaturation in the groundwater. Biswas et al. (2012) reported similar observation in the eastern part of the Ganges basin. Like manganese, smithsonite ($ZnCO_3$) also indicates near saturation in these wells. Further, near saturation is also observed in the willemite (Zn_2SiO_4). The saturation indices of mineral phases evident that the water quality is governed by weathering of carbonate and silicate minerals along with oxides and hydroxide phases (i.e. Fe)

Ion activities, calculated by the geochemical modeling, are employed to draw mineral stability diagrams to describe the equilibrium status of silicate weathering products formed from incongruent dissolution of silicates with groundwater (Stumm and Morgan 1996). In this aquifer, clay-water interaction is very common because RSB is formed by the alluvial deposits. Groundwater samples are plotted in the stability diagram of the partial system $Na_2O–Al_2O_3–H_2O–SiO_2$ and $CaO–Al_2O_3–H_2O–SiO_2$ to explain the reactions governing the system (Nesbitt and Young 1984; Rogers 1989; Rajmohan and Elango 2004). Groundwater samples clustered predominantly in the Kaolinite field and few of them in the Kaolinite-Gibbsite interface (Fig. 18.6). Hence, the water chemistry is influenced by the kaolinite clay formations and explained below.

$$\underset{\text{Albite}}{2NaAlSi_3O_8} + 11H_2O + 2CO_2 \leftrightarrow \underset{\text{Kaolinite}}{Al_2Si_2O_5(OH)_4} + 2Na + 2HCO_3 + 4H_4SiO_4$$

$$\underset{\text{Ca - smectite}}{6CaAl_2SiO_{10}(OH)_2} + 2H^+ + 23H_2O \leftrightarrow \underset{\text{Kaolinite}}{7Al_2Si_2O_5(OH)_4} + Ca^{2+} + 8H_4SiO_4(a) + 8H_4SiO_4$$

$$\underset{\text{Kaolinite}}{Al_2Si_2O_5(OH)_4} + 5H_2O \leftrightarrow 2Si(OH)_4 + \underset{\text{Gibbsite}}{2Al(OH)_3}$$

Based on sediments analysis using XRD, Shah (2014) identified the occurrence of silicate minerals (feldspar, kaolinite, quartz, montmorillonite, muscovite and goethite) in the Varanasi, Ganges Basin.

As mentioned earlier, ion exchange reactions are also affected the water quality in the RSB. The ion exchange reactions are classified into cation exchange

[Na(K)-Clay + $Ca^{2+}(Mg^{2+})_{aq}$ = $2Na^{+}(K^{+})_{aq}$ + Ca(Mg)-Clay] and reverse ion exchange (RIE) [$Na^{+}(K^{+})_{aq}$ + Ca(Mg)-Clay = Na(K)-Clay + $Ca^{2+}(Mg^{2+})_{aq}$]. Ion exchange reactions can be explained by Na/Cl ratio and chloro-alkaline indices (CA1 and CA2; Schoeller 1977). In this study, Na/Cl ratio is less than one in 26 samples (70%) and highlight the role of RIE processes. CA1 {CAI1 = [Cl − (Na + K)]/Cl} and CA2 {CAI2 = [Cl − (Na + K)]/[Cl + HCO_3 + SO_4 + NO_3]} are calculated in this study. In this calculation, positive and negative values denote RIE and cation exchange, respectively. Results suggest that 20 wells (54%) show positive indices (Fig. 18.4). Hence, RIE and cation exchange are contributed well; however, former is predominant in this aquifer. Besides, Cl corrected Na + K is plotted against HCO_3 and SO_4 corrected Ca and Mg to validate the role of ion exchange reactions in this aquifer (Fisher and Mulican 1997). Figure 18.4 depicts negative slope (−1.15) with strong correlation ($r^2 = 0.95$) and prove that ion exchange reactions governed the water chemistry in the shallow wells along with mineral dissolutions.

