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Monitoring of Persistent Organic Pollutants in Hydrosphere of Pakistan

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Pakistan Council of Research in Water Resources (PCRWR)

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Table of Contents

Executive Summary xi

Chapter 1: Introduction 1

1. Introduction 1

Chapter 2: Generalized Methodology 4

2. General Methodology 4

2.1 Sampling Design 4

2.1.1 Study Area Characteristics and Sampling Design 4

Chapter 3: Monitoring of Organo-Chlorine Pesticide 11

3.1 Introduction 11

3.2 Methodology: 11

3.2.1 Water and Biota Sampling 11

3.2.2 Pre-treatment of Samples for OCPs 12

3.2.3 Testing of Water and Biota Samples for OCPs 12

3.2.4 OCPs Data Extraction and Interpretation 12

3.3 Results and Discussion 13

3.3.1 OCPs in Surface Water (2007) 13

3.3.2 The LOD and LOQ of Test Method 13

3.3.3 Level of OCPs in Water 13

3.3.4 OCPs in Surface Water (2008) 15

3.3.5 OCPs in Biota (2007-2008) 18

3.4 Conclusions 22

Chapter 4: Polychlorinated Biphenyls & Polybrominated Diphenyl Ethers 23

4.1 Introduction 23

4.2 Materials and Methods 24

4.2.1 Monitoring of PCBs (2009) 24

4.2.2 Monitoring of PBDEs (2011) 25

4.3 Results and Discussion 27

4.3.1 PCBs in Surface Water (2009) 27

4.3.2 PBDEs in Sediments (2009) 31

4.4 Potential Health Impacts 32
4.5 Conclusions 33
Chapter 5: Monitoring of Per-Fluorinated Compounds 34
5.1 Introduction: 34
5.2 Materials and Methods 35
5.2.1 Water Sampling (2013-14) 35
5.2.2 Sampling of Surface Water, Groundwater and Sediments Samples (2016) 36
5.2.3 Sampling of Water, Sediment and Biota (2017-18) 37
5.2.4 Sampling of Water, Sediment and Biota (2018-19) 39
5.3 Results and discussion 39
5.3.1 PFCs in Surface Water (2013-15) 39
5.3.2 Levels of PFCs in Surface Water (2013-15) 41
5.3.3 PFCs in Groundwater Sources (2015-16) 44
5.3.4 PFCs in Surface Water and Sediments (2015-16) 46
5.3.5 PFCs in Surface Water, Sediments and Fish (2017-18) 47
5.3.6 PFCs in Water, Sediments and Fish (2018-19) 54
5.4 Potential Health Effects 58
5.5 Conclusions 58
Chapter 6: Overall Conclusions and the Way Forward 59
6.1 Overall Conclusions 59
6.2 The Way Forward 60
6.2.1 Monitoring 60
6.2.2 Regulatory 60
6.2.3 Awareness and Behaviour Change 60
References 61
Annexures 65

List of Figures

Figure 1.1: Sources of Persistent Organic Pollutants (POPs) in the Environment 1

Figure 2.1: Map showing River Indus and its tributaries 4

Figure 3.1: Concentration of OCPs (ng/L) above LOQs in surface water sites during dry season and wet season (2007) 14

Figure 3.2: Concentration of OCPs (ng/L) in surface water sites during dry and wet seasons (2008) 16

Figure 3.3: Characterisation of ΣOCPs (ng/L) in surface water sites during dry season (2008) 17

Figure 3.4: Characterisation of ΣOCPs (ng/L) in surface water sites during wet season (2008) 18

Figure 4.1: Sources of release of PCBs in the environment 23

Figure 4.2: Sediment samples collection from various sites of monitoring areas 26

Figure 4.3: Concentration of PCBs (ng/L) in surface water (2009) 29

Figure 4.4: Characterisation of distribution of ΣPCBs (ng/L) in surface water sites during wet season (2009) 30

Figure 4.5: PCBs in marine environment and accumulation in Sea life (Adopted from Allsopp et al., 2008) 31

Figure 5.1: Contaminated sites resulting in release of PFCs in the environment 34

Figure 5.2: Schematic diagram showing the complete process of pre-treatment for PFCs analysis 36

Figure 5.3: Pre-treatment of sediment samples for PFCs 37

Figure 5.4: Biota Sample Pre-treatment for PFCs in National Water Quality Laboratory Islamabad 38

Figure 5.5: Concentration of PFOA (ng/L) in surface water sites (2013-15) 42

Figure 5.6: Concentration of PFOS (ng/L) in surface water sites (2013-15) 42

Figure 5.7: Characterisation of distribution of ΣPFCs (ng/L) in surface water sites during dry season (2013-15) 43

Figure 5.8: Characterisation of distribution of ΣPFCs (ng/L) in surface water sites during wet season (2013-15) 44

Figure 5.9: Concentration of PFCS (ng/L) above LOQs in groundwater (2015-16) 45

Figure 5.10: Characterisation of distribution of ΣPFCs (ng/L) in groundwater sources (2015-16) 45
Figure 5.11: Concentration of PFCS (ng/L) above LOQs in surface water sites (2015-16)..... 46
Figure 5.12: Characterisation of distribution of ΣPFCs (ng/L) in surface water sources (2015-16)..... 47
Figure 5.13: Concentration of PFCS (ng/L) in surface water during wet season (2017-18) 49
Figure 5.14: Characterisation of distribution of ΣPFCs (ng/L) in surface water sources in wet season (2017-18)..... 50
Figure 5.15: Concentration of PFCS (ng/L) in surface water sites in dry season (2017-18) 51
Figure 5.16: Characterisation of distribution of ΣPFCs (ng/L) in surface water sources in dry season (2017-18) 51
Figure 5.17: Characterisation of distribution of ΣPFCs (ng/L) in sediments in wet season (2017-18)..... 52
Figure 5.18: Concentration of PFC (ng/L) in sediments during dry season (2017-18) 53
Figure 5.19: Characterisation of distribution of ΣPFCs (ng/L) in sediments in dry season (2017-18) 53
Figure 5.20: Concentration of PFCS (ng/L) in groundwater (2018-19)..... 55
Figure 5.21: Characterisation of distribution of ΣPFCs (ng/L) in groundwater sources in wet season (2018-19) 55
Figure 5.22: Concentration of PFCs (ng/L) in surface water sites in wet season (2018-19) 56
Figure 5.23: Characterisation of distribution of ΣPFCs (ng/L) in surface water sites in wet season (2018-19)..... 57

List of Tables

Table 1.1: Compounds restricted in Stockholm Convention as POPs 2

Table 2.1: Sampling plan for monitoring of POPs from 2005-19 6

Table 3.1: LOQ for OCPs in Water (2007) 13

Table 3.2: LOQ and minimum and maximum OCPs in water (2008) 15

Table 3.3: LOQs, minimum and maximum concentrations of OCPs (ng/g) in shrimps 18

Table 3.4: LOQs, minimum and maximum concentrations of OCPs (ng/g) in Squids 19

Table 3.5: Minimum and maximum concentration of OCPs (ng/g) in Sea Bass 20

Table 4.1: LOQs, minimum and maximum concentration (ng/L) of PCBs in surface water samples (2009) 28

Table 4.2: Concentration (ng/L) of PBDEs in sediment samples 32

Table 5.1: LOQs & LODs of PFCs determined for surface water samples testing (2015-16) 39

Table 5.2: Percent recovery rates of PFCs standards (2015-16) 40

Table 5.3: LOQs & LODs of PFCs in surface water samples (2017-18) 48

Table 5.4: LOQ & LOD of PFCs in surface water samples (2018-19) 54

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Abbreviations and Acronyms

General	CNU	Chonnam National University
	FWHM	Full Width Half Maximum
	GIS	Geographic Information Systems
	HPLC	High Performance Liquid Chromatography
	LC-MS/MS	Liquid Chromatography-Mass Spectrometry/Mass Spectrometry
	NWQL	National Water Quality Laboratory
	PCRWR	Pakistan Council of Research in Water Resources
	QA/QC	Quality Assurance/Quality Control
	SD	Standard Deviation
	UNU	United Nations University
	UNU-ISP	UNU Institute of Sustainability and Peace
	USEPA	United States Environmental Protection Agency
	LOQ	limit of quantification
	LOD	Limit of Detection
	GCMS	Gas Chromatograph Mass Spectrometer
Units of measurement	µg/L	Micro gram per litre
	ml	Millilitre
	ng/g	Nano-gram per gram
	ng/L	Nano-gram per litre
	m/z	Mass to charge ratio
	3S	3x Standard Deviation
	10S	10x Standard Deviation
Compounds	DCM	Dichloromethane
	DDE	Dichlorodiphenyl dichloroethylene
	DDT	Dichlorodiphenyl trichloroethane
	HCB	Hexachlorobenzene
	OCPs	Organo-Chlorine Pesticides
	PBDE's	Polybrominated diphenyl ethers

PCB’s	Polychlorinated biphenyls
PFASs	Per fluoro alkylated substances
PFBA	Perfluorobutanoic acid
PFC’s	Perfluorinated compound
PFNA	Perfluorononoic acid
PFHxA	Perfluorohexanoic acid
PFOA	Per fluorooctanoic acid
PFOS	Per fluorooctanesulfonic acids
α HCH	alpha-Hexachlorocyclohexane
β HCH	beta-hexachlorocyclohexane
γ-HCH	*gamma*-hexachlorocyclohexane (Lindane)
BHC	Benzene hexachloride
HCH	Hexachlorocyclohexane
DCM-NaOH	Dichlomethane-sodium hydroxide
H_2SO_4	Sulfuric Acid
MeOH	Methyl Alcohol

Executive Summary

Persistent Organic Pollutants (POPs) are organic compounds that are resistant to environmental degradation through chemical, biological and photolytic processes. Because of their persistence, POPs bio-accumulate with potential adverse impacts on human health and the environment. Considering these concerns, the international community adopted the Stockholm Convention on Persistent Organic Pollutants in 2001, which entered into force in 2004. This convention requires 171 signatory countries including Pakistan to take measures to eliminate or reduce the release into the environment of over twenty POPs. Following this, the United Nations University Institute for Sustainability and Peace (UNU-ISP) and the Shimadzu Corporation, Japan have partnered with national institutions across Asia to monitor and manage POPs to better implement the Stockholm Convention.

Over the past 15 years from 2005 to 2019, the UNU-ISP project on Environmental Monitoring and Governance in the Asian Coastal Hydrosphere has helped ten Asian partner countries including Pakistan to enhance overall scientific capacity in POPs research. The monitoring of POPs in the environment water, sediment, biota and drinking water has also been undertaken in Pakistan.

PCRWR in collaboration with UNU-IAS (United Nation University Institute of Advance Studies) has monitored four groups of POPs from 2005-2019 in the surface water bodies of Pakistan (five rivers and Arabian Sea) at 37 strategic sites. Besides water and sediments samples, aquatic organisms such as shrimps, squid (*Sepioteuthis Lessonia*) and sea bass (*Lates Calcarifer*) were also collected. During these years, 213 surface water, 28 groundwater, 80 sediments and 32 biota samples were collected and analysed for organo-chlorine pesticide (OCPs) in 2005 to 2008; Poly Chlorinated Biphenyl's (PCBs) in 2009, Poly Brominated Diphenyl Ethers (PBDEs) in 2010 and Per Fluorinated Compounds (PFCs) in 2013-19.

