ORGANIC MICROPOLLUTANTS IN THE RIVER YAMUNA AND RANNEY WELLS IN CENTRAL DELHI

Ph.D. THESIS

by

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DEPARTMENT OF CIVIL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY ROORKEE
ROORKEE-247 667, INDIA
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A THESIS

Submitted in partial fulfilment of the
requirements for the award of the degree
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in

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CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in this thesis entitled "**ORGANIC MICROPOLLUTANTS IN THE RIVER YAMUNA AND RANNEY WELLS IN CENTRAL DELHI"** in partial fulfilment of the requirements for the award of the Degree of Doctor of Philosophy and submitted in the **Department of Civil Engineering** of the Indian Institute of Technology Roorkee, Roorkee is an authentic record of my own work carried out during a period from December, 2009 to December, 2015 under the supervision of Dr. Indu Mehrotra, Professor (Retd.), and Dr. Pradeep Kumar, Professor, Department of Civil Engineering, Indian Institute of Technology Roorkee, Roorkee.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other Institution.

(SOMA KUMARI)

This is to certify that the above statement made by the candidate is correct to the best of our knowledge.

(Indu Mehrotra) Supervisor	(Pradeep Kumar) Supervisor

The Ph.D. Viva-Voce Examination of **Soma Kumari**, Research Scholar, has been held on **August 16th, 2016.**

Chairman, SRC **Signature of External Examiner**

This is to certify that the student has incorporated all the corrections in the thesis.

Signature of Supervisors **Head of the Department**

Date:

This thesis is dedicated to my parents and supervisors

for their endless love, support and encouragement.

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ABSTRACT

Due to prevalent use of pharmaceuticals, pesticides, herbicides, personal care products, hormones, petroleum hydrocarbons, and industrial chemicals, surface water bodies get polluted. In conventional drinking water treatment process, removal of OMPs is not been in practice. Riverbank filtration (RBF) on the other hand is able to remove/reduce the OMPs through the processes such as filtration, sorption, acid-base reaction, hydrolysis, biochemical reactions etc. RBF is a process where wells adjacent to the rivers draw water that is a mixture of ground water and filtered river water.

The thesis has been organized into six chapters. **Chapter 1** describes the background and motivation of the study. Contamination of fresh water resources with thousands of persistent organic micropollutants (OMPs) is a matter of concern. Challenges are that their numbers and concentrations are increasing and vary widely from place to place. Conventional water treatment processes are not adequate to remove the OMPs. Additional operations are required to remove OMPs to produce potable water. The result is an increase in the cost of drinking water. Natural filtration such as riverbank filtration (RBF) or Lake Bank filtration (LBF) is reported as a useful alternative for the attenuation of OMPs.

The database related to the OMPs that are present in a polluted Indian River is not available. It, therefore, led to quantifying the OMPs in the polluted stretch of the river Yamuna in central Delhi. Also, to find out their frequencies of occurrence, and concentration ranges. It became imperative to investigate the impacts of the polluted river on the well field comprising of eight Ranney wells (RWs) in the vicinity of the study site of the Yamuna. Therefore, the focus of the study was towards the assessment of pollution, measurement of OMPs present in the water of the Yamuna River and nearby eight RWs. Experimental results and outcomes of each phase of the study are presented in four chapters (Chapters 2-5) and conclusions of the study in Chapter 6.

In the first phase, the pollution of the Yamuna River along with the quality of the water from eight RWs near Akshardham temple in Delhi was assessed in the monsoon and non-monsoon of the year 2013-2014. The sampling schedule, analysis protocol, and results are presented in **Chapter 2**. An attempt has also been made to establish the connectivity between the river and

RWs by monitoring the stable isotopes $\delta^{18}O$ and $\delta^{2}H$ of the water samples. The $\delta^{18}O$ concentration of the river water in non-monsoon was significantly more than the monsoon. The monsoon river water coincided with the local meteoric water line (LMWL). The signature of non-monsoon river water was different from the LMWL. The water from the wells in the monsoon was marginally lighter than the non-monsoon water. Similar differences were found in the electrical conductivity (EC) of the water from the river and the RWs. The EC of non-monsoon river water was 3 to 4 times the EC of the monsoon water whereas EC of the monsoon and non-monsoon RWs water was either same or marginally different.

The river and RWs water responded positively to the bacterial pollution. However, total coliform and E. coli in the well water was around 5 log less than the river water in both non-monsoon and the monsoon seasons. The organic pollution of the river was more than the well water. The average DOC of 17 mg/L in the non-monsoon was reduced to around 2 mg/L in all the RWs except NR-I. Ultraviolet absorption at 254 nm (UV-254) and specific UV absorbance (SUVA) followed the same trend as of DOC. Results suggest that in the case of contaminated source waters, RBF is an effective pre-treatment option for the production of drinking water. However, further treatment of filtrate is necessary.

In developing countries, where river waters, in general, are impacted by wastewater, agriculture runoff, identification/quantification of OMPs has not been attempted. Given diverse nature, sources and effects of the OMPs, it deemed necessary to monitor OMPs in the river and well waters. Chapters 3 and 4 present the sampling protocol and measurement of OMPs by GC-MS in the river and well waters. The occurrence of OMPs in the Yamuna water in non-monsoon and the monsoon months is discussed in **Chapter 3**. Chapter 4 deals with the monitoring data of OMPs in the well water. Fifty-seven OMPs that were identified included the pharmaceutically active compounds (PhACs), pesticides, endocrine disrupting chemicals (EDCs), phthalates, personal care products (PCPs), fatty acids, food additive, hormones and trace organics present in hospital wastes. The two observations that were quite noteworthy regarding monitoring of OMPs are as under:

(i) Ten out of fifty-seven OMPs were detected in the monsoon but were not at all detected in non-monsoon

(ii) The concentration of forty-seven out of fifty-seven OMPs was more in the monsoon samples than non-monsoon samples.

In general, during monsoon season OMPs were present in much lower concentration in river water due to high dilution. But in the present study OMPs concentrations were found high due to surface runoff from the polluted catchment area. The reason for this contradiction could not be correlated with the octanol-water partition coefficients (log K_{ow}), solubility, and polar/non-polar characteristics of the OMPs. It could be due to the sorption of OMPs onto the sediments in an extensive network of interconnected drains and river during the low flow (~ 19 m^3/s) conditions in non-monsoon months. During the high flow conditions (~ 507 m^3/s), scouring of deposited sediments possibly results in erosion and dissolution of OMPs in the river water. In general, compared to rivers of Europe and United States of America, much higher concentrations of OMPs were found in the river Yamuna.

OMPs present in eight RWs were also quantified over a period of one year from Aug. 2013 to Aug. 2014. Results are presented in **Chapter 4**. Filtrates collected from RWs were although contaminated with OMPs, the concentrations were found to be much lower than the river water. Number of OMPs detected, their frequencies of occurrence and concentrations in RWs reduced substantially compared to river water. Among different RWs, in general, number of OMPs detected their frequencies of occurrence and concentrations correlated very well with the distance of RWs from the river. Larger the distance, lesser the number of OMPs detected and lower the concentrations. In spite of high concentrations (~ 50 μg/L) in river water of 3-acetamido-5-bromobenzoic acid, 1- dodecanethiol, diethyl phthalate, palmitic acid, and adenine, they were detected to be < 1 μg/L in samples from RWs. Only few OMPs e.g. simazine and aldrin, sometime exceeded 1 μg/L in RWs. Compared to other OMPs, in general, EDCs, PCPs, phthalates, fatty acids and food additives appeared more frequently in more number of RWs but in significantly lower concentrations than present in river water. Among hormones, only estriol detected once in RW P-4. Some of the OMPs e.g. adenine were never detected in any of the RWs.

The OMPs in the river water are likely to move through the aquifer. The fate depends on the nature of the OMP as well as the characteristics of the aquifer. Keeping this in view the fate of fifteen OMPs that were frequently detected in the Yamuna River water at Central Delhi was investigated under abiotic (predominantly adsorption) and biotic (mainly bio-sorption/bio-degradation) conditions in columns packed with the aquifer material. The OMPs tested on the column RBF wells. The list included pharmaceuticals and their raw materials, endocrine disruptors, steroids, OMPs found in hospital wastes, and personal care products structurally belonging to acrylates, neutral organics, amines, phenols and fatty acids. The findings of the column runs and experimental details are presented in **Chapter 5**. Columns were packed with aquifer material that was taken out from the laterals of the M-15 RW, during its cleaning operation. Among different OMPs, dimethyl maleate, benzoic acid, guanine, and lomustine were found to be more mobile than estriol, decanoic acid, 1-tridecanol, 1- eicosanol, triclosan, stearic acid and cetyl alcohol. The mobility depends on the polarity of the OMPs. The retardation factor of non-polar OMPs is more than the polar ones. However, the mobility of the OMPs is considerably restricted in the biotic column. Retardation factors (R_d) for OMPs varied widely in adsorption column from 3 to 772. In biosorption column, R_d ranged from 6 to 1692 showing better removal except for benzophenone.

Core findings of the dissertation along with limitations of the investigations carried out and a short note on future scope of the work are summarized in **Chapter 6**.

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Abbreviations	**Expansion**
ABA	L-2- aminobutyric acid
ABBA	3-acetamido-5-bromobenzoic acid
ADE	Adenine
ALD	Aldrin
AOX	Adsorbable Organic Halogens
APHA	American Public Health Association
ATG	N-acetylglycine
ATZ	Atrazine
BA	Benzoic acid
BBPH	Benzyl butyl phthalate
BEN	Benzophenone
BHBH	3,5-di-tert-butyl-4- hydroxy-benzaldehyde hemihydrate
BOD	Biochemical Oxygen Demand
BTC	Breakthrough Curves
CA	Clofibric acid
CGWB	Central Ground Water Board
CHC	Clenbuterol hydrochloride
COD	Chemical Oxygen Demand
CPCB	Central pollution control board
CSE	Centre for Science and Environment
CTA	Cetyl alcohol
DA	Diacetone alcohol
DBPs	Disinfection by-products
DEA	Decanoic acid
DEBD	N,N’-diethyl-2-butene-1,4-diamine
DFS	Diphenyl sulfone
DHC	Dopamine hydrochloride
DISA	3,5-diiodosalicylic acid
DMAB	4-(dimethylamino) benzaldehyde
DMM	Dimethyl maleate
DOC	Dissolved Organic Carbon
DPH	Diethyl phthalate
DS	Diclofenac sodium
DTAP	2,4- Di-tert-amylphenol
DTH	1-dodecanethiol
E.Coli	Escherichia Coli
EC	Electrical conductivity
EDCs	Endocrine Disrupting Chemicals
EDCs	Endocrine Disrupting Chemicals
EDS	α-Endosulfan
EFC	6-ethyl-3-formylchromone
EH	Esculin hydrate
EIC	1-eicosanol
ENE	Estrone
EOL	Estriol
GC-MS	Gas Chromatography-Mass Spectroscopy
GEM	Gemfibrozil
GFF	Glass Fiber Filters
GMWL	Global Meteoric Water Line
GUA	Guanine
HBA	3,5- di-tert-butyl-4-hydroxybenzyl alcohol
HMBA	5-hydroxy-2-methylbenzoic acid
HPC	Heptachlor

HPD	1-heptadecanol
HP-LC	High Performance Liquid Chromatography
HXD	1-hexadecanol
IBF	Ibuprofen
KHP	Potassium Hydrogen Phthalate
KTP	Ketoprofen
LA	Linoleic acid
LBF	Lake Bank Filtration
LC-MS	Liquid chromatography–Mass Spectrometry
LME	N-(tert-butoxycarbonyl)-L-leucine methyl ester
LMS	Lomustine
LMWL	Local Meteoric Water Line
LOQ	Limit of Quantification
MBGL	Meter Below Ground Level
MBHD	Methyl 16-bromohexadecanoate
MBZ	Metribuzin
MSTFA	N-Methyl-N-(trimethylsilyl) trifluoroacetamide
NTU	Nephelometric Turbidity Unit
OMPs	Organic micropollutants
OMTS	Octamethyltrisiloxane
PA	Palmitic acid
PCH	1-Pyrrolidino-1-Cyclohexane
PCPs	Personal Care Products
PhACs	Pharmaceutically Active Compounds
PTM	Pyridine, 2,4,6-trimethyl-
RBF	Riverbank Filtration
RWs	Ranney Wells
SA	Salicylic acid
SMZ	Simazine
SPE	Solid Phase Extraction
STA	Stearic acid
SUVA	Specific Ultraviolet Absorbance
TBA	Terbuthylazine
TC	Total Coliform
TMP	2,2,6,6-tetramethyl-4-piperidone
TPO	Triphenyl phosphine oxide
TRD	1-tridecanol
TRI	Triclosan
VSMOW	Vienna Standard Mean Ocean Water

LIST OF SYMBOLS

Symbol	Meaning
A	Cross-sectional area of the column
ρ_b	Bulk density
f_{oc}	Fraction of organic carbon
C_u	Uniformity coefficient
C	Concentration at time t
C_o	Initial Concentration
V	Volume of Column
m	Mass of Aquifer material
K_{ow}	Octanol-Water Partition Coefficient
R_d	Retardation Coefficient
K	Partition Coefficient
$\delta^{18}O$	Stable isotope of oxygen
$\delta^{2}H$	Stable isotope of Hydrogen
ϵ_b	Porosity
K_{OC}	Organic carbon-water partition coefficient
µ	micro
T	breakthrough time of tracer
t	breakthrough time of OMP

CHAPTER 1
Introduction

1.1. ORGANIC MICROPOLLUTANTS

Presence of organic micropollutants (OMPs) in the water resources is an emerging challenge to the persons responsible for water supply. OMPs mainly include pharmaceutically active compounds, pesticides and herbicides, personal care products, hormones, petroleum hydrocarbons, industrial chemicals etc. The discharge of partially treated and untreated sewage, industrial effluents, and agricultural runoff are the main sources of these pollutants in the water bodies (Heberer et al., 2002). Presence of OMPs in the water is of great concern because of their persistence, toxicity (particularly when present as complex mixture), endocrine disrupting effect, transportability (Harrad, 2001) and antibiotic resistance of microorganisms. To date, discharge guidelines and standards do not exist for most of the OMPs present in the water bodies. Conventional sewage/wastewater treatment has not been found to be adequate for the removal of OMPs. In such cases, entry of OMPs in surface and underground water resources is not ruled out. Water treatment as practiced in developing countries particularly in India is also not sufficient and appearance of river-borne OMPs at the consumer’s tap is not ruled out. River or lake bank filtration (RBF/LBF) can be a good alternative for the production of potable drinking water.

1.2. RESEARCH GAP

In developing countries like India, detailed identification and quantification of OMPs in sewage-impacted river waters, often used for water supply has not been attempted. Their occurrence in water supply wells hydraulically connected to such rivers is also not studied. In addition, variation of OMPs in-non monsoon and monsoon months is not reported. This is important for countries like India where rains, in general, are restricted to 2-3 months of monsoon and rivers carry high discharges and bulk of the water during monsoon. Also, retardation of OMPs (when present together in a mixture) during passage through aquifer is not studied.

1.3. OBJECTIVE

Keeping above research gap in mind the objective of the present work was (a) to study the occurrence of OMPs in contaminated surface water and RWs located close to the bank of the river, (b) their variations during non-monsoon and monsoon, and (c) attenuation/retardation during passage through the aquifer.

1.4. SCOPE OF STUDY

Study site: Due to discharge of untreated and treated sewage, industrial effluents and agricultural runoff in River Yamuna, its stretch close to Nizamuddin Bridge/Akshardham Temple in Central Delhi is considered to be highly polluted (CPCB, 2012). In urban flood plain of the Yamuna, close to this site, a number of Ranney wells (RWs) are located for tapping the unconfined aquifer for municipal water supply. Sewage impacted River Yamuna and eight RWs were selected for the study. Accordingly, scope of the study was defined as:

- To analyse the water quality of the river Yamuna and RWs in non-monsoon and monsoon months over a period of one year (2013-2014) for stable isotopes ($\delta^{18}O$ and $\delta^{2}H$), microorganisms, turbidity, DOC, and UV-absorbance at 254 nm (UV-254). Also, to identify and quantify OMPs present in water samples collected from the river Yamuna and RWs.
- To run column experiments under abiotic (predominantly adsorption) and biotic (predominantly bio-sorption/bio-degradation) conditions to determine retardation factors for the most frequently detected OMPs in river water/RWs.

1.5. OUTLINE OF THE DISSERTATION

The core of the thesis comprises individual chapters that are organized in the form of manuscripts submitted/under review in four referred journals. The pollution of the Yamuna River along with the quality of the water from eight RWs near Akshardham temple in Delhi was assessed in the monsoon and non-monsoon of 2013-2014. An attempt has been made to establish the connectivity between the river and RWs by monitoring the stable isotopes of the water samples. The results in terms of EC, turbidity, DOC, UV-absorbance, SUVA, coliforms are presented in **Chapter 2**. The occurrence of OMPs in the Yamuna water in non-monsoon and the monsoon months is discussed in **Chapter 3**. Results regarding quantification of OMPs present in eight RWs are discussed in **Chapter 4**. Data regarding OMPs in river water is discussed in detail in Chapters 3 and part of it is reappearing in a different form in Chapter 4. This repetition could not be avoided as a comparison of the occurrence of OMPs in river water and RWs was warranted in Chapter 4. The findings of the column runs and experimental details are presented in **Chapter 5**. Methodology used for the extraction and detection of OMPs is repeatedly presented in Chapters 3, 4 and 5. Since the thesis is a compilation of independent research papers submitted to different journals, this repetition was unavoidable. **Chapter 6** summarizes the overall findings of the research.

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CHAPTER-2
Natural Filtration of Polluted River Water for Municipal Use

Submitted to the Journal of Sustainable Water Resources Management (Springer)

ABSTRACT

The objective of the present study is to assess changes in water quality due to bank filtration of the contaminated river water. During riverbank filtration (RBF), surface water moves towars underground passage due to high pumping rate of water from the wells located in the adjacent aquifer. During the travel through subsurface, surface water gets purified due to number of processes such as filtration, adsorption, biodegradation and mixing with local ground water. To meet the objective water samples from the Yamuna River and eight Ranney wells (RWs) near Akshardham temple in Delhi, India were analysed in non-monsoon and the monsoon seasons. The proportion of the bank filtrate drawn by the RWs was determined by monitoring $\delta^{18}O$ and $\delta^{2}H$, the stable isotopes of the water samples. The $\delta^{18}O$ concentration of the river water in non-monsoon was significantly more than that of monsoon water. The water from the wells during monsoon was marginally lighter than that of non-monsoon water. An attempt has been made to establish the hydraulic connectivity between the river and RW using $\delta^{18}O$ data. Total coliform were reduced by more than 5 and 4 log in non-monsoon and monsoon respectively. E-coli were reduced by more than 5 log in both the seasons. The organic pollution of the river was also reduced considerably. The average DOC of around 17 mg/L in the non-monsoon was reduced to around 2 mg/L in all the RWs except NR-I. Ultraviolet absorption at 254 nm (UV-254) and specific UV absorbance (SUVA) followed the same trend as of DOC. Results suggest that in case of contaminated source waters, riverbank filtration (RBF) is an effective pre-treatment option for the production of drinking water. However, further treatment of filtrate is necessary.

Keywords: Riverbank filtration, Polluted river water, Ranney wells, River Yamuna, Stable isotopes, Coliforms, DOC, UV-254, Specific UV absorbance (SUVA).

2.1. INTRODUCTION

The unsaturated (vadose) zone and saturated depths are two most relevant physical media controlling the movement of water and pollutants. Contaminants arising from municipal and hazardous waste landfills, suburban septic systems, mining and petroleum production, and agriculture, filter through the vadose zone. Microbes, plant roots (rhizosphere), macrofauna (earthworms, ants and termites), humic matter and minerals reduce the concentration of contaminants. The vadose zone is potentially capable of blocking or/and degrading contaminants flowing in deep water.

In natural or riverbank filtration (RBF), the river water travels through the riverbed and bank that serve as a natural filter and contaminants are removed by filtration, sorption, biodegradation, etc. The dilution of the filtrate with the local ground water further alters the quality of the filtrate (Hiscock and Grischek 2001). The turbidity, bacteria, organic impurities, etc. present in the polluted river water are removed during natural filtration. RBF is either a complete treatment as practiced in many places in Europe or a pre-treatment as prevalent in the USA. It is a well accepted simple and a low cost treatment (or pre-treatment) technique, in use for more than 100 years along the rivers Rhine, Elbe and Danube (Grischek et al. 1998, Kühn and Müller 2000).

The RBF production wells are of different types. There are vertical wells, horizontal collector wells with radials, inclined wells, large-diameter dug wells and small devices such as Uttaranchal koops/wells (Dash 2011). For water supply, Ranney wells (RWs), also known as radial or horizontal collector wells, are in use in India since the early-1970s. The range of variation in the dimensions of RWs is given in Table 2.1. Globally; RWs have been placed in three different ways: (a) wells some distance away from the river with their laterals fully extended within the aquifer as practised in European countries (Hunt et al. 2003), (b) wells constructed close enough to the bank such that some of the laterals are partially below the bed as used in the United States (Grischek et al. 2003, Hunt et al. 2003) and (c) wells placed in the middle of the river as popular in India (Singh et al. 2010, Kumar et al. 2012).

Table 2.1. Variation in the dimensions of Ranney wells (Based on data from Hunt et al. 2003)

Well Yield (m^3/s)	Depth of the concrete caisson (m)	Diameter of the concrete caisson (m)	Diameter of laterals (m)	Number of laterals	Total length of laterals (m)*
0.0044-1.75	10->38	3-6	0.20-0.30	2-14	100-750

**Length of an individual lateral is restricted to 75 m.*

In India, RBF wells have been installed on the banks of many rivers/lakes during past four decades (Dash et al. 2008, Sprenger et al. 2008, Dash et al. 2010, Lorengen et al. 2010, Singh et al. 2010, Cady 2011, Kumar et al. 2012, Cady et al. 2013, Gupta et al. 2015). However, in the past 25 years, pollution load in several rivers has increased gradually due to rapid industrialisation, urbanisation, population growth and inadequate wastewater treatment facilities. It has resulted in the deterioration of the quality of the bank filtrate too at many places (Singh et al. 2010, Kumar et al. 2012). Natural filtration systems originally conceived for the attenuation of turbidity and microbes are now facing challenges due to the presence of the higher concentrations and a wider variety of contaminants in source waters. In few cases, this has resulted in bank filtrate not conforming to drinking water quality standards (Singh et al. 2010) and closure of RBF well (Saph Pani 2012).

There are a few reports on the treatment of polluted water by natural filtration or RBF. Cosovic et al. (1996) conducted the study on the polluted Gorjak stream, a tributary of the Sava River in Croatia. The river receives industrial effluent from the baker’s yeast and pharmaceutical production. The COD of the river water was found to vary from 870 to 5330 mg/L. The COD of the water from the well at 5 m from the river was 3-5 mg/L. The residual organics were identified as fulvic and humic substances. Miettinen et al. (1998) showed that high molecular weight organic fraction of the water of Lake Kallavesi, Finland was reduced during bank filtration. Attenuation of organic fraction reduced the formation of halogenated compounds during chlorination. Reduction of organic carbon content of the source water was found to be strongly dependent on the filtration distance. Contaminants get adsorbed into the clay particles and due to longer residence time, either degraded by microorganisms or transformed into the less harmful compound due to chemical degradation. Wu et al. (2007) studied the effectiveness of RBF of heavily polluted water of Kuihe River in China. The biochemical processes in the saturated percolation zone could remove about 95 % of nitrogen present in the river water.

Water quality improvement during bed filtration of the polluted water of the river Yamuna was studied by Singh et al. (2010) and Kumar et al. (2012) at Mathura, India. Coliforms, color and organics measured as DOC and UV-254 of the river water were reduced by more than 50%. It was concluded that RBF can eliminate the need for a pre-chlorination step and thereby decrease the formation of adsorbable organic halogens (AOX) and disinfection by-products (DBPs). The performance of an RBF system on polluted river Kali, in southern India (Karnataka) was studied by Cady (2011) and Cady et al. (2013). Results showed 88 % to more than 99% removal of bacteria in the RBF production well water. Heavy metal concentrations were also found to decrease during RBF.

RBF has been in use around Akshardham Temple in Central Delhi for approximately four decades. Over this period, water quality of river Yamuna has gradually degraded. Yamuna River has been extensively studied over several decades for its quality and sources of pollution (Karn and Harada 2001, CPCB 2006, Kaushik et al. 2008, Sprenger et al. 2008, Mandal et al. 2010, Lorengen et al. 2010, Mutiyar et al. 2011, Sehgal et al. 2012, CPCB 2012 etc.). As per the report from the Central Pollution Control Board (CPCB, 2012), only ~1558 ML/d of sewage was being treated in Delhi in 2012. The remaining ~2242 ML/d of untreated sewage was being discharged into the river Yamuna. Karn and Harada (2001) estimated discharges from the industries in Delhi as 300 ML/d. Sewage contains a wide variety of dissolved and suspended impurities (food and vegetable wastes, plant nutrients from chemical soaps, washing powders etc.) and these discharges lead to high amount of pollutants in the Yamuna . The resulting water pollution deteriorates the aquatic ecosystem. Although the Yamuna water quality has been studied extensively, however, a comprehensive study on water quality of bank filtrate is lacking. It is relevant as filtrate is utilized for drinking.

The present study, therefore, is confined (i) to the analysis of the proportion of river bank filtrate in the RWs water (based on stable isotope δ^{18}O and δ^{2}H data) and (ii) to the assessment of the improvement in quality of river water after bank filtration. To investigate these two aspects water quality of the river Yamuna and Ranney wells was evaluated. Water samples were collected in non-monsoon and monsoon months of the year 2013-14 and analysed for stable isotopes ($\delta^{18}O$ and $\delta^{2}H$), microorganisms, turbidity, DOC, and UV-absorbance at 254 nm (UV-254).

2.2. SITE DESCRIPTION

The present study was carried out in a well field having nine RWs in Central Delhi located on the left bank of the river Yamuna around Akshardham Temple (Fig. 2.1). A typical cross section of the well field, across RWs P-3, P-4, P-5 and P-6 is shown in Fig. 2.2. As the river Yamuna travels through Delhi, its (a) flow decreases due to substantial withdrawal of the clean water at an upstream location, Wazirabad Barrage and (b) quality deteriorates due to the release of domestic and industrial wastewaters by 22 major drains. The 22-km stretch of the Yamuna in Delhi, which is less than even 2% of the length of the river (1376 km), contribute over 80 percent of the pollution load (CSE 2007). The entire stretch of the river Yamuna has been monitored at 19 locations for six years from 1999-2005 (CPCB 2006). The data reveals that compared to the other sites, Yamuna has the highest level of pollution at Nizamuddin (28°35'N, 77°17'E), close to Akshardham Temple. Well field around Akshardham Temple was particularly preferred as (a) the Yamuna is reported to be the most contaminated (Sprenger et al. 2008; Lorenzen et al.; 2010). BOD is as high as 51 mg/L (CPCB 2012) (b) it has 9 operating RWs, and (c) a deep unconfined aquifer exist between the river and RWs. Relevant details of the RWs in the well field are compiled in Table 2.2.

The Yamuna flood plain of Delhi comprises of younger alluvium overlying older alluvium. The thickness of younger alluvium varies from ~70 m in the northern part of the flood plain to 30-40 m in the southern part of the flood plain. The composition of the younger alluvium is mainly a mixture of medium-to-coarse sand, silt, clay and kankar (local name of small calcareous concretions mixed with small gravels) (Chatterjee et al., 2009).The major water-bearing horizon is fine to coarse-grained sand with kankar. The thickness of fresh water zone varies from 30-85 m (CGWB, 2006). Hydraulic conductivities of the newer alluvium are in the range of 2×10^{-4} to 7×10^{-4} m/s (Chatterjee et al., 2009).