Impact of land use pattern on shallow aquifer

Groundwater quality in the RSB is affected by the surface contamination sources. High dissolved CO_2 value in the shallow wells (average −1.9 > atmospheric CO_2) suggests that the groundwater is contaminated by the vertical leakage of wastewater from various contamination sources from surface (drainage/sewage lines, domestic wastewater and other sources) (Sinha and Saxena 2006; Mukherjee et al. 2007). Sinha and Saxena (2006) also reported high free CO_2 and low dissolved oxygen in the shallow aquifer. Similar observations are also stated by the Raju et al. (2009), Nandimandalam (2012) and Khan et al. (2015).

In this study, dissolved silica is not varying with depth and justify that the depth wise variation is not due to silicate weathering alone. Figure 18.3 displays that shallow wells have high Cl, NO_3, SO_4, HCO_3 and K. Further, undersaturation is observed in the sulphate (gypsum and anhydride) and chloride (halite) minerals in the groundwater. Hence, shallow wells are more vulnerable to surface pollution sources. Excessive fertilizers (NPK, muriate of potash, gypsum) application, irrigation return flow and domestic sewage water are claimed the enrichment of the above parameters in the shallow well water. In the Muzaffarnagar district (Uttar Pradesh), high chloride and sulphate are noticed in the groundwater due to wastewater derived from chemical fertilizers and sugar factories (Tyagi et al. (2009). During the fieldwork, it is found that domestic sewage water is directly discharged into the ground/ditches near to hand pumps/houses and storage of animal waste by the local populace. Other studies also reported that high nitrate in the groundwater is derived from these sources (Somasundaram et al. 1993; Chakraborti et al. 2011; Raju et al. 2009; Tyagi et al. 2009; Nandimandalam 2012; Khan et al. 2015). Nitrate in the groundwater is governed by the nitrification and denitrification processes. Nitrification (oxidation of ammonium and organic matter degradation) results acidic proton, which is neutralized by the carbonates and silicates in the vadose zone. Denitrification observes the acidic proton and increases pH in the water. In the study region, nitrification is predominant process in the shallow aquifer. Vertical infiltration of wastewater from land surface and nitrification processes induce mineral weathering and ion exchange reactions in the vadose zone, which resulted the enrichment of major ions and nitrate in this aquifer. Water types ($CaMgHCO_3$ (n = 17) > CaMgCl (n = 15)) and correlation between Cl^- and SO_4^{2-} with major ions justify this argument. Likewise, high fluoride in these wells are likely derived from surface (evaporated water from surface, clays in ceramic industries and phosphatic fertilizers) (Datta et al. 1996; Sinha and Saxena 2006; Misra and Mishra 2007; Kundu and Mandal 2009) because F^- shows significant positive correlation with Cl^-.

Groundwater management

Groundwater development and management is an immediate task to preserve the shallow aquifer in the RSB. This study recommends the following options to preserve groundwater resources.

- Periodic groundwater quality monitoring is a right option to protect and manage the aquifer.
- Care should be taken during the hand pumps/tube wells installation to avoid the vertical leakage from wastewater accumulated in the ground. Wastewater accumulation is noticed during fieldwork.
- Local populace should be trained for disposal and reuse of animal waste (i.e. cow dung) to protect the aquifer. Huge heap of animal waste storage is observed during fieldwork.
- Managed Aquifer Recharge (MAR) and rainwater harvesting methods should be implemented in the village and household level to improve the water quality and aquifer storage.
- Unused wells and surface structures (i.e. ponds, pits) can be used as a groundwater recharge options.
- Village level awareness program will be carried out about water borne diseases, water demand, water quality and waste management to protect the shallow aquifer.
- Smart agricultural practices (high production with less water and agrochemicals) will be introduced in the local populace to save water and protect water quality.