Monitoring of OCPs in 2006-07 revealed that 6 (31%) and 5 (27%) of surface water samples in dry and wet seasons, respectively had OCPs residues. Likewise, 50% of 10 shrimps samples were detected with OCPs residues (range: 1.98-4.44 ng/g).

During 2008, 4 (21%) of the total 19 surface water (range: 8.42-12.45 ng/L) and all of the biota samples (range: 3.26-57.61 ng/g) showed presence of OCPs in dry season. In wet season, 5 (26%) of the 19 surface water samples revealed detection of OCPs.

PCBs were detected at 12 (63%) surface water sources of strategic importance in 2009. Whereas, in 2010, sediments collected from the same strategic locations showed presence of PBDEs in 94% of the samples.

Initial monitoring of PFCs in 2013-14 indicated 96% of the 48 surface water samples collected during wet and dry seasons contaminated with PFCs (PFOA & PFOS) in the range of 0.23-12.15 ng/L. During 2015-16, PFOAs, PFOS and other compounds of PFCs were also detected in surface water, groundwater and sediments. Besides PFOA and PFOS, a significant concentration of PFBA and PFHxA have also been

detected in 53% of the groundwater sources (range: 0.3-1.24 ng/L) mainly used for drinking purpose. Similarly 47% of the surface water samples (range: 0.27-1.71 ng/L) were also found to have PFCs.

During 2017-18, 29 of 35 surface water samples collected during dry and wet seasons and 14 of 26 sediments samples in both seasons showed presence of PFCs. In case of biota, only Rawal lake indicated presence of PFCs in a fish sample.

In conclusion, almost all types of POPs were detected in surface, sediments and biota at strategically important sites in Pakistan such as Head Sidhnai, Head Sulemanki, Tarbela dam, Taunsa barrage, Head Tarimu, Hub dam and Kabul river, Head Panjnad, Rawal lake, and Arabian Sea. Since quality of river water has direct link with the health of the whole ecosystem including human, soil, crops, livestock, wildlife and aquatic life, it should be protected from all kind of organic pollutions. These contaminants are closely associated with the excessive use of pesticides, expanding oil, industrial and energy sectors, with their obvious potential for the emission of POPs. This has raised particular concern as POPs can lead to serious health effects including certain cancers, birth defects, dysfunctional immune and reproductive systems and greater susceptibility to disease.

Chapter 1: Introduction

1. Introduction

Persistent Organic Pollutants (POPs) are organic compounds of anthropogenic origin that resist degradation and accumulate in the food-chain. They are produced as pesticides and chemicals in various industrial processes. These can also be unintentionally released from incomplete combustion or reaction processes.

Exposure to POPs can take place through diet, environmental exposure or accidents. POPs can accumulate in the fatty tissues of living organisms including humans and are found at higher concentrations in the food chain (Figure 1.1). The exposure of POPs can cause death and serious health effects such as disruption of the endocrine, reproductive, and immune systems, neuro-behavioural disorders; different kind of cancers including breast cancer (Alharbi et al., 2018).

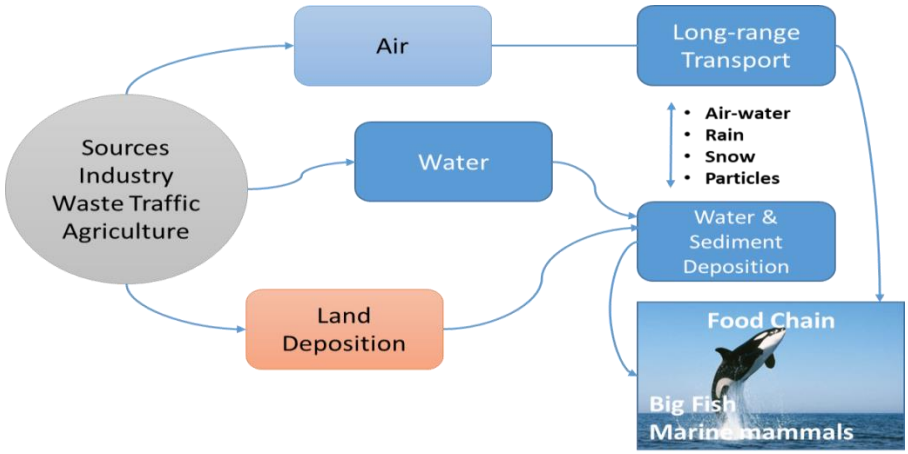


Figure 1.1: Sources of Persistent Organic Pollutants (POPs) in the Environment

Regardless of their origin, POPs are a global concern because they present a transboundary problem. Once POPs are discharged into the environment they can easily cross national boundaries and can be transported over long distances in the atmosphere, resulting in widespread distribution across the earth, including regions where they have never been used.

For example, an Indian state Kerala reported to have major health deterioration of the local community and the neighbouring fauna due to heavy overuse of pesticides. For the last 25 years, nearly 2.2 million litres of endosulfan was applied through air-spray to grow cashewnuts in 1500 acres (Singh et al., 2019), which badly effects the whole ecosystem. More than 500 people were badly affected. Cancer, miscarriage in women neurological disorder, epilepsy etc. were common in the area. Likewise, in Jaipur (Rajasthan, India) babies were born with brain abnormalities due to absence of folic acid in mothers, destroyed by pesticides. Therefore, farmers in these regions used chemicals for commercial crops but grew a separate crop, without using chemicals for their personal use (Singh and Jheeba, 2020).

In developing countries, major POPs contaminated sites have resulted from the

stockpiles of pesticides and their disposal sites. Green peace has also reported about the stockpiles of POPs in Pakistan and these are available in market with different names and brands (Baqar et al., 2017). DDT, Dieldrin, Heptachlor along with other harmful chemicals are illegally sold in the markets (Muti-ur-Rahman et al., 2018). Though, DDT was banned in 1994 in Pakistan, however, it is still reported to be illegally imported and used in agriculture. Moreover, there are various dumping sites of obsolete pesticides located in big cities.

Pakistan and India share the transboundary water. It may also result in flow of POPs from contaminated sites to intact sites. For example, drains discharging into Pakistan territory, particularly Hudiara drain originating from India, carry all kinds of pollutants including Persistent Organic Pollutants (POPs) which ultimately discharge into the already almost dry River Ravi (Imran et al., 2018). The Basel Convention, which entered into force on 5th May, 1992, states that the transboundary movement of hazardous wastes and other wastes need to be reduced to the minimum, consistent with the environmentally sound and efficient management of such wastes, in a manner which will protect human health and the environment against the adverse effects (UNEP Environmental Law, 1989). Transport of POPs through transboundary rivers and drains requires proper monitoring by the riparian countries with mutual understanding.

In response to concerns on POPs pollution, the international community in 2001 adopted the Stockholm Convention on POPs, which entered into force in 2004 (UNU, 2011). The Convention is a global treaty that aims to protect human health and the environment from the hazardous effects of POPs. This convention, to which 171 countries are now party, also requires them to take measures to eliminate or reduce release into the environment of over twenty POPs (Table 1.1). The Convention also aims to ensure the sound management of their stockpiles and wastes.

Table 1.1: Compounds restricted in Stockholm Convention as POPs

Types of Chemicals	Restricted Compounds
Pesticides	aldrin, chlordane, DDT, dieldrin, endrin, heptachlor, hexachlorobenzene (HCB), mirex, toxaphene; chlordecone, alpha hexachlorocyclohexane, beta hexachlorocyclohexane, lindane (γ-HCH) and pentachlorobenzene
Industrial chemicals	hexachlorobenzene, polychlorinated biphenyls (PCBs); hexabromobiphenyl, hexabromodiphenyl ether and heptabromodiphenyl ether, pentachlorobenzene, perfluorooctane sulfonic acid (PFOS), its salts and perfluorooctane sulfonyl fluoride, tetrabromodiphenyl ether and pentabromodiphenyl ether (PBDE)
By-products	hexachlorobenzene; polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/PCDF), and PCBs. alpha hexachlorocyclohexane, beta hexachlorocyclohexane and pentachlorobenzene

This Stockholm Convention (SC) requires 171 signatory countries including Pakistan to take measures to eliminate or reduce the release into the environment of over twenty POPs. Pakistan has signed the SC on POPs on December 06, 2001, ratified the Convention on April 17, 2008 which entered into force in July 2008. Article 11 of the SC requires each party to undertake appropriate research, development, monitoring and cooperation pertaining to persistent organic pollutants. Following this, United Nation University (UNU), Tokyo, Japan and Shimadzu Corporation, Japan in 1996 initiated a project on Environmental Monitoring and Governance in the Asian Coastal Hydrosphere in Japan, Korea, China, Malaysia, Singapore, Indonesia, Taiwan, Thailand, Vietnam and Philippine to monitor the POPs. PCRWR as Pakistani partner entered in this monitoring network on October 21, 2005 and monitored rivers and Arabian Sea costal line, riverine sediments, and aquatic organisms with the aim to take measures to eliminate or reduce release of these POPs into the environment. The specific objectives of this monitoring research were as below:

a. Assessment of different groups of POPs such as Organo-Chlorine Pesticide (OCPs), Poly Chlorinated Biphenyl's (PCBs), Poly Brominated Diphenyl Ethers (PBDEs) and Per Fluorinated Compounds (PFCs) in environmental matrices.
b. Identification of threats of POPs to human and environmental health and to inform policy makers, government leaders, international organizations and civil society.
c. Propose strategies to control and prevent POPs pollution and safeguard human health.

These study objectives are closely aligned with the SDG 6 (clean water and sanitation), SDGs 3 (good health and well-being), SDGs 8 (decent work and economic growth), SDGs 9 (industry, innovation and infrastructure) and SDGs 12 (responsible consumption and production).

Chapter 2: Generalized Methodology

2. General Methodology

The methodology comprised sampling design, sampling of surface water, sediments, biota and/or groundwater under different monitoring phases of POPs (2005-19), samples transportation, laboratory processing and testing and data interpretation.

2.1 Sampling Design

2.1.1 Study Area Characteristics and Sampling Design

The river system of Pakistan originates from the snow-covered Himalayan and the Karakoram Range and is comprised five main rivers (Jhelum, Chenab, Ravi, Sultej and Indus) that pass mainly through the Punjab province. A brief description of these rivers is given in relation to possibility of contaminants origin and transport due to which sampling was designed in such a way to cover the whole river system of Pakistan (Figure 2.1).