Table 2.2. Details of RWs (based on records/personal communication with officials of Delhi Jal Board)

Ranney wells[1] (Fig. 1)	**Distance from the bank[2](km)**	**Year of Installa-tion**	**Total depth of well (m)**	**Number of radials[3](Layers, laterals/layer)**	**Length of each lateral (total length of laterals in a well)(m)**
P-3	0.5-0.6	1972	19.20	10 (1)	30 (300)
V-8	1.0-1.2	1975	21.64	10 (1)	30 (300)
P-4	1.2-1.4	1975	28.95	10 (1)	30 (300)
NR-II	1.8-2.0	2001	31	20 (2, 10 laterals/layer)	30 (600)
P-5	1.8-2.0	1975	19.81	10 (1)	30 (300)
M-15	2.0-2.2	1975	25	24 (3, 8 laterals/layer)	60 (1440)
NR-I	2.0-2.2	2006	24.38	20 (2, 10 laterals/layers)	30 (600)
P-6	2.4-2.5	1975	19.05	10 (1)	30 (300)
M-16	3.8-4.0	1975	25	24 (3, 8 laterals/layer)	60 (1440)

[1] *P- Patparganj, V- Vikas Marg, NR- Nizamuddin Railway, M- Mayur Vihar*
[2] *Shortest distances from the bank measured from the Google Earth in non-monsoon.*
[3] *Diameter of all the laterals = 0.2 m*

2.3. MATERIALS AND METHODS

Water samples from the river Yamuna (at Nizamuddin and ITO Bridges) and all the RWs (Fig. 2.1) were collected between August 2013 and August 2014. Due to 8-9 mg/L of NH_4^+ in water, the operation of the RW P-3 was stopped in November 2013 (Saph Pani 2012). Samples of water from P-3 could not be collected beyond November 2013. The data from P-3 collected from August to November has, therefore, not been reported. Samples from RWs M-15 and M-16 were collected during March 2013 to August 2014, therefore the results for the same duration is reported. A total of 16 sampling were organised, 7 in the monsoon (2.5 months, mid July-September) and 9 in non-monsoon (9.5 months, October-mid July). If any of the RWs was not in operation at the time of the sampling, it was purged for at least 20 minutes prior to the sampling. Samples were collected in glass bottles for organics and polypropylene bottles for other physicochemical water quality parameters. Samples for microbial analysis were collected in sterilised glass bottles. For stable isotope analysis, samples were collected in polypropylene bottles of 15 mL capacity ensuring that there was no air entrapped in the bottles. Electrical conductivity (EC), pH and temperature were measured on site with a portable multi-parameter probe (HQ40d, Hach, Loveland, USA). Water samples were transported within 8 hours to the Environmental Engineering Laboratory, IIT

Roorkee for the analysis of bacteria, turbidity, and organics. Total coliform (TC) and E. coli were measured using IDEXX Colilert -18 and Quanti-Tray method. For all other parameters, samples were stored at 4^{o}C and analysis was completed within 48 hours after sampling. Parameters were analysed as per the methods prescribed in the Standard Methods (APHA, 2005).

For the determination of DOC and UV-254, samples were filtered through 0.45 µm filter paper and analysed using TOC-VCSN total organic carbon analyzer (Shimadzu) and Hach DR-5000 UV-VIS spectrophotometer with 10 mm quartz cell respectively. Specific UV-absorbance (SUVA) was calculated as the ratio of UV-254(1/m) to DOC (mg/L). Turbidity was measured using Hach 2100 AN Turbiditimeter.

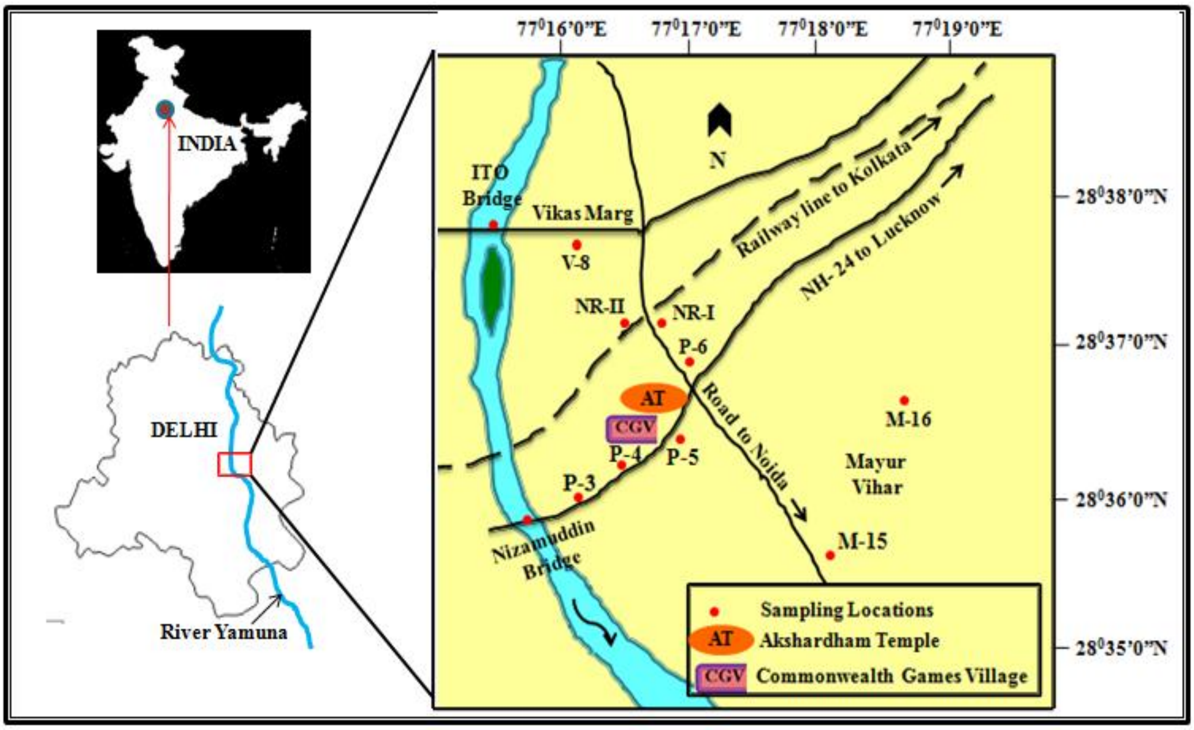

Fig. 2.1. Well field around Akshardham Temple on the left bank of the River Yamuna and the 11 sampling locations (2 on river Yamuna and 9 RWs).

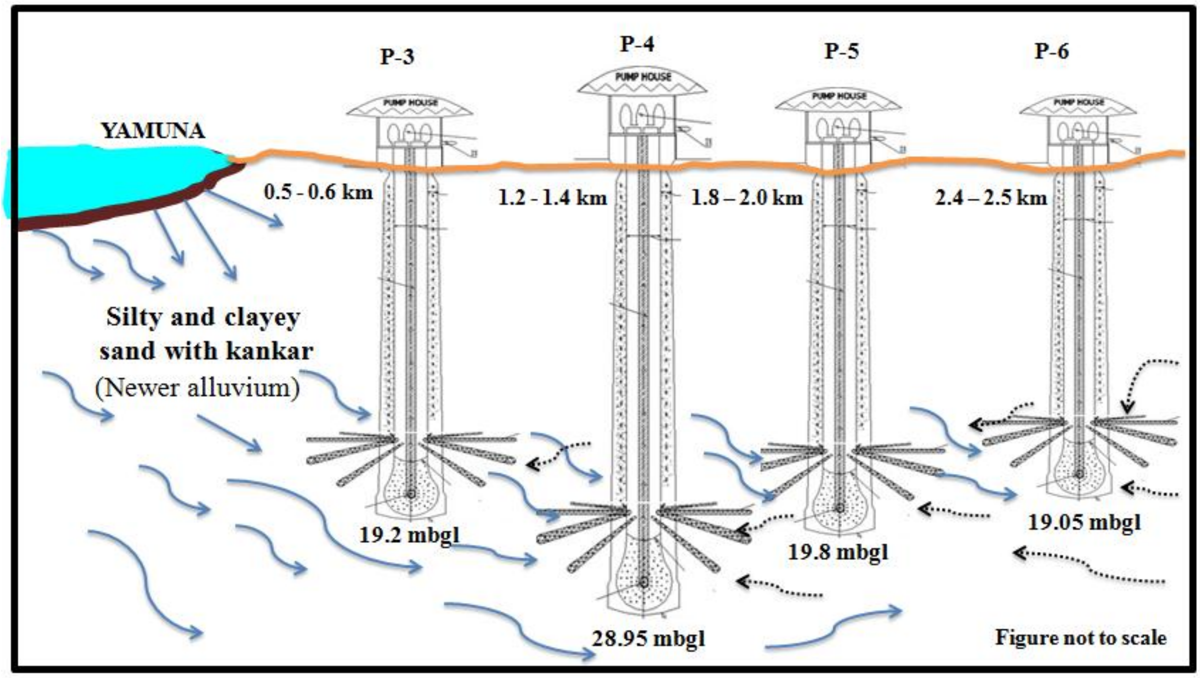

Fig. 2.2. Cross-section of the well field, across RWs P-3, P-4, P-5 and P-6 (mbgl= meter below ground level; horizontal distances are the shortest distance from the river bank from Google Earth).

Stable isotopes ($\delta^{18}O$ and $\delta^{2}H$) were determined using a dual inlet isotope ratio mass spectrometer (GV Instruments, Isoprime) at National Institute of Hydrology, Roorkee. Samples were equilibrated with Pt-H_2 and CO_2 to measure $\delta^{18}O$ and $\delta^{2}H$ respectively (Epstein and Mayeda 1953, Brenninkmeijer and Morrison 1987). The isotopes are reported as a per mil difference (δ ‰) relative to the international Vienna Standard Mean Ocean Water (VSMOW). The precisions in the measurement of $\delta^{18}O$ and $\delta^{2}H$ were ±0.1 ‰ and ±1 ‰ respectively.

2.4. RESULTS AND DISCUSSIONS

Results are presented in four sections. The first section deals with the isotopic composition of the samples. The observations from the on-site measurement have been put in the next section. Thereafter, removal of turbidity and coliform has been discussed. Observations related to the attenuation of the organic impurities have been incorporated in the last section.

2.4.1 Stable isotope

2.4.1.1 Seasonal variation

The temporal variation of $\delta^{18}O$ for water from the river and RWs is presented in Fig.2.3. The perusal of the data indicates significant difference between the values of $\delta^{18}O$ of the monsoon and non-monsoon river water. The average values of $\delta^{18}O$ of the monsoon and non-monsoon river water are −9.25 and −7.28 respectively. The monsoon values are related to the rainfall. Higher is the rainfall lesser is the value. The $\delta^{18}O$ of −11.09 of the sample in August 2013 corresponds to the flood conditions. Dalai et al. (2002) have also found the depleted $\delta^{18}O$ values of the river Yamuna water by 0.5-1.5 ‰ in the monsoon compared to the summer months. The seasonal variation in $\delta^{18}O$ of the well water is in a narrow range (Figs. 2.3 and 2.4).

Also, $\delta^{18}O$ and $\delta^{2}H$ of the river water in the monsoon months coincide with the local meteoric water line (LMWL) (Fig. 2.5). The river is fed primarily by the rain water. The non-monsoon $\delta^{18}O$ and $\delta^{2}H$ of Yamuna water are shifted towards the heavier side of the LMWL. The high values could be due to the evaporative enrichment and/or different source water. The physicochemical analysis indicates high conductivity and substantial organic pollution of the Yamuna water during non-monsoon (Figs. 2.6 and 2.8). Conductivity of the river water during non monsoon is 3 to 4 times conductivity of The conductivity of the river water in non-monsoon is three to four times the monsoon water conductivity (Fig. 2.6). The high conductivity and organic pollution of the river water coupled with the isotopic signatures (Fig. 2.5) point towards a different source water rather than the evaporative enrichment.

The water quality data is in conformity with the operation of the water supply schemes upstream of the Akshardham well field. The glacial melt feeding the Yamuna in non-monsoon is diverted to the Wazirabad, and Chandrawal water works through the Wazirabad barrage that is located 15 km upstream of the well field. Also, 22 drains join the river between the Wazirabad barrage and the well field. The river in this stretch is polluted. It carries the water from the drains.

2.4.1.2 Spatial variation

Average values with standard errors of $\delta^{18}O$ of the water samples from the river and RWs are presented in Fig. 2.4. The data suggests that during non-monsoon, the water from all the RWs is (i) lighter than the river water and (ii) heavier than the corresponding monsoon water. In an

RBF field, the well water is generally heavier than the river water. The non-monsoon observation for the present well field, however, is unusual.

The maximum difference between monsoon and non-monsoon values of δ^{18}O has been observed for the river water. As far as the other wells are concerned, the difference in the case of water from the V-8, P-4, and NR-II RWs is more than the other well waters. These three wells are at a distance of less than 2 km from the river whereas the other wells are at a distance ranging from 2 to 4 km (Table 2.2). It, therefore, suggests that the RWs close to the river receive more river water than the wells away from the river. Water in the wells that are away from the river is in equilibrium with the aquifer. Also, the river discharge during non-monsoon is small as most of the water upstream of the well field is diverted to the water works.

Among the wells, the water from the NR-I is lighter than the other well water. The NR-I is at a distance of 2-2.2 km away from the river. The NR-I may receive rain water through infiltration and/or river water through the sub-surface flow. The observed isotopic composition of the water from the other wells could be due to the mixing of the river water and NR-I water as well as travel time.

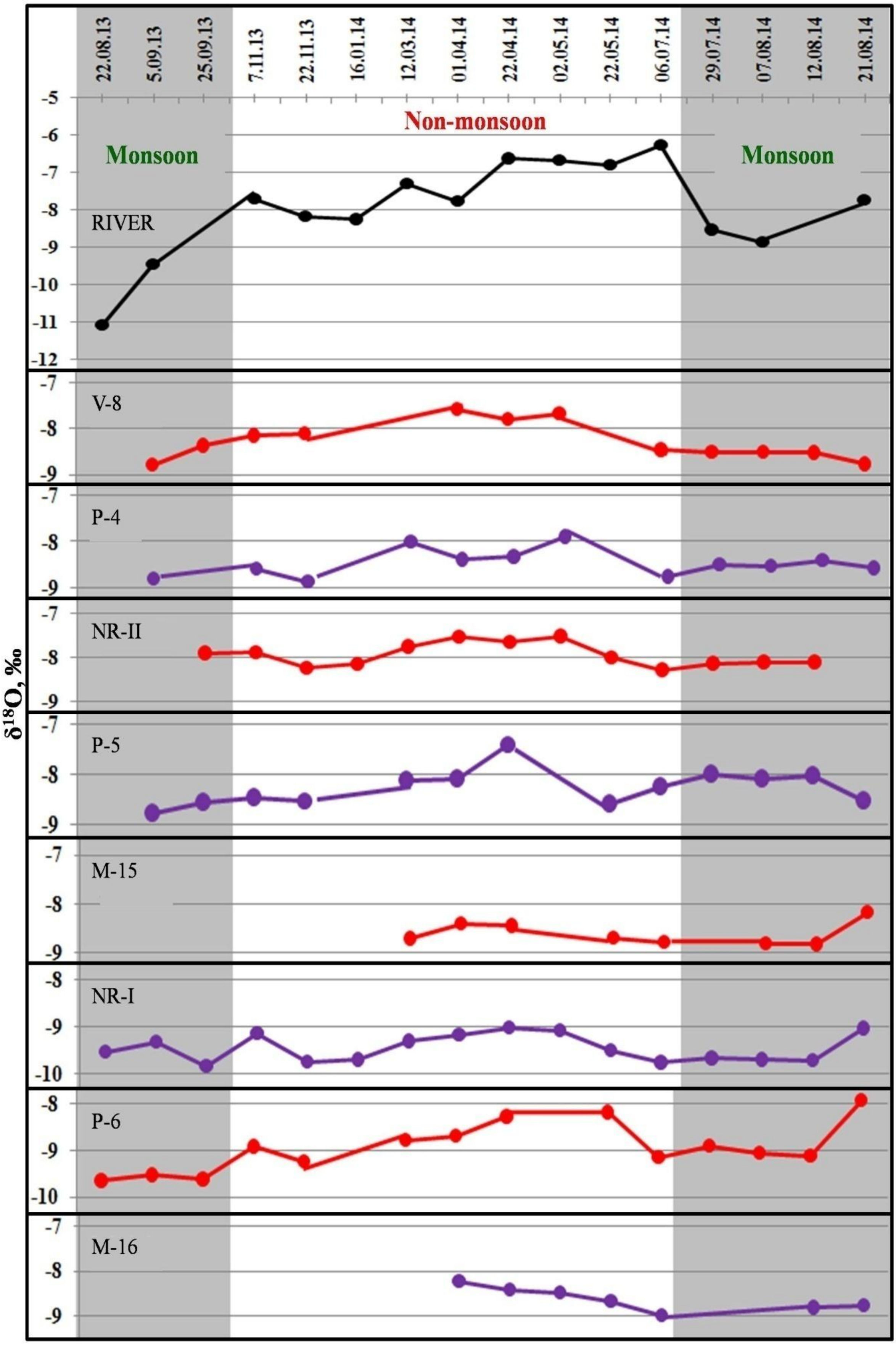

Fig. 2.3. River Yamuna and Ranney wells: temporal variation of δ^{18}O

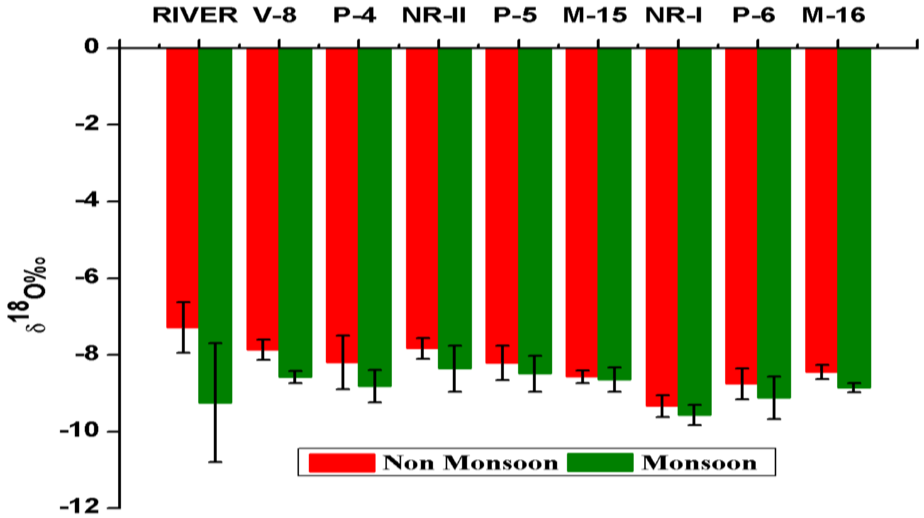

Fig. 2.4. River Yamuna and Ranney wells: average values of $\delta^{18}O$ with standard error

2.4.1.3 Mixing Ratios

The mixing ratios in the wells, therefore, have been calculated from the $\delta^{18}O$ of the NR-I and the river water using the mass balance method (Eq. 2.1). The values of mixing ratio for different seasons are presented in Table 2.3.

$$\frac{Q_{River}}{Q_t} = \frac{\delta^{18}O\ RW - \delta^{18}O\ NR\text{-}I}{\delta^{18}O\ River - \delta^{18}O\ NR\text{-}I} \qquad \textbf{(2.1)}$$

Where,

$\frac{Q_{River}}{Q_t}$ = fraction of the river water in the well water
$\delta^{18}O$ RW = average $\delta^{18}O$ of the RW water for which mixing ratio is to be calculated
$\delta^{18}O$ River = average $\delta^{18}O$ value of river water
$\delta^{18}O$ NR-I = average $\delta^{18}O$ value of the NR-I water

In the monsoon season, calculations indicate contribution of river water in a few RWs are more than 100% (Table 2.3). Calculations indicate more than the 100% of the river water in a few RWs in the monsoon season (Table 2.3). One of the implications of this observation could be that these wells receive river water through the subsurface flow and/or rainwater through infiltration. The signature of the water, however, changes due to evaporative enrichment or mixing of some other water. The evaporative enrichment could be due to long travel time, which has not been estimated in the present study. Nevertheless, Lorenzen et al. (2010) reported the travel time of ~ 8 months from an observation well located at a distance of 50 m from the river bank. RWs, however, are at a distance of more than 50 m. The travel time, therefore, is expected to be greater than eight months. The fraction of the river water in the wells has been calculated by taking values of $\delta^{18}O$ of the river water, NR-I water and the RW water for the same months. The monsoon lasts for 2-3 months and travel time is more than the monsoon period. Therefore, the effect of the same monsoon water on the RWs water may not simultaneously appear in the same year. The non-monsoon RWs water being lighter than the river water could also be because of the long travel time. Since these wells are in an unconfined aquifer, the mixing of rainwater through infiltration cannot be ruled out.

2.4.1.4 Deuterium excess (d)

According to Dansgaard (1964) the deuterium excess (d), on the basis of global meteoric water line (GMWL) is defined by Eq. 2.2. However, d-excess, as well as the slope of correlation for local lines, are different.The d value (from Eq. 2.2) for the Yamuna water in the Himalayan ranges varies from 5.2‰ to 17.3 ‰ (Dalai et al. 2002). The long-term average *d* value for New Delhi precipitation from Eq. 2.2 is about 8.5‰, and during non-monsoon (October), it is >10‰ (Araguas et al. (1998). The values of slope and d-excess depend on the humidity conditions. Evaporative trends have a slope between 2 and 5 depending on the relative humidity. The Higher value of *d* in the precipitation is the consequence of low humidity conditions (Clark and Fritz 1997).

$$d = \delta^{2}H - 8\,\delta^{18}O \qquad (2.2)$$

LMWL for Delhi is given by the Eq. 2.3

$$4.6 = \delta^{2}H - 7.2\,\delta^{18}O \qquad (2.3)$$

Eq. 2.3 provides the baseline to compare the isotopic composition of the river (surface water) and RWs water (sub-surface water). The $\delta^{18}O$ and $\delta^{2}H$ data shown in Fig. 2.5 indicate the following:

- The monsoon data for the river and RWs water are close to the LMWL for Delhi.
- The LMWL can describe the river data in the monsoon except the outlier corresponding to the flood event of Aug 2013.
- The non-monsoon data is within −10‰ of the LMWL i.e. d value from the Eq. 2.3 ranges between 4.6 to – 5.4 ‰ (+4.6 – 10 = -5.4).
- Most of the data points other than the monsoon river and a few RW data exhibit oxygen enrichment.

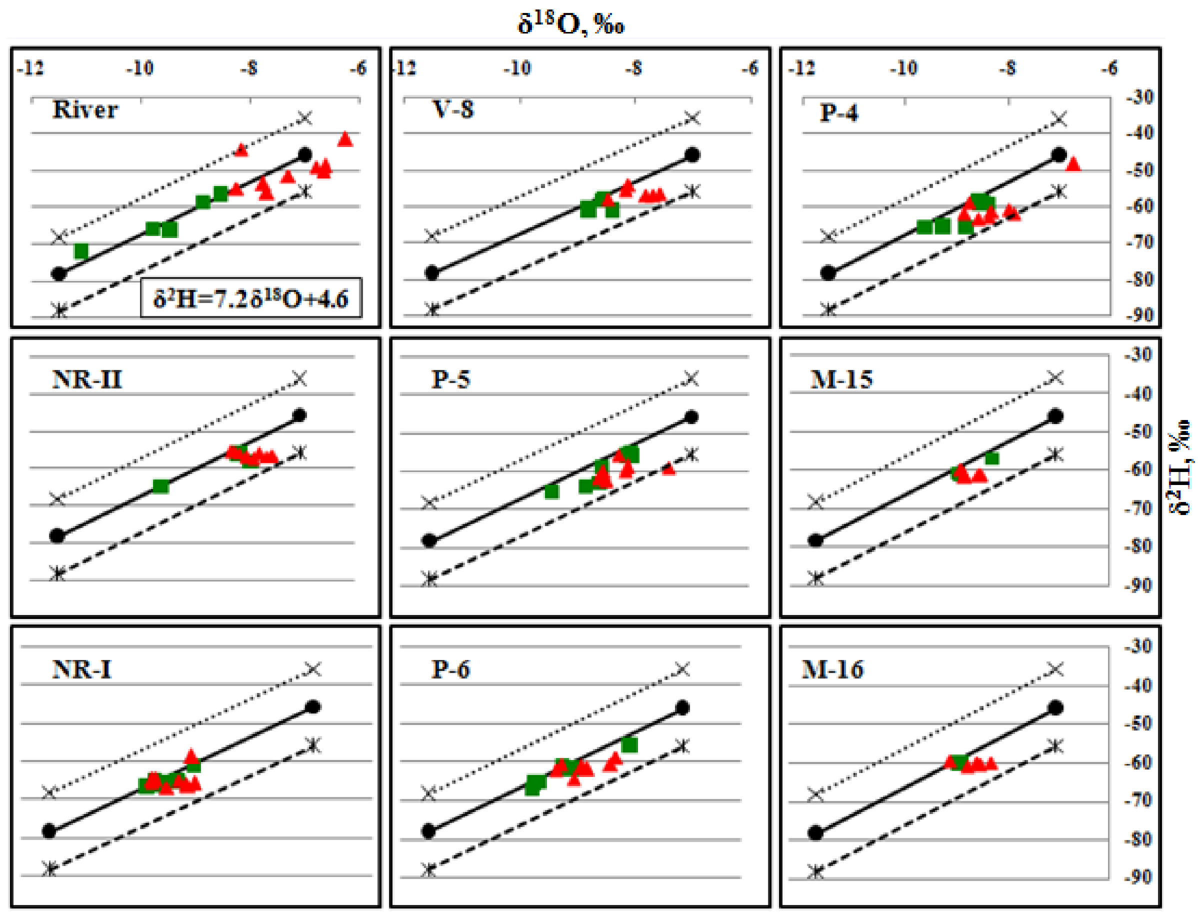

Fig. 2.5. $\delta^{18}O$ and $\delta^{2}H$ data for the Yamuna and RWs. The equation for LMWL for Delhi is shown with the river data. (◆LMWL ■ Monsoon ▲ Non monsoon)

Table 2.3. Proportion of river water in the filtrate collected from RWs in different seasons

	V-8	P-4	NR-II	P-5	M-15	P-6	M-16
Non-monsoon(%)	77	63	78	59	40	33	46
Monsoon (%)	100% *					59	95

**The proportion of the river water in the water from the RWs during monsoon months has been calculated to range from 100 to 115%. It has, therefore, been taken as 100%.*

The $\delta^{18}O$ and $\delta^{2}H$ for the individual RW water have not been found to be correlated due to oxygen enrichment as well as mixing. Since the non-monsoon river water is a mixture of the glacier melt and the waste water, it is not described by LMWL. All the data show oxygen enrichment resulting decrease in d-excess from +4.6 to a minimum of -5.4 (Fig. 2.5). The d-excess for the water decreases with the oxygen enrichment, provided the slope does not change. The range of d-excess calculated from the data shown in Fig. 2.5 using Eq. 2.3 is given in Table 2.4. The minimum values of d intercept for all the non-monsoon samples are negative i.e. oxygen enrichment is significant enough to decrease d value more than 4.6 (Eq. 2.3, LMWL). The oxygen enrichment for the monsoon samples is less than the non-monsoon. Higher is the oxygen enrichment lesser is the d-excess. The maximum value of d-excess for the monsoon RWs water is mostly less than the LMWL value of 4.6. The oxygen enrichment could be due to the evaporation of water or mixing of water that is rich in $\delta^{18}O$. The negative value of d-excess has been reported for the lake water (Yuan et al. 2011).

2.4.2. On-site measurement

2.4.2.1 Temperature and pH

Temperature of the Yamuna river water during non-monsoon was observed in the range of 15.2 (winter) to 32.5°C (summer) whereas during monsoon temperature varied from 29.2 to 32.1°C. However, a wide range of variation from winter to summer was not observed for RWs water. The temperature of the water from the RWs ranged from 26 to 30°C. pH of the river water ranged from 7.39 to 8.35 and for RWs from 6.74 to 8.32.

2.4.2.2 Electrical conductivity (EC)

The electrical conductivity of the river water is significantly different during monsoon and non-monsoon seasons. The information extracted from the EC data is as under:

- The EC values of the monsoon and non-monsoon river water are around 400 and 1400 µs/ cm respectively.
- The EC of the monsoon RW water is more than the river water. It may be due to the mineralization of the river water during the sub-surface flow (Dash et al. 2010).
- There is not much difference in the magnitude of EC of the monsoon and non-monsoon well water except that the scatter in data is large for the water from the RWs P-4 and P-5 (Table 2.5 and Fig. 2.6).

Table 2.4. River Yamuna and RWs: Deuterium-excess (d)

d (‰)	**River**	**V-8**	**P-4**	**NR-II**	**P-5**	**M-15**	**NR-I**	**P-6**	**M-16**
Non-monsoon	(−2.12) - (+4.74)	(−1.74) - (+4.60)	(−5.00) - (+4.39)	(−2.47) - (+4.15)	(−5.71) - (+3.71)	(−0.36) - (+3.71)	(−0.65) - (+6.81)	(−0.92) - (+5.30)	(−0.83) - (+5.26)
Monsoon	(+2.03) - (+5.00)	(−0.70) - (+3.30)	(−2.10) - (+3.53)	(−1.25) - (+2.68)	(−1.28) - (+2.59)	(+2.03) - (+2.96)	(+1.88) - (+4.60)	(+2.40) - (+4.30)	(+3.22) - (+3.24)

Table 2.5. River Yamuna and RWs: average EC and standard deviation in non-monsoon and monsoon

EC(µS/cm)	**River**	**V-8**	**P-4**	**NR-II**	**P-5**	**M-15**	**NR-I**	**P-6**	**M-16**
Non-monsoon									
Average	1416	1267	868	1289	959	1285	1109	769	1583
SD	±416	±68	±88	±20	±99	±100	±37	±21	±37
Monsoon									
Average	436	1181	939	1336	1031	1356	1138	787	1652
SD	±95	±36	±247	±36	±215	±14	±45	±12	±8

Scatter may be due to connectivity to the river. The analysis of isotope data suggests connectivity of other wells along with P-4, P-5 (Table 2.5). EC, however, of NR-I, NR-II, M-15, M-16 and P-6 is stable i.e. data is not scattered. The water is in equilibrium with the aquifer material. Observed difference in the response of water samples to isotope and EC could be due to the difference in travel time or mixing of the river water with the water other than the NR-I water. Mixing ratios have been calculated using isotope data of the river and NR-I water. With the limited data available, it is difficult to comment on this aspect.