18.6 Conclusions

Groundwater quality in the shallow unconfined aquifer is deteriorated by the natural and man-made activities. Results of this study suggest that the groundwater quality is governed by the carbonate and silicate weathering reactions in the RSB. Ion activity ratios and stability diagrams suggest that kaolinite, formed from silicate weathering reactions, is governed the water chemistry in this region. In addition, ion exchange reactions also contributed well in groundwater quality variation. Saturation indices reveal that carbonate minerals are saturated/over saturated whereas fluorite, halite and sulphate minerals are under saturated in this aquifer. Besides, carbonates, oxides and hydroxides phases have substantial contribution in trace metals occurrence in the groundwater. In addition to natural processes, high concentrations of Cl^-, SO_4^{2-}, NO_3^-, Cu, Mn, Fe and Cr and dissolved CO_2 justify that vertical infiltration of wastewater (derived from domestic sewage water, irrigation return flow, animal waste accumulation) leads to mineral weathering, ion exchange reactions and nitrification in the vadose zone, which increases pollutants load in groundwater. The present study concluded that well planned groundwater management program is required to secure the shallow aquifer in the RSB.

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Chapter 19
Water Governance: A Pragmatic Debate of 21st Century; An Indian Perspective

Omi Kumari and Manish Kumar

19.1 Introduction

The study of human evolution has come up with many questions on the sustainability of life on earth. In geography, researchers are investigating the pattern of human settlement. Since human understood water is the basic necessity of life, the human population started concentrating beside rivers, today almost every prominent cities are found to be residing on the side of a river. In India, the presence of rivers or streams and other wetlands is the primary reason for population growth over here from centuries. But, today the perception of water has been changing, and these changes are very complicated. On the launch of International Decade for Action, "*Water for Sustainable Development 2018–2028*" United Nations chief has said that "*Water cannot be taken for granted*" (UN 2018). We have seen several times how various climatic zones in the world have faced severe problems such as drought and floods. There is a pressing question, is it water unavailability which is causing stress or the improper management of water is the prominent problem?

Water cannot be put in the category of something which is going to extinct; it must be understood that this basic necessity of life belongs to renewable resources. Water has been unconsciously exploited by humankind, and this current ongoing craptastic management is an added burden to its scope and quality. People and governance are the two main pillars of water resource management. This chapter will primarily analyze the debate on water management system in India. The question of water governance and its sense of persuasion will bring together the

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sentiments on water availability, its utility, organizational behavior, and the captivity for its management.

Groundwater is a primary source of water in many parts of the world, and in India groundwater is the most often source of freshwater (Shankar et al. 2011). Since India emerged as the largest user of groundwater, and as World Bank has also stated India's on the "*brink of severe water crisis*" (UN News 2018), these devastating statements on water resources took a pragmatic place in the debate of our existence. The problem of water challenges in the country has taken the space where we have to address the prime factors of governance and factors affecting the uses and utility of water. The farmers are migrating in the search of water and the employment are being lost due to the crisis of water in the several regions of the country (Matthew 2009). This chapter will also try to understand the people's perception of future water availability, and governmental efforts to resolve the complication.

Nowadays people are demanding for the safety of water bodies in the country. Awareness among the young population has been seen in many parts of the country which is a very positive sign of attitude. Many people have come forward to protect our natural resources. In India, the sense of understanding is varying in every particular situation. It was observed that the action and perception of the individual in everyday life are very different especially for the utilization of natural resources such as water, soil, trees etc. Many cases in India has been seen when local people are found to be detached from their native natural resources. The governing factor and high demand for such resources is the prime reason for intervention in people's life. Though there are several cases found where industries and firms are found to be ruining water quality, there are specific measures that are made for water governance. The proper resource utilization starts from home and so, the community and local people. The pressure for saving nature and its proper usage is one of the perspectives which caused governments to have strict laws and policies. In the ground perspective, it creates a picture of uneasiness among the people using the resources. It was concluded that when law restricts indigenous people for the utilization of natural resources, it creates a sense of detachment among them. This discernment is one of the factors which is lowering down the tendency for bothering about their natural environment.