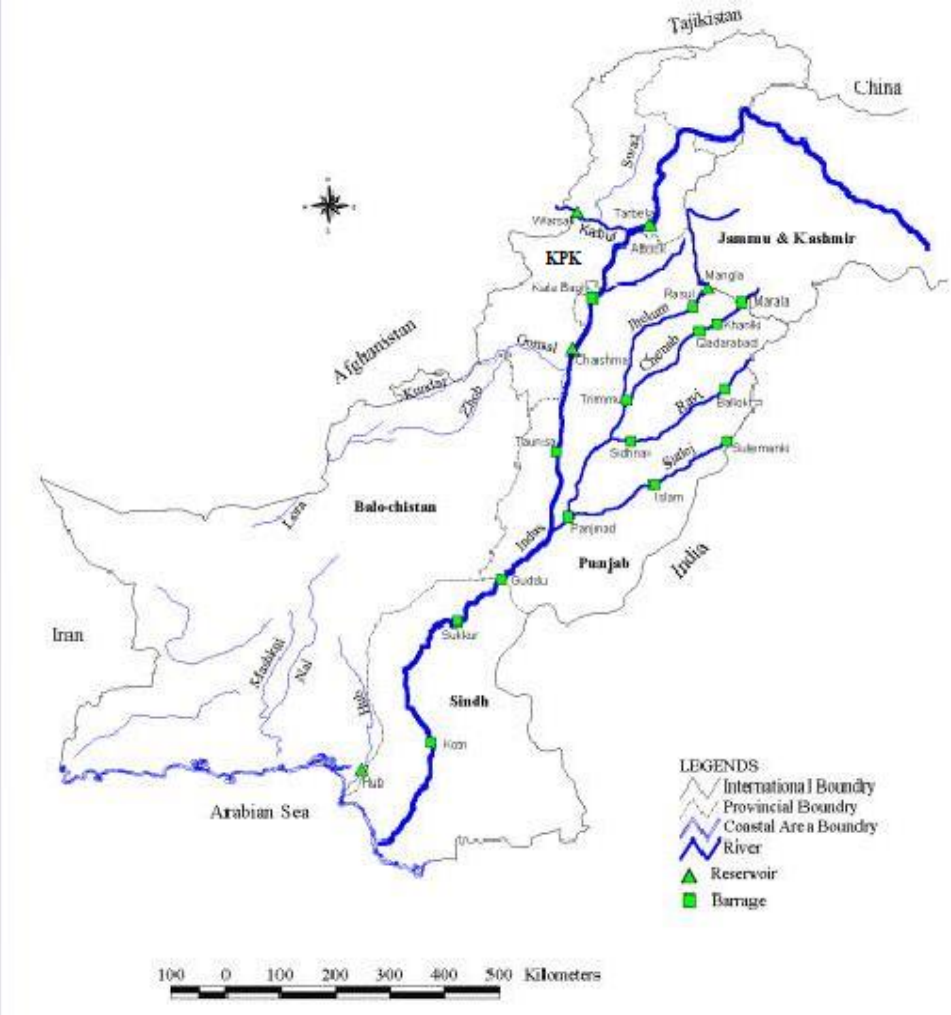


Figure 2.1: Map showing River Indus and its tributaries

River Jhelum is nearly 774 km long and is a tributary of River Chenab. It originates from the south-eastern part of Kashmir valley and flows through Srinagar before entering Pakistan. Along its course, it is joined by the largest tributary of the Neelam River near Muzaffarabad. River Jhelum also has many dams and barrages constructed on it. Mangla dam was constructed in 1967. It has a storage capacity of 9.12 billion m^3 (7.39 million acre ft). Rasul Barrage and Tarimu Barrage are also built on the Jhelum River.

The Sutlej River with 550 km length flows through the historic crossroad region of Punjab in northern India and Pakistan. It is located north of the Vindhya Range, south of the Hindu Kush segment of the Himalayas, and east of the Central Sulaiman Range (Kapur, 2020).

The Chandra and Bhaga rivers in the upper Himalayas join to form the Chenab river. Chenab flows through Jammu and Kashmir and then joined by the Jhelum river at Tarimu. It merges with the Sutlej near Uch Sharif in Pakistan. The Chenab River is nearly 960 km long (Krishna, 2021).

The river Ravi, through south-west region of Indian Punjab, flows along the Indo-Pak border and enters Pakistan. It is nearly 720 km long (Iqbal et al., 2018).

The Indus River with a total length of 3,180 km flows from north to south. It originates from the Tibetan plateau near Lake Mansarovar in China and runs through Jammu and Kashmir, enters the Gilgit-Baltistan region. It flows through the entire length of the country and finally drains into the Arabian Sea (Aslam, 2019). All other rivers join the Indus River at different locations. Some other tributaries of the Indus are: Astor River, Balram River, Gilgit River, Kabul River, Tanubal River and the Zanskar River (Usman et al., 2021).

Municipal, agricultural and industrial effluents and solid wastes are being discharged into these rivers mostly without any treatment. Therefore, these rivers bring pollution from across the country. Thus, sampling sites were selected in such a way to measure POPs pollution in each of these rivers and at the strategic locations.

To measure the load of POPs in each river and to give coverage to most of the surface water bodies and possible pollution sources, 19 sites were selected initially on main rivers and Arabian Sea coastal line for sampling of water, biota and sediments (Table 2.1).

Table 2.1: Sampling plan for monitoring of POPs from 2005-19

Sr. #	Source	Site	Lat - Long	Reason of site selection
1.	Indus River	Kharmang	3444.293 ° E 7 610.550 ° N	It is a point where transboundary contamination can be determined in upper Indus catchment area. The point at which Indus river enters Pakistan from Indian occupied Jamu & Kashmir.
2.	Indus River	Bunji	3339.995 ° E 74 37.653 ° N	Impacts of domestic and agricultural waste was previously identified in water and sediment samples collected from Bunji River Near Bunji bridge Gilgit, a tributary of River Indus.
3.	Indus River	Tarbela Dam	34° 07' 52 ° E 72 ° 48' 08 ° N	Tarbela dam is one of the world's largest dams and supplies 16% of Pakistan's electricity and is constructed on River Indus in KP. The water is mainly used for electric power generation and small-scale agricultural activities. At this point the level of pollution can be identified coming from the upper Indus basin and from hydropower generation.
4.	Indus River	Taunsa Barrage	30° 30' 41 ° E 70 ° 51' 07 ° N	Middle of the Punjab, where chemical, pharma, food, wheat and rice processing industries are present.
5.	Indus River	Guddu Barrage	28° 58' 27 ° E 68 °51' 38 ° N	All the rivers join before entering this barrage, having industrial, agricultural and domestic wastes of the Punjab.
6.	Indus River	Kotri Barrage	25° 26' 22 ° E 68° 08' 35 ° N	Site is in the centre of Sindh, where Indus river along its tributaries carries all the pollution (domestic, industrial and agricultural wastes) from Punjab and some pollution from Sindh.

Sr. #	Source	Site	Lat - Long	Reason of site selection
7.	Indus River	End point of river Indus near Thatta	24º 41' 04 º E 67º 58' 26 º N	This is the entry point of River Indus into Arabian Sea. Polluted water from Punjab, Sindh and other parts of the country enters into the Arabian sea at this site.
8.	Lake/ Reservoir	Manchar Lake	26º44,09 º E 67 69,90 º N	Manchar is a beautiful shallow lake located in district Jamshoro, Sindh. The lake collects water from numerous small streams in the Kirthar Mountains and empties into the Indus River. The lake provides livelihood to thousands of fisherfolk, near village Kot Lashari Bobak railway station. Currently, the lake is undergoing environmental degradation hazardous to human and aquatic life.
9.	Lake/ Reservoir	Keenjhar Lake	2491,48 º E 68 07,27 º N	Water samples were collected from the mid of Keenjhar Lake. One of the largest fresh water lake in Pakistan supplying water to Karachi and is also under degradation due to effluents disposal.
10.	Dam/ Reservoir	Hub Dam	2524,84 º E 67 12,51 º N	Hub Dam is situated in Karachi and at Sindh and Baluchistan borders and is a source of drinking water to Karachi city.
11.	Kabul river	Warsak Dam	34 10.311 º E, 71 25.975 º N	This dam was built on Kabul river entering in Pakistan from Afghanistan and supplies irrigation water.
12.	Lake/ Reservoir	Rawal Dam	3342.630 º E, 73 07.502 º N	The municipal waste enters in Rawal dam from Banigala, Constitutional Avenue and Quaid-e-Azam University (QAU) without any treatment and required assessment. The Rawal Dam water is being supplied for drinking to Rawalpindi district after treatment by Water and Sanitation Agency (WASA) Filtration Plant.

Sr. #	Source	Site	Lat - Long	Reason of site selection
13.	Lake/ Reservoir	Simly Dam	34 42.885 º E, 73 19.955 º N	Simly Dam was constructed on the Soan River and supplies water for domestic consumption to Islamabad. The water stored in this dam is fed by the melting snow & natural springs of Murree hills.
14.	Jhelum River	Mangla Dam	33 09 18 º E 73 40 02 º N	Located at Mangla and main purpose is power generation and agriculture.
15.	Jhelum River	Head Rasool	32 41 07 º E, 73 31 27 º N	Central Punjab region where agricultural runoff, industrial and domestic waste is heavily disposed of into the river.
16.	Jhelum River	Neelum-Jhelum	3428′13 º E, 70 49 ′36 º N	At the confluence of river Neelum to river Jhelum this sampling location identifies any type of contamination coming from AJK agricultural areas.
17.	Chenab River	Head Marala	32 º 40 04 º E, 74 28 06 º N	Agricultural practices and cottage industries exist. Sample was collected to see POPs originating from such sources in central Punjab.
18.	Chenab River	Qadirabad	32º 19 00 º E, 72 º 41 14 º N	Industrial and domestic wastes from northern Punjab possibly polluting the river
19.	Chenab River	Head Tarimu	31 41 02v º E, 71 5111 º N	Jhelum river joins the Chenab at this site and all the wastes of northern areas are assessed for POPs obtaining sample from this point.
20.	Ravi River	River Ravi (Lahore), on Indian border	31 36 53 º E, 74 16 08 º N	At this site the river enters Pakistan from India and pollution added by Indian side is monitored.

Sr. #	Source	Site	Lat - Long	Reason of site selection
21.	Ravi River	Head Baloki	31 13 12 º E, 71 51 40 º N	All the wastes of Lahore region come into river at this point. It is also a rich industrial and agricultural zone such as. leather, chemicals, agrochemicals, petrochemicals and pharma, textile wastes and run off from wheat & rice fields.
22.	Ravi River	Sidhnai Head	32 40 04 º E, 74 28 06 º N	Located at the southern side of Punjab, where, all the industries of central and southern Punjab pollute the river. Cultivation of wheat, rice, cotton and vegetables may result in runoff and contaminate the river.
23.	Sutlaj River	Head Sulemanki	30 41 43 E, 72 31 57 N	Agricultural wastes and run off from cotton, wheat, rice, vegetables fields as well as from agro-chemical industries are expected to be polluting the river.
24.	Sutlaj River	Head Islam	29 49 43 º E, 72 32 57 º N	-do-
25.	Sutlaj River	Head Panjnad	29 20 36 º E, 71 01 25 º N	A site where all the rivers of Punjab join each other and is thought to be the most contaminated area in Punjab. All of the domestic, industrial and agricultural waste is thought to be high in this region.
26.	Arabian Sea site No I	Arabian Sea Near Coast Guard Post Shah Bunder	24 09 35 º E, 67 53 56 º N	Domestic, agricultural and industrial wastes of the whole country come to Arabian sea through river Indus and its tributaries.
27.	Arabian Sea site No II	Near Zaman Jat village	24 10 29 º E, 67 53 05 º N	-do-
28.	Arabian Sea site No III	Near Allah Warayo Bhatti Village	24 10 29 º E, 67 53 05 º N	-do-

Sr. #	Source	Site	Lat - Long	Reason of site selection
29.	Thatta	Thatta City Area	24.748058 º E 67.927541 º N	Drinking water samples collected from the shallow ground water sources of Thatta city to figure out the impacts of agricultural chemicals in drinking water sources of Thatta city
30.	Karachi	Karachi City Area	24.93159 º E, 67.125499 º N	To assess contamination of restricted chemicals from industrial sources in water supplies of Karachi
31.	Hyderabad	Hyderabad city Area	33.67379 º E, 73.0655021º N	To assess contamination of restricted chemicals from agricultural practices in water supplies of Hyderabad city.
32.	Attock	Attock city Area	33.790956 º E, 72.358133 º N	Drinking water samples collected from the ground water sources of Attock city to identify the level of agricultural contaminants sources.
33.	Bahawalpur	Bahawalpur City Area	29.39347 º E, 71.709138 º N	Drinking water samples collected from the shallow ground water sources to assess the presence of POPs
34.	Lahore	Lahore City Area	31.591888 º E, 74.459051 º N	–do-
35.	Multan	Multan City Area	30.156523 º E, 71.571379 º N	-do-
36.	Jhelum	Jhelum City Area	32.924865 º E, 73.720097 º N	–do-
37.	Kasur	Kasur City Area	31.133101 º E, 74.45989 º N	–do-

In total, 213 surface water samples, 28 groundwater samples, 80 sediment samples, 32 biota samples were collected over a period of 2005 to 2019 under four phases of monitoring of POPs and analysed for 67 compounds. Phase-wise results of different groups of POPs such as organo-chlorine pesticide (OCPs) in 2005 to 2008; Poly chlorinated Biphenyl's (PCBs) in 2009, Poly brominated diphenyl Ethers (PBDEs) in 2010-11 and Per Fluorinated Compounds (PFCs) in 2014-19 alongwith complete monitoring and findings of each group of compounds is given in the subsequent chapters.