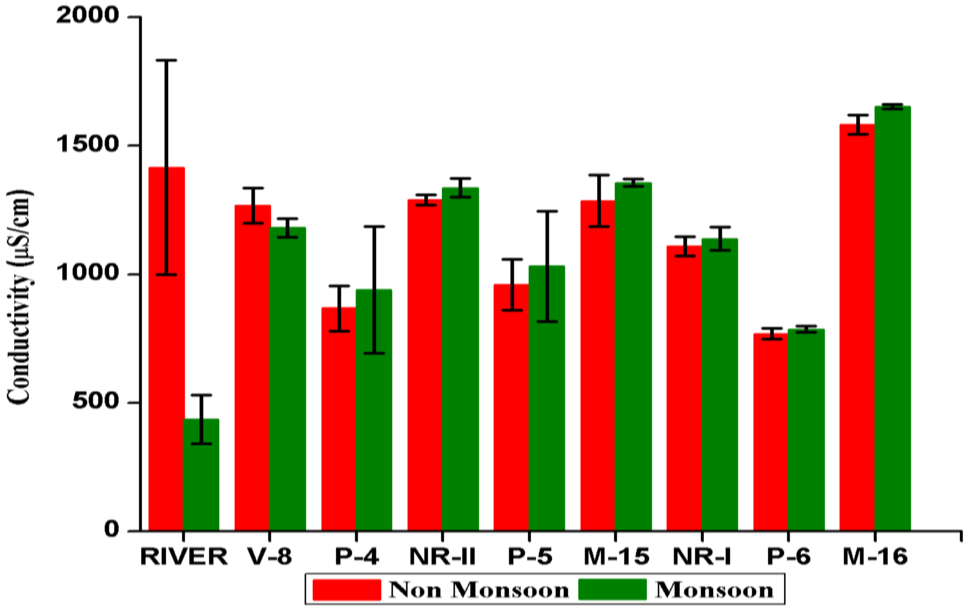

Fig. 2.6. River Yamuna and Ranney wells: average EC with standard error in non-monsoon and monsoon

2.4.2.3 Removal of coliform and turbidity

Coliforms

Bacterial contamination of water samples measured as total coliform and E. coli are presented in Fig. 2.7. Coliform count of the river water has been found to be between (i) log 6 and 7 in the non-monsoon and (ii) log 5 and 6 in the monsoon. The coliform counts in the monsoon river water are reduced by around 1 log due to the dilution. In non-monsoon, river primarily carries treated/untreated wastewater. Water samples from RWs were found to be bacteriologically contaminated in both the seasons. However, compared to river water counts of coliform were significantly low. Bacterial attenuation as noticed in the water from the RWs was more than log 5 and log 4 during non-monsoon and monsoon respectively. Like total coliform, average E.coli counts were also found one log less in monsoon compared to non-monsoon (Fig. 2.7). In the water from RWs, decrease in E-coli was more than 5 log both in non-monsoon and monsoon seasons. Despite 4-5 log removal of coliforms, the water of from the RWs cannot be classified as safe for drinking. Disinfection is essential.

Turbidity

Turbidity of the river water exhibits a broad range of variation. Ranney well water turbidity is mostly less than 2 (Table 2.6). The turbidity of the well water is in compliance with the drinking water standard IS: 10500 (2012) (acceptable limit 1 NTU).

Table 2.6. River Yamuna and RWs: Turbidity of the water samples in non-monsoon and monsoon

Turbidity (NTU)	**River**	**V-8**	**P-4**	**NR-II**	**P-5**	**M-15**	**NR-I**	**P-6**	**M-16**
Non- monsoon	16-158	<2				4.3	<2		
Monsoon	164 -1552	<2				3	<2		

2.4.2.4. Aqueous **Organics**

Aqueous organics have been monitored by measuring DOC and UV-254. Organics have further been characterized by estimating SUVA from DOC and UV-254. The perusal of the data in indicates the following:

River water

- DOC has been found to vary from about 2 to 66 mg/L.
- DOC of the monsoon samples is between 3 and 8 mg/L. Non-monsoon samples except January 2014 sample had DOC ranging from 5 to 15 mg/L. The DOC of the January sample was 66 mg/L.
- The numerical value of UV-254 (m^{-1}) for all the samples except January sample is more than the corresponding DOC (mg/L).
- SUVA values (L/mg.m) of the (i) monsoon samples are around one and (ii) non-monsoon samples are greater than 2.

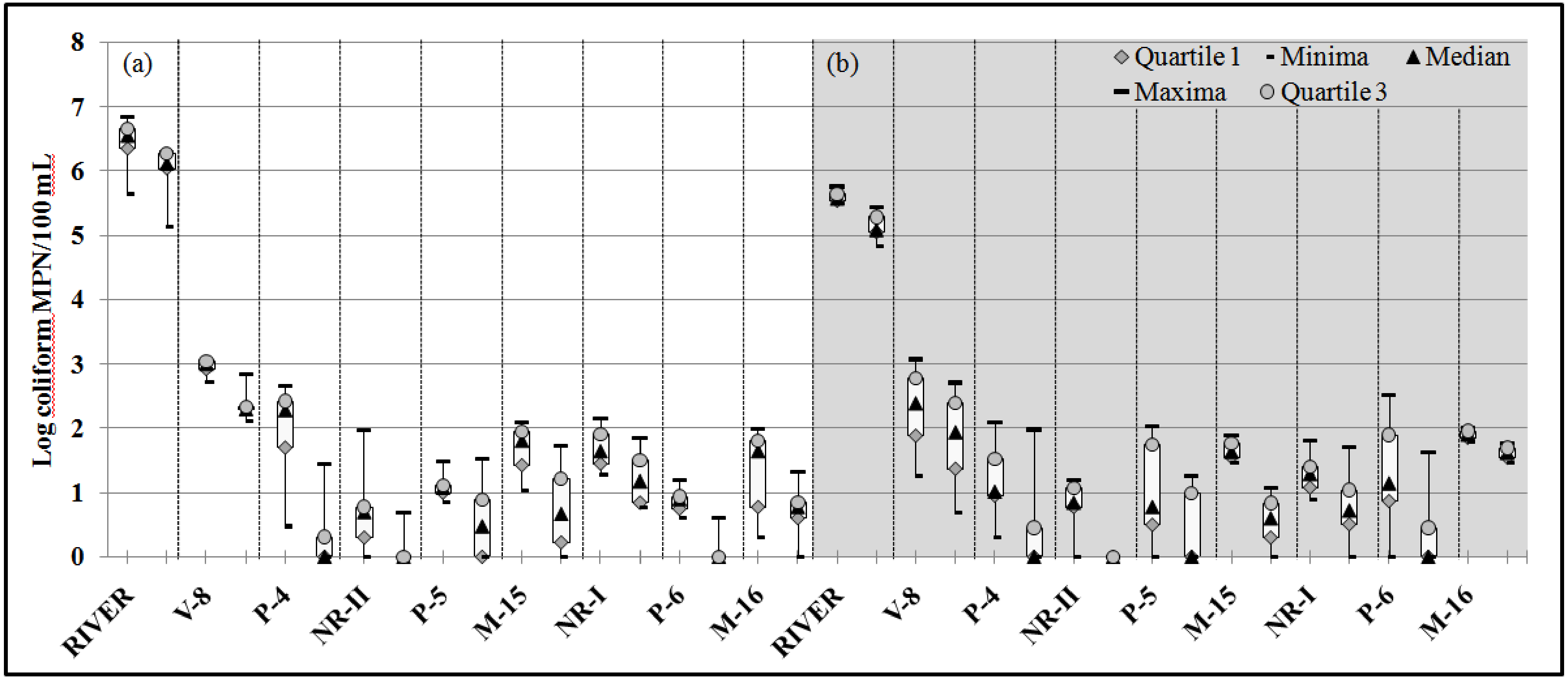

Fig. 2.7. River Yamuna and Ranney wells: total coliform and E. coli for (a) non-monsoon and (b) monsoon (in each vertical column the first box-plot represents total coliform and the second one is for E.Coli)

It is evident that the nature of the aqueous organics is different in the monsoon and non-monsoon samples. It is quite clear as the river carries rainwater in the monsoon and substantial amount of wastewater in the non-monsoon. It corroborates the observations and conclusion derived from the isotope and EC data. The SUVA value greater than two indicates the presence of hydrophobic aromatic compounds in water (Table 2.7). These compounds are removed during bank filtration. The SUVA of the filtered water is less than 2.

Ranney Wells Water

- The water from the NR-I is different compared to other wells.
- DOC of the NR-I is in the range from 6 to 14 mg/L.
- The average DOC of the non-monsoon NR-I samples is more than that of monsoon samples (Fig. 2.8).
- UV-254 of all the NR-I samples except one monsoon sample is less than two m^{-1}, and SUVA is less than one. The residual organics in NR-I water are hydrophilic in nature as the hydrophobic organics would be sorbed by the aquifer material (Ruffino and Zanetti 2009).
- The DOC of the water from the other wells is mostly less than 2 mg/L. There are three out of about fifty observations that have recorded DOC greater than 2 mg/L.
- UV-254 of the water has been found to vary from 0.1 to less than four m^{-1}.
- There is no definite trend in the SUVA values. SUVA values are from 0.04 to about 2 L/mg.m.

The German Technical and Scientific Association for Gas and Water (DVGW) has recommended maximum concentration of DOC of 2 mg/L for drinking water. Frimmel, (2002) has mentioned that if DOC concentration is maintained < 2 mg/L, trihalomethane (THM) guideline of 100 µg/L does not exceeded. The water from the NR-I has to be treated for DOC removal prior to use for domestic consumption. Another RW on the bed of the river Yamuna is located at Mathura, 155 km downstream of Delhi. The DOC of the river water is reduced by about 59-78% during bed filtration. The filtrate DOC of 1.65-6.30 mg/L has been reported (Kumar et al. 2012). At both places, river water is heavily polluted, and filtrate needs post treatment to get consistent filtrate DOC <2 mg/L.

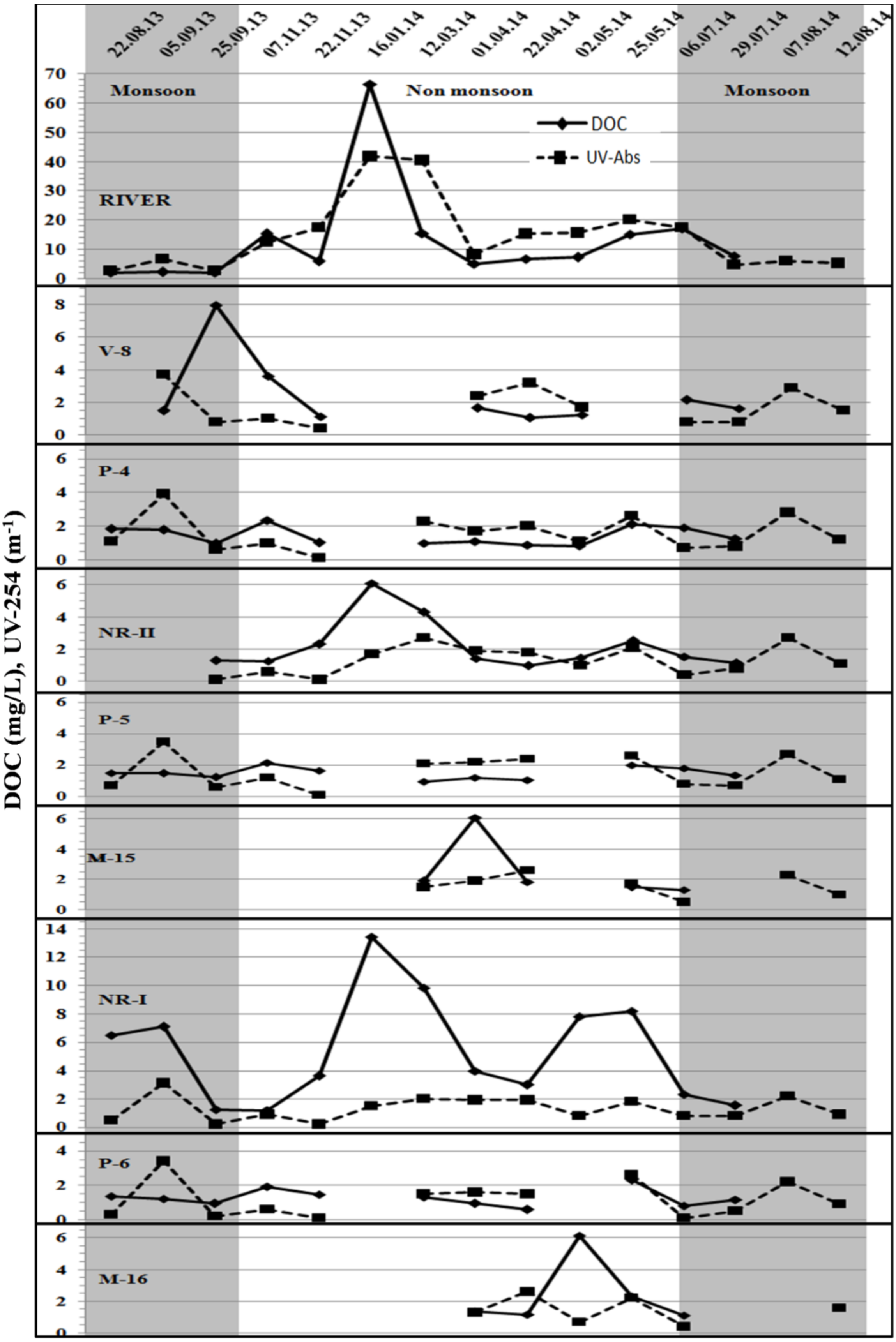

Fig. 2.8. River Yamuna and Ranney wells: Temporal DOC and UV-Abs plots for non-monsoon and monsoon.

Table 2.7. DOC, UV-254 and SUVA values of the water samples

	River	V-8	P-4	NR-II	P-5	M-15	NR-I	P-6	M-16
DOC (mg/L)									
Non - monsoon	17.24 ±19.06	1.79 ±0.97	1.39 ±0.62	2.43 ±1.70	1.53±0.48	2.53±2.00	5.92±4.09	1.34±0.61	2.42±2.13
Monsoon	3.58±2.85	3.68±3.70	1.45±0.42	1.21±0.12	1.37±0.13	-	4.08±3.13	1.17±0.17	-
UV-254 (m^{-1})									
Non - monsoon	21.04±11.90	1.58±1.06	1.44±0.86	1.37±0.88	1.63±0.94	1.64±0.76	1.31±0.65	1.14±0.92	1.44±0.94
Monsoon	4.80±1.69	1.94±1.30	1.73±1.32	1.18±1.10	1.55±1.24	1.65±0.92	1.28±1.12	1.25±1.28	-
SUVA (L/mg.m)									
Non - monsoon	1.70±0.77	1.16±0.99	1.22±0.81	0.71±0.54	1.26±0.85	0.81±0.43	0.32±0.24	1.00±0.84	0.92±0.73
Monsoon	1.57±1.01	1.03±1.29	1.02±0.79	0.39 ±0.45	0.97±0.94	-	0.30±0.21	0.91±1.24	-

2.5. CONCLUSIONS

Based on the study, following conclusions were drawn:

- The non-monsoon river water is polluted. It is heavier than the monsoon river water as well as water from the RWs. The non-monsoon river water has a significant wastewater discharge from the drains.
- The effect of the monsoon river water on the water from the RWs is not seen due to the long travel time (more than 8 months).
- The d-excess (from LMWL Eq. 2.3) decreases from +4.6 to -5.4 with oxygen enrichment.
- The water from RWs away from the river is in equilibrium with the aquifer. These wells do not respond to seasonal fluctuations in the river water due to the travel time that is expected to be in years.
- In spite of the considerable amount of turbidity in the source water during monsoon (> 1500 NTU), goal of achieving prescribed limits of turbidity through RBF is attainable.
- Even in case of source waters contaminated by wastewaters (non-monsoon average DOC >15 mg/L), attenuation of organics in terms of DOC < 2 mg/L through RBF is possible.
- However, in case of contaminated source water (rich in organics), coliform survive over long distances in the aquifer. Production of coliform free filtrate does not seem to be a realistic target. Post-treatment of filtrate is a must.
- Overall, it could be summarized that in case of contaminated surface waters, natural filtration alone is not adequate for the production of guaranteed safe and wholesome drinking water. Further treatment of riverbank filtrate is necessary. Results suggest that in such cases, the value of RBF as an effective pre-treatment step could not be undermined.

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CHAPTER-3

Occurrence of Organic Micropollutants (OMPs) in the River Yamuna, Delhi, India

Under Review in the Journal of Hydrology (Springer)

ABSTRACT

In developing countries, identification/quantification of organic micropollutants (OMPs) has not been attempted in river waters impacted by wastewaters. Given the diverse nature and sources of the OMPs, the objective of the present study was to identify and quantify OMPs present in heavily contaminated River Yamuna. Fifty-seven OMPs that were identified included the pharmaceutically active compounds (PhACs), pesticides, endocrine disrupting chemicals (EDCs), phthalates, personal care products (PCPs), fatty acids, food additive, hormones and trace organics present in hospital wastes. The two observations that were quite noteworthy regarding monitoring of OMPs were: (i) Fifty-six OMPs were detected in the monsoon while only forty-seven were found in the non-monsoon (ii) The concentration of forty-seven out of fifty-seven OMPs was more in the monsoon samples than non-monsoon samples. These observations were contrary to the general understanding that the OMPs in the monsoon samples due to the high dilution should be present in much lower concentrations in river water. The reason for this contradiction could not be correlated with the octanol-water partition coefficients (log K_{ow}), solubility, and polar/non-polar characteristics of the OMPs. It could be due to the sorption of OMPs onto the sediments during the low flow (~ 19 m^3/s) conditions. During the high flow conditions (~ 507 m^3/s), scouring of deposited sediments possibly results in erosion and dissolution of OMPs in the river water. In general, compared to rivers of Europe and United States of America, much higher concentrations of OMPs were found in the river Yamuna.

Keywords: Organic micropollutants (OMPs); Pharmaceutically active compounds (PhACs); Endocrine disrupting chemicals (EDCs); Phthalates; Personal care products (PCPs); River Yamuna.

3.1. INTRODUCTION

Increasing contamination of freshwater resources with thousands of organic micropollutants (OMPs) is a key environmental concern. Using surface waters having low flows and contaminated with municipal sewage for drinking water production has a potential risk of water being contaminated with OMPs. Pharmaceutically active compounds (PhACs), endocrine disrupting compounds (EDCs), personal care products (PCPs), industrial chemicals, etc. have been identified in the environment in last few decades (Snyder et al., 2008).

Since OMPs are not completely removed during conventional wastewater treatment of municipal sewage, they find their way into the surface water systems. PhACs, household chemicals and hormones are released to the environment even after passing through the wastewater treatment facilities (Halling-Sorensen et al., 1998). Pharmaceuticals such as analgesics and antipyretics are excreted from the body either in their native form or as biotransformed forms as polar molecules (Zuehlke et al., 2007) which are not removed during municipal treatment and find a way into the receiving water bodies (Heberer and Stan, 1997, Daughton and Ternes, 1999, Kim et al., 2007). Effluents from hospitals, agriculture runoff, landfill leachate, etc. (Verstraeten et al., 2002) also find their way into water bodies. The application of animal wastes in the agriculture fields results in the presence of veterinary drugs in surface water bodies due to runoff (Meyer et al., 2000). In Berlin, 24 h composite sampling was done for different sewage treatment plants (STPs) to observe the removal of different PhACs during treatment processes. The results showed, 8-17 %, removal of clofibric acid, carbamazepine and diclofenac whereas 99.9 % removal of caffeine was observed (Heberer, 2002). Estrogens such as estrone, estriol and 17β-estradiol were found at very low concentrations (ng/L) in treated effluents from STPs in Brazil, Canada, Germany and Italy (Heberer, 2002). Many researchers studied the occurrences of OMPs such as PhACs, PCPs, EDCs, phenols in the wastewater (Heberer et al., 1998, 2001), surface water (Kalkhoff et al., 1998, Daughton and Ternes, 1999), groundwater (Lange et al., 2000) and drinking water (Heberer and Stan, 1996, Lange et al., 2000).

According to Schwab (2005) presence of low concentrations (ng/L) of PhACs in the aquatic environment does not pose much risk to the human health. However, low concentrations of these chemicals in the aquatic system can cause antibacterial resistance. The detrimental effect of long-term exposure to the mixture of PhACs, EDCs, PCPs and other OMPs in the aquatic environment as well as on the human health is currently not fully understood. According to Villanueva et al. (2014), many pharmaceuticals and personal care products (PPCPs) and industrial chemicals can cause chronic toxicity to the human health even at a concentration below 1 µg/L.

Where surface water is contaminated with municipal discharges, recharged groundwater has the potential risk of contamination with OMPs (Heberer et al., 2001). To protect aquatic ecosystem and drinking water resources, monitoring and quantification of sewage born pollutants are needed. Kaushik et al. (2008) analyzed samples from the Yamuna in Delhi and found traces of pesticides such as HCH and DDT, well within Indian permissible limits of 1000 ng/L. Agarwal et al. (2006) reported a high impact of urbanization and industrialisation on the overall pollution status of the river and reported the presence of polycyclic aromatic hydrocarbons (PAHs) in sediments of the Yamuna in Delhi. OMPs such as alkanes, phthalates, fatty acids, and pharmaceuticals were also found in Yamuna water in a qualitative analysis (Techneau D 5.2.6).

Very little is known about the environmental occurrence and fate of PhACs, PCPs and other OMPs after their use in day to day life. These contaminants currently have no regulatory standards for their presence in the wastewater streams or public water supplies because of lack of the database on their occurrence. In developing countries, complete identification and quantification of OMPs in sewage-impacted river waters, often used for water supply, has not been attempted. The objective of the present study, therefore, was to identify and quantify OMPs present in surface water heavily contaminated by municipal wastewater from a metropolis. The scope of the work included analysis of water samples collected from the river Yamuna for OMPs over a period of one year. Accordingly, the study presents a data set of 57 OMPs which mainly included PhACs, pesticides, EDCs, phthalate, PCPs, fatty acids, food additive, hormones and hospital wastes in a heavily polluted Indian River, Yamuna. Seasonal variation during non- monsoon and monsoon months are also summarized.

3.2. SITE DESCRIPTION

Delhi is the eighth largest metropolises in the world with over 16.7 million inhabitants (excluding urban clusters at the outskirts) according to the census of 2011. The 22 km long stretch of the Yamuna in Delhi is bound by a Wazirabad barrage at its upstream end and Okhla barrage on its downstream end. To meet the drinking water demand of the city, water is withdrawn from the upstream barrage at Wazirabad and no fresh water is released in non-monsoon months. Due to a combined discharge from domestic, industrial and agricultural activities, stretch downstream of Wazirabad barrage is highly polluted. In the present study, river samples were collected from this polluted stretch around Nizamuddin Road Bridge in Central Delhi. The bulk of the Delhi wastewater is discharged upstream of the location selected. In urban flood plain of the Yamuna, close to Nizamuddin Bridge, a number of Ranney wells are located for tapping the unconfined aquifer for municipal water supply. Wells are suspected of a withdrawing mixture of river and ground waters. Although river water is supposed to get purified during its travel/passage through the aquifer, however, the possibility of the presence of waterborne pollutants, particularly OMPs, in drinking water is not ruled out.

3.3. MATERIALS AND METHODS

Sixteen samplings were organized between Aug. 2013 and Aug. 2014, 7 in monsoon and 9 in the non-monsoon. Water samples from the river Yamuna were collected in glass bottles. Samples were transported within 8 hours to the Environmental Engineering Laboratory, IIT Roorkee and stored at 4^{o} C. The analysis was completed within 48 hours after sampling.

3.3.1. Extraction of Trace Organics

Water samples (1 L each) were filtered through glass fiber filters (GFF). The OMPs in the samples were extracted using solid phase extraction (SPE) cartridges (Bond Elut Plexa, 200 mg, 6 mL, Agilent Technologies, India) using a 12 port vacuum manifold unit (Agilent Technologies, India).

Before sample loading, SPE cartridges were conditioned successively with 3 mL 50:50 (v/v) ethyl acetate: acetone, 3 mL methanol and demineralised water. Water samples were loaded under vacuum onto the cartridges at a flow rate of 5 to 8 mL min^{-1}. After sample loading, cartridges were washed with 5% methanol-water and dried under vacuum for 10 minutes. OMPs were eluted with three successive solvents, 3 mL of ethyl acetate, 3 mL of ethyl acetate: acetone (50:50; v/v) and 3 mL hexane. After elution, the collected extracts were evaporated under a gentle stream of nitrogen gas to the final volume of 100 – 150 μL. Samples were incubated at 70° C for 35 min followed by the addition of 70 μL N-Methyl-N-(trimethylsilyl) trifluoroacetamide (MSTFA) for derivatization.

3.3.2. *Determination of Trace Organics*

The trace organics were quantified by a calibration curve method for each sample. The extraction recoveries were determined separately for each OMP by spiking samples at 50 ng/L before extraction. Gas chromatographic separation coupled with mass spectrometry (GC-MS) analysis was performed using Varian 450 GC 240 MS equipped with a split/splitless injector 1079. VF-5MS capillary column (Varian) of length 30 m, internal diameter (ID) 0.25 mm, coated with a 0.25 μm film of 5% diphenyl, 95% dimethylpolysiloxane was used. The ultrapure helium (99.999%) used as a carrier gas was maintained at a constant flow of 1 mL min^{-1}, the transfer-line was held at 250°C. 2 μL samples were injected in splitless mode. For GC separation, the sequence of the temperature program was: (i) started at 80°C (held for 2 min) (ii) then set at 5°C min^{-1} to 180°C (held for 5 min); (iii) set at 5°C min^{-1} to 250°C (held for 5 min); (iv) set at 5°C min^{-1} to 280°C and then was held isothermally at 280°C for 5 min. The gas chromatograph was coupled to an ion trap mass spectrometer operated under electronic impact (EI) mode at 70 eV using scan mode, scan range (from 50–1000 amu).

3.4. RESULTS AND DISCUSSION

3.4.1. OMPs: Characteristics, Limit of Quantification and Frequencies of Occurrence

The partitioning properties of OMPs play a major role in their transport and mobility in the environment. Partition coefficients have been measured in many solvent water systems (Sato and Nakajima, 1979; Pezzagno et al., 1985). However, the octanol-water partition coefficient (K_{OW}) is the most widely accepted coefficient. K_{OW} describes the hydrophobic or hydrophilic nature of aqueous organic compounds (Schwarzenbach et al., 1983). According to Edzwald and Tobiason, (1999), the log K_{OW} of hydrophobic organic compounds is greater than two (>2) and that of hydrophilic compounds is less than two (<2).

Initially, qualitative analysis of the Yamuna water and water samples collected from eight nearby Ranney wells was carried out to identify the OMPs for few months. Based on the screening, 57 OMPs that were detected in every sampling campaign either in river water or water samples from Ranney wells or both were selected for further quantification. The identified OMPs included the PhACs, pesticides, EDCs, phthalates, PCPs, fatty acids, a food additive, hormones and hospital wastes. For the sake of summarizing the results and discussion, OMPs along with their characteristics have been listed in Tables 3.1 to 3.3. An abbreviation for each compound is also given, and same is used in the text. Limit of quantification (LOQ), category (polar/non-polar) and frequency of their occurrence in non-monsoon and monsoon are also presented in Tables 3.1 to 3.3. Log K_{ow} values of OMPs varied from –2.54 to 8.70 representing highly hydrophilic to highly hydrophobic compounds (Tables 3.1 to 3.3). The solubility of identified OMPs also varied widely from almost insoluble (0.001 mg/L) to highly soluble (1×10^6 mg/L). Out of 57 OMPs, 54 % were polar, and 46 % were non-polar. OMPs mainly belonged to acids, amines, phenols, esters, aldehydes, triazines and halides. Frequencies of occurrence of OMPs during non-monsoon and monsoon are also given in Tables 3.1 to 3.3.. While ENE, a hormone, was the most frequently detected OMP in non-monsoon and monsoon (sixteen out of sixteen times), PCH, a PhAC did not appear even once. Apart from ENE, only PA, a fatty acid, appeared 100% of the time in non-monsoon (nine out of nine times) and EDS, a pesticide, BBPH, a phthalate, and EOL, a hormone, 100% of the times in monsoon (seven out of seven times). Six PhACs and four pesticides were absent during non-monsoon and one PhAC and one fatty acid during monsoon.