There have been many times authorities have stated about the non-cooperation of people in the development process. This chapter aims to find out the understanding of this particular gap between the involvement and concern of the authority and people. The poor water management in India has now become the compelling argument to discuss on, and this chapter will try to understand the debate on the governance of water in India. This chapter will analyze India's water problem through people's perception of water governance and the analysis of hydrologist, academicians, government reports, and policymakers. Is the crisis of unavailability of water is real, or there are other factors which aroused the situation at this level? (Express News Service 2017).

19.2 An Understanding of Water as a Natural Resource in India

Since the time India emerged as the largest user of groundwater for agriculture, and domestic purpose, environmental agencies are working actively to improve the quality of water to make it available for the future generation (Shankar et al. 2011). The quality of groundwater is found to be drinkable in many places, and lack of availability of piped water supply from rivers in the homes made people depend on groundwater. Knowingly or unknowingly Indian people became habituated with using groundwater. Another factor was the pollution in the major rivers. The colour and odour were changing, and people felt safe while using groundwater. At present, various types of contaminants from anthropogenic activities are depleting the quality of groundwater which raises a question on the safety of groundwater. The governance of water in India was always a problem because there were many middlemen between people and government. But, the government has always been blamed for this situation. People in India consider rivers as deity such as river Ganga and Yamuna. How come people pollute the same river which is sanctified in their culture? While talking with some of the specialist and officers of Delhi Pollution Control Committee (DPCC) on water governance and people perception, it was found that officers are also evenly judging this situation and asking for more researches for its prevention. There is a difference in the deeds and opinion of people. The understanding of water as a natural resource and should be used for the legitimate purpose is the primary question that needs to be addressed before coining the term water crisis.

On the report of Environmental Performance Index (EPI) 2018, The Ministry of state has given comments on groundwater 'Different weight and the difference in the methodology used implies that ranking rivers are not comparable, and have their limitations'. "Under the category water resources, the only indicator shows is wastewater treatment, which puts developed countries on the top since it is a measure of the capacity to address a problem" (Parelkar 2018). If the statement of the ministry of state will be refined, then some facts can be understood while understanding the problem of water in India. According to the researcher, India measures water quality through mechanical method whereas developed countries are using technically advanced digital instruments which give them reports on water quality in every given time. Ministry also defined how the lack of wastewater treatment capacity has caused developing countries to sink into the poor category. The scientist community indeed decides indicators, and there should not be many measurement indicators for different countries. The index taken by EPI is the ideal indicator which is certainly not favoring any specific nation, and it needs to be understood by the ministry that this vulnerable situation requires action rather than the statement on biasedness in indicators and error in the measurement techniques.

Indian rivers are polluted, especially river Yamuna, and Ganga has repeatedly ranked among the top ten polluted rivers in the world (Help Save Nature Staff 2018). The understanding of the river's significance in Indian culture and the public way of treating a stream is very disgraceful. A large chunk of contamination from various sources such as Industries and household wastes is polluting the river water at a massive level. 'The Ganga is the most sacred river in India', and it is also one of the most polluted in the world.

Can a river get their rights for themselves? There was a huge debate when Uttarakhand High Court was declaring their rights as a legal entity. Researchers have asked questions, what kind of power will be given to the river? (Kothari and Bajpai 2017). This idea of granting rights to the river has come initially from New Zealand. The primary question was what will be the rights of a river, and how these rights will be protected? It is clear that the Indian rivers are sacred and violated in many terms, then how will the rights will get implemented? The Uttarakhand High court has named many parent offices (The Chief Secretary, State of Uttarakhand, Director NAMAMI Ganga Project, Director (NMCG), Advocate General, State of Uttarakhand, Director (Academics), Chandigarh Judicial Academy, and Supreme Court) which are supposed to take care of the river. These laws are not unique, this idea has been received from the policies for water governance of New Zealand, and it is found that in New Zealand Iwi people fought for the safety of Whanganui River and it looks likely that they will take their parenthood seriously (Kothari and Bajpai 2017). But, can it happen in India, aren't the suggested departments and offices were previously involved in the rejuvenation of river water? The complications of the new law in India is sensible, and it will surely get compared with the river management in New Zealand; potentially there has been a various divergence in implementation and regulation in India, and unless these points are not fixed such decisions will only be on the paper.