Chapter 3: Monitoring of Organo-Chlorine Pesticide

3.1 Introduction

Organochlorine pesticides such as dichloro-diphenyltrichloroethane (DDT), polychlorinated biphenyl, and hexachlorobenzene (HCB) are a globally concerned group of chemicals. These have well known persistence in the environment and may show variations in their chemical structures and toxicity mechanisms. Besides their persistency, they can be dispersed by air and re-deposited. For instance, some organochlorine gets deposited in food commodities, aquatic lives and soil after covering long distances. Organochlorines have extremely strong bonds between their chlorine and carbon components and are attracted to fats. They are also highly insoluble in water and during rains can be transported through runoff. When used, OCPs can spread into the environment via direct application, contaminated waste disposal, incinerator emissions or runoff.

OCPs have been reported to be distributed in the surface and groundwater, soil, plants, animals, and humans, causing disturbances in the endocrine, reproductive, neurologic, and immunologic systems and may also be an oncogenic (Chen et al., 2020). Considering the wide spectrum health hazards and persistence properties, the monitoring of OCPs in 19 fixed surface water sites during pre and post monsoon seasons was undertaken in 2007 and 2008. Standard protocols provided by the United Nation's University and Shimadzu Corporation were followed for samples collection, transportation, extraction, testing and quality control.

3.2 Methodology:

3.2.1 Water and Biota Sampling

Sampling for OCPs was performed in both dry (April-May) and wet seasons (July-August) during 2007 and 2008. The temperature recorded during samples collection ranged from 35-40 °C and 28-48 °C in dry and wet seasons (2007), respectively. The dry weather temperature in 2008 was recorded as 30-40 °C and during wet season this was 24 to 38 °C. Thirty eight water samples from 19 fixed sites were collected in pre-cleaned 2 litres glass bottles. Ten samples of squids were collected with the help of Fisheries Department, Karachi. However, only 10 samples of 18 cm length and on average 700 g weight were selected for OCP analysis. Due to the unavailability of shrimps in the selected rivers, shrimps found in the Arabian Sea were sampled from the market.

All collected samples were kept under controlled temperature in insulated ice boxes and were immediately transported to the National Water Quality Laboratory, PCRWR Islamabad. The questionnaire/sample collection proforma were filled with the information related to each sampling site, sample types, sample ID, sample code,

GPS reading, date and time of sample collection along with the description of the surrounding areas of the river, usage of source water, point sources of industrial and municipal waste entering in the river.

3.2.2 Pre-treatment of Samples for OCPs

N-Hexane was used for liquid-liquid, solid phase extractions (SPE) and other processes. The extraction was further processed with rotary evaporator followed by SPE and nitrogen concentrator. Each water sample was reduced with nitrogen sample concentrator to 1 ml and analysed. Biota samples tissues (5 g) were weighed and processed with aceto-nitrile, homogenizer and SPE-C-18 with Silica cartridges for homogenization and clean-up processes. Then ethyl acetate and hexane were used to extract the OCPs in the presence of sodium chloride. SPE-NH_2 was used for further clean-up of extracted OCPs in hexane. After concentrating to 1 ml with nitrogen, the samples were analyzed.

3.2.3 Testing of Water and Biota Samples for OCPs

The OCPS in water, sea bass, shrimps and squids samples were identified and quantified on Gas Chromatograph Mass Spectrometer (GC-MS) (Shimadzu, model QP2010 chromatographic column-capillary DB-5, 30 m x 0.32 mm id x 0.25 mm of film thickness) using selected ion monitoring (SIM) mode.

DDT-^{13}C was used as a spiking agent and the range for percent recovery was set as 70 to 130%. Phenanthrene d10 and Chrysene d12 were used as internal standards. Calibration standards of concentration 10, 50, 100 and 200 µg/L were used for method's calibration. Internal standards of Phenanthrene d10 and Chrysene d12 of 50 µg/L were used in all calibration standards of OCPs. All standards were spiked with 100 µg/L of *p,p'*- DDT^{13}C to check the recovery of *p,p'*-DDT^{13}C in samples.

The pre-treated samples were analyzed for Alpha BHC, Beta BHC, Gamma BHC, Delta BHC, Hexachloro-benzene, Heptachlor, trans-Chlordane, cis-Chlordane, Aldrin, Dieldrin, Endrin, *o,p'*- DDD, *p,p'*- DDD, *o,p'*- DDE, *p,p'*-DDE, *o,p'*- DDT, *p,p'*-DDT and Mirex.

3.2.4 OCPs Data Extraction and Interpretation

It has been observed that values at low concentration (10 ng/L and below) showed little deviations from linearity in calibration. Low concentration of Dieldrin and Endrin were integrated manually. The peaks of these two OCPs were broad and showed other shoulder peaks. To minimize this problem in calibration, the weighted regression was kept on 1/c (instrument option as suggested by Shimadzu). A standard of 10 ng/L was run after every 20 samples. Repeatability was checked while injecting 2 µl of 10 ng/L standards and limit of detection (LOD) of method (3S) was calculated from repeatability. Limit of Quantification (LOQ) was set as 10S from repeatability. OCPs detected above 3S but below 10S were reported as traces.

3.3 Results and Discussion

3.3.1 OCPs in Surface Water (2007)

OCPs were quantified by analysing different compounds including Dieldrin, Aldrin, *p,p*–DDT, *o,p'*- DDT, *o,p'*- DDE, *p,p'*- DDE, *o,p'*- DDD and *p,p'*- DDD in 38 water samples.

3.3.2 The LOD and LOQ of Test Method

Internal quality procedures were applied to produce valid logical results. Calibration curve slope and laboratory fortified blank methods were conducted to determine the limit of detection (LOD) and limits of quantification (LOQ). The limit of quantification is almost 10 times higher than limit of detection. Table 3.1 shows LOQs of compounds of OCPs. Test data of water samples was compared with these LOQs.

Table 3.1: LOQ for OCPs in Water (2007)

Compounds	LOQ (ng/L)
Heptachlor	1.68
Aldrin	1.48
trans-chlordane	2.61
cis-chlordane	2.20
Dieldrin	6.24
Endrin	7.92
Hexachlorobenzene	2.18
p,ṕ-DDT	2.27
o,ṕ-DDT	2.64
o,ṕ-DDE	1.47
p,ṕ-DDE	1.86
p,ṕ-DDD	1.45
p,ṕ-DDD	2.13
o,ṕ-DDT	1.39

3.3.3 Level of OCPs in Water

OCPs were detected in 6 (31%) and 5 (27%) of the surface water samples in dry and wet seasons, respectively. In dry season (Figure 3.1), two OCP compounds such as aldrin (18.2 ng/L) and dieldrin (138 ng/L) were detected at the Islam Headworks (River Sutlej). In wet season, both compounds were again detected at the same sites with comparatively reduced concentrations of aldrin from 18.2 ng/L

to 5.94 ng/L and dieldrin from 138 ng/L to 55.3 ng/L. The Sutlej River enters into Pakistan near Kasur district. However, its all water is being used by India due to the Indus Waters Treaty. Two irrigation link canals, Bulloki-Sulemanki Link Canal and Pakpattan-Islam Link Canal, join the river to irrigate southern Punjab. Both link canals carry industrial and municipal wastewater to the river from nearby urban and industrial areas including the Kasur and Pakpattan districts. The effect of pollution of municipal and industrial discharges in the river becomes hazardous in certain reaches as depicted from the OCP levels at Head Islam. The Pandoki drain in Kasur district, with an average discharge of 2.46 m^3/s (86.95 cusecs) is the main continuous source of the Sutlej's pollution. Municipal wastewater from Bahawalnagar, Okara, Bahawalpur and Vehari districts also join the Sutlej. As these districts are mostly agricultural, excessive use of fertilizers and pesticides are possibly adding OCPs in surface water. During wet season, the surface flows reach the river – carrying large quantities of the several contaminants.

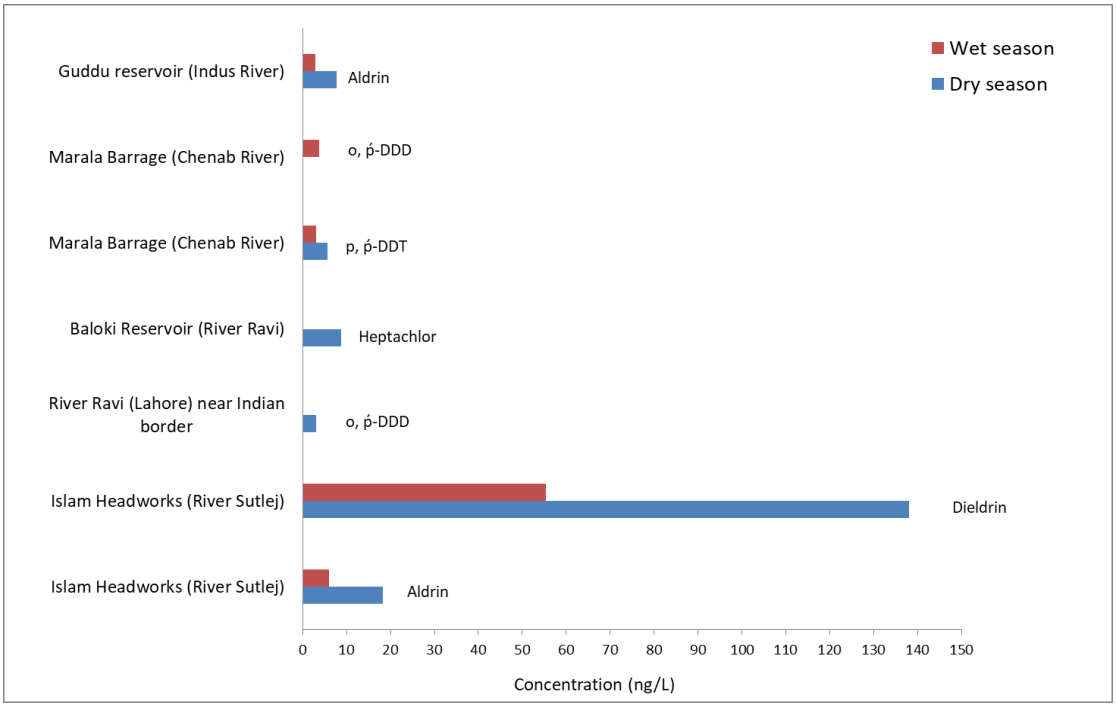


Figure 3.1: Concentration of OCPs (ng/L) above LOQs in surface water sites during dry season and wet season (2007)

- The sampling site of river Ravi (Lahore) near Indian border showed presence of *o,ṕ-DDD* (3.02 ng/L), while heptachlor (8.75 ng/L) was detected at the Baloki Reservoir in dry season. In wet season, there was no detection of OCPs at both sites (Figure 3.1). River Ravi, a transboundary river has a strategic significance for being bordered by an intensive agricultural region i.e. Rachna Doab and Bari Doab, and also the most polluted river of Pakistan.
- In the Chenab River, *p,ṕ-DDT* (5.61 ng/L) was detected at sampling site of Marala Barrage (Figure 3.1). This concentration level decreased to 3.09 ng/L in

post-monsoon monitoring. In addition, *o,ṕ*-DDD (ng/L) was also detected at the same site. Most of the fertile area lies near the bank of River Chenab and is famous for it's highly productive Kharif and Rabi crops. Cotton is the main Kharif cash crops where farmers spray different pesticides and herbicides. This may be a possible reason for higher levels of banned OCPs in the river Chenab.