3.4.2. OMPs: Temporal Variations/ Average Concentrations/ Concentration Ranges

Temporal variations of OMPs are presented in Figs. 3.1 to 3.3 and their average concentrations during non-monsoon and monsoon months are given in Fig. 3.4. It is quite clear from the temporal variations and the average values that forty-seven out of fifty-seven OMPs exceeded in monsoon samples compared to non-monsoon samples. Based on average concentrations, OMPs have been divided into three categories/ranges: (a) <1 μg/L, (b) 1-10 μg/L and (c) > 10 μg/L in Table 3.4. Following observations were recorded from Table 3.4:

- The concentration of several OMPs like EFC, LME, BA, TMP, ABA, HBA, DMAB, DTAP, DPH, CTA, STA, OMTS, MBHD, ATG, GUA, and ADE was < 1 μg/L or 1-

10 μg/L in non-monsoon. However, the concentration of these OMPs was 1-10 μg/L or >10 μg/L in the monsoon.

- OMPs such as CA, DS, GEM, KTP, IBF, ALD, MBZ, ATZ, and SMZ were detected only in the monsoon.

It was quite contrary to the understanding that during monsoon due to the high dilution of the river water, OMPs should be present in much lower concentrations in river water. Even the nine out of ten OMPs that were not detected at all in any of the samples during non-monsoon appeared in monsoon. The reason for this contradiction could not be correlated to their log K_{ow}, solubility, polar/non-polar characteristics of the OMPs reported in Tables 3.1 to 3.3. A study of the large, densely populated catchment of River Yamuna in Delhi was carried out to find the possible reasons.

3.4.3. OMPs: Likely Reasons of Increase/ Appearance during Monsoon

As per CPCB (2012) around 3800 ML sewage is generated every day of which only around 40% is treated through 17 sewage treatment plants. Also, around 220 ML/d industrial waste is generated for which 13 common effluent treatment plants have been established. Treated and untreated wastewaters are discharged into 22 open surface drains those subsequently discharge into the river downstream of Wazirabad barrage. During nine non-monsoon months, the river carries mainly wastewater. Contrary to this, during three months of monsoon, around 80% the water flows into it. Accordingly, significant variations in water quality are observed. BOD of the polluted river water from 2001-Aug. 2012, in Delhi stretch, ranged from 3-99 mg/L. In Yamuna River, desirable limit of BOD in Delhi is 3 mg/L (CPCB, 2012). However, under the given circumstances where complete sewage treatment is not feasible, and dilution water (from upstream barrage) in the river is not available during non-monsoon, achievement of this target is difficult in near future.

Table 3.1. Detected pharmaceuticals in the Yamuna [$^{\#}$NM (9) = non monsoon (total no. of samples=9), M (7) =monsoon (total no. of samples=7)]

S. No	Name of the compound (Abbreviations in bold)	MW (g/mol)	log K_{ow}	Water solubility (mg/L)	P-polar, NP-non polar	Class	LOQ (µg/L)	Number of times appeared$^{\#}$	
								NM (9)	M (7)
	Pharmaceuticals								
1	Clofibric acid **(CA)**	214.64	2.57	582.5	P	Neutral organics-acid	0.1	ND	2
2	Diclofenac sodium **(DS)**	296.15	4.51	4.518	P	Neutral organics-acid	0.05	ND	3
3	Gemfibrozil **(GEM)**	250.33	4.77	4.964	P	Neutral organics-acid	0.09	ND	1
4	Ketoprofen **(KTP)**	254.28	3.12	120.4	P	Neutral organics-acid	0.1	ND	3
5	1-pyrrolidino-1-cyclohexane **(PCH)**	151.14	3.09	1743	NP	Aliphatic amines	0.4	ND	ND
6	Ibuprofen **(IBF)**	206.28	3.97	41.05	P	Neutral organics-acid	0.2	ND	3
7	Lomustine **(LMS)**	233.70	2.83	111.3	P	Aliphatic amines	0.04	1	4
8	6-ethyl-3-formylchromone **(EFC)**	202.20	1.84	1143	NP	Aldehydes	0.06	5	3
9	Pyridine, 2,4,6-trimethyl- **(PTM)**	121.18	1.88	4.917e+004	NP	Neutral organics	0.2	5	5
10	Salicylic acid **(SA)**	138.12	2.26	3808	P	Phenols-acid	0.1	4	2
11	Dopamine hydrochloride **(DHC)**	189.64	-	--	P		0.06	4	5
12	N-(tert-butoxycarbonyl)-L-leucine methyl ester **(LME)**	245.31	3.18	48.71	P	Esters	0.05	5	5
13	Clenbuterol hydrochloride **(CHC)**	313.65	-	-	P	-	0.1	4	1
14	3-acetamido-5-bromobenzoic acid **(ABBA)**	-	-	-	P	Neutral organics-acid	0.4	1	4
15	3,5-di-tert-butyl-4- hydroxy-benzaldehyde hemihydrate **(BHBH)**	486.68	-	-	NP	-	0.2	2	3
16	3,5-diiodosalicylic acid **(DISA)**	389.91	4.56	4.71	P	Phenols-acid	0.08	1	4
17	L-2- aminobutyric acid **(ABA)**	103.12	-2.54	1.438e+005	P	Aliphatic amines-acid	0.1	2	3
18	2,2,6,6-tetramethyl-4-piperidone **(TMP)**	155.24	0.43	3.14e+005	P	Aliphatic amines	0.1	1	6
19	Benzoic acid **(BA)**	122.12	1.87	2493	P	Neutral organics-acid	0.09	4	5
20	Dimethyl maleate **(DMM)**	144.12	0.74	1.877e+004	P	Acrylates	0.2	3	2

Table 3.2. Detected pesticides, EDCs and phthalates in the Yamuna [*P-polar, NP-non-polar, #NM (9)-non-monsoon (total no. of samples=9), M (7) =monsoon (total no. of samples=7)]

S. No	Name of the compound (Abbreviation)	MW (g/mol)	log K_{ow}	Water solubility (mg/L)	P/ NP*	Class	LOQ (μg/L)	Number of times appeared#	
								NM (9)	M (7)
Pesticides									
1	Terbuthylazine **(TBA)**	229.70	3.21	55.4	NP	Triazines	0.1	4	3
2	1-dodecanethiol **(DTH)**	200.40	6.18	0.22	NP	Thiols (mercaptans)	0.07	6	3
3	α-Endosulfan **(EDS)**	406.92	3.83	1.48	NP	Vinyl/allyl halides	0.2	8	7
4	Aldrin **(ALD)**	364.90	6.50	0.014	NP	Vinyl/allyl halides	0.1	ND	2
5	Heptachlor **(HPC)**	373.31	6.10	0.027	NP	Vinyl/allyl halides	0.06	1	3
6	Metribuzin **(MBZ)**	214.28	1.70	1304	NP	Hydrazines	0.3	ND	5
7	Atrazine **(ATZ)**	215.68	2.61	214.1	NP	Triazines	0.1	ND	5
8	Simazine **(SMZ)**	201.65	2.18	589.9	NP	Triazines	0.08	ND	3
EDCs									
1	5-hydroxy-2-methylbenzoic acid **(HMBA)**	152.14	1.60	1.216E+004	P	Phenols-acid	0.1	5	3
2	3,5- di-tert-butyl-4-hydroxybenzyl alcohol **(HBA)**	236.35	3.56	312.6	P	Benzyl alcohols	0.2	6	4
3	Diphenyl sulfone **(DFS)**	218.27	2.61	313.6	NP	Neutral organics	0.09	3	4
4	N,N'-diethyl-2-butene-1,4-diamine **(DEBD)**	142.24	1.06	1.032e+005	NP	Aliphatic amines	0.07	5	4
5	2,4- Di-tert-amylphenol **(DTAP)**	234.37	6.31	0.4441	NP	Phenols	0.1	7	6
6	Triphenyl phosphine oxide **(TPO)**	278.28	3.10	62.76	NP	Neutral organics	0.1	5	5
7	4-(dimethylamino) benzaldehyde **(DMAB)**	149.19	1.89	2177	NP	Aldehydes	0.2	3	3
8	Diacetone alcohol **(DA)**	116.16	-0.34	6.512e+005	NP	Neutral organics	0.1	4	4
9	Benzophenone **(BEN)**	182.21	3.18	103.3	NP	Neutral organics	0.08	6	1
Phthalate									
1	Diethyl phthalate **(DPH)**	222.24	-	-	NP	-	0.07	3	6
2	Benzyl butyl phthalate **(BBPH)**	312.36	4.73	0.95	NP	Esters	0.05	8	7

Table 3.3. Detected PCPs, fatty acids, food additive, hormones and hospital waste in the Yamuna [*P-polar, NP-non-polar, # NM (9)-non-monsoon (total no. of samples=9), M (7) =monsoon (total no. of samples=7)]

S. No	Name of the compound (Abbreviations)	MW (g/mol)	log K_{ow}	Water solubility (mg/L)	P/NP*	Class	LOQ (µg/L)	Number of times appeared#	
								NM (9)	M (7)
PCPs									
1	Esculin hydrate **(EH)**	358.29	-	-	P	-	0.1	5	4
2	Stearic acid **(STA)**	284.47	8.23	0.0035	NP	Surfactants	0.07	3	5
3	Octamethyltrisiloxane **(OMTS)**	236.53	4.80	0.1495	NP	Neutral organics	0.08	5	1
4	1-tridecanol **(TRD)**	200.36	5.26	4.53	P	Neutral organics	0.1	1	2
5	Cetyl alcohol **(CTA)**	242.44	6.73	0.1495	P	Neutral organics	0.1	2	3
6	1-hexadecanol **(HXD)**	-	-	-	P	-	0.09	1	2
7	1-heptadecanol **(HPD)**	256.46	7.23	0.047	P	Neutral organics	0.3	1	5
8	1-eicosanol **(EIC)**	298.54	8.70	0.0015	P	Neutral organics	0.06	3	1
9	Triclosan **(TRI)**	289.54	4.76	4.62	P	Phenols	0.09	3	2
Fatty acid									
1	Palmitic acid **(PA)**	256.42	7.17	0.04	P	Surfactants	0.1	9	5
2	Methyl 16-bromohexadecanoate**(MBHD)**	349.34	7.59	0.002	NP	esters	0.08	5	3
3	Linoleic acid **(LA)**	280.44	7.05	0.037	P	Surfactants	0.3	4	2
4	Decanoic acid **(DEA)**	172.26	4.09	47.89	P	Surfactants	0.07	4	ND
Food additive									
1	N-acetylglycine **(ATG)**	117.10	-1.02	7.68e+005	P	organic-acid	0.07	6	3
Hormones									
1	Estrone **(ENE)**	270.36	3.13	146.8	P	Phenols	0.2	9	7
2	Estriol **(EOL)**	288.38	2.45	440.8	P	Phenols	0.2	7	7
Hospital waste									
1	Adenine **(ADE)**	135.13	-0.05	4739	NP	Imidazoles	0.6	5	5
2	Guanine **(GUA)**	151.13	-1.77	1e+006	NP	Imidazoles	0.1	2	6

Wastewater disposal system in Delhi is quite different compared to developed countries. Treated and untreated wastewaters are first discharged into the network of open drains which ultimately take it to river Yamuna. Longest drain is the Nazafgarh drain. It was originally a storm water drain or rivulet. Presently, it carries untreated and treated wastewaters. It traverses a distance of about 40 km before joining River Yamuna. 38 tributary drains discharge into Najafgarh drain. Out of 2064 ML/d wastewater generated in Najafgarh basin, the treatment capacity exists for only 1305 ML/d. Out of the installed capacity, only about 629 ML/d is utilized thus leaving 1335 ML/d of sewage to join Najafgarh drain without any treatment and ultimately flowing into the river (CPCB, 2012).

In the present study, river samples were collected around Nizamuddin Bridge in Central Delhi. Most of the drains discharge into the Yamuna before Nizamuddin Bridge. It is clear that wastewater travels considerable distances (in some cases even more than 100 km) through the extensive network of connecting open drains and river. Khim et al. (1999), Khim et al. (2001), Koh et al. (2002), Davide et al. (2003), Venkatesan et al. (2010) and Wang et al. (2014) have reported accumulation of OMPs in the sediments of different rivers impacted by municipal and industrial wastewaters. In the present case too, it appears that OMPs adsorb onto the sediments in long stretches of open drains and river during the low flow conditions.

Stull et al. (1996) found remobilization of DDTs and PCBs from heavily contaminated sediments in the deeper strata as the reason of their widespread presence in the Santa Monica and San Pedro basins in California, USA. Zeng and Venkatesan (1999) also suggested that historically deposited DDTs in the Palos Verdes shelf gets remobilized upward in the sedimentary strata and consequently re-suspend into the water column. Venkatesan et al. (2010) suggested that contaminated particles could be dispersed upward by bio-diffusion and carried during strong flow events. Davide et al. (2003) investigated major elements, nutrients and trace metals in the bed sediments and their suspension along the River Po (Italy) during normal and high flow conditions. During normal summer months, discharge was found to range from 1200-1450 $m^3 s^{-1}$ whereas it exceeded 3000 $m^3 s^{-1}$ during 30 days of high flow condition. Both nutrients and trace metals were found to concentrate in river bed sediments during normal flow conditions and decreased in the sediments under high flow conditions due to flushing of contaminated bed sediments. Re-suspension of coarser material from the bottom sediments during flood conditions is also reported.

Table 3.4. Categorization of OMPs according to their ranges of average concentrations in the Yamuna in non-monsoon and monsoon months

S. No	Compounds Group	River water: range of average concentrations of compounds					
		<1 µg/L		**1-10 µg/L**		**>10 µg/L**	
		NM	M	NM	M	NM	M
1	Pharmaceuticals	EFC, SA, LME, BA BHBH, ABA, TMP.	GEM, SA, BHBH, DISA.	LMS, PTM, DHC, CHC, DISA, DMM.	CA, KTP, IBF, LMS, EFC, PTM, DHC, LME, CHC, ABA, TMP, BA, DMM.	ABBA.	DS, ABBA.
2	Pesticide	HPC.	ALD, HPC, MBZ.	TBA, EDS.	TBA, DTH, EDS, ATZ, SMZ.	DTH.	-
3	EDCs	HBA, DMAB.	BEN.	HMBA, DFS, TPO DEBD, DTAP, DA, BEN.	HMBA, HBA, DFS, DA DEBD, TPO, DMAB.	-	DTAP.
4	Phthalate	DPH.	-	BBPH	BBPH.	-	DPH.
5	PCPs	CTA.	TRI.	EH, STA, OMTS, TRD, HXD, EIC, TRI.	EH, TRD, CTA, HXD, HPD, EIC.	HPD.	STA, OMTS.
6	Fatty acids	MBHD.	-	PA, DEA.	PA, MBHD, LA.	LA.	-
7	Food additive	ATG.	-	-	ATG.	-	-
8	Hormones	-	EOL.	ENE, EOL.	ENE.	-	-
9	Hospital waste	GUA.	-	ADE.	GUA.	-	ADE.

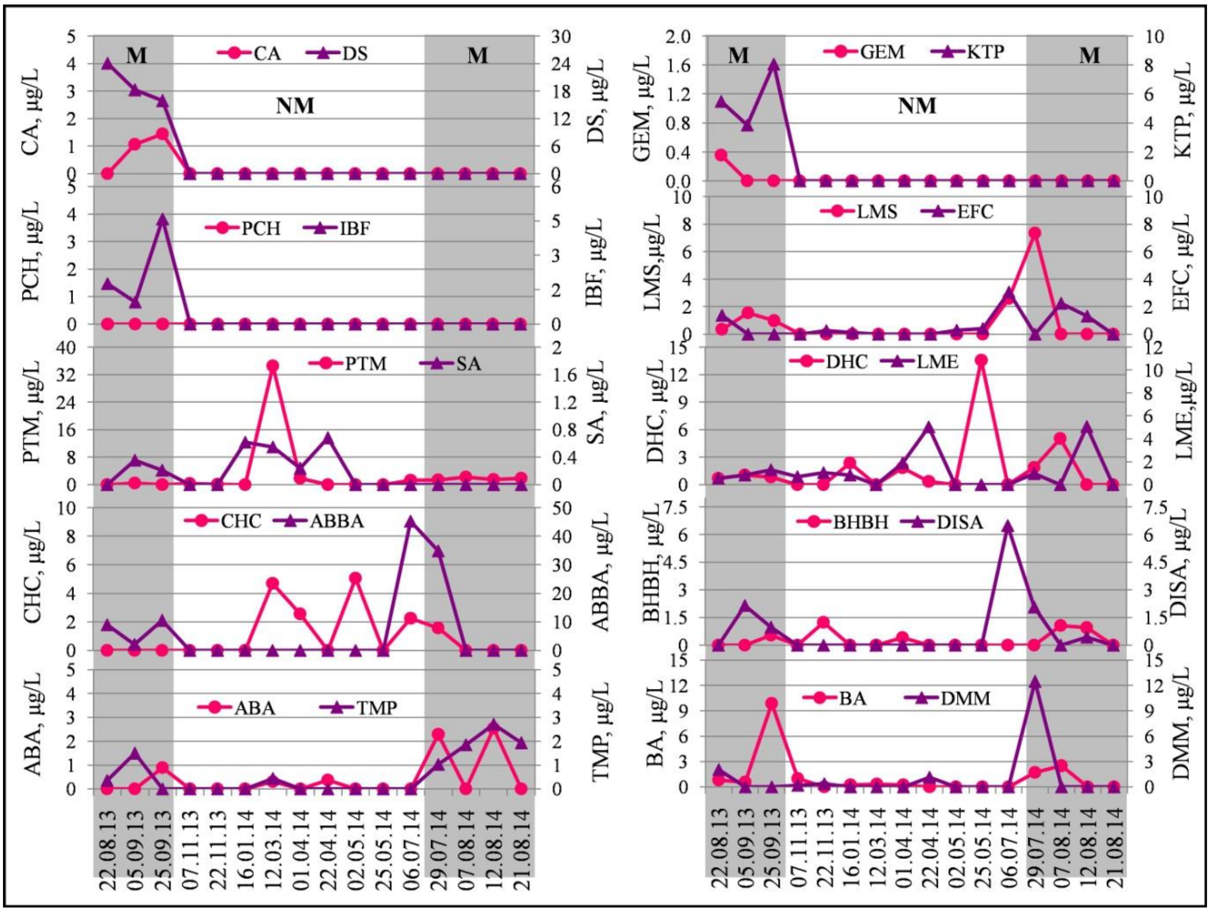


Fig. 3.1. Temporal variation of pharmaceuticals in the Yamuna

In the present study, results show that even the polar OMPs adsorb during low flow and appear in greater concentrations during high flow. Pradhan et al. (2015) have demonstrated that partitioning of the mixture of compounds is different from the individual compound. It appears that OMPs adsorb onto the sediments in an extensive network of interconnected drains and river during the low flow (~ 19 m^3/s) conditions in non- monsoon months. During the high flow conditions (~ 507 m^3/s), scouring of deposited sediments possibly results in erosion and dissolution of OMPs in the river water.

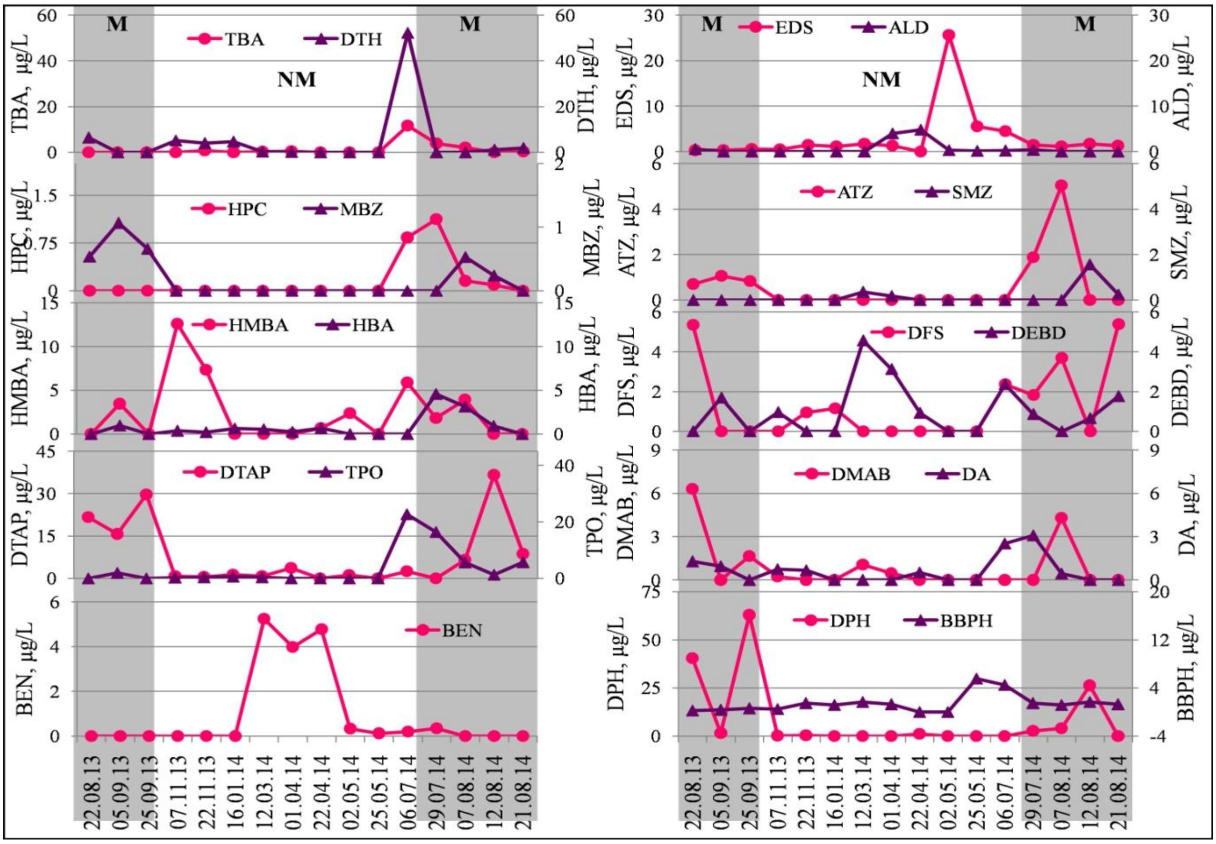


Fig. 3.2. Temporal variation of pesticides, EDCs and phthalates in the Yamuna

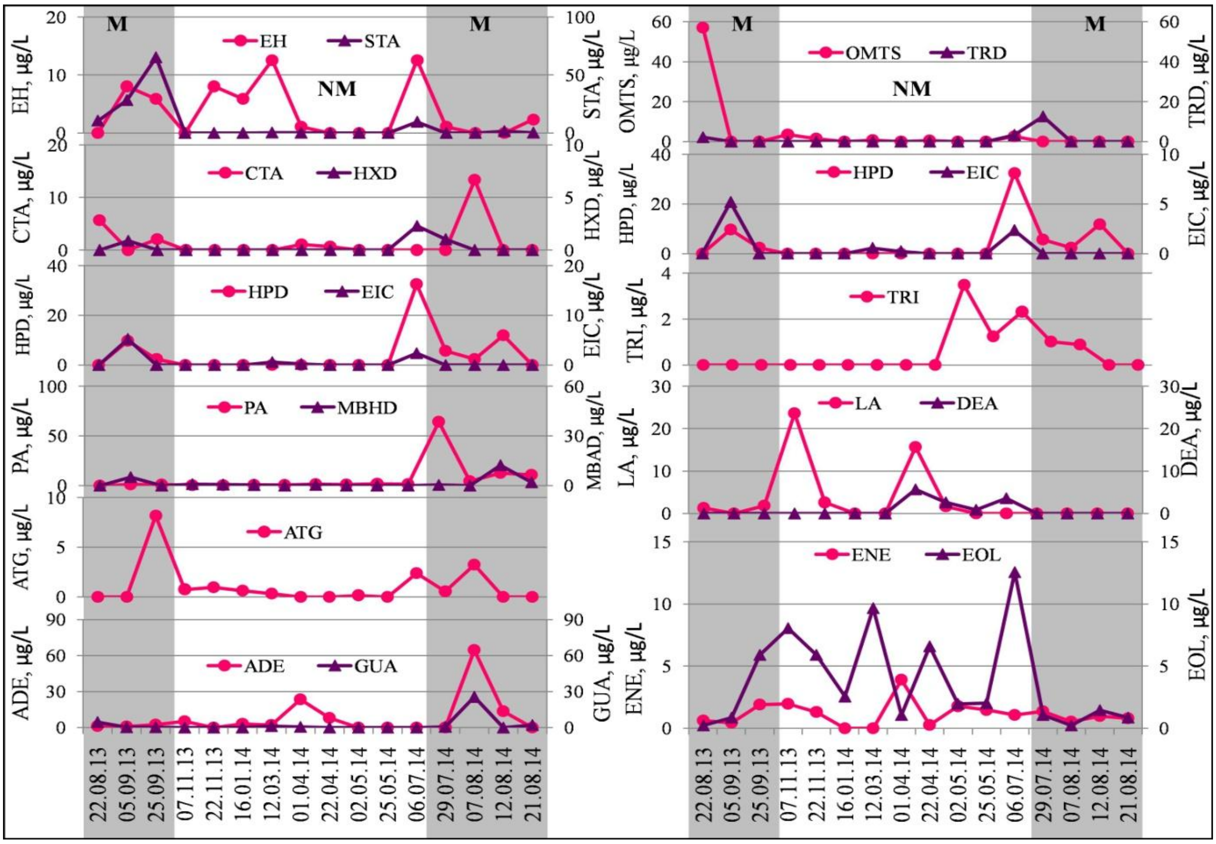


Fig. 3.3. Temporal variation of PCPs, fatty acids, food additive, hormones and hospital waste in the Yamuna

3.4.4. Occurrence of Selected OMPs in Different Rivers

Over the last two decades, some selected OMPs have been detected in different rivers. Maximum reported concentrations of these OMPs along with their concentrations found in Yamuna water during the present investigation are summarized in Fig. 3.5. It is quite clear, in general, that compared to Europe and the United States, much higher concentration of OMPs are present in the Yamuna. Despite many publications on the occurrence of OMPs in surface waters (range: ng/L to μg/L), neither their effects on the environment and human health, in particular, are reported, nor limits have been prescribed for their presence in surface waters. Oaks et al. (2004) have proposed that the exposure to the residues of veterinary diclofenac are responsible for the decline of Oriental white-backed vultures (OWBV).