19.3 Groundwater Challenges in Country

Groundwater is the primary source of water in India. According to Central Ground Water Board (CGWB), the majority of groundwater in India are found to be fresh; except for the region beside sea coast in Gujarat and some areas where surface water is in extensive use; this area includes some parts of Punjab, Haryana, Uttar Pradesh, Andhra Pradesh, Rajasthan, Karnataka, M.P, and Tamilnadu.

On an annual basis, India receives precipitation of 4000 Billion m^3 including snowfall, and the runoff was counted around 1869 Billion m^3 in the river. In the data of 1997 per capita, water availability was 1869 m^3/year. The water availability was found highest in Brahmaputra basin 14,057 m^3/year/person, and lowest in Sabarmati basin 307 m^3/year/person (CGWB). Himalaya being on the north of India is the primary factor behind this high amount of precipitation in the country.

According to the report by CGWB-2013, the past four decades has come up with a massive change in the groundwater extraction in the country. The data shows that the dug wells in between 1951 and 2001 has been increased from 3.86 million to 9.62 million, and tube wells from 3000 to 8.35 million. Figure 19.1 is showing

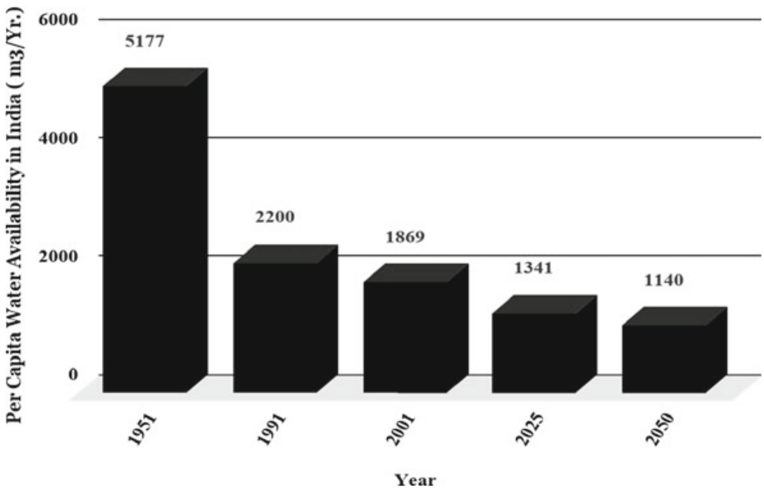

Fig. 19.1 Per capita water availability in India

water availability in India throughout these periods. The prediction of water availability for 2025 and 2050 indicates it is miserable lowering down.

Three Indian states (Punjab, Haryana, and Uttar Pradesh) accounts for 57% of the tube wells; this area falls in the region of Indo-Gangetic plain (IIT K). This region is well known for high yielding of crops in the country. Agriculture needs a high amount of water, and the less accessibility to surface water is the primary reason this area become dependent on groundwater.

19.4 Drinking Water Analysis of Indian States

The less availability of supply water (tap water) to the rural households has made this significant group of the Indian population depends on other sources of drinking water. The use of tube wells and a hand pump is very often in the rural part of the country, and through the available data of 1986–87, it was found that people have managed to drink water from other sources. The 67% of Indian population lives in the rural settlement, so it will be more precise to understand the water condition if we will focus on the rural areas of the country (India Population 2018). The vital point was noted that the rural and urban percentage of population availing water supply has been in very distinctive, it can be seen in Fig. 19.2 taken from National Sample Survey Organization (NSSO) (1986–1987). The rural population in the states like Punjab and West Bengal, approximately 3/4th of the population were depended on tube wells or hand pump. Figure 19.2 analyses the tap water used for drinking purpose in particular Indian states and all India. It was found that only 16% of Indian rural population was using tap water in 1986–87.