- In the Indus River, aldrin (7.69 ng/L) was detected at the sampling site of Guddu reservoir in pre-monsoon season (Figure 3.1). In post-monsoon, this concentration decreased to 2.91 ng/L. Again the indiscriminate discharges of untreated municipal and industrial wastewater could have resulted in presence of OCPs in addition to other physico-chemical and biological contaminates. The Indus River dolphin is one of the world's most endangered freshwater river dolphin as their numbers specifically at lower part of the Indus has declined as a result of water pollution (Gareth and Azra, 2020). Presence of restricted OCPs may further pose risks to these endangered species.
- The sum of OCP compounds as ∑OCPs was higher in the dry season compared to the wet season at above mentioned sites. This may be due to dilution effect and higher resident time of the sediment transported during dry season.
- No OCPs were detected in the River Jhelum and the Arabian Sea in both seasons (Figure 3.1).

3.3.4 OCPs in Surface Water (2008)

In 2008, 19 fixed sites were assessed for 18 OCPs such as α-BHC, β-BHC, γ-BHC, δ-BHC, hexachlorobenzene, heptachlor, cis-chlordane, trans-chlordane, aldrin, dieldrin, endrin, o,ṕ-DDD p,ṕ-DDD, o,ṕ-DDE p, ṕ-DDE, o,ṕ-DDT p,ṕ-DDT and mirex. LOQs of these OCPs are given in Table 3.2.

Table 3.2: LOQ and minimum and maximum OCPs in water (2008)

Sr No.	Compounds	LOQ (ng/L)	Pre-monsoon		Post monsoon	
			Min.	Max.	Min.	Max.
1.	α- BHC,	1.90	<1.90	12.5	<1.90	8.26
2.	β BHC	5.19	<5.19	<5.19	<5.19	<5.19
3.	γ-BHC,	4.50	<4.50	<4.50	<4.50	<4.50
4.	δ-BHC	7.97	8.42	8.79	<7.97	<7.97
5.	Heptachlor	7.44	<7.44	<7.44	<7.44	<7.44
6.	Hexachlorobenzene	3.25	<3.25	<3.25	<3.25	<3.25
7.	Aldrin	4.03	<4.03	<4.03	<4.03	<4.03
8.	trans-chlordane	5.94	<5.94	<5.94	<5.94	<5.94
9.	cis-chlordane	6.35	<6.35	<6.35	<6.35	<6.35

Sr No.	Compounds	LOQ (ng/L)	Pre-monsoon		Post monsoon	
			Min.	Max.	Min.	Max.
10.	Dieldrin	5.56	<5.56	<5.56	<5.56	<5.56
11.	Endrin	14.3	<14.3	<14.3	<14.3	<14.3
12.	*o,ṕ*-DDE	6.35	<6.35	<6.35	<6.35	<6.35
13.	*p,ṕ*-DDE,	6.63	<6.63	<6.63	<6.63	<6.63
14.	*o,ṕ*-DDD	22.4	<22.4	<22.4	<22.4	<22.4
15.	p,ṕ-DDD	3.93	<3.93	<3.93	<3.93	<3.93
16.	o,ṕ-DDT	4.11	<4.11	<4.11	<4.11	<4.11
17.	p,ṕ-DDT	7.12	<7.12	<7.12	<7.12	7.92
18.	mirex	2.80	<2.80	<2.80	<2.80	<2.80

LOQs, minimum and maximum have indicated the presence of α- BHC, δ-BHC, and o,ṕ-DDT. The analytical data revealed that α-BHC (12.45 ng/L) was detected in dry season in surface water sites of head Sulemanki, δ-BHC at Kotri (8.79 ng/L), Sidhnai (8.42 ng/L) and, *p,ṕ*-DDT (7.92 ng/L) at Baloki (Figure 3.2).

In post-monsoon (wet season), α-BHC was found at Tarbela (8.26 ng/L) and reduced at head Sulemanki (2 ng/L) and p,ṕ-DDT at Baloki (7.92 µg/L) as shown in Figure 3.2.

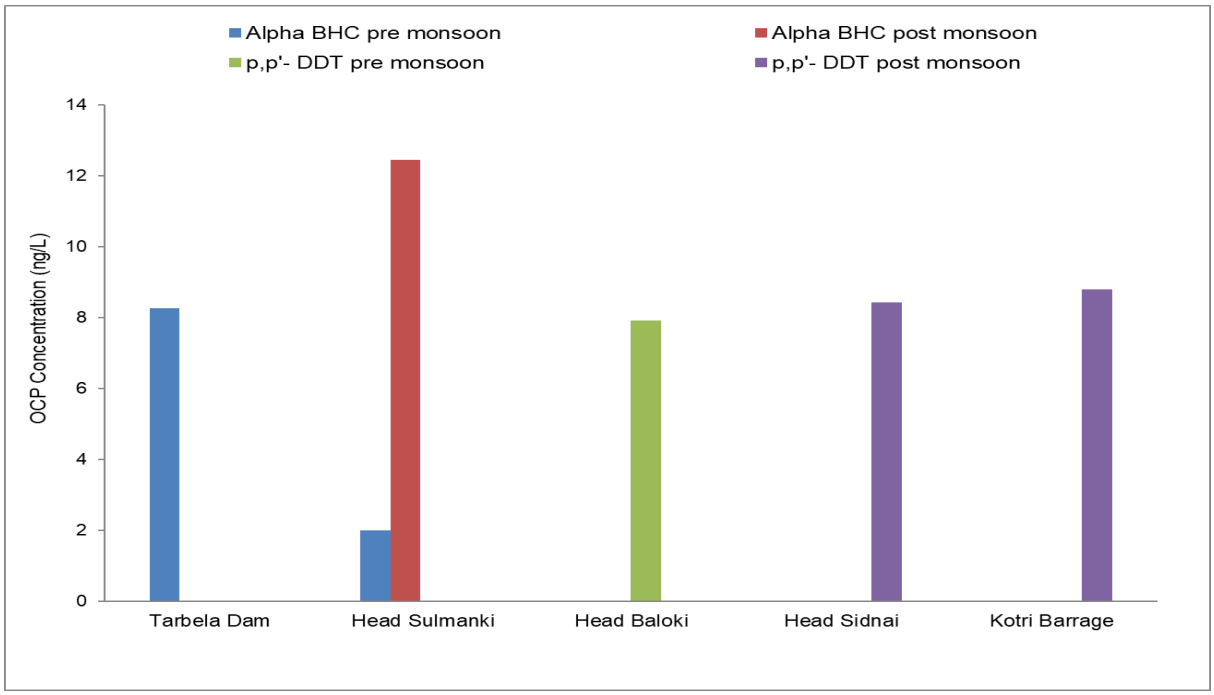


Figure 3.2: Concentration of OCPs (ng/L) in surface water sites during dry and wet seasons (2008)

The summation of OCPs has also indicated presence of OCPs at six sites (three sites in dry and three sites in wet season) (Figures 3.3 and 3.4). The concentrations of OCPs were slightly higher in the wet season indicating that the increasing runoff during the summer might bring the chemical residues from soils to water bodies. α-BHC is the only compound found in both sampling seasons. Benzenehexachloride (BHC) is also called hexachlorocyclohexane (HCH), whilst γ-BHC is called Lindane, a pesticide used for the treatment of food crop, seed, livestock and pets. Lindane also acts as pharmaceutical product to kill lice and treat scabies. The detection of Lindane (γ-BHC) in the surface water sources indicates possibility of utilization of this banned compound as pesticide or as lice and scabies treatment solutions. Presence of γ-BHC is a matter of concern due to its reported neurotoxicity and carcinogenicity in humans (Agus et al., 2021).

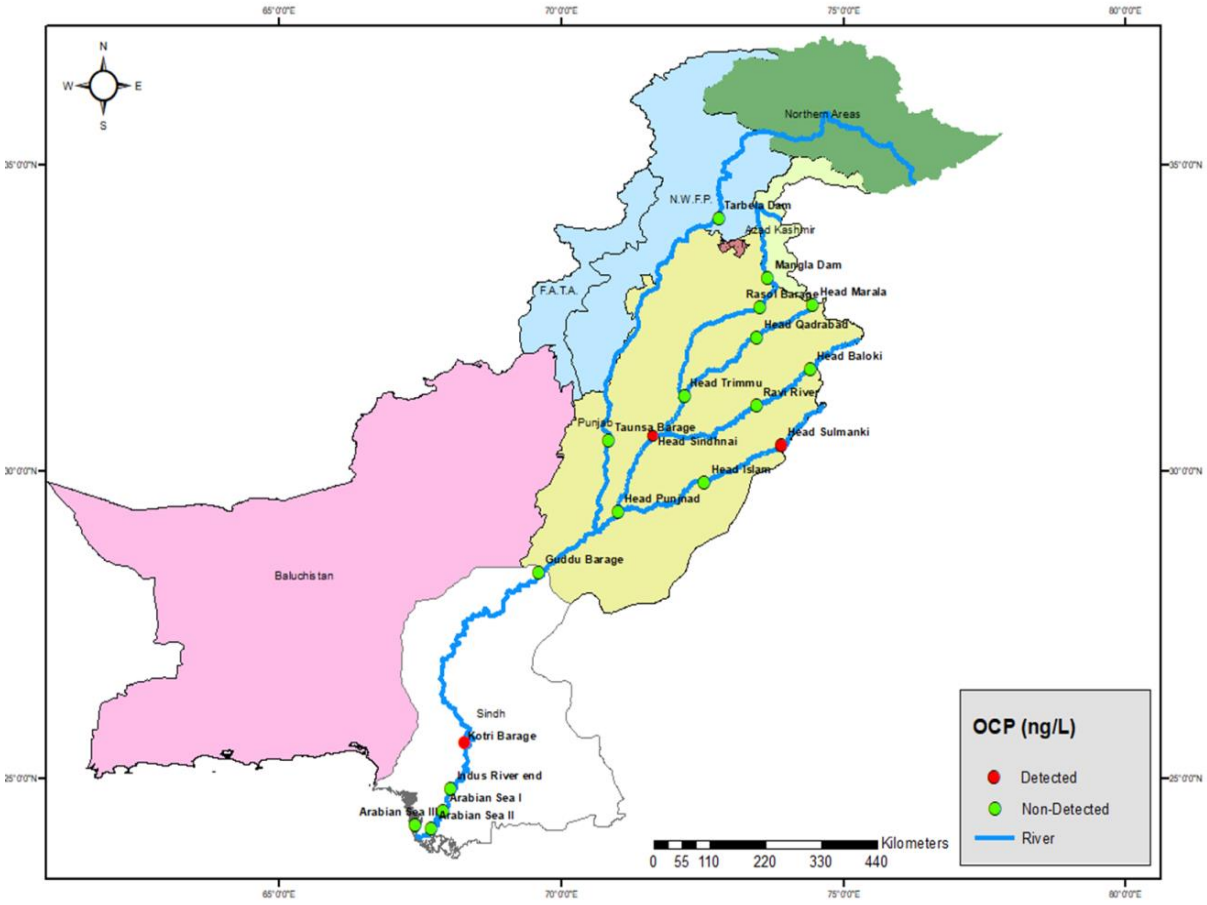


Figure 3.3: Characterisation of ΣOCPs (ng/L) in surface water sites during dry season (2008)