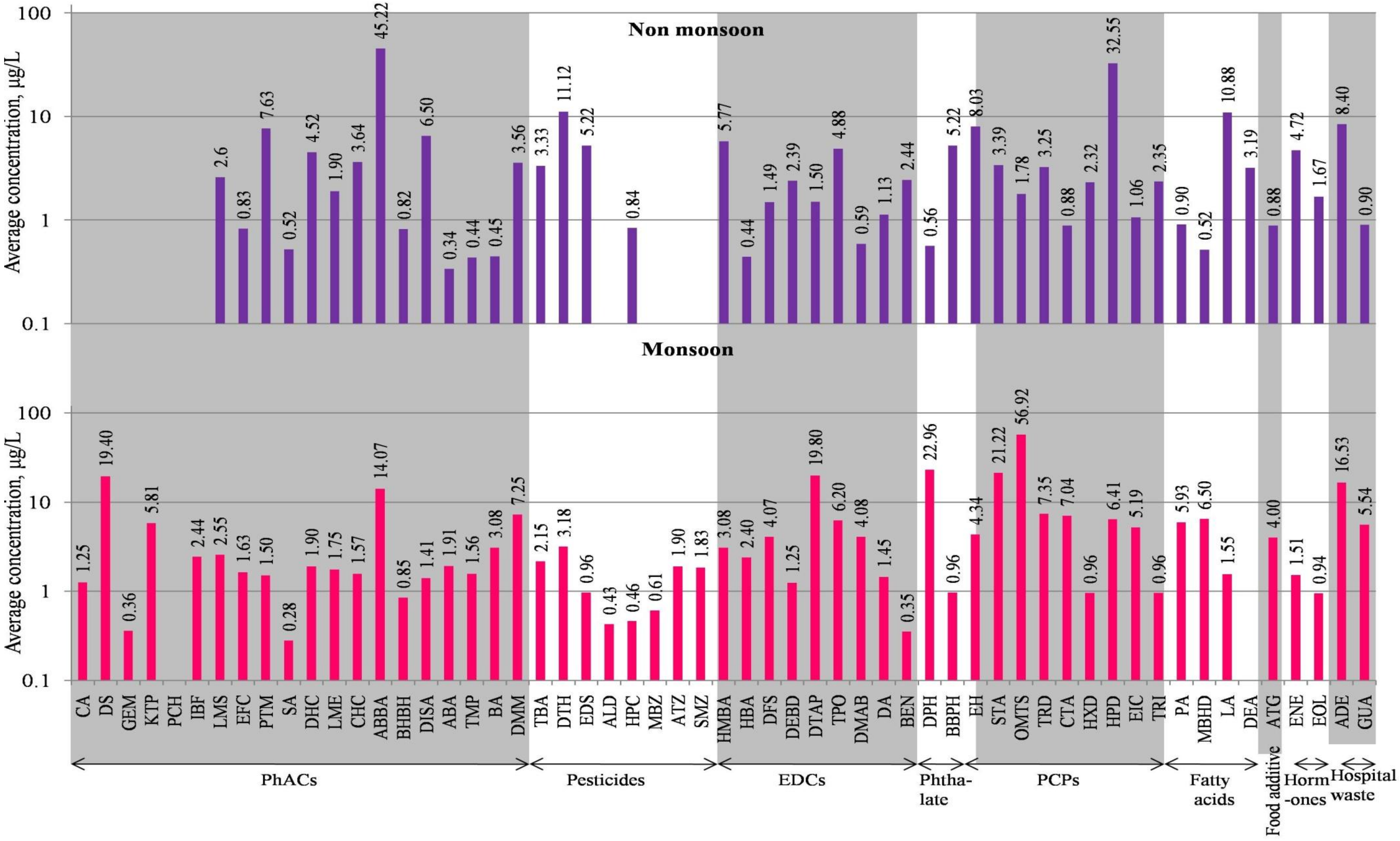
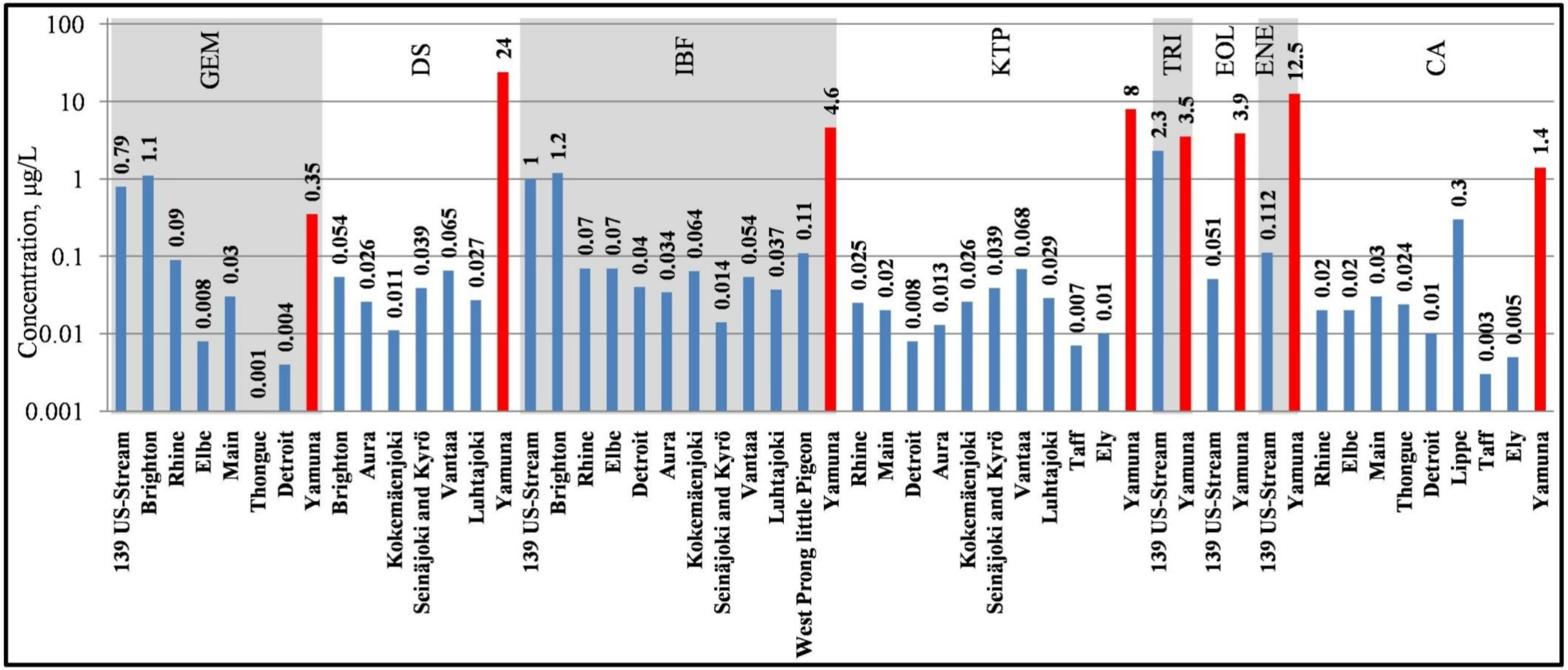


Fig. 3.4. Average concentrations of detected OMPs in the Yamuna during non-monsoon and monsoon months



1	139 US-Stream	Kolpin et al. (2002);
2	Brighton	Hoppe-Jones et al. 2010
3	Rhine (CA)	Walreven and Laane (2008), Ternes (1998)
	Rhine (GEM)	Weil and Knepper (2006), Walreven and Laane (2008)
	Rhine (KTP)	Walreven and Laane (2008)
	Rhine (IBF)	Weil & Knepper (2006), Walreven & Laane (2008), Ternes (1998)
4	Elbe	Weigel et al. (2004)
5	Main	Ternes (1998)
6	Thongue	Rabiet et al. (2006)
7	Detroit	Tabe et al. (2009)
8	Aura	Vieno 2007
9	Kokemäenjok	Vieno 2007
10	Seinäjoki and Kyrö	Vieno 2007
11	Vantaa	Vieno 2007
12	Luhtajoki	Vieno 2007
13	Lippe	Dsikowitzky et al. (2004)
14	Taff	Kasprzyk-Hordern et al. (2008)
15	Ely	Kasprzyk-Hordern et al. (2008)
16	West Prong little Pigeon	Yu and Chu (2009)
17	Yamuna	Present study

Fig. 3.5. Maximum reported concentrations of OMPs in the surface waters

3.5. CONCLUSION

- Fifty-six OMPs were detected in the monsoon while only forty-seven were found in non-monsoon. The concentration of forty-seven out of fifty-seven OMPs was more in the monsoon samples than non-monsoon samples.
- It was quite contrary to the general understanding that during monsoon due to the high dilution, OMPs should be present in much lower concentrations in river water. The reason for this contradiction could not be correlated with their respective characteristics (log K_{ow}, solubility, polar/non-polar, etc.).
- OMPs perhaps adsorb onto the sediments in extensive network of interconnected drains and river during the low flow conditions in non-monsoon months. Results show that even the polar OMPs follow this trend. During the high flow conditions, scouring of deposited sediments results in dissolution of these compounds in the river water.
- In general, compared to rivers of Europe and United States, much higher concentrations of OMPs were found in the Yamuna.

3.6. ACKNOWLEDGEMENTS

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CHAPTER-4

Organic Micropollutants (OMPs): Occurrence In Ranney Wells In Central Delhi, India

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ABSTRACT

Organic micropollutants (OMPs) have been detected in aquatic systems worldwide. In the present study, OMPs present in eight Ranney wells (RWs) in Central Delhi, India were screened and quantified. Fifty-seven detected OMPs in river Yamuna and RWs were identified as pharmaceutically active compounds (PhACs), pesticides, endocrine disrupting chemicals (EDCs), phthalates, personal care products (PCPs), fatty acids, food additive, hormones and those organics present in hospital wastes in trace quantities. Number of OMPs detected, their frequencies of occurrence and concentrations in RWs reduced substantially compared to river water and correlated well with the distance of RWs from the river. Larger the distance, lesser the number of OMPs detected and lower their frequencies of occurrence and concentrations. In spite of significant levels (~ 50 μg/L) in river water of 3-acetamido-5-bromobenzoic acid, 1- dodecanethiol, diethyl phthalate, palmitic acid, and adenine, they were detected to be < 1 μg/L in RWs. Only a few OMPs e.g. simazine and aldrin, sometimes exceeded 1 μg/L in RWs. Compared to other OMPs, in general, EDCs, PCPs, phthalates, fatty acids and food additive appeared more frequently in the larger number of RWs. Among hormones, only estriol appeared once that too only in one of the RWs. Some of the OMPs e.g. adenine were not detected in any of the RWs.

Keywords: Organic micropollutants (OMPs), River Yamuna, Ranney Wells (RWs).

4.1. INTRODUCTION

Disposal of partially treated or untreated wastewaters into the natural water bodies increases the risk of contamination of drinking waters. As wastewaters are biologically and chemically complex, they pose problems for the ecology and human health such as toxicity, endocrine disruption and antibiotic resistance (Martinez 2009, Gust et al. 2013, Rosi-Marshall et al. 2013).River/lake-bank filtration (RBF/LBF) is either used as a pre-treatment or complete treatment for the production of drinking water (Grünheid et al., 2005, Eckert and Irmscher, 2006). At Lake Müggelsee in Berlin, Germany, LBF is being used for the treatment of drinking water for almost 100 years (Grischek et al., 1998). According to Sontheimer (1980), RBF has been in use as a pre-treatment step along the Rhine for more than 75 years. RBF as a pre-treatment step was initially intended for the removal of turbidity and microorganisms. Detection of organic micropollutants (OMPs) in the surface waters in recent times has raised the interest of researchers to explore the capacity of RBF/LBF in removing OMPs. Understanding of the environmental fate and transport of OMPs is necessary to protect the human health and aquatic ecosystems. Attenuation of pharmaceuticals present in the effluent-impacted surface waters used for the drinking water production has been reported by Lin et al. (2006), Brown et al. (2009), and Barber et al. (2013).

RBF of contaminated surface water result in the presence of OMPs in the groundwater as well as in drinking water, even though the concentration of these compounds were found very low (Heberer 2002, Reemtsma et al., 2006). Studies conducted by researchers reported the presence of many OMPs mainly pharmaceuticals, pesticides and industrial chemicals in the bank filtrate (Heberer et al. 2004, Verstraeten et al. 2003).Removal/reduction of OMPs during RBF mainly depends on microbial degradation, adsorption and travel time to the production well. Contaminants that are not degradable, generally appear in the bank filtrate. Polar contaminants such as PhACs, pesticides etc. leach into the groundwater. Non polar contaminants such as steroid hormones, synthetic musk compounds etc. are adsorbed in the aquifer, and thus do not leach and appear in drinking water (Heberer, 2002). Where surface water is contaminated with municipal discharges, recharged ground water has potential risk of contamination with OMPs (Heberer et al. 2004). Studies conducted by researchers have shown that in RBF system, many of the OMPs degraded or removed but OMP such as carbamazepine shown resistant to degradation

(Scheytt et al. 2006, Maeng et al. 2011). Kunkel and Radke (2011) conducted a tracer study using six pharmaceutical compounds in a small stream in Sweden and reported elimination of ibuprofen and clofibric acid whereas over a 16.4 km stretch of study, no attenuation of bezafibrate, diclofenac, metoprolol and naproxen was reported. Individual PhACs present in the aquatic environment in ng/L does not pose a risk to human health (Schwab 2005). However, the health risk of a mixture of pollutants (PhACs, EDCs, and PCPs) is currently unknown.

Fate and transport of OMPs of different origin/characteristics present as a mixture in river water, ultimately leading to Ranney wells (RWs) or consumer’s tap, has not been studied. The objective of the present investigation, therefore, was to explore the attenuation of OMPs during passage through aquifer from heavily contaminated surface water to RWs. Understanding fate during soil passage is essential to assess the degree of post-treatment required. The scope of the work included determination of OMPs in the water samples collected from the river Yamuna and RWs, located at varying distances, over a period of one year. Accordingly, the study presents a detailed data set of OMPs found in river Yamuna during non-monsoon and monsoon seasons and their attenuation during passage through the aquifer. As per author’s knowledge, in developing countries, identification and quantification of OMPs in polluted river waters and their attenuation as they travel towards production wells has not been attempted.

4.2. SITE DESCRIPTION

Within Delhi, Yamuna River is highly contaminated with sewage and industrial wastewaters. As per CPCB (2012) around 3800 ML sewage is generated every day of which only around 40% is treated. During non-monsoon months, the river carries mainly wastewater in its 22 km long stretch inside Delhi, as clean water is withdrawn for water supply, before the river enters into the city. Contrary to this, during three months of monsoon, around 80% the water flows into it. In Central Delhi, in the urban floodplain of River Yamuna number of RWs are being used to tap the unconfined aquifer (Fig. 4.1). Eight RWs (V-8, P-4, NR-II, P-5, M-15, NR-I, P-6 and M-16) were selected for the study. Wells were established between 1972 and 2006 and are located up to a distance of around 3.9 km from the bank of the river. Fig. 4.2 gives a conceptualized profile of the well field representing well numbers and their approximate distances from riverbank during non-monsoon. Layers of laterals and their

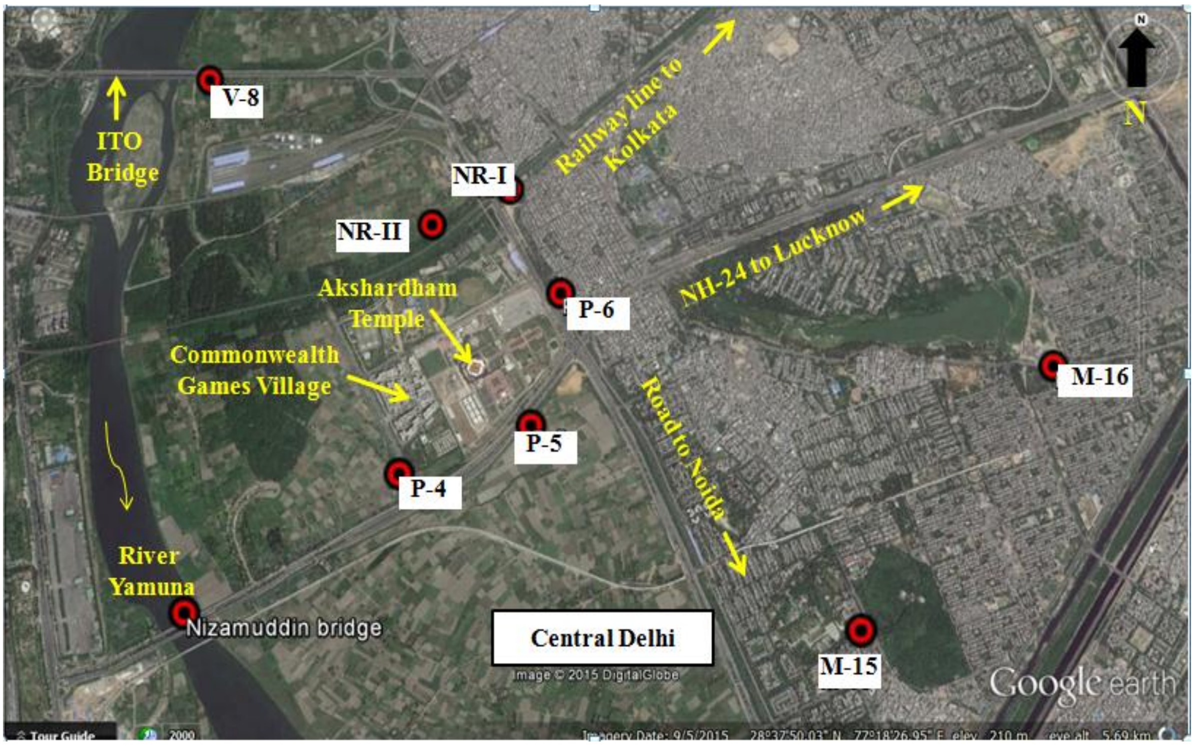


Fig. 4.1. Google Earth map of the study area showing 9 sampling locations: (i) River Yamuna at Nizamuddin Bridge and (ii) 8 Ranny wells (V-8, P-4, NR-II, P-5, M-15, NR-I, P-6 and M-16).

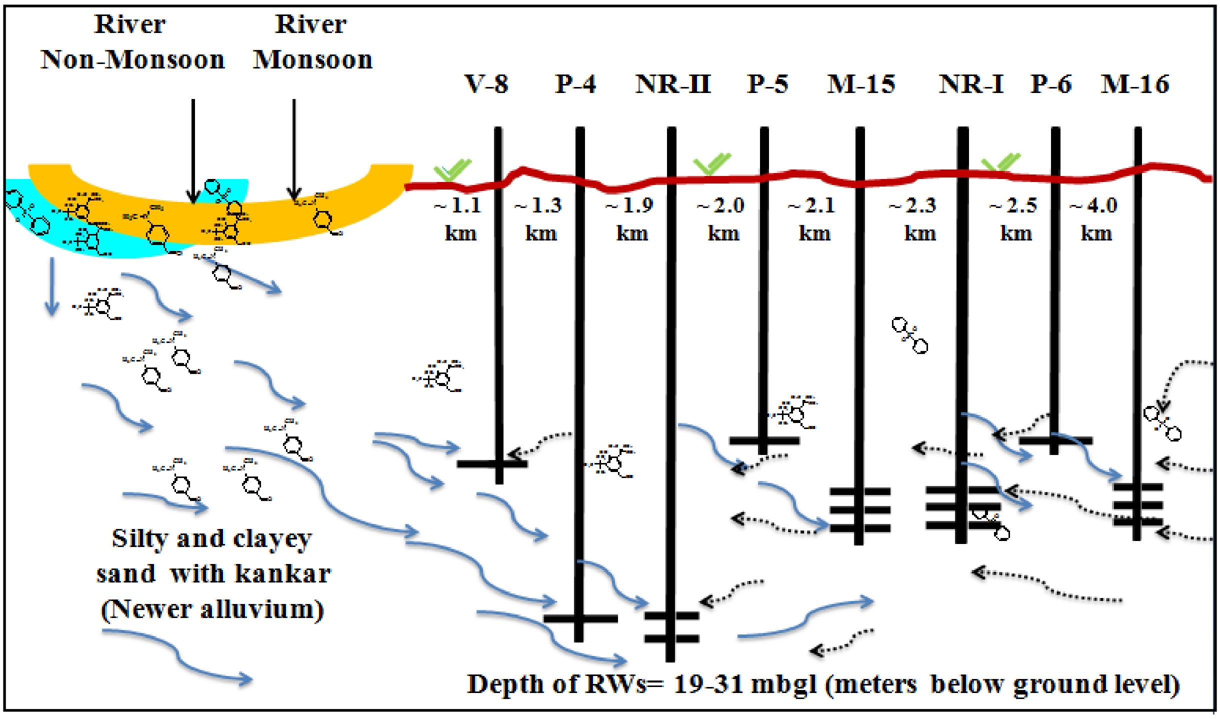


Fig. 4.2. Conceptualized profile of the well field representing well numbers and their approximate distances from riverbank during non-monsoon.

numbers and lengths vary from one RW to another. The number of layers of laterals varies from 1-3, the number of laterals from 10-24, length of individual laterals from 30-60 m and total length in a RW from 300-1440 m. Aquifer/newer alluvium has the thickness up to about 80 m and transmissivity from 730-2100 m^2 /day (Sprenger and Lorenzen, 2014).The composition of the younger alluvium is mainly a mixture of medium-to-coarse sand, silt, clay and kankar (local name of small calcareous concretions mixed with small gravels) (Chatterjee et al., 2009). The major water-bearing horizon is fine to coarse-grained sand with kankar. The thickness of fresh water zone varies from 30 to 85 m (CGWB, 2006). RWs are used for municipal water supply.

4.3. MATERIALS AND METHODS

To assess the OMPs, samples from the river and eight RWs were collected during non-monsoon and monsoon months between Aug. 2013 and Aug. 2014. Seven sampling were organized in monsoon and 9 in non-monsoon months. Water samples were collected in glass bottles and were transported to the Environmental Engineering Laboratory, IIT Roorkee within 8 hours and stored at 4^oC. Analysis was completed within 48 hours after sampling to avoid the loss or degradation of OMPs.

4.3.1. Extraction of OMPs

1 L water sample from each sampling location was filtered through glass fiber filters (GFF). The OMPs in the samples were extracted on solid phase extraction (SPE) cartridges (Bond Elut Plexa, 200 mg, 6 mL, Agilent Technologies, India) using a 12 port vacuum manifold unit (Agilent Technologies, India). Before sample loading, SPE cartridges were conditioned in the two steps using: (a) 3 mL, 50:50 (v/v) ethyl acetate: acetone and (b) 3 mL, 5:95 (v/v) methanol: demineralised water. Flow rate in the vacuum manifold was maintained at 5 to 8 mL/min. After sample loading, cartridges were first washed with 5% methanol-water and later dried under vacuum for 10 minutes. Elution of OMPs from cartridges was carried out using three solvents in succession: (a) 3 mL of ethyl acetate, (b) 3 mL of ethyl acetate: acetone (50:50; v/v) and (c) 3 mL hexane. After elution, the collected extracts were evaporated under a gentle stream of nitrogen gas to the final volume of 100 – 150 μL. Samples were incubated at 70°C for 35 min followed by the addition of 70 μL N-Methyl-N-(trimethylsilyl) trifluoroacetamide (MSTFA) for derivatization. For derivatization, 70 μL N-

Methyl-N-(trimethylsilyl) trifluoroacetamide (MSTFA) was added to each sample. It was followed by incubation at 70°C for 35 min.

4.3.2 Determination of OMPs

Detection of OMPs was done using gas chromatographic separation coupled with mass spectrometry (GC-MS: Varian 450 GC 240 MS). It was equipped with a split/split less injector 1079 and VF-5MS capillary column (Varian) of length 30 m, internal diameter (ID) 0.25 mm, coated with a 0.25 μm film of 5% diphenyl, 95% dimethylpolysiloxane. Calibration curve method was used to quantify OMPs. The flow of ultrapure helium (99.999%) was maintained at 1 mL/min and the transfer-line was held at 250°C. Samples (2 μL) were injected in splitless mode. For GC separation, the sequence of the temperature program followed was: (a) started at 80°C (held for 2 min), (b) then set at 5°C/min to 180°C (held for 5 min), (c) set at 5°C/min to 250°C (held for 5 min) and (d) set at 5°C/min to 280°C (held isothermally at 280°C for 5 min). The gas chromatograph was coupled to an ion trap mass spectrometer operated under electronic impact (EI) mode at 70 eV using scan mode (scan range 50–1000 amu).

4.4. RESULTS AND DISCUSSION

4.4.1. Qualitative analysis

To begin with water samples from river Yamuna and RWs were screened for four months to identify the OMPs. Based on the results of the qualitative analysis, OMPs those were detected in every sampling campaign at least in one of the samples (i.e. in Yamuna river water or water samples from eight RWs) were selected for further quantification. This preliminary exercise led to the identification of 57 OMPs (Table 4.1). The identified OMPs included the PhACs, pesticides, EDCs, phthalates, PCPs, fatty acids, food additive, hormones and those trace organics present in hospital wastes. OMPs have been arranged in Table 4.1 in descending order of their frequency of occurrence in Yamuna water during monsoon. This particular criterion to tabulate OMPs was selected based on the following subsequent observations:

(a) The concentration of 46 OMPs out of 57 was found to be higher in monsoon samples compared to non-monsoon samples,

(b) 9 OMPs were detected only during monsoon and

(c) 55 OMPs were found to be present in river water during monsoon while only 47 were present during non- monsoon.

The same criterion has been followed in the subsequent tabulation of the data (Tables 4.2-4.4) and further plotting of the results (Figs. 4.3-4.5). To tabulate the results and for simplifying the presentation, OMPs have been abbreviated as given in Table 4.1.

4.2.2. OMPs: Quantitative assessment

- Frequency of occurrence and average concentrations of (a) PhACs, (b) pesticides, EDCs and phthalates and (c) PCPs, fatty acids, food additive, hormones and trace organics found in hospital wastes (in µg/L) in the river Yamuna and RWs are given in Tables 4.2, 4.3 and 4.4 respectively. Their respective box plots of spatial variations during non-monsoon and monsoon for river Yamuna and RWs are shown in Figs. 4.3, 4.4 and 4.5. From Tables 4.2-4.4 and Figs. 4.3-4.5, it is quite clear that:
- (a) Number of OMPs detected, (b) their frequencies of occurrence and (c) concentrations in RWs reduced substantially compared to river water.
- A perusal of the data also reveals that among the RWs, in general, the number of OMPs detected their frequencies of occurrence and concentrations correlated very well with the distance of RWs from the river. Larger the distance, lesser the number of OMPs detected and lower the levels. For example in a closer well, P-4 (~1.2 km) around 85% of PhACs (17 out of 20) were detected while, in a distant well, M-16 (~4 km), only 45% (9 out of 20) PhACs were found.

Particular observations regarding each group are discussed separately in Sections.

4.2.2.1 PhACs: Occurrence in RWs

Among the PhACs, the highest concentration in river water was recorded for 3-acetamido-5-bromobenzoic acid (ABBA) (45.2 µg/L, non-monsoon). It was detected in only four of the RWs (NR-II, P-5, P-6, M-16) that too it was always <1 µg/L.

- Concentrations of diclofenac sodium (DS) also exceeded 10 µg/L (19.4 µg/L, monsoon) in river water. It was observed in only 3 RWs (P-4, P-5, P-6) and reduced exponentially to very low level, around 0.2 µg/L. Ketoprofen (KTP) was found in > 40% of river water samples during monsoon in the range of 3.85-8.07 µg/L.

However, KTP was never detected in any of the samples from any of the RWs, either in non-monsoon or monsoon.

- Diclofenac sodium (DS), gemfibrozil (GEM) and clofibric acid (CA)were not detected in RWs during non- monsoon.
- In general, following PhACs appeared more frequently in higher number of RWs: 2,2,6,6-tetramethyl1-4-piperidone (TMP), N-(tert- butoxy carbonyl)-L-leucine methyl ester (LME), lomustine (LMS), pyridine, 2,4,6-trimethyl- (PTM), 3,5-diiodosalicylic acid (DISA), 3,5-di-tert-butyl-4- hydroxy-benzaldehyde hemihydrates (BHBH).