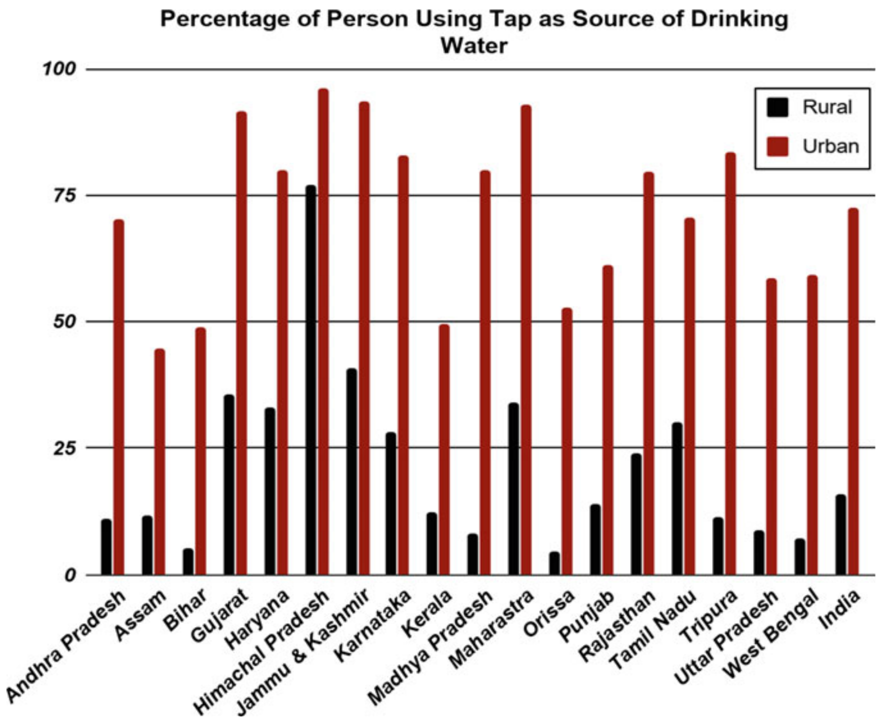

Fig. 19.2 Percentage of person using tap as source of drinking water. *Source* NSSO (1989)

Figure 19.2 shows a variation in the availability of piped water supply (through tap) in the rural and urban population. The urban area has a very different scenario then the rural area in all states including the overall population of India. 72.43% of the population was getting tap water in the urban sector while in the rural sector the percentage was around 16%. In Fig. 19.3 the data shows the condition of the rural percentage of the population who can get supplied water for drinking purpose. This data is carried out from the Strategic Plan—2011 to 2022 of Department of Drinking Water and Sanitation—Rural Drinking Water, Ministry of Rural Development (MRD). This survey was carried out in 2008–2009 and found from the 65th survey by the National Statistical Organization (NSO) where some points are highlighted by the Ministry of Rural Development on the drinking water coverage of Indian states. It was found that eight states of India have less than 10% of piped water supply to the rural population.

In rural areas of the country around 33% of people are getting piped water supply, where wealthier people account for the 32% of total water supply, and only 1% of water is used by the poor people. There have been many changes in the data found from 1986–87 to 2008–09; this seems very positive in many states of India. The data of the year 1986–87 was showing less than 35% of supplied water for almost every states of India. But, in the data of 65th round of National Sample