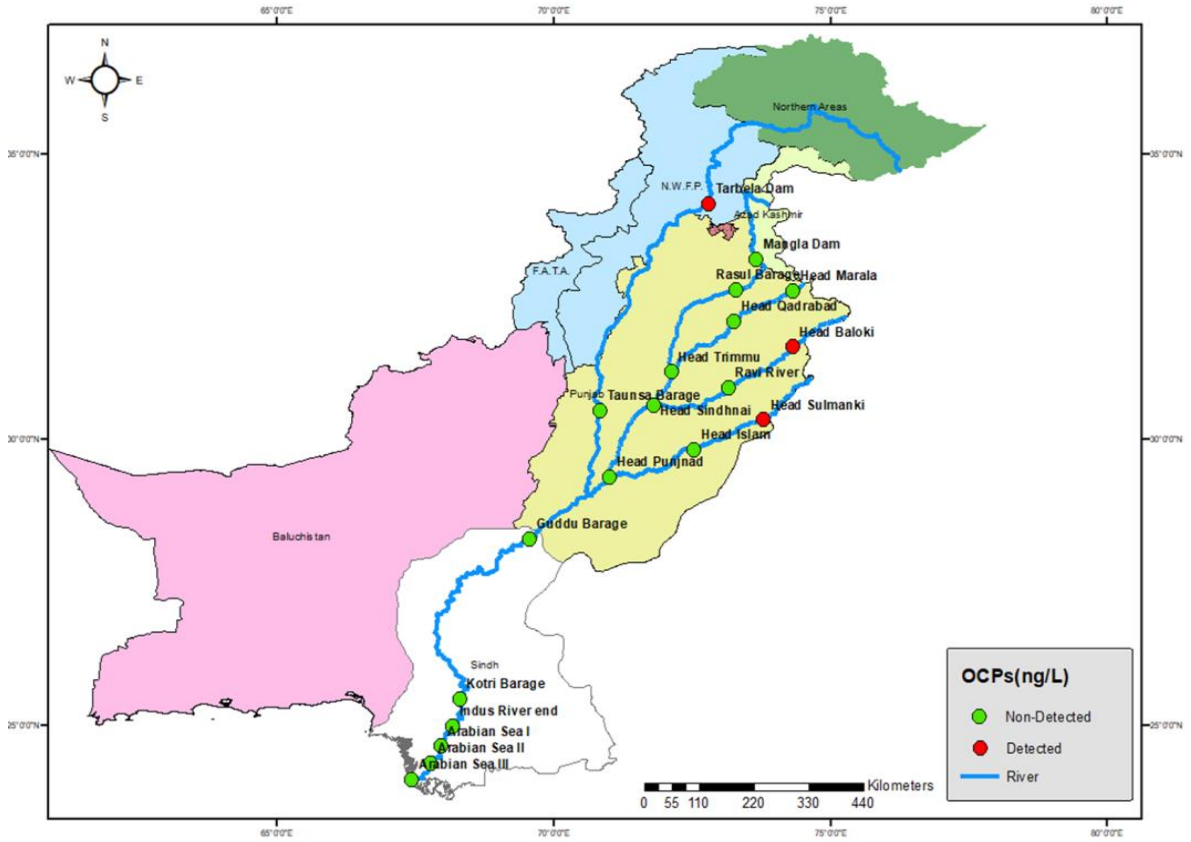


Figure 3.4: Characterisation of ΣOCPs (ng/L) in surface water sites during wet season (2008)

3.3.5 OCPs in Biota (2007-2008)

OCPs in Shrimps

A total of 10 shrimps samples were analysed and these samples were injected with 20 ng/g of surrogate DDT-^{13}C. The range of DDT-^{13}C was set as 25 to 35 ng/g. Comparison of LOQs with minimum and maximum of different OCPs indicated the presence of two compounds i.e. *o,ṕ*-DDE and *p,ṕ*-DDE in shrimps samples purchased from local market in Karachi (Table 3.3).

Table 3.3: LOQs, minimum and maximum concentrations of OCPs (ng/g) in shrimps

Sr No.	Compounds	LOQ (ng/g)	Minimum	Maximum
1.	Heptachlor	1.68	<1.68	<1.68
2.	Aldrin	1.48	<1.48	<1.48
3.	*trans*-chlordane	2.61	<2.61	<2.61
4.	*cis*-chlordane	2.20	<2.20	<2.20

Sr No.	Compounds	LOQ (ng/g)	Minimum	Maximum
5.	Dieldrin	6.24	<6.24	<6.24
6.	Endrin	7.92	<7.92	<7.92
7.	Hexachlorobenzene	2.18	<2.18	<2.18
8.	*o,ṕ*-DDE	1.47	1.98	4.44
9.	*p,ṕ*-DDE	1.86	<1.86	2.44
10.	*o,ṕ*-DDD	1.45	<1.45	<1.45
11.	p,ṕ-DDD	2.13	<2.13	<2.13
12.	o,ṕ-DDT	2.64	<2.64	<2.64
13.	p,ṕ-DDT	2.27	<2.27	<2.27
14.	Mirex	1.39	<1.39	<1.39

OCPs in Squids

Analysis of 10 samples of squids (*Sepioteuthis Lessonia*) for 18 OCPs showed recoveries of *p,ṕ*-DDT-^{13}C in 4 samples beyond 100%, while 6 samples were below 100% recovery. *p,ṕ*-DDT was detected in 2 samples in the range of 13.5 to 15.2 ng/g, whilst *o,ṕ*-DDT was detected as 8.79 to 9.06 ng/g. The recoveries of α-BHC and hexachlorobenzene exceeded 70% in all 10 samples. The concentration of hexachlorobenzene varied from 7.17 to 16.3 ng/g. The concentrations of α-BHC ranged from 4.52 to 15.5 ng/g (Table 3.4). γ-BHC was detected in three samples only, while p, ṕ-DDE was detected in 9 samples in the range of 20.4 to 57.6 ng/g. Its concentration was relatively higher than other OCPs and indicates the absorption of OCPs in Sea life.

Table 3.4: LOQs, minimum and maximum concentrations of OCPs (ng/g) in Squids

Sr No.	Compounds	LOQ (ng/g)	Minimum	Maximum
1.	α- BHC,	1.90	4.52	15.5
2.	β BHC	5.19	<5.19	<5.19
3.	γ-BHC,	4.50	15.6	21.1
4.	δ-BHC	7.97	<7.97	<7.97
5.	Heptachlor	7.44	<7.44	<7.44
6.	Hexachlorobenzene,	3.25	7.17	16.4
7.	Aldrin	4.03	<4.03	<4.03
8.	trans-chlordane	5.94	<5.94	<5.94
9.	cis-chlordane	6.35	<6.35	<6.35

Sr No.	Compounds	LOQ (ng/g)	Minimum	Maximum
10.	Dieldrin	5.56	<5.56	<5.56
11.	Endrin	14.3	<14.3	<14.3
12.	*o,ṕ*-DDE	6.35	<6.35	42.2
13.	*p,ṕ*-DDE,	6.63	20.4	57.6
14.	*o,ṕ*-DDD	22.4	<22.4	<22.4
15.	p,ṕ-DDD	3.93	<3.93	<3.93
16.	o,ṕ-DDT	4.11	8.79	9.06
17.	p,ṕ-DDT	7.12	13	15.2
18.	Mirex	2.80	<2.80	<2.80

OCPs in Sea Bass

The sea bass species (*Lates Calcarifer*) selected by the UNU-ISP project for sampling were not common in Pakistan. Therefore, only two samples could be collected from the Arabian Sea with the help of Fisheries Department, Karachi. The samples were analyzed in duplicate by using head and tail parts used for extraction and analysis of OCPs. α-BHC and *p,p'*-DDE were detected in all four parts of samples. Minimum and maximum concentrations of OCPs in sea bass samples (Table 3.5) showed the presence of four OCPs such as α- BHC, *p,ṕ*-DDE, hexachlorobenzene and β-BHC beyond the LOQ level.

Table 3.5: Minimum and maximum concentration of OCPs (ng/g) in Sea Bass

Sr No.	Compounds	LOQ (ng/g)	Minimum	Maximum
1.	α- BHC	1.90	3.26	12.4
2.	β BHC	5.19	<5.19	25.9
3.	γ-BHC	4.50	<4.50	<4.50
4.	δ-BHC	7.97	<7.97	<7.97
5.	Heptachlor	7.44	<7.44	<7.44
6.	Hexachlorobenzene	3.25	7.51	13.8
7.	Aldrin	4.03	<4.03	<4.03
8.	trans-chlordane	5.94	<5.94	<5.94
9.	cis-chlordane	6.35	<6.35	<6.35
10.	Dieldrin	5.56	<5.56	<5.56
11.	Endrin	14.3	<14.3	<14.3
12.	*o,ṕ*-DDE	6.35	<6.35	<6.35

13.	*p,ṕ*-DDE	6.63	21.7	49.9
14.	*o,ṕ*-DDD	22.4	<22.4	<22.4
15.	p,ṕ-DDD	3.93	<3.93	<3.93
16.	o,ṕ-DDT	4.11	<4.11	<4.11
17.	o,ṕ-DDT	7.12	<7.12	<7.12
18.	Mirex	2.80	<2.80	<2.80

Overall, the *p,p'*-DDE was the dominant OCPs contaminant detected in all of the biota samples followed by α–BHC and γ-BHC in sea bass and squid samples, respectively. This shows the presence of these OCPs in Arabian Sea as well as their absorption in the bodies of sea life. These results imply that the bioaccumulation of OCPs in sea biota is species-specific due to their ecological characteristics such as feeding habits and habitat. Organochlorine pesticides including DDT remained widely in use in Pakistan as pesticide, herbicide and fungicide. These OCPs can persist in the environment for 10-15 years. Compared to water, OCPs are more soluble in the fatty tissues and the chemical properties of lipid solubility results in the ability to pass through biological phospholipid membranes and bioaccumulation in the fatty tissues of living organisms.