Table 4.1. OMPs found in river Yamuna / Ranney Wells and their abbreviations

S.N	Compound (Abbreviation)	SN	Compound (Abbreviation)
PhACs		4	N,N’-diethyl-2-butene-1,4-diamine **(DEBD)**
1	2,2,6,6-tetramethyl-4-piperidone **(TMP)**	5	Diphenyl sulfone **(DFS)**
2	Benzoic acid **(BA)**	6	3,5- di-tert-butyl-4-hydroxybenzyl alcohol **(HBA)**
3	Dopamine hydrochloride **(DHC)**	7	4-(dimethylamino) benzaldehyde **(DMAB)**
4	N-(tert-butoxycarbonyl)-L-leucine methyl ester **(LME)**	8	5-hydroxy-2-methylbenzoic acid **(HMBA)**
5	Pyridine, 2,4,6-trimethyl- **(PTM)**	9	Benzophenone **(BEN)**
6	3-acetamido-5-bromobenzoic acid **(ABBA)**		***Phthalates***
7	3,5-diiodosalicylic acid **(DISA)**	1	Benzyl butyl phthalate **(BBPH)**
8	Lomustine **(LMS)**	2	Diethyl phthalate **(DPH)**
9	L-2- aminobutyric acid **(ABA)**		***PCPs***
10	3,5-di-tert-butyl-4- hydroxy-benzaldehyde hemihydrate **(BHBH)**	1	1-heptadecanol **(HPD)**
11	Diclofenac sodium **(DS)**	2	Stearic acid **(STA)**
12	6-ethyl-3-formylchromone **(EFC)**	3	Esculin hydrate **(EH)**
13	Ibuprofen **(IBF)**	4	Cetyl alcohol **(CTA)**
14	Ketoprofen **(KTP)**	5	1-hexadecanol **(HXD)**
15	Clofibric acid **(CA)**	6	1-tridecanol **(TRD)**
16	Dimethyl maleate **(DMM)**	7	Triclosan **(TRI)**
17	Salicylic acid **(SA)**	8	1-eicosanol **(EIC)**
18	Clenbuterol hydrochloride **(CHC)**	9	Octamethyltrisiloxane **(OMTS)**
19	Gemfibrozil **(GEM)**		***Fatty acid***
20	1-pyrrolidino-1-cyclohexane (PCH)	1	Palmitic acid **(PA)**
Pesticides		2	Methyl 16-bromohexadecanoate **(MBHD)**
1	α-Endosulfan **(EDS)**	3	Linoleic acid **(LA)**
2	Atrazine **(ATZ)**	4	Decanoic acid **(DEA)**
3	Metribuzin **(MBZ)**		***Food additive***
4	1-dodecanethiol **(DTH)**	1	N-acetylglycine **(ATG)**
5	Heptachlor **(HPC)**		***Hormones***
6	Simazine **(SMZ)**	1	Estrone **(ENE)**
7	Terbuthylazine **(TBA)**	2	Estriol **(EOL)**
8	Aldrin **(ALD)**		***Hospital waste***
EDCs		1	Guanine **(GUA)**
1	2,4- Di-tert-amylphenol **(DTAP)**	2	Adenine **(ADE)**
2	Triphenyl phosphine oxide **(TPO)**		
3	Diacetone alcohol **(DA)**		

Table 4.2. Frequency of occurrence and average concentrations of pharmaceutically aactive compounds (µg/L) in river Yamuna and Ranney Wells**.**

S. No	Compo-unds	Seas-on	**River** $9^{\S},7^{\#}$	**V-8** $6^{\S},5^{\#}$	**P-4** $8^{\S},7^{\#}$	**NR-II** $9^{\S},5^{\#}$	**P-5** $7^{\S},7^{\#}$	**M-15** $5^{\S},3^{\#}$	**NR-I** $9^{\S},7^{\#}$	**P-6** $7^{\S},7^{\#}$	**M-16** $5^{\S},2^{\#}$
Pharmaceutically active compounds (PhACs)											
1	TMP	NM	***1***,0.44	*	***4***,0.3	***1***,0.2	***3***,0.2	*	***5***,0.3	*	*
		M	***6***, 1.56	*	*	***3***,0.3	*	***2***,0.5	***4***,0.3	*	***2***,0.3
2	BA	NM	***4***,0.45	*	***4***,0.4	***1***,0.2	***3***,0.4	***1***,0.5	*	***3***,0.3	*
		M	***5***, 3.08	*	*	***4***,0.3	*	***1***,0.1	*	***3***,0.7	*
3	DHC	NM	***4***, 4.52	***1***,0.6	*	***1***,0.4	***1***,0.8	*	***1***,0.4	*	*
		M	***5***, 1.90	*	***1***,0.6	*	***1***,0.5	*	*	***2***,0.2	*
4	LME	NM	***5***,1.90	***4***,0.2	*	***3***,0.3	*	*	***3***,0.3	*	*
		M	***5***, 1.75	***5***,0.2	***1***,0.3	***3***,0.2	***2***,0.2	*	***5***,0.2	***1***,0.1	*
5	PTM	NM	***5***, 7.63	*	***2***,0.2	*	***2***,0.2	***1***,0.5	*	***2***,0.6	*
		M	***5***, 1.50	*	***2***,0.6	*	***2***,0.3	***1***,0.4	*	***3***,0.7	***2***,0.6
6	ABBA	NM	***1***, 45.2	*	*	***7***,0.5	***7***,0.2	*	*	***7***,0.2	*
		M	***4***, 14.1	*	*	*	***6***,0.2	*	*	*	***2***,0.4
7	DISA	NM	***1***, 6.50	*	***1***,0.5	***4***,0.3	*	*	***4***, 2.6	***3***,0.2	***3***,0.2
		M	***4***,1.41	*	***1***,0.4	***3***,0.5	*	***3***,0.6	***1***,0.1	*	*
8	LMS	NM	***1***, 2.6	*	*	***3***,0.4	*	*	***3***,0.6	*	*
		M	***4***, 2.55	***1***,0.5	***2***,0.5	***1***, 1.3	***1***,0.6	***1***,0.4	***3***,0.5	***2***,0.2	*
9	ABA	NM	***2***,0.34	*	***3***,0.1	*	***1***,0.1	*	***3***,0.3	*	***2***,0.7
		M	***3***, 1.91	***4***,0.4	*	***1***,0.6	*	*	***2***,0.3	*	*
10	BHBH	NM	***2***,0.82	*	***1***,0.8	***1***,0.9	*	*	***3***,0.3	*	*
		M	***3***,0.85	***2***,0.3	***1***, 1.8	*	***3***,0.2	***1***,0.8	*	***2***,0.3	***1***,0.4
11	DS	NM	*	*	*	*	*	*	*	*	*
		M	***3***,19.4	*	***2***, 1.8	*	***3***,0.5	*	*	***2***,0.2	*
12	EFC	NM	***5***,0.83	*	*	***1***,0.4	*	*	*	*	*
		M	***3***, 1.63	*	***2***,0.1	***3***,0.3	***2***,0.3	*	*	***2***,0.2	*
13	IBF	NM	*	*	*	*	*	*	*	*	***3***,0.4
		M	***3***, 2.44	*	***1***,0.4	*	***1***,0.7	*	*	*	*
14	KTP	NM	*	*	*	*	*	*	*	*	*
		M	***3***, 5.81	*	*	*	*	*	*	*	*
15	CA	NM	*	*	*	*	*	*	*	*	*
		M	***2***, 1.25	*	***1***,0.5	*	***1***,0.4	*	*	***1***, 1.3	*
16	DMM	NM	***3***, 3.56	***1***,0.5	***3***, 1.7	*	***1***, 2.3	***2***, 1.7	***4***,0.6	*	*
		M	***2***, 7.25	***4***,0.3	***2***,0.5	*	***2***,0.4	*	*	***2***,0.4	*
17	SA	NM	***4***,0.52	***2***,0.2	*	*	*	*	*	*	***1***, 2
		M	***2***,0.28	*	***2***,0.2	*	*	*	*	***2***, 1.3	***2***, 1.7
18	CHC	NM	***4***, 3.64	***2***, 2.7	*	***2***,0.6	*	*	***1***, 2.9	*	*
		M	***1***, 1.57	*	*	***2***,0.2	*	*	***2***,0.3	*	*
19	GEM	NM	*	*	*	*	*	*	*	*	*
		M	***1***,0.36	*	***1***,0.5	*	*	*	*	*	*
20	PCH	NM	*	*	*	*	*	*	*	***1***,0.2	**6**,0.8
		M	*	*	***4***,0.7	*	*	*	*	***3***,0.9	*

*(§Number of samples collected in non-monsoon (NM), # Number of samples collected in monsoon (M), * Not detected. First digit in the column (bold & italic) represents the number of times compound detected and the subsequent value the average concentration)*

4.2.2.2. Pesticides, EDCs and phthalates: occurrence in RWs

Pesticides

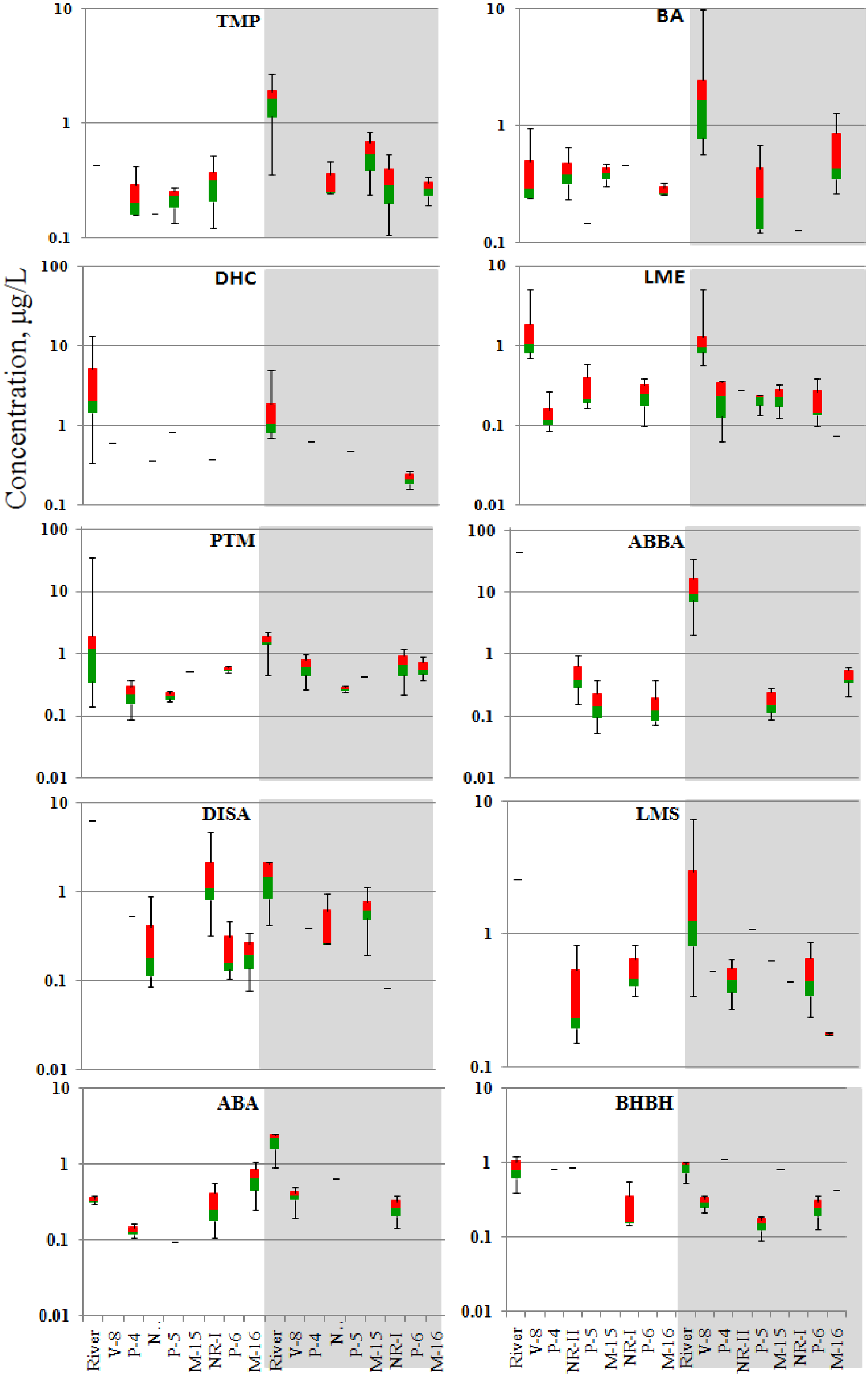
- Only 50 % of the pesticides were detected in river water in non-monsoon compared to monsoon. Among them, only 1-dodecanethiol (DTH) was found to exceed 10 µg/L (52.3 µg/L). However, in spite of high concentrations in both non-monsoon (0.12-52.3) and monsoon (1.09-6.43), it was detected to be < 1 µg/L in all samples from RWs.
- Only simazine (SMZ) and aldrin (ALD), sometimes exceeded 1 µg/L in RWs. All other pesticides were always found to be < 1 µg/L in RWs in spite of their higher concentrations in river water.
- Among the pesticides, most prominently detected ones in RWs were: α-Endosulfan (EDS) and terbuthylazine (TBA).
- Least detected pesticides among the analyzed ones were: atrazine (ATZ), metribuzin (MBZ) and heptachlor (HPC).

EDCs

- Among EDCs, 2, 4-di-tert-amylphenol (DTAP), triphenyl phosphine oxide (TPO) and 5-hydroxy-2-methylbenzoic acid (HMBA) were occasionally detected to be > 10 µg/L in river water but always < 10 µg/L in water samples collected from RWs.
- Compared to other OMPs, in general, the occurrence of EDCs in river and RWs was more frequent. Also, EDCs were detected in number of RWs.

Phthalates

- Maximum recorded concentrations of both the detected phthalates, diethyl phthalate (DPH, 0.2-62.8 µg/L) and benzyl butyl phthalate (BBPH, 0.27-25.6 µg/L) were > 10 µg/L in river water. Unlike other OMPs, they appeared in most of the RWs during both the seasons but in significantly lower concentrations than present in river water. DPH in RWs ranged from 0.07-1.70 µg/L and BBPH from 0.05-78 µg/L. Only one value of BBPH (78 µg/L) in V-8 exceeded the concentrations found in river water.


Concentration, µg/L
TMP
BA
DHC
LME
PTM
ABBA
DISA
LMS
ABA
BHBH
100
10
1
0.1
0.01
River
V-8
P-4
N..
P-5
M-15
NR-I
P-6
M-16
River
V-8
P-4
N..
P-5
M-15
NR-I
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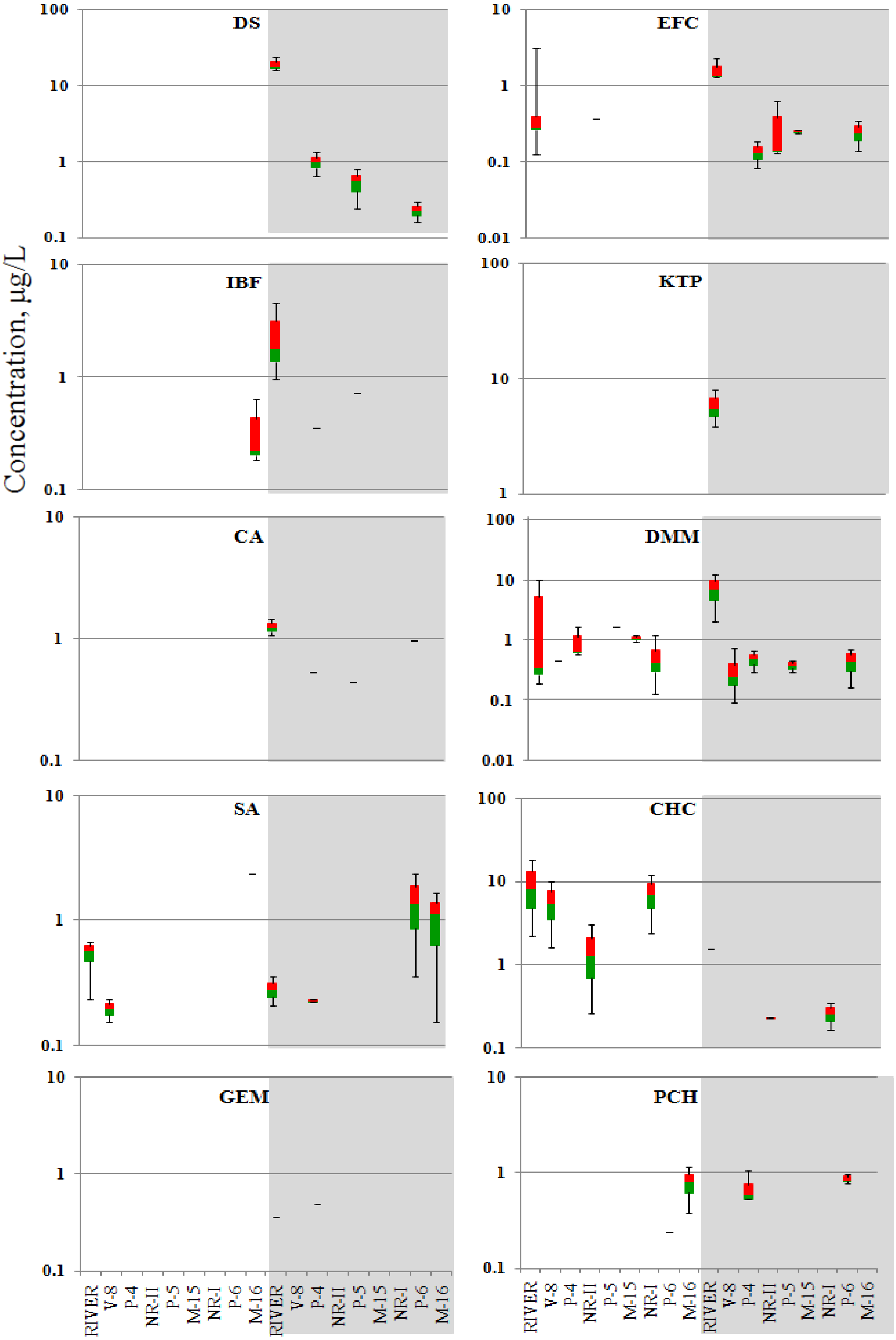


Fig. 4.3. Yamuna River and RWs: box plots of spatial variations of PhACs during non-monsoon and monsoon. For monsoon, variations are shown in gray shade.

4.2.2.3. PCPs, fatty acids, food additive, hormones and hospital wastes: Occurrence in RWs

PCPs

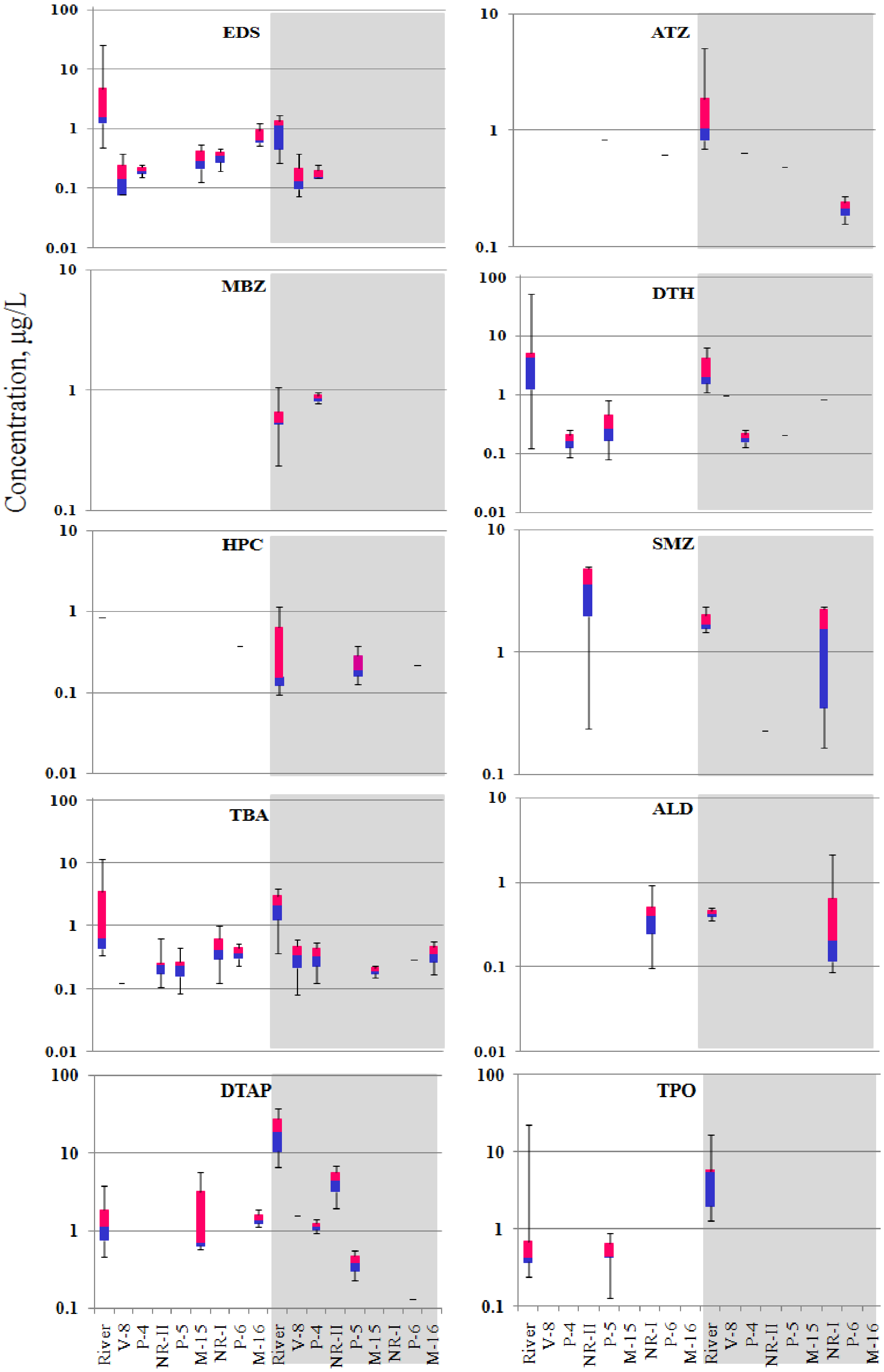
- Maximum observed concentration of three of the PCPs i.e. 1-heptadecanol (HPD), stearic acid (STA) and octamethyltrisiloxane (OMTS) were found to be >10 μg/L in river water. In spite of their higher concentrations in river water, most of the PCPs were detected in the range of < 1 μg/L in RWs.
- Like EDCs, PCPs were also detected in most of the RWs in both the seasons, but in lower concentration

Fatty acids and Food Additives

- The maximum concentration of palmitic acid (PA) in river water was found to be 64.3 μg/L while methyl 16-bromohexadecanoate (MBHD) and linoleic acid (LA) were also detected > 10 μg/L. In general, these OMPs appeared quite frequently in RWs but in significantly lower concentrations, in most cases < 1 μg/L.

Hormones and trace organics present in hospital wastes

- Among all the OMPs detected in the present study, hormones such as estrone (ENE) and estriol (EOL) were detected most frequently in river water in both non-monsoon and monsoon. However, only EOL appeared once in P-4 among all the RWs.
- Concentrations of both the trace organics from hospital wastes i.e. adenine (ADE) and guanine (GUA) were detected as high as 64 μg/L and 25.5 μg/L respectively. However, ADE was never detected in any of the samples from RWs.


Concentration, µg/L
EDS
ATZ
MBZ
DTH
HPC
SMZ
TBA
ALD
DTAP
TPO
100
10
1
0.1
0.01
River
V-8
P-4
NR-II
P-5
M-15
NR-I
P-6
M-16
River
V-8
P-4
NR-II
P-5
M-15
NR-I
P-6
M-16

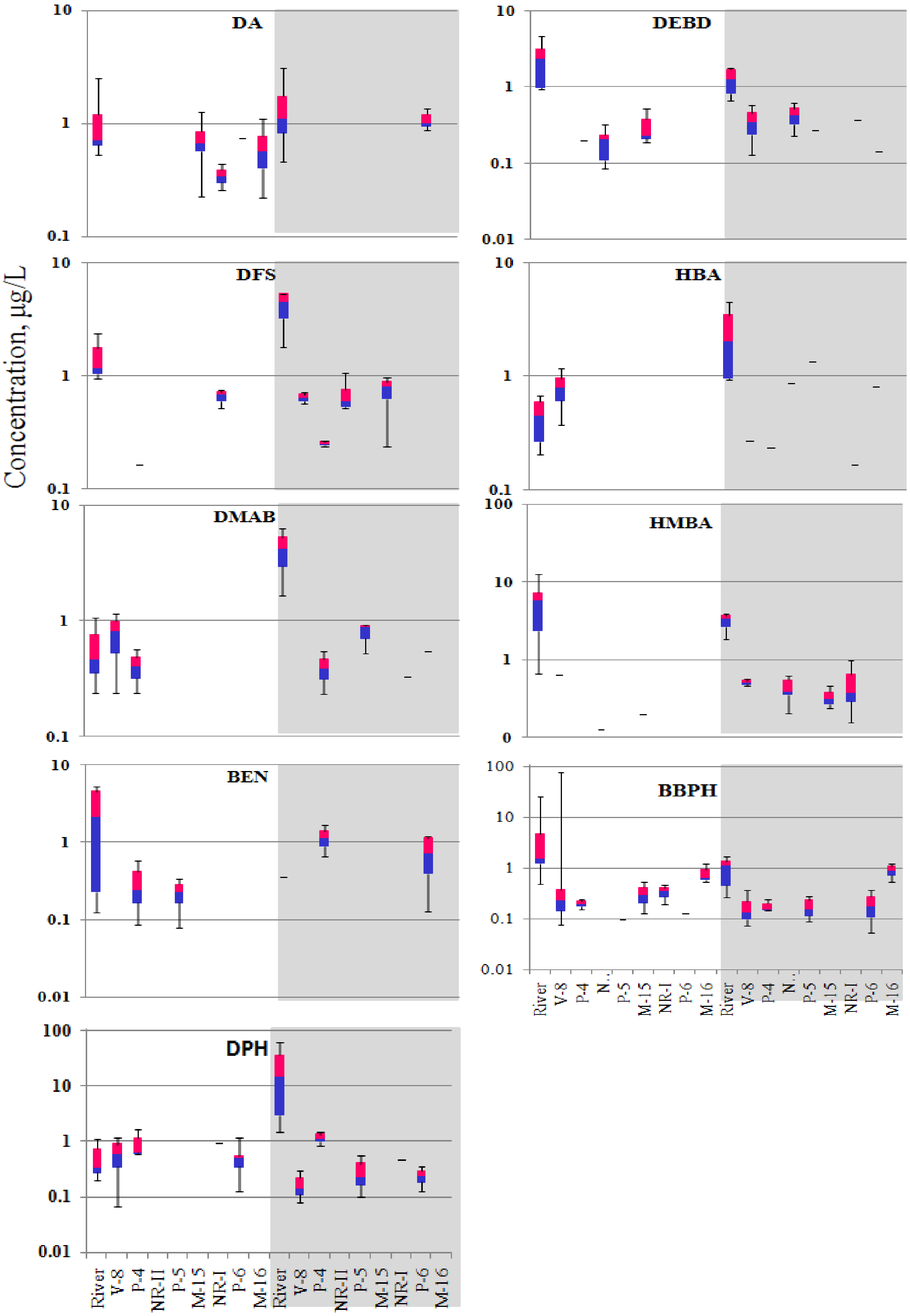
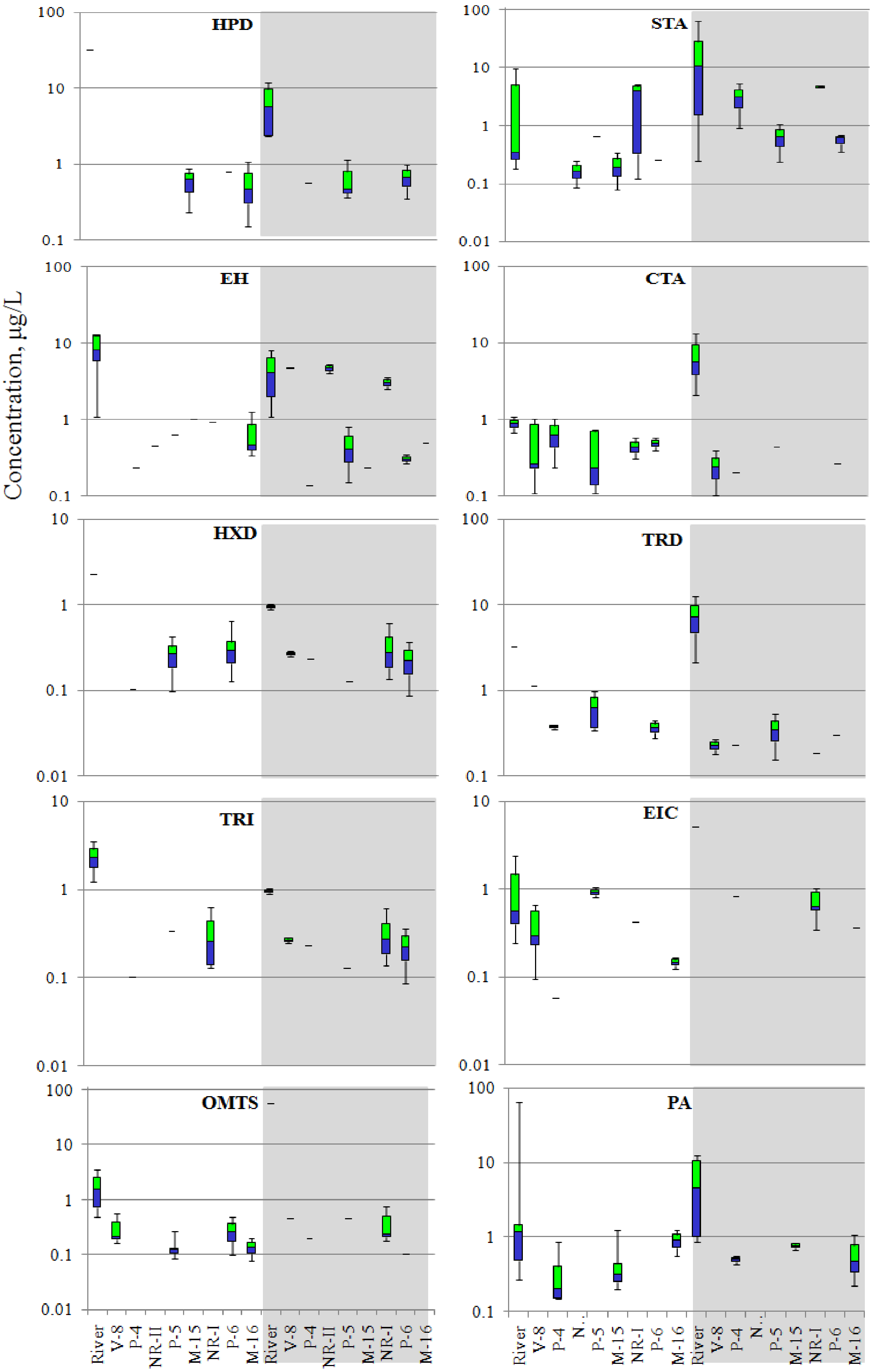


Fig. 4.4. Yamuna and RWs: box plots of spatial variations of pesticides, EDCs and phthalates during non-monsoon and monsoon. For monsoon variations are shown in gray shade.