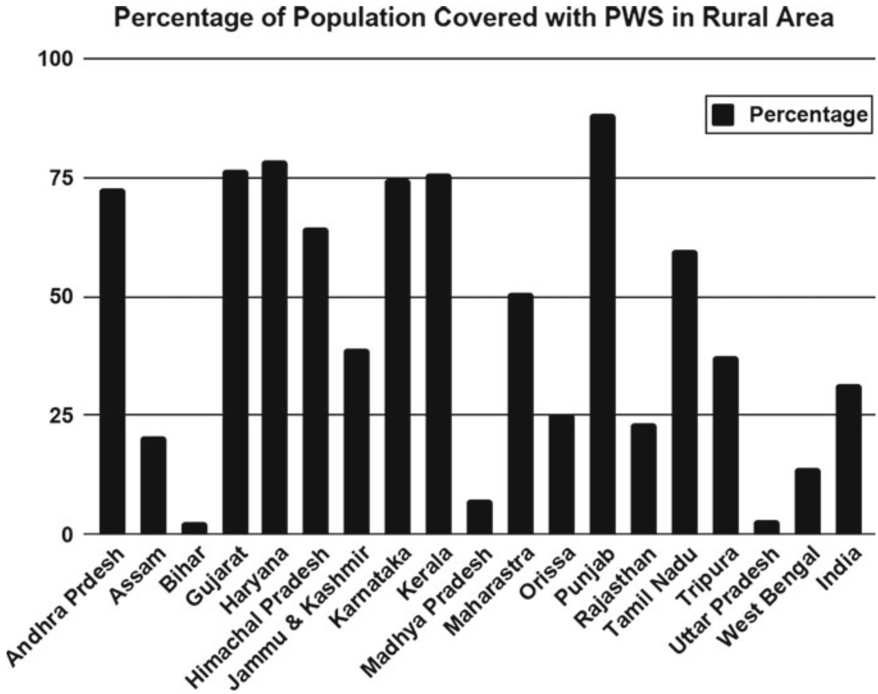

Fig. 19.3 Percentage of population covered with PWS in rural area. *Source* MDWS (2013)

Survey Organization (NSSO), it was found that many states have jumped to the hike of more than 60% of rural piped water supply. Some states like Andhra Pradesh who had only 11% of water supply in the rural region are now supplying 78%, in Punjab, 80% of the rural population were using tube wells in 1986–87, but in recent data, 89% of the population was using piped water. Some states are still shrinking on the bottom in terms of water supply like Bihar, Uttar Pradesh, and Jharkhand which has less than 5% of piped water supply in rural areas.

The condition of drinking water availability and efforts of the government to the citizen is clearly understood through the analysis of data, 'the better governance always leads to a better outcome for the citizen'. The southern, and North-Eastern states have done comparatively very well in terms of providing water supply to the rural population.

19.5 A General Analysis of Water Quality in India

According to NITI Aayog report on 14th June 2018, India is suffering from worst water crisis; report says that around 600 million people in India are suffering from high level of water stress, and 0.2 million people are dying due to lack of access to

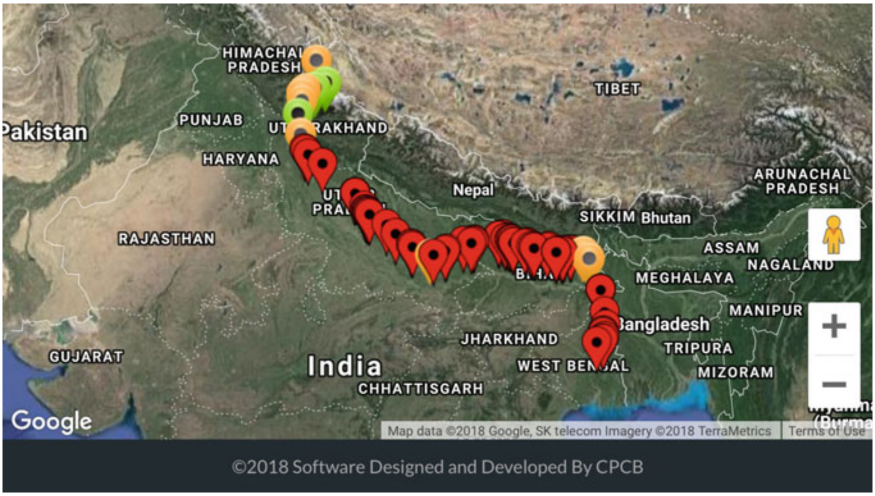

Fig. 19.4 Quality of Ganges water flowing through different Indian states. *Source* CPCB

safe water (India Population 2018). From the data released by the Central Pollution Control Board (CPCB) in 2013, the sewage generation from class one cities was 2601.3 MLD against the treatment capacity of 1192.4 MLD (CPCB 2013). The sewage generation is far more than the total treatment capacity, which contaminates and degrade the water quality; and this is a clear indicator of the unsafe condition for water. On the picture released by CPCB, there were several comments that were received on the water quality of Ganges. The water quality is shown in the colour of red and green; the green colour shows the safe condition of water and red colour indicates the water is not fit for bathing and drinking (Fig. 19.4).