The proportion of different forms of OCPs also reflects the composition profile in the environment. Source tracking of OCPs in the river system is very important to mitigate the possible hazards to human and aquatic life. During the green revolution in the country, some of the OCPs were imported from Europe and the USA in later 1960s and early 1970s. Dichlorodiphenyltrichloroethane (DDT) and benzene hexachloride (BHC) were locally produced. In this period, responsibility of pesticide imports and distribution was shifted from public to private sector in 1980 and subsidies on pesticides were eliminated. As such no mechanism was developed by the government for these stockpiles comprising banned compounds like OCPs. Similarly, restricting the production or usage of DDTs and other OCPs after Pakistan signed the Stockholm Convention on the Persistent Organic Pollutant in 2001 left behind the large stock of banned pesticides (Alamdar et al., 2014). About 6033 metric tons of outdated pesticides were left in Pakistan (Crawford et al., 2022), which according to Ministry of Climate Change are now estimated to be reduced to 275 tons (134 tons in Sindh, followed by 66 tons in Punjab, 60 tons in Baluchistan and 15 tons in KP). However, a Netherlands-funded programme in Pakistan carried out by the German Agency for Technical Cooperation has identified 917 tons of obsolete pesticides in 133 stores in Punjab (Sana et al., 2021). Major part of these large stocks of obsolete pesticides is situated in areas of intensive agricultural region including cash crop cultivated areas. Since stockpiles are located in towns or villages and near water bodies, there are high probability of their leakage from old, rusted and broken containers posing potential risks to human and environment (Sajid, 2018).

Potential Health Implications

Human exposure to OCPs is through inhalation from environment and ingestion from contaminated foods, such as fish, dairy products and other foods with higher fat contents. OCPs exposure has been reported to cause wide range of effects on human and environmental health as listed below;

a) Long-term exposure in humans can have serious health effects, including damage to the liver, kidney, thyroid gland, bladder, and central nervous system as well as serious reproductive problems (Yilmaz et al., 2020).

b) DDT has been reported to cause disastrous effects on the reproductive abilities of birds, fish, and marine animals, and thus it was banned.

c) Aldrin is a pesticide applied to soils to control termites, grasshoppers, corn rootworm, and other pests. Humans are mostly exposed to aldrin through dairy products and animal meats.

d) Dieldrin was the second most common pesticide in pasteurized milk which can result in adverse health effects such as headaches, giddiness, muscle twitching, convulsions, and loss of consciousness in workers spraying dieldrin (Daniel, 2007).

e) USEPA has estimated that exposure of aldrin and dieldrin through drinking water at concentrations of 0.0046 ng/L and 0.0044 ng/L, respectively would result in a lifetime cancer risk of 10^{-6} (Kuzmanovic et al., 2014).

3.4 Conclusions

The trends of OCPs in different environmental matrices (water, sediments, biota) of Pakistan reveals that α-HCH, β-HCH dichlorodiphenyltrichloroethane (DDT), and endosulfans were the most persistent OCPs residues in aquatic environment. Of different OCP types, highest levels of DDT may be due to the fact that a large amount of it was produced and used in the previous decades and the usage still continues in different areas of the country. Even banning after years ago in the developed world, extensive use of OCPs containing pesticides continue in Pakistan and possibly also in neighbouring countries.

Future research should prioritize testing of OCPs in the biomarkers and food chain, especially in areas where OCPs are used frequently. Training of farmers and other users on handling, storage and disposal of pesticides is also needed to control this issue.

Chapter 4: Polychlorinated Biphenyls & Polybrominated Diphenyl Ethers

4.1 Introduction

Polychlorinated biphenyls (PCBs), a group of 209 congeners, are a family of hydrophobic chlorinated compounds characterized by high persistence, toxicity, bio-accumulative properties and widespread distribution in the environment. Considering the best dielectric properties, thermal stability, and resistance to oxidation, PCBs were used as cooling fluids in capacitors, transformers, and other electrical and non-electrical products such as transmission fluids, plastics, lubricants, adhesives, pigments/paints, and other metal coating compounds (Trinh and Chang, 2018). These compounds were first synthesized in 1929 and used extensively for different industrial applications during 1970s. Its manufacturing, processing and distribution was banned in the USA. Despite this ban, evidence showed presence of their residues in the environment indicating continuous usage (Davies and Delistraty, 2016). It is estimated that more than half of the PCBs produced have been released into the environment through sources indicated in Figure 4.1 (National Research Council, 2001).

Figure 4.1: Sources of release of PCBs in the environment

Untreated industrial and domestic wastewater transports the PCBs to rivers and linked tributaries. PCB congeners have a strong affinity to bind with suspended matter particulates in the aquatic environment and eventually, sink and accumulate in the sediments (Mahmood et al., 2014).

Polybrominated diphenyl ethers (PBDEs) are a class of synthetic halogenated organic compounds used in numerous polymer-based commercial and household products including textiles, furniture and electronics to enhance their flame ignition resistance and to meet fire safety standards (Ni et al., 2013). PCBs and PBDEs have attracted more and more attentions due to their potential toxicity, durability and bioaccumulation. Considering this, PCBs and PBDEs were monitored in the water bodies and sediments with the following objectives:

a) Assessment of status and spatio-temporal variations of PCBs and PBDEs in the river system.

b) Providing samples, data, and other information to assist in developing risk management practices for reducing exposure to PCBs and PBDEs.

4.2 Materials and Methods

4.2.1 Monitoring of PCBs (2009)

4.2.1.1 Water Sampling for PCBs

Samples collection, extraction and analysis were performed following SOPs given in the manual "Determination of PCB in water by GCMS, UNU-ISP Shimadzu Japan, 2009". As per sampling plan, 19 sampling sites were selected from rivers and Arabian Sea along the coast line (Figure 2). In November and December 2009, only surface water samples were collected from these locations having temperature of 14 to 34 °C (Annexure III). Samples were collected in 1 litre amber colored glass bottles. Replicate samples in one litre bottle were collected from each location to get total volume of two litres. These samples in insulated ice boxes, kept away from direct sunlight, were immediately transported to the National Water Quality Laboratory, PCRWR Islamabad, where the samples were refrigerated. Within next 3 days, these samples were processed for extraction and analysis.

4.2.1.2 Pre-treatment of Water Samples

Replicate water samples collected in glass bottles were extracted with hexane and then cleaned with 44% H_2SO_4 coated silica SPE cartridges.

4.2.1.3 Calibration Standards

PCBs were analyzed on Shimadzu GC/MS-QP 2010, Japan. Calibration standards of selected congeners were used for method calibration on GCMS. These included PCBs, CB-l (2-Chlorobiphenyl), CB-4 (2,2'-Dichlorobiphenyl) & 10 (2,6-Dichlorobiphenyl), CB-8 (2,4'-Dichlorobiphenyl), CB-18 (2,2',5-Trichlorobiphenyl), CB-44 (2,2',3,5'-Tetrachlorobiphenyl), CB-37 (3,4,4'-Trichlorobiphenyl), CB-74 (2,4,4',5-Tetrachlorobiphenyl), CB-99 (2,4,4',5-Tetrachlorobiphenyl) & 150 (2,2',3,4',6,6'-Hexachlorobiphenyl), CB-118 (2,3',4,4',5-Pentachlorobiphenyl), CB-153 (2,2',4,4',5,5'-Hexachlorobiphenyl), CB-156 (2,3,3',4,4',5-Hexachlorobiphenyl), CB-189

(2,3,3',4,4',5,5'-Heptachlorobiphenyl), CB-195 (2,2',3,3',4,4',5,6-Octachlorobiphenyl), CB-194 (2,2',3,3',4,4',5,5-Octachlorobiphenyl), 'CB-206 (2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl) and CB-209 (Decachlorobiphenyl).

4.2.1.4 Data Extraction and Interpretation

On the basis of isotope dilution methods, total PCBs were calculated by excel software, provided by the Shimadzu Corporation, Japan. For the recovery check, ^{l3}C labelled surrogated standards were used. Perylene-d12 was used as internal standard. 4 µL of 10 µg/L standard were injected for repeatability studies. 3S (3XSD) and l0S (10XSD) were calculated from repeatability studies.10S was designated as the limit of quantification (LOQ) and 3S as the instrument detection limit (IDL). LOQs of CB#189, CB#195, CB#194, CB#206 and CB#209 were bit higher than the rest of the PCBs. Repeatability studies of surrogated standards showed a gradual increase from lower to higher molecular weight of PCBs.

4.2.2 Monitoring of PBDEs (2011)

4.2.2.1 Sediments Sampling for PBDEs

Sediment samples were collected in February, 2011 from the pre-selected 19 sites of selected rivers and coastal line for monitoring of PBDEs (Figure 4.2). Detail of sampling sites is given at Annexure IV. Glass bottles of 100 ml were used for sediments collection and were kept in insulated ice boxes to keep away from direct sunlight at low temperature and transported immediately to laboratory, where these samples were stored in freezers at -20 °C.

Sediments collection from river

Sediments samples field observations

Sediments samples bottles labelling

Figure 4.2: Sediment samples collection from various sites of monitoring areas

4.2.2.2 Pre-treatment and Testing of Sediment Samples

Completely dried sediment samples of 10 g were extracted in a Soxhlet extractor with toluene. Dichloromethane (DCM)-H_2SO_4 and DCM-NaOH solutions were used for sequential extractions. DCM was exchanged with hexane and further clean-up was done with florisil SPE cartridges. The extracts were analysed by GC/MS using the isotopic dilution method via SIM mode. Activated florisil and silica gel were used by activating them in an oven at 150°C for three days. Glass wool was kept at 450°C for four hours in a muffle furnace to make it dry and free of residues. Retention times of alkane were used for the predictions of retention times of targeted PBDEs.

4.2.2.3 PBDEs Calibration Standards

For calibration, tri-BDE (BDE-028), tetra-BDE (BDE-47), penta-BDE (BDE-l00), penta-BDE (BDE-99), hexa-BDE(BDE-154), hexa-BDE(BDE-l53), hepta-BDE(BDE-183) and deca-BDE(BDE-209) standards were used. On the basis of calibration, ∑PBDEs were calculated by Microsoft Excel formula provided by the Shimadzu Corporation, Japan.

4.2.2.4 Quality Control Recovery Data

Repeatability studies of five samples spiked with 10 µg/L standard passed criteria for recovery %RSD of native BDEs (except deca-BDE 209), whereas labelled BDEs fail to qualify the same criteria. Average percent recovery of both native BDEs and labelled BDEs did not pass the criteria.

This study shows that only deca-BDE 209 accounts for 84% of total concentration of PBDEs, otherwise only two BDE congeners (penta-99 and hepta-183) were found at four sites (Mangla, Sulemanki, Rasool and Tarimu).