Table 4.3. Frequency of occurrence and average concentrations of personal care products, fatty acids, food additive, hormones and hospital waste (µg/L) in river Yamuna and Ranney Wells.

S. No	Compo-unds	Seas-on	**River $9^{\S},7^{\#}$**	**V-8 $6^{\S},5^{\#}$**	**P-4 $8^{\S},7^{\#}$**	**NR-II $9^{\S},5^{\#}$**	**P-5 $7^{\S},7^{\#}$**	**M-15 $5^{\S},3^{\#}$**	**NR-I $9^{\S},7^{\#}$**	**P-6 $7^{\S},7^{\#}$**	**M-16 $5^{\S},2^{\#}$**
Personal care products (PCPs)											
1	HPD	NM	1,32.5	*	*	*	*	*	*	1,0.8	*
		M	5, 6.41	*	1,0.6	*	3,0.7	*	*	2,0.7	*
2	STA	NM	3, 3.39	*	*	2,0.1	1,0.7	3,0.2	5, 3.9	1,0.3	*
		M	5,21.2	*	2, 3.8	*	2,0.7	*	2, 5.3	3,0.6	*
3	EH	NM	5, 8.03	*	1,0.6	1,0.5	1,0.6	1, 1.9	1,0.91	*	3,0.7
		M	4, 4.34	2, 5.8	1,0.1	3, 5.6	3,0.5	1,0.2	2, 3.4	2,0.3	1,0.5
4	CTA	NM	2,0.88	5,0.5	2,0.6	*	5,0.4	*	3,0.4	2,0.5	*
		M	3,7.04	3,0.2	1,0.2	*	1,0.4	*	*	1,0.3	*
5	HXD	NM	1, 2.32	*	1,0.1	*	6,0.3	*	*	5,0.3	*
		M	2, 0.96	2,0.3	1,0.2	*	1,0.1	*	4,0.3	2,0.2	*
6	TRD	NM	1,3.25	1,1.3	2,0.4	*	5,0.6	*	*	2,0.4	*
		M	2,7.35	2,0.2	1,0.2	*	2,0.4	*	1,0.2	1,0.3	*
7	TRI	NM	3, 2.35	*	1,0.1	*	1,0.4	*	4,0.3	*	*
		M	2,0.96	2,0.3	1,0.2	*	1,0.2	*	4,0.3	2,0.2	*
8	EIC	NM	3, 1.06	5,0.4	1,0.1	*	2,0.9	*	1,0.4	*	2,0.2
		M	1, 5.19	*	1,0.8	*	*	*	5,0.7	*	1,0.4
9	OMTS	NM	5, 1.78	3,0.3	1,0.2	*	5,0.1	*	*	3,0.3	2,0.1
		M	1,56.9	1,0.5	1,0.2	*	1,0.5	*	3,0.4	1,0.1	*
Fatty acids											
1	PA	NM	9, 7.95	*	4,0.4	*	*	5,0.5	*	*	2,0.9
		M	5, 5.93	*	2,0.5	*	*	2,0.8	*	*	2,0.6
2	MBHD	NM	5,0.52	4,0.2	2,0.3	*	4,0.3	*	*	*	3, 2.2
		M	3, 6.50	3,0.6	1,0.4	*	1,0.1	*	*	2,0.4	*
3	LA	NM	4,10.9	*	*	*	*	1, 6.3	*	*	*
		M	2, 1.55	*	*	*	*	3, 2.7	*	*	*
4	DEA	NM	4, 3.19	1,0.2	6,0.6	*	*	*	7, 3.9	1,0.1	*
		M	*	4,0.2	*	*	3,0.4	*	*	6,0.3	*
Food additive											
1	ATG	NM	5,0.88	*	1,0.3	*	*	*	*	*	*
		M	3, 4.00	2,0.4	1,0.2	3,0.4	1,0.7	2,0.3	1, 1.8	2,0.4	*
Hormones											
1	ENE	NM	9, 4.72	*	*	*	*	*	*	*	*
		M	7, 1.51	*	*	*	*	*	*	*	*
2	EOL	NM	7, 1.67	*	*	*	*	*	*	*	*
		M	7,0.94	*	1,0.5	*	*	*	*	*	*
Hospital waste											
1	GUA	NM	2,0.90	*	*	*	5,0.8	*	*	3,0.4	*
		M	6, 5.54	*	1, 2.6	*	2, 4.8	*	*	1,1.7	*
2	ADE	NM	5, 8.40	*	*	*	*	*	*	*	*
		M	5,16.5	*	*	*	*	*	*	*	*

*(§Number of samples collected in non-monsoon (NM), # Number of samples collected in monsoon (M), * Not detected. First digit in the column (bold & italic) represents the number of times compound detected and the subsequent value the average concentration)*


Concentration, µg/L
HPD
100
10
1
0.1
STA
100
10
1
0.1
0.01
EH
100
10
1
0.1
CTA
100
10
1
0.1
HXD
10
1
0.1
0.01
TRD
100
10
1
0.1
TRI
10
1
0.1
0.01
EIC
10
1
0.1
0.01
OMTS
100
10
1
0.1
0.01
PA
100
10
1
0.1
River
V-8
P-4
NR-II
P-5
M-15
NR-I
P-6
M-16
River
V-8
P-4
NR-II
P-5
M-15
NR-I
P-6
M-16
River
V-8
P-4
N..
P-5
M-15
NR-I
P-6
M-16
River
V-8
P-4
N..
P-5
M-15
NR-I
P-6
M-16

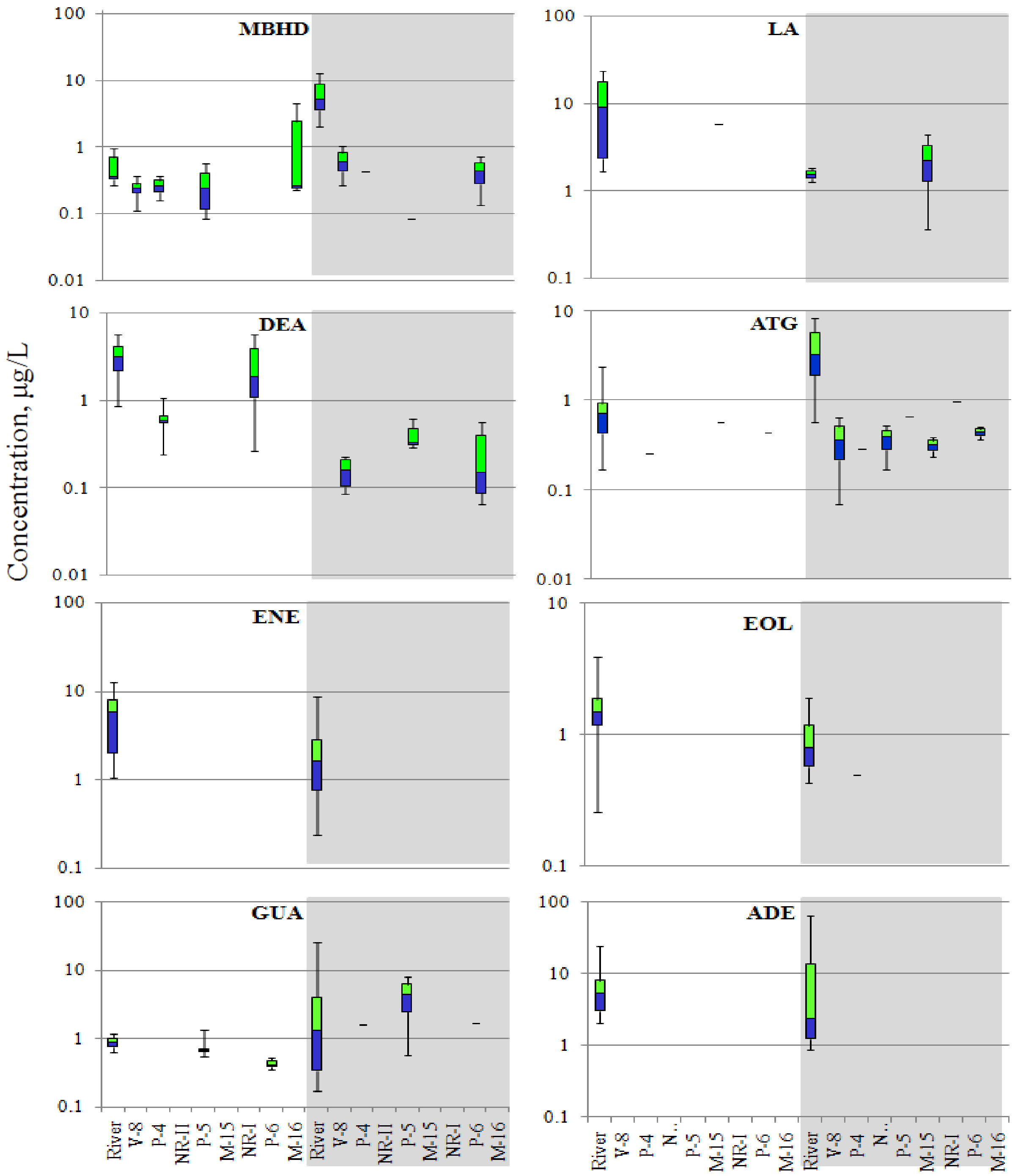


Fig. 4.5. River Yamuna and RWs: box plots of spatial variations of PCPs, fatty acids, food additive, hormones and trace organics found in hospital wastes during non- monsoon and monsoon. For monsoon variations are shown in gray shade.

4.5. CONCLUSION

- Fifty-seven detected OMPs in river Yamuna and RWs were identified as pharmaceutically active compounds (PhACs), pesticides, endocrine disrupting compounds (EDCs), phthalates, personal care products (PCPs), fatty acids, food additives hormones and those organics present in hospital wastes in trace quantities.
- Number of OMPs detected, their frequencies of occurrence and concentrations in RWs reduced substantially compared to river water. Among different RWs, in general, number of OMPs detected, their frequencies of occurrence and concentrations correlated very well with the distance of RWs from the river. Larger the distance, lesser the number of OMPs detected and lower the concentrations.
- In spite of high levels (~50 μg/L) in river water of 3-acetamido-5-bromobenzoic acid, 1- dodecanethiol, diethyl phthalate, palmitic acid, and adenine, they were detected to be < 1 μg/L in water samples from RWs.
- Only a few OMPs e.g. simazine and aldrin, sometime exceeded 1 μg/L in RWs.
- Compared to other OMPs, in general, EDCs, PCPs, phthalates, fatty acids and food additives appeared more frequently in number of RWs but in significantly lower concentrations than present in river water.
- Among hormones, only estriol appeared once in a RW.
- Some of the OMPs e.g. adenine were never detected in any of the RWs.

4.6. ACKNOWLEDGEMENTS

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CHAPTER-5

Fate of 15 wastewater originated organic micropollutants in a sand column

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ABSTRACT

The present investigation is on the assessment of the fate of 15 organic micro-pollutants (OMPs) under abiotic (predominantly adsorption) and biotic (predominantly bio-sorption/bio-degradation) conditions in columns packed with the aquifer material. The motivation behind this work was to predict the fate of the OMPs during subsurface flow/riverbank filtration (RBF). Columns were packed with aquifer material that was taken out from the laterals of a Ranney or RBF well, M-15 during its cleaning operation. OMPs that were selected for the study were frequently detected in the river Yamuna at Central Delhi, M-15 and other nearby RBF wells. The list included pharmaceuticals and their raw materials, endocrine disruptors, OMPs found in hospital wastes, steroid and personal care products structurally belonging to acrylates, neutral organics, amines, phenols and fatty acids. Among different OMPs, dimethyl maleate, benzoic acid, guanine and lomustine were found to be more mobile than estriol, decanoic acid, 1-tridecanol, 1- eicosanol, triclosan, stearic acid and cetyl alcohol. The mobility depends on the polarity of the OMPs. The retardation factor of non-polar OMPs is more than the polar ones. However, the mobility of the OMPs is considerably restricted in the biotic column. Retardation factors (R_d) for OMPs varied widely in adsorption column from 3 to 772. In biosorption column, R_d ranged from 6 to 1692 showing better removal except for benzophenone.

Keywords: Riverbank filtration; Non-polar and polar OMPs; Adsorption; Biosorption; Retardation; Octanol/water partition coefficient.

5.1. INTRODUCTION

There has been a growing concern regarding increasing numbers as well as concentrations of pharmaceuticals, pesticides, personal care products, endocrine disruptors, etc. in the natural environment. These compounds are collectively known as organic micro-pollutants (OMPs), (Kümmerer, 2009; Calisto and Esteves, 2009). OMPs find their ways into the aquatic environment through sewage disposal, industrial discharges and overland flow during rain (Ying et al., 2009; Boxall, 2004). Trace concentrations of these OMPs in aquatic environment have synergistic impacts on human health and aquatic life (Heberer et al., 2002; Kümmerer, 2009).To ensure a reliable and safe drinking water supply, removal of these contaminants from water is essential (Kim et al., 2007; Madden et al., 2009).

OMPs are removed to some extent in the conventional wastewater treatment plants (Daughton and Ternes, 1999). Such compounds, however, are not removed by the conventional water treatment. Advanced treatment technologies that can eliminate OMPs from water are not economically viable. Natural treatment processes such as river/lake bank filtration (RBF/LBF) are cost-effective. Filtration through the aquifer material attenuates OMPs from the source water (Heberer et al., 2004; Grünheid and Jekel, 2005; Schmidt et al., 2007; Massmann et al., 2008; Maeng et al., 2010; Maeng et al., 2011a; Benotti etal., 2012). RBF is a well accepted and efficient technique for the pre-treatment of surface water for drinking water production throughout the world including India (Dash et al., 2008). Factors that influence the removal of OMPs are redox conditions (Banzhaf et al., 2012), cation exchange capacity of the soil (Schaffer et al., 2012a,b), biomass rich and biomass deficient aquifer (Flemming, 1995), temperature, and the nature of the OMPs. RBF system in Ohio, USA was studied by Benotti et al. (2012). OMPs such as pharmaceuticals, endocrine disruptors (EDCs) and pesticides were removed by 90% during aquifer passage. Fate and removal of meprobamate, atrazine, sulfamethoxazole, diazepam, carbamazepine tris (2-chloroethyl) phosphate (TCEP), and phenytoin were further investigated in the laboratory. Results from the column study indicated 20% to 80% removal of most of the compounds except carbamazepine, sulfamethoxazole and atrazine.

The fate or removal of OMPs has been understood through bench-scale column runs. Patterson et al. (2011) evaluated the fate of the nine polar OMPs in a soil containing low organic carbon content and estimated values of retardation coefficient (R_d) between 1.0 and

1.2. However, the behaviour of the OMPs in the biotic column was different. Under aerobic condition, bisphenol A, 17β-estradioland iohexol rapidly degraded (half life<1 day) whereas iodipamide was persistent. Carbamazepine, oxazepam, N-nitrosomorpholine, N-nitrosodimethylamine did not degrade in any of the conditions and resulted in the half-life of >50 days.

Banzhaf et al. (2012) in their column experiments demonstrated the effect of nitrates on the degradation of sulfamethoxazole, carbamazepine, diclofenac and ibuprofen. Cation exchange capacity of the soil plays a significant role in the sorption of cationic OMPs and pH influences the sorption of ionizable compounds into aquifer sediments (Schaffer et al., 2012a, b). Column experiments performed by Maeng et al. (2011b) were to differentiate the biodegradation and sorption processes of pharmaceutically active compounds (PhACs). The findings suggest biodegradation to be an important mechanism for the removal of PhACs during passage through the soil.

Soil column study was conducted by Bertelkamp et al. (2013) using 14 OMPs to compare sorption and biodegradation behaviour of the compounds. R_d for most of the compounds was found close to 1. The presence of ether and carbonyl group in the OMP increased its biodegradability whereas presence of amines, ring structures and sulphur group decreased the biodegradability. In another soil column study, Bertelkamp et al. (2015) investigated the sorption and biodegradation behaviour of the mixture of 20 OMPs and did not observe biodegradation after 75 days of column operation.

Onesios and Bouwer (2012) assessed biofilm-based removal of the mixture of 14 pharmaceuticals and personal care products (PPCPs). The authors observed 95% removal of biphenylol, p-chloro-m-cresol, chlorophene, 5-fluorouracil, gemfibrozil, ibuprofen, ketoprofen, naproxen, triclosan and valproic acid. RBF thus is a well-suited technique for the removal of PPCPs from the surface water. According to Flemming (1995) bacteria excrete extracellular polymeric substances (EPS) that lead to the formation of a biofilm over the soil grains. The biofilm increases sorption of charged or polar OMPs.

Burke et al. (2013) chose frequently detected OMPs in the water bodies of Berlin, Germany, to perform column experiments. R_d of 20 OMPs that include psychoactive drugs, phenazone type pharmaceuticals, β-blockers, phenacetine, N-methylphenacetine, tolyltriazole and paratoluenesulphonamide, was determined through the column runs. β-blockers such as atenolol, propranolol and metoprolol showed the tendency to adsorb onto the aquifer sand. Experimentally determined R_d values for these compounds varied from 6 to 9. Other compounds having R_d value between 1 and 2 showed a low sorption affinity.

A large quantity of treated or untreated sewage is discharged into the river Yamuna during its passage through Delhi. Results of the field investigations carried out by authors prior to this study showed the presence of some OMPs in the water samples collected from the river Yamuna at Central Delhi and nearby RBF wells. The fate of the OMPs depends on nature of the OMP and the aquifer conditions. Therefore, a necessity was felt to explore the behaviour of the fifteen most frequently found OMPs in the Yamuna water and the well water in the vicinity. Given this, the present study aims at determining the R_d of fifteen most frequently detected OMPs under abiotic (predominantly adsorption) and biotic (predominantly bio-sorption/bio-degradation) column conditions. Also, to find out the correlation, if any, between R_d and octanol-water partition coefficient (log K_{ow}) of the OMPs. Abiotic conditions were established by suppressing microbial activity/biodegradation. Biotic conditions were created by encouraging the growth of microorganisms (Onesios and Bouwer 2012).

5.2. MATERIALS AND METHODS

5.2.1. Aquifer material: source and analysis

Aquifer material used as a sorbent was collected from a depth of 18 m from one of the radial collector wells (M-15) ($28^{o}36'$N and $77^{o}17'$E) located in Mayur Vihar at New Delhi, India. Well was established in 1975 and is located in the flood plains of river Yamuna at around 2.1 km from the bank of the river. Total depth is 25 m. It has 24 laterals (60 m each) in 3 layers of 8 laterals each; having a total length of 1440 m. The aquifer material was collected in April 2014 during the periodic cleaning of caisson and laterals. The sieve analysis of the aquifer material was carried out at the Geotechnical Laboratory, IITR, Roorkee, India. The Brunauer–Emmett–Teller (BET) surface area and the average cross-sectional area were determined using Micromeritics ASAP 2020 BET surface area analyser. Organic carbon content of the sediment was measured by the Shimadzu-SSM-5000A-TOC-V_{CSN} analyser.

5.2.2. Column set-up and acclimatization

Height, inner diameter and volume of both the acrylic columns: A (abiotic) and B (biotic) were 30 cm, 2 cm and 94.2 cm^3 respectively. Flow rate through the columns was maintained in the range of 0.031-0.034 cm^3/s. Pre-wetted columns were wet-packed with aquifer material in small increments and rammed mildly at each step. Experiments were carried out at room temperature (28-35^oC). Columns were covered with a black sheet to prevent algal growth and loss of OMPs due to the photochemical reactions. Columns were operated in up flow mode to ensure saturated conditions throughout the experimentation. The columns packed with the aquifer material were first equilibrated for ten days with water collected from the Upper Ganga Canal (UGC), Roorkee, to attain the natural aquifer conditions. Subsequently the adsorption column-A was fed with tap water containing 400 mg/L sodium azide (NaN_3, Merck, Germany) to inactivate the biomass inside the column. The biosorption column-B was fed with surface water collected from the UGC, spiked with 200 µg/L sodium acetate ($CH_3COONa.3H_2O$, Merck, Germany) to enhance biological growth (Bertelkamp et al., 2013; Qureshi et al., 2001; Wunder et al., 2011). After 56 days of conditioning, columns attained a steady state in terms of almost constant UV-absorbance at 254 nm (UV-254).

5.2.3. Tracer test

The effective porosity, pore volume and mean pore water velocities in both the columns were determined using NaCl (Merck) as a tracer. The initial electrical conductivity (EC) of the tracer solution was taken as 1854 µS/cm, and the EC at the outlet was measured with a conductivity meter (Hach 40 Q D).

5.2.4. OMPs studied

OMPs included pharmaceutical ingredients (dimethyl maleate, benzoic acid, lomustine, and salicylic acid), EDCs (diacetone alcohol, benzophenone), trace organics found in hospital wastes (adenine and guanine), steroid (estriol) and PCPs (stearic acid, 1-tridecanol, cetyl alcohol, 1-eicosanol, triclosan, decanoic acid). Structurally, these compounds belong to the acrylates, neutral organics, amines, phenols and fatty acids groups.

5.2.5. Preparation of feed water containing OMPs

Separate stock solutions of fifteen OMPs were prepared by dissolving 5 mg/L in one litre of tap water. A feed solution having 0.5 µg/L of each compound was prepared by adding one mL stock solution of each OMP in 10 L tap water. Before using, feed solution was stirred for a minimum of 20 hours each time for thorough mixing of all the OMPs. Same was fed as inlet water after the columns attained the steady state.

5.2.6. Operation of columns with influent containing OMPs

After 56 days of conditioning and obtaining stable absorbance readings (UV-254) of the effluents from Columns A and B, influent water containing the target OMPs (500 ng/L each) was passed through the columns. Feed water was prepared daily and pumped through the columns using peristaltic pumps (Micllins). Experiments were terminated after 11 days once the breakthrough was obtained for most of the OMPs.

5.2.7. Extraction of OMPs

250 mL of the inlet feed and outlet of the columns were collected in glass bottles and filtered through glass fibre filters (GFF). The OMPs in the samples were extracted on solid phase extraction (SPE) cartridges (Bond Elut Plexa, 200 mg, 6 mL, Agilent Technologies) using a 12 port vacuum manifold unit (Agilent Technologies).

Before sample loading, SPE cartridges were conditioned successively with three mL 50:50 (v/v) ethyl acetate: acetone, three mL methanol and demineralised water. Water samples were loaded under vacuum onto the cartridges at a flow rate of 5 to 8 mL/min. After sample loading, cartridges were washed with 5% methanol-water and dried under vacuum for 10 minutes. OMPs were eluted with three successive solvents, 3 mL of ethyl acetate, 3 mL of ethyl acetate: acetone (50:50; v/v) and 3 mL hexane. After elution, the collected extracts were evaporated under a gentle stream of nitrogen gas to the final volume of 100-150 µL. Samples were incubated at 70^{o}C for 35 min followed by the addition of 70 µL N-Methyl-N-(trimethylsilyl) trifluoroacetamide (MSTFA) for derivatization. The concentration of the OMPs in the influent and effluent was measured daily for 11 days.

5.2.8. Measurement of OMPs

Gas chromatographic separation coupled with mass spectrometry (GC-MS) was used to detect the analytes. The OMPs were quantified by calibration curve method for each sample. The extraction recoveries were determined separately for each OMP by spiking samples at 50 ng/L before extraction. GC–MS analysis was performed using Varian 450 GC 240 MS equipped with a split/splitless injector 1079 and VF-5MS capillary column (Varian) of length

30 m, internal diameter (ID) 0.25 mm, coated with a 0.25 μm film of 5% diphenyl, 95% dimethylpolysiloxane. The ultra pure helium (99.999%) used as the carrier gas was maintained at a constant flow of 1 mL min^{-1}; the transfer line was held at 250^{o}C. 2 μL samples were injected in splitless mode. For GC separation, the sequence of the temperature program was: - (i) started at 80^{o}C (held for 2 min) (ii) then set at 5^{o}C/min to 180^{o}C (held for 5 min); (iii) set at 5^{o}C/min to 250^{o}C (held for 5 min); (iv) set at 5^{o}C/min to 280^{o}C and then was held isothermally at 280^{o}C for 5 min. The gas chromatograph was coupled to an ion trap mass spectrometer operated under electronic impact (EI) mode at 70 eV using scan mode, scan range (from 50-1000 amu).

5.3. RESULTS AND DISCUSSION

5.3.1. Characteristics of the aquifer material

Characteristics of the aquifer material from the sieve analysis along with surface area are given in Table 5.1. The column packing material is classified as sand with an effective size of 0.23 mm. According to Carmody et al. (2007), BET surface area of the sand varies from 1 to 5 m^2/g. The BET surface area of the aquifer material used for column packing has been estimated to be 1.6 m^2/g. The effective porosity and the pore water velocity obtained for Column A and B from the tracer test are compiled in Table 5.2.

Table 5.1. Characteristics of the aquifer material

Parameter	Unit	Value
Bulk density (ρ_b)	kg/L	1.62
Fraction of organic carbon (f_{oc})	%	0.47
Effective size (d_{10})	mm	0.23
Average grain size (d_{50})	mm	0.42
60 percentile diameter (d_{60})	mm	0.50
Uniformity coefficient (C_u)	-	2.17
BET surface area	m^2/g	1.60

Table 5.2. Results from tracer test

Columns	**Darcy Velocity (cm/s)**	**Breakthrough time (T) at C/C_0=0.5 (h)**	**Effective porosity**	**Pore water velocity (cm/s)**
A	0.01	0.33	0.40	2.5×10^{-2}
B	0.011	0.28	0.38	2.9×10^{-2}

5.3.2. Breakthrough curves and retardation factor

Breakthrough curves (BTC) of OMPs along with that of tracer are given in Figs. 5.1, 5.2 and 5.3. R_d, the ratio of the velocity of water to the velocity of the OMP, is calculated using Eq.5.1. Also, R_d depends on the partition coefficient, K (L/kg) as given by Eq. (5.2) (Worch et al., 2002). Partition coefficient, K, is the ratio of solid phase concentration to the solution phase concentration.

$$R_d = t/T \qquad (5.1)$$

Where, t = breakthrough time of OMP at C/C_0= 0.5

T = breakthrough time of tracer at C/C_0= 0.5

C_0 = initial concentration of OMP

C = concentration of OMP at a given time

$$\frac{K\rho_b}{\epsilon_b} + 1 = R_d \qquad (5.2)$$

Where, ρ_b (bulk density, kg/L) = m/V

m = mass of aquifer material in the column (kg),

V = volume of the column (L)

ϵ_b= porosity (dimensionless).

Values of R_d from Eq. 5.1 and K from Eq. 5. 2 for OMPs are given in Table 5. 3. A perusal of data in Table 5.3 indicates two groups of OMPs. Group one includes OMPs those have R_d values ≤ 5 in the abiotic column. All these OMPs except DMM are polar in nature. The R_d of the other group of OMPs is > 50, and most of the OMPs in this category are non-polar.