The question of unsafe water of Ganges was asked in every print, and electronic media, where the problem of Ganges water is unsafe for drinking and bathing were discussed, and some of the points were being noted (Ashok 2018a, b). The trend of bathing in holy river Ganges is not getting prevention, neither there is any news from the government. Compelling fact is, the public is not accepting the fact that Ganges water is not safe for bathing in most of the places. It should be recommended to the government that they should release an advertisement to prevent people from using the unsafe water, and educate to understand to use the natural resource wisely.

19.6 Conclusion

The study shows how the water becomes problematic when there is less governance. The management of water has come up as the main issue when we talk about water problems. As the study showed the problem of water in rural areas, it has measured how some of the states have done magnificent work in making water reach to the households. Some of the states have a deplorable condition, and clearly, this is a sign of bad governance. The most significant stretch of Ganges passes through Uttar Pradesh and Bihar, and in this region, the condition of Ganges water is found to be very poor, and these two states have also ranked lowest in the water supply.

The inadequate water supply is a problem though there are some places in India where the amount of supplied water is more than the need of an ordinary person, and Delhi tops in the list. The renowned hydrologist Professor Biswas have discussed the water governance and strategy of Delhi from the 1950s and showed how Delhi lagged every bit in management, and now a failure. It is fascinating to know that in the 1950s water supply in Delhi was better than Tokyo and Osaka, and it was comparable to the city like Singapore. At present Singapore is one of the most excellent examples of water management in the world (Biswas and Tortajada 2014). A few years back Delhiites were getting 2–3 h of water supply, but in the present date, they have an unlimited water supply with two kinds of supply water tap in the various settlement. According to the people, the water from one is for drinking purpose and another for other household purposes. The excess supply of water in a settlement is not a good symbol of governance. A human needs 70 L per person per day for a living a decent life (WHO Regional Office for South-East Asia). Delhi has been in stress of water for very long time, and this long-term discomfort in Delhi because of water, always needed the best management rather than quick fix temporary solution of purchase of the high amount of water, and moreover, the new government came up with new policies and governance. When we go through the wastewater management and condition of streams flowing through the territory of Delhi, this situation seems to be alarming and can be considered as the hazard for the long term.

When we talk about sustainability, some points were needed to be learned that people are still not capable of altering their actions. Several factors in India is a puzzling problem since people think the “Ganges water is never going to be dirty” or “air will get cleaned by their own”. 67% of the population living in India is in a rural settlement, where people depend on their efforts to extract water from a bore well, tube well or hand pumps. There are several cases found where people do not consider supplied water well qualitatively enough to use for the household purpose. In a talk with the senior officer, it was found that they tried to provide water to the households in Guwahati, but the acceptance of water in the houses was very less. This unfaithful situation where people are not accepting the service is stressful, but there are several unanswered questions with these sentiments of Indian People for their lost faith in Government. When the government officials were asked which water they will prefer they have answered as groundwater is a safer approach. River water is contaminated, groundwater is depleting, and conditions are going worse in India.

Management is not always one-sided, but there needs to have cooperation among all stakeholders. A cumulative talk between government authorities and the public can be a possible solution. There is a need to have more governance and security of water according to public needs. If there are rights given to the river, or people are taking parts in the management, what impact will it have in the water management? There are several fundamental questions India needs to address while talking about the water crisis in the country. With the phenomena of stressed life of water from its journey of precipitation to the sea, it covers many aspects of human's attitude which includes everyone from an individual to the top officials. While the Indian government keep on shouting about the water crisis in the country, in reality, it is a crisis of water management.

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