Table 5.3. Experimentally determined values of R_d and K for adsorption and biosorption

No	OMPs (Abbreviation; Category [a])	From column experiments						From literature [b]		
		Adsorption				**Biosorption**		log K_{ow}	Water solubility (at 25^0C) mg/L	Molecular Weight (MW) g/mol
		R_d	K, (L/kg)	log K_{oc}		R_d	K, (L/kg)			
1	Diacetone alcohol (DA; P)	3.20	0.54	2.06	**Rd≤5**	18.2	4.02	-0.34	6.512e+005	116.16
2	Adenine (ADE;P)	3.40	0.59	2.09		12.7	2.73	-0.05	4739	135.13
3	Guanine (GUA; P)	3.60	0.64	2.13		10.1	2.13	-1.77	1e+006	151.13
4	Benzoic acid (BA; P)	3.80	0.69	2.16		9.80	2.06	1.87	2493	122.12
5	Dimethyl maleate (DMM; NP)	4.40	0.83	2.24		6.80	1.35	0.74	1.877e+004	144.12
6	Lomustine (LMS; P)	5.00	1.10	2.36		6.00	1.17	2.83	111.3	233.70
7	Salicylic acid (SA; P)	50.0	11.4	3.38	**Rd>50**	220	51.2	2.26	3808	138.12
8	Benzophenone (BEN; NP)	122	29.7	3.80		-	-	3.18	103.3	182.21
9	Estriol (EOL; P)	124	28.7	3.78		189	44.0	2.45	440.8	288.38
10	Decanoic acid (DEA; NP)	561	138	4.46		630	147	4.09	47.89	172.26
11	1-Tridecanol (TRD; NP)	709	174	4.56		834	195	5.26	4.53	200.36
12	1-Eicosanol (EIC; NP)	740	182	4.58		1146*	268	8.70	0.001	298.54
13	Triclosan (TRI; NP)	743	183	4.58		828	194	4.76	4.621	289.54
14	Cetyl alcohol (CTA; NP)	756*	177	4.57		1150*	269	6.73	0.149	242.44

[a] *P: Polar; NP: Non- polar*

[b] *Royal Society of Chemistry (2015)*

* *Projected value as $C/C_0=0.5$ was not achieved till the end of the experiment*

5.3.3. OMPs having $R_d \leq 5$ (abiotic column)

Of various OMPs tested, R_d (abiotic) of GUA, DA, ADE, DMM, BA and LMS is in the range from 3.2 to 5 (Fig. 5.1). The K calculated from Eq. 5.2 has been found to vary from 0.54 to 1.1 L/kg. However, the log K_{ow} of these compounds exhibits a broad range of variation from -1.77 to 2.83 (Table 5.3). Several researchers have demonstrated that K_{oc} is empirically correlated to K_{ow} (Kenaga and Goring, 1980; Worch, 2004). Therefore, K_{ow} and K_{oc} should exhibit nearly the same range of variation. Nevertheless, Pradhan et al. (2015) have demonstrated that partitioning of the mixture of compounds is different from the individual compound. As seen from the data, the R_d and K (abiotic) values of GUA, DEA, ADE and BA are between 3.2 to 3.8 and 0.54 L/kg to 0.69 L/kg respectively. The BTC of these 4 compounds overlap each other and appear as a single compound (Fig. 5.2). Therefore, the K_{ow} of individual compounds cannot be correlated to R_d and K. The K_{ow} of the mixture of compounds can be correlated to sorption parameters (Pradhan et al., 2015).

The organic content of the material packed in the biotic column B is expected to be more than that of the abiotic column as surface water spiked with sodium acetate was initially fed to enhance the biological growth. The R_d of the OMPs on the biotic column, therefore, is in the range from 6 to 18.2 as compared to 3.2 to 5 on sorption column. It may, however, be noted that R_d on sorption column increases from DA (compound 1) to LMS (compound 6). The trend is reversed on the biosorption column. R_d decreases from DA (compound 1) to LMS (compound 6). From these observations, it can be generalized that a high mobility on a sorption column is decreased considerably on a biosorption column. Biofilm or extracellular polymers facilitate the retention of hydrophilic OMPs more than the hydrophobic OMPs. It is in accordance with the analysis carried out by Flemming (1995). He stated that the extracellular polymeric substances secreted by bacteria led to the formation of a biofilm over the soil grains, which increases sorption of charged or polar OMPs.

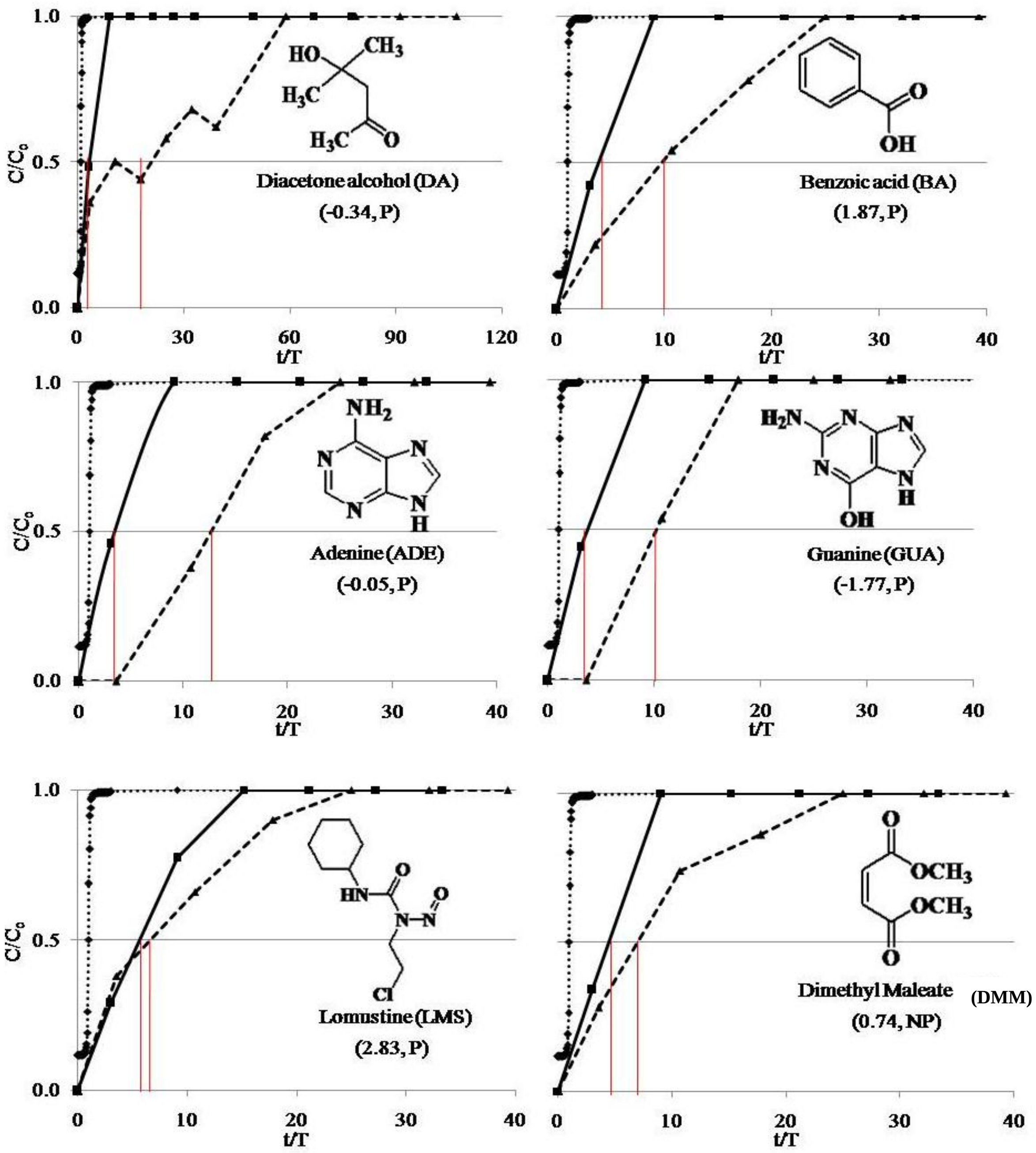


Fig. 5.1. BTCs of the tracer and OMPs having R_d ≤5 under abiotic and biotic conditions (Values in parenthesis are log K_{ow} and group of compounds P: Polar; NP: Non-polar) (◆ Tracer ■ Abiotic ▲ Biotic)

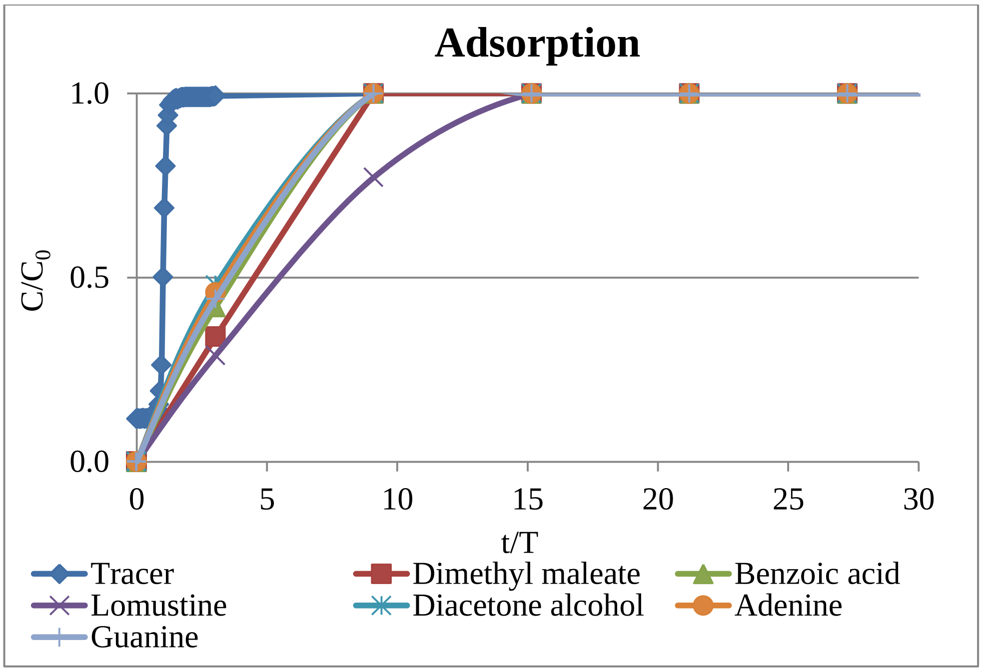


Fig. 5.2. BTCs of the tracer and OMPs having $R_d \leq 5$ under abiotic

5.3.4. OMPs having R_d >50 (abiotic column)

The second category of the OMPs has $R_d > 50$. It includes salicylic acid (SA), benzophenone (BEN), estriol (EOL), decanoic acid (DEA), 1-tridecanol (TRD), 1-eicosanol (EIC), triclosan (TRI), cetyl alcohol (CTA). All the OMPs except salicylic acid (SA) and estriol (EST) in this category are (i) non-polar and (ii) have the solubility ≤ 0.1 mg/L. Log K_{ow} of these OMPs lies in the range of 2.26 to 8.70 (Table 5.3). BTCs of OMPs under abiotic and biotic conditions are shown in Fig. 5.3.

A perusal of BTCs in Fig. 5.3 indicates that out of nine OMPs, SA, BEN and EST attained C/C_0 equal to one in less than 11 days of the column operation. Other OMPs (DEA, TRD, EIC, TRI, CTA) were not completely eluted from the abiotic or biotic column due to low solubility and a high value of K_{ow}. The solubility and log K_{ow} of these six OMPs are less than 0.1 mg/L and more than four respectively. Elution from the biotic column was less than the abiotic column. Bertelkamp et al. (2015) studied the behaviour of 20 OMPs that included pharmaceuticals, herbicides, insecticides, and a solvent on the biotic and abiotic columns for 75 days. They did not observe biodegradation of any of the OMPs. Onesios and Bouwer (2012), however, found 81-87 % removal of TRI in biological processes during column experiment. Retention, removal or R_d of OMPs depends on the nature of the OMP, nature of the mixture as assessed by K_{ow} and the solubility. Non-polar OMPs have high retardation (R_d) values ranging from 122 to 772 and 630 to 1692 under abiotic and biotic conditions respectively. R_d values indicate their low mobility. From the observed values of R_d for non-polar OMPs, it is concluded that the movement of these OMPs into an RBF system is negligible. It may take several years to reach these contaminants to the abstraction wells through the sandy aquifer, hydraulically connected to contaminated surface water.

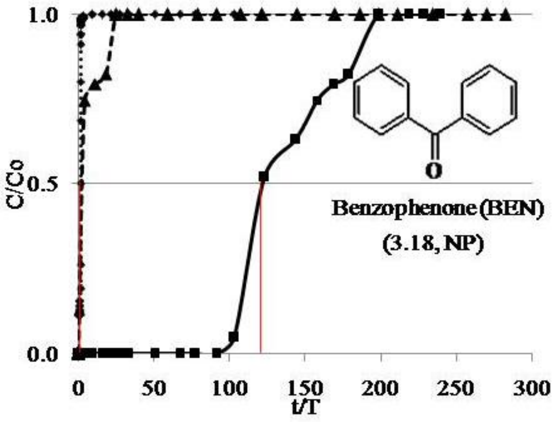
Column experiments were conducted by Seders Dietrich et al. (2013) to analyse molecular weight (MW) distributions of the humic substance rich-dissolved organic matter (DOM) in column influent and effluent. The study concluded that R_d increased with increasing MW, except for the highest-MW fraction. However, the observed result indicates that MW did not have any significant effect on OMP sorption (R_d) in this study (Table 5.3).

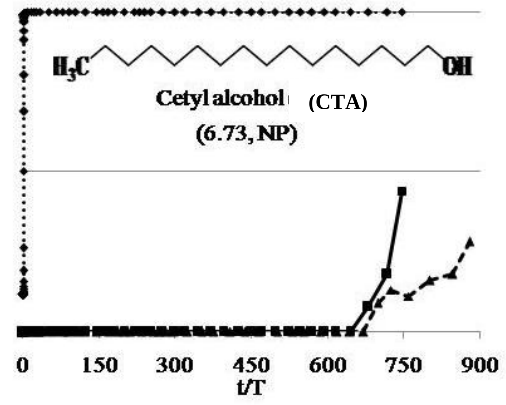
5.3.5. Correlations between log K_{ow} and log R_d for hydrophobic compounds

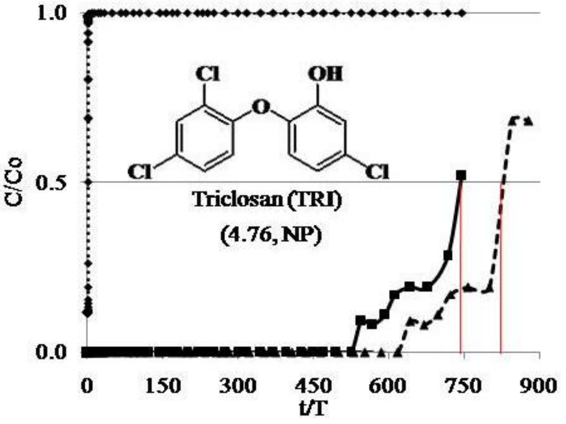
In general, higher the hydrophobicity of the compound, higher is the adsorption (Worch et al., 2002). Therefore, the correlation between log R_d and log K_{ow} can be useful. Fig. 5. 4 show the correlation between log R_d and log K_{ow} for the hydrophobic OMPs having log $K_{ow} > 2$ and R_d values > 50.

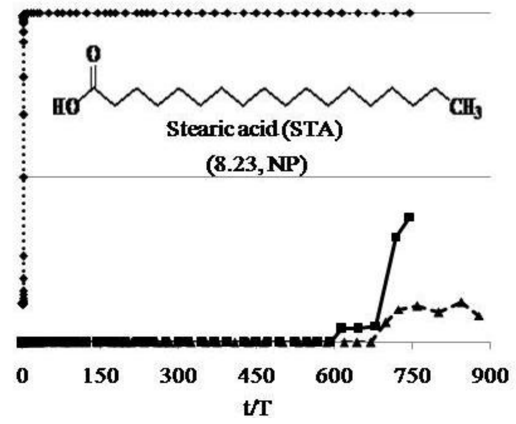
5.3.6. Fate of OMPs during subsurface flow through sandy aquifers

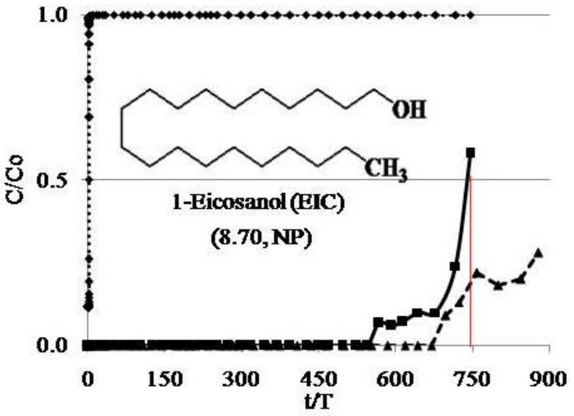
Based on the values of R_d, higher mobility can be expected for the OMPs of category one, viz. DMM, BA, GUA and LMS. As a result, a potential of these compounds leaching into the groundwater and to the RBF well cannot be neglected. Therefore, water treatment facilities have to be optimized for the removal of these compounds. The aquifer material showed a very high degree of removal for EOL, DEA, TRD, EIC, TRI and CTA. Organic compounds containing hetero atoms (as O, N and S) in its structure interact with electron deficient species present in the sand in the form of natural organics, doesn't allow such compounds to elute out quickly from the column. Such an interaction is one of the reasons for higher retardation values in the case of biotic column. In the biotic column, bacterial growth may enhance the content of organic matter due to their metabolic activities, and thereby retardation of OMPs increased.

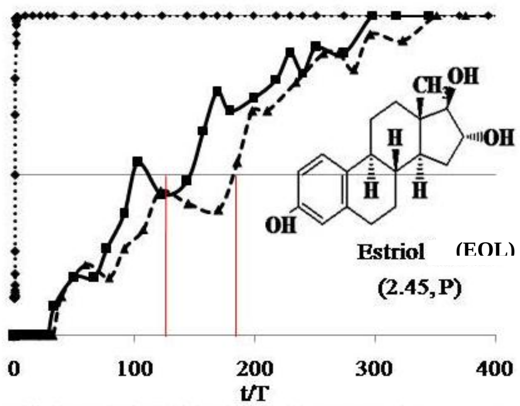

1.0
0.5
0.0
C/Co
0
50
100
150
200
250
300
t/T
Benzophenone (BEN)
(3.18, NP)
O

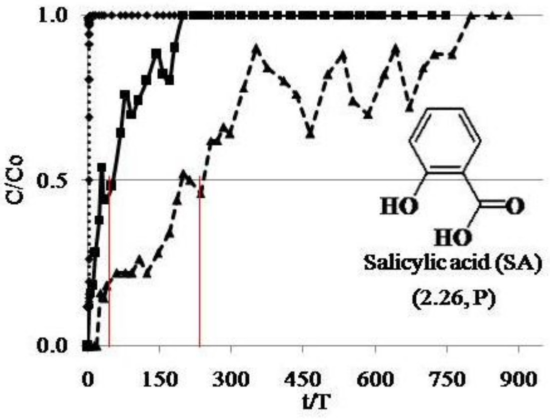

H_3C
OH
Cetyl alcohol (CTA)
(6.73, NP)
0
150
300
450
600
750
900
t/T

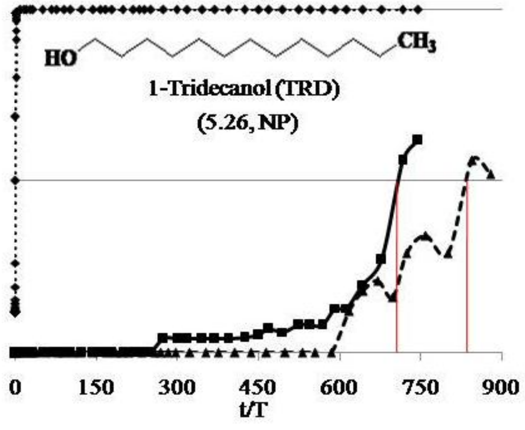

1.0
0.5
0.0
C/Co
Cl
OH
O
Cl
Cl
Triclosan (TRI)
(4.76, NP)
0
150
300
450
600
750
900
t/T


O
HO
CH_3
Stearic acid (STA)
(8.23, NP)
0
150
300
450
600
750
900
t/T


1.0
0.5
0.0
C/Co
OH
CH_3
1-Eicosanol (EIC)
(8.70, NP)
0
150
300
450
600
750
900
t/T


CH_3
OH
OH
H
H
H
OH
Estriol (EOL)
(2.45, P)
0
100
200
300
400
t/T


1.0
0.5
0.0
C/Co
HO
O
HO
Salicylic acid (SA)
(2.26, P)
0
150
300
450
600
750
900
t/T


HO
CH_3
1-Tridecanol (TRD)
(5.26, NP)
0
150
300
450
600
750
900
t/T

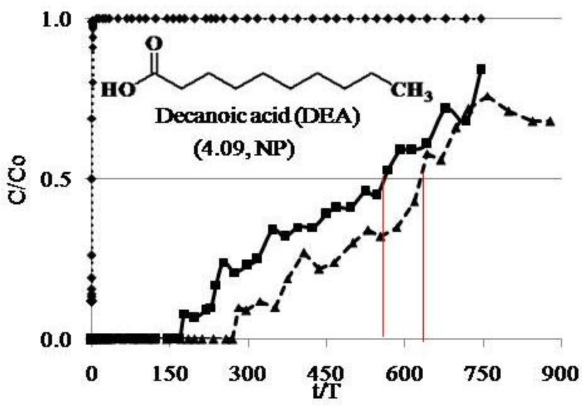


Fig. 5. 3. BTCs for the OMPs having $R_d > 50$ under abiotic and biotic conditions along with the BTC for the tracer. (Values in parenthesis are log K_{ow} and group of compound P: Polar; NP: Non- polar) (◆ Tracer ■ Abiotic ▲ Biotic)

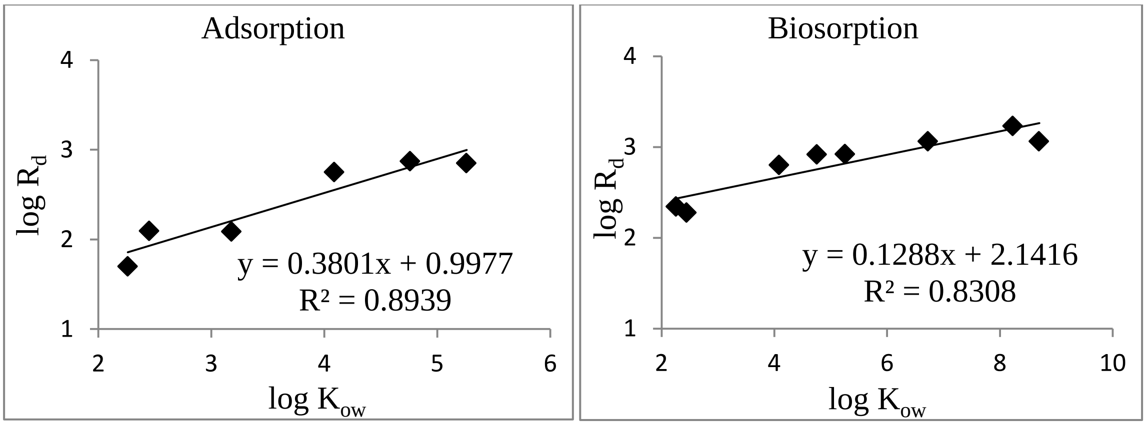


Fig. 5.4. OMPs: correlation between log K_{ow} and log R_d (Correlation applicable to compounds having log $K_{ow} > 2$ and R_d values > 50)

Column experiments are the simplified simulation of field conditions. Experimentally determined values of R_d shows only one-dimensional transport behaviour of the contaminant. Multi-directional mixing and diffusion are not considered. So, R_d values obtained, approximates the transport velocity of contaminants with respect to the velocity of the water.

To the best of the author's knowledge, R_d values of studied OMPs in RBF system were determined for the first time in the current study. These results provide valuable information regarding residence time required for the removal of OMPs in the RBF system and post-treatment necessary for the public water supply.

5.4. CONCLUSION

- Out of the OMPs studied DMM, BA, GUA, DA, ADE, and LMS were found to be more mobile ($R_d < 5$) than EOL, DEA, TRD, EIC, TRI, SA and CTA ($R_d > 50$).
- In general, R_d was found to depend on polarity. R_d of non polar OMPs was found to be more than the polar ones with a few exceptions.
- In general, OMPs with low values of K_{ow} (< 2) and R_d (< 5) present in the water as a mixture tend to lose their identity and behave as a single compound.Therefore, for individual compounds, K_{ow} can't be corelated to R_d, K etc.
- Compared to sorption (R_d = 3-772), mobility of OMPs decreases significantly during biosorption (R_d = 6-1692).
- Results indicate that MW did not have any significant effect on R_d.
- Although R_d values for all the OMPs were > 3, the occurrence of some of the polar OMPs in bank filtrate cannot be neglected after some time. However, non-polar OMPs may take several years to travel to abstraction wells through the sandy aquifer. Additional treatment for OMPs is required before public distribution.

5.5. ACKNOWLEDGEMENTS

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CHAPTER-6
Conclusions

6.1 Natural filtration of contaminated river water through the aquifer for the production of drinking water

- The non-monsoon river water is heavier than the water from the RWs. The non-monsoon river water has a significant wastewater discharge from the drains.
- In spite of the considerable amount of turbidity in the source water during monsoon (> 1500 NTU), goal of achieving prescribed limits of turbidity through RBF is attainable.
- Even in the case of source waters consistently contaminated by wastewaters (non-monsoon average DOC >15 mg/L), attenuation of organics in terms of DOC < 2 mg/L through RBF is possible.
- However, in the case of contaminated source water (rich in organics), coliform survive over long distances in the aquifer. Production of coliform free filtrate does not seem to be a realistic target. Post-treatment of filtrate is a must.
- Overall, it could be summarized that in the case of contaminated surface waters, natural filtration alone is not adequate for the production of guaranteed safe and wholesome drinking water. Further treatment of riverbank filtrate is necessary.

6.2 Occurrence of OMPs in the River Yamuna and Ranney wells in Central Delhi, India

- Fifty-seven detected OMPs in river Yamuna and RWs were identified as pharmaceutically active compounds (PhACs), pesticides, endocrine disrupting compounds (EDCs), phthalates, personal care products (PCPs), fatty acids, food additives hormones and those organics present in hospital wastes in trace quantities.
- In river water, fifty-six OMPs were detected in the monsoon while only forty-seven were found in non-monsoon. The concentration of forty-seven out of fifty-seven OMPs was more in the monsoon samples than non-monsoon samples.
- It was quite contrary to the general understanding that during monsoon due to the high dilution, OMPs should be present in much lower concentrations in river water. The

reason for this contradiction could not be correlated with the octanol-water partition coefficients (log K_{ow}), solubility, and polar/non-polar characteristics of the OMPs. It could be due to the sorption of OMPs onto the sediments during the low flow (~ 19 m^3/s) conditions. During the high flow conditions (~ 507 m^3/s), scouring of deposited sediments possibly results in erosion and dissolution of OMPs in the river water. Results show that even the polar OMPs follow this trend.

- In general, compared to rivers of Europe and United States, much higher concentrations of OMPs were found in the Yamuna.
- Number of OMPs detected, their frequencies of occurrence and concentrations in RWs reduced substantially compared to river water and correlated well with the distance of RWs from the river. Larger the distance, lesser the number of OMPs detected and lower their frequencies of occurrence and concentrations.
- In spite of high levels (~50 μg/L) in river water of 3-acetamido-5-bromobenzoic acid, 1- dodecanethiol, diethyl phthalate, palmitic acid, and adenine, they were detected to be < 1 μg/L in water samples from RWs.
- Only a few OMPs e.g. simazine and aldrin sometimes exceeded 1 μg/L in RWs.
- Compared to other OMPs, in general, EDCs, PCPs, phthalates, fatty acids and food additives appeared more frequently in the number of RWs but in significantly lower concentrations than present in river water.
- Among hormones, only estriol appeared once in a RW.
- Some of the OMPs e.g. adenine were never detected in any of the RWs.
- Based on the results, bank filtration seems to be quite effective in attenuation of OMPs.

6.3 Fate of wastewater originated OMPs in a sand column

- Out of the OMPs studied dimethyl maleate, benzoic acid, guanine, diacetone alcohol, adenine, and lomustine were found to be more mobile ($R_d < 5$) than estriol, decanoic acid, 1-tridecanol, 1- eicosanol, triclosan, stearic acid, salicylic acid and cetyl alcohol ($R_d > 50$).
- In general, R_d was found to depend on polarity. R_d of non-polar OMPs was found to be more than the polar ones with a few exceptions.

- In general, OMPs with low values of K_{ow} (<2) and R_d (<5) present in the water as a mixture tend to lose their identity and behave as a single compound. Therefore, for individual compounds, K_{ow} can't be correlated to R_d, K etc.
- Compared to sorption (R_d = 3-772), the mobility of OMPs decreases significantly during biosorption (R_d= 6-1692).
- Results indicate that MW did not have any significant effect on R_d.
- Although R_d values for all the OMPs were >3, the occurrence of some of the polar OMPs in bank filtrate cannot be neglected after some time. However, non-polar OMPs may take several years to travel to abstraction wells through the sandy aquifer. Additional treatment for OMPs is required before public distribution.

6.4 SCOPE FOR FURTHER RESEARCH

- In the present work, it is suggested that OMPs adsorb onto the sediments during the low flow (~ 19 m^3/s) conditions. During the high flow conditions (~ 507 m^3/s), scouring of deposited sediments possibly results in erosion and dissolution of OMPs in the river water. This results in the appearance of larger number of OMPs in monsoon months in river water in greater concentrations. Although it is supported with the help of studies carried out elsewhere during high and low flows, however, a detailed study including analysis of sediments is warranted.
- Data regarding attenuation of OMPs in natural aquifer is presented in Chapter 4 while retardation of 15 most frequently occurring OMPs in lab scale sand columns is discussed in Chapter 5. There is a need to study the correlation between field and laboratory data.
- Water quality of tributaries and drains contributing wastes to the river Yamuna in Delhi need to be studied to identify the probable sources of OMPs.