4.2.2.5 PBDEs Data Extraction and Interpretation

- For QA/QC, degradation of *p,p-DDT* was checked, which was within limits.
- Auto-tuning results were within the limits, where Full Width Half Maximum (FWHM), detector voltages, base peak, relative intensity o f m/z 69 and mass number shift at *m/z* 131.0, 219.0, 414.0, 502.0 and 614.0 were checked and found within limits.
- Instrument performance was checked with the help of mass number shift of deca-BDE, degradation of p,p-DDT, tailing factor ^{13}C penta BDE (BDE-99L) and sensitivity of native and labelled the BDEs.
- The mass number shift of m/z 719.5, 799.5 and 959.4 were less than ± 0.3.
- Column performance was checked and was found in range.
- Sensitivity of 10 µg/L standard was checked and found in limits. In batch analysis of samples, 100 µg/L standards were used to check the calibration of the instrument.
- For the limit of quantifications (LOQ), five samples were spiked with 1 ml of 10 µg/L, labelled surrogate, labelled surrogate and internal standard were analyzed individually. The repeatability of native BDEs were kept under 20%. 10S was designed as LOQ.
- For the linearity of calibration check, %RSD was kept within 20%.
- Average percent recoveries of native BDEs (except deca-BDE 209) were found within range but labelled BDEs show variations in both in average percent recovery and %RSD allowance. The native BDEs showed low percent recoveries and within range %RSD, whereas average percent recoveries of labelled BDEs were within limit (except deca-BDE) but the allowance for %RSD (except deca-BDE) varies slightly from 20%.

4.3 Results and Discussion

4.3.1 PCBs in Surface Water (2009)

LOQs, minimum and maximum concentration (ng/L) of individual selected congeners of PCBs in surface water samples is given in Table 4.1. Percent recovery studies showed that only octa and nona CBs (PCB#l94 and PCB #206) have standard deviation (SD) more than 5 (7.31 and 6.42, respectively): other PCBs have shown SD of <5%. The most prevalent compound is CB-37 followed by CB-1, CB-18 and CB-74.

Table 4.1: LOQs, minimum and maximum concentration (ng/L) of PCBs in surface water samples (2009)

Sr. No.	PCBs Congener	PCBs Compound	LOQ	Minimum	Maximum
1	CB 1	Monochlorobiphenyls	2.40	2.61	14.2
2	CB 10 & 4	Dichlorobiphenyls	1.90	ND	ND
3	CB 8	Dichlorobiphenyls	2.20	ND	7.54
4	CB 18	Trichlorobiphenyls	1.30	1.89	12.1
5	CB 44	Tetrachlorobiphenyls	0.90	1.06	3.30
6	CB 37	Trichlorobiphenyls	1.20	1.30	17.7
7	CB 74	Tetrachlorobiphenyls	1.70	1.83	5.36
8	CB 99 & 150	Hexachlorobiphenyls	1.70	ND	ND
9	CB 118	Pentachlorobiphenyls	1.30	ND	5.69
10	CB 153	Hexachlorobiphenyls	2.40	ND	ND
11	CB 156	Hexachlorobiphenyls	2.70	ND	ND
12	CB 189	Heptachlorobiphenyls	4.80	ND	ND
13	CB 195	Octachlorobiphenyls	4.70	ND	ND
14	CB 194	Nonachlorobiphenyl	5.90	ND	ND
15	CB 206	Decachlorobiphenyls	4.00	ND	ND
19	CB 209	Decachlorobiphenyls	6.60	ND	ND

Comparing the samples test data with LOQs (Table 4.1) reveals the detection of PCBs within the range of 1.06 to 17.72 ng/L. Maximum concentration of CB-37 (17.72 ng/L) was found at Taunsa Barrage followed by 8.69 ng/L at Arabian Sea coast line sampling site I, 6.43 ng/L at Head Islam and 5.67 ng/L at Mangla Dam (Figure 4.3).

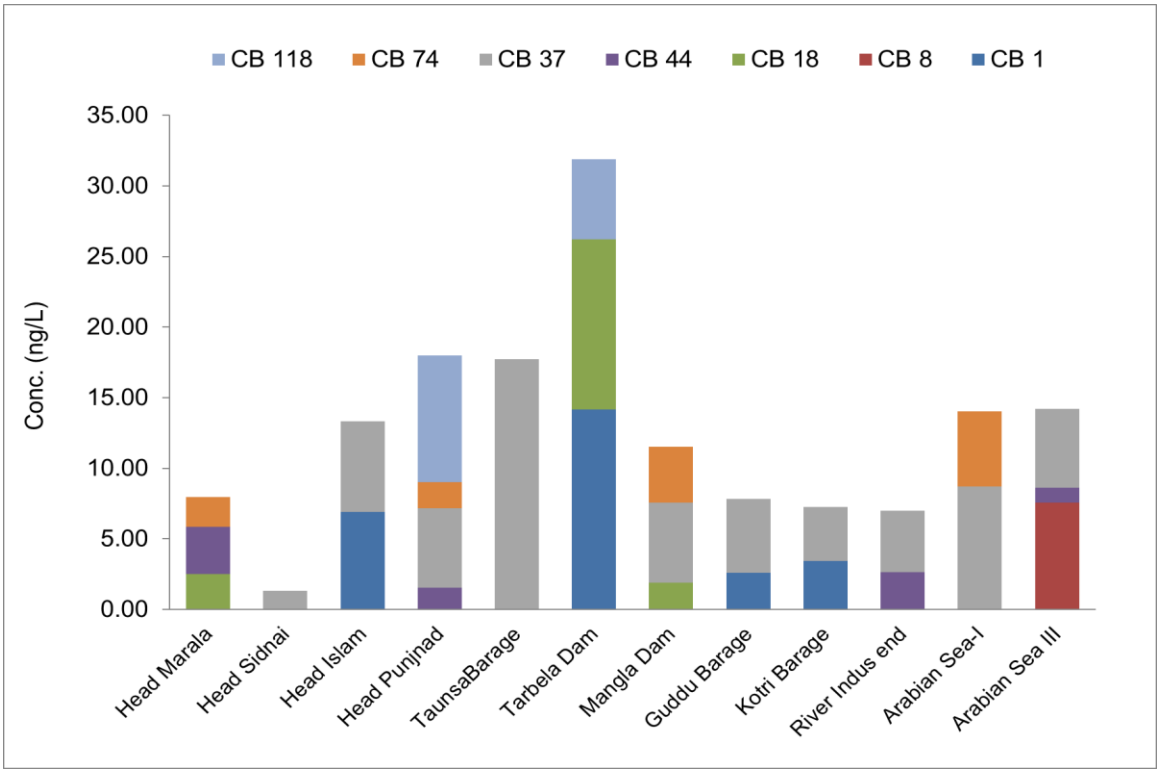


Figure 4.3: Concentration of PCBs (ng/L) in surface water (2009)

The highest concentration of CB-1 (14.16 ng/L) at Tarbela was followed by 6.91 ng/L at Head Islam and 3.4 ng/L at Kotri. The highest concentration of CB-18 was found at Tarbela Dam (12.05 ng/L) followed by 2.52 ng/L at Head Marala and 1.89 ng/L at Mangla Dam. Similarly highest concentration of CB-74 (5.35 ng/L) was detected at Arabian Sea site I followed by 3.93 ng/L at Mangla Dam. Whereas, the CB-118 (5.68 ng/L), CB-8 (7.54 ng/L) and CB-44 (3.304 ng/L) were only detected at Tarbela Dam, Arabian Sea site II and Head Marala, respectively. The insulating and cooling agents in electrical equipment (capacitors and transformers and transformer oil containing PCBs) are probably the major sources of PCBs contamination specifically at Mangla and Tarbela dams. Out of 19 samples, 12 (63%) were detected with PCBs and thus considered as contaminated as depicted in the characterisation of PCBs (Figure 4.4).

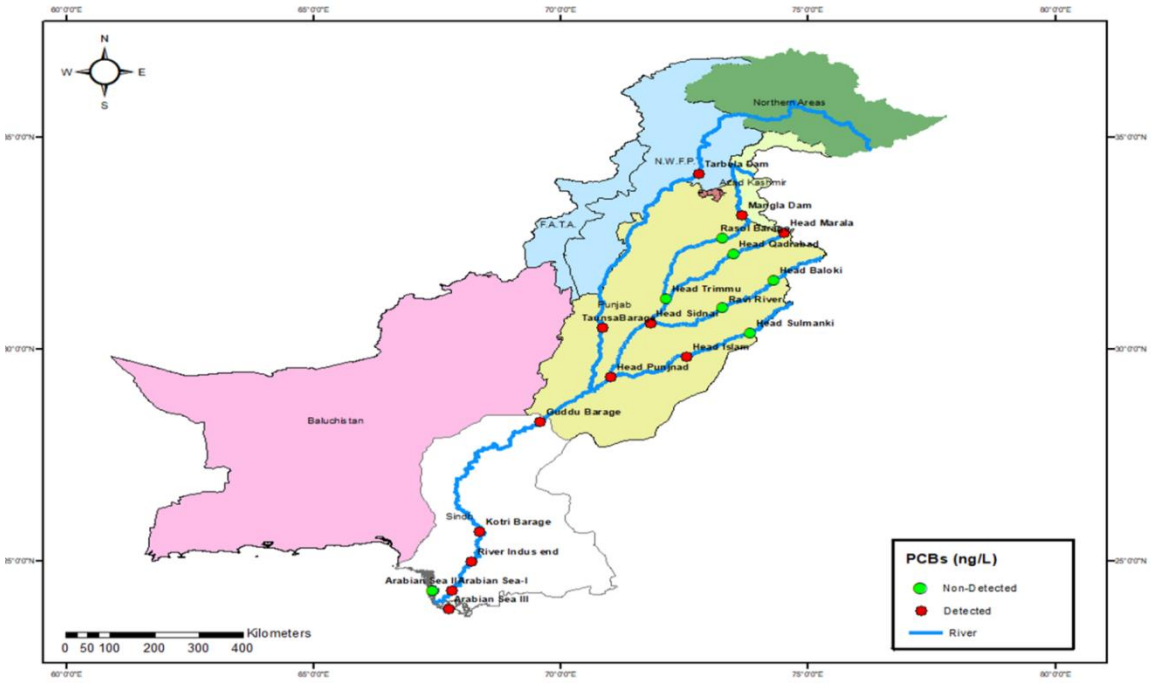


Figure 4.4: Characterisation of distribution of ΣPCBs (ng/L) in surface water sites during wet season (2009)

In general, ΣPCBs revealed Tarbela dam (31.90 ng/L) to be the most contaminated site due to 2-Chlorobiphenyl (CB-1), 2,2',5-Trichlorobiphenyl (CB-18), and 2,3',4,4',5-Pentachlorobiphenyl (CB-118) followed by the Taunsa Barrage (17.72 ng/L), Arabian Sea (14.21 ng/L), Head Islam (13.34 ng/L) Mangla Dam (11.5 ng/L), Head Panjnad (9.01 ng/L), Head Marala (7.96 ng/L), Guddu Barrage (7.82 ng/L), Kotri Barrage (7.24 ng/L), end of Indus river (7 ng/L) and Head Sidhnai (1.3 ng/L) probably due to release from the hydropower plants. The electrical appliances and leakages from transformer oil could be the potential source of PCBs contamination in the above mentioned water bodies. This form of environmental pollution with negative influence on human health would not be possible without the utilization of high-voltage industrial electrical equipment having dielectric fluids contaminated with different polychlorinated biphenyl isomers.

PCB congeners have a strong affinity to bind with suspended matter particulates in the aquatic environment and eventually, sink and accumulate in the sediments (Gardes et al., 2020). Thus, hydropower, industrial and domestic discharges are possibly disposing the PCBs to water bodies and environment in Pakistan. Such PCBs bio-accumulate in various lower trophic organisms moving up the food chain through plankton, bivalve mollusks, fish, reptiles, marine mammals, birds and terrestrial mammals as conceptualized in Figure 4.5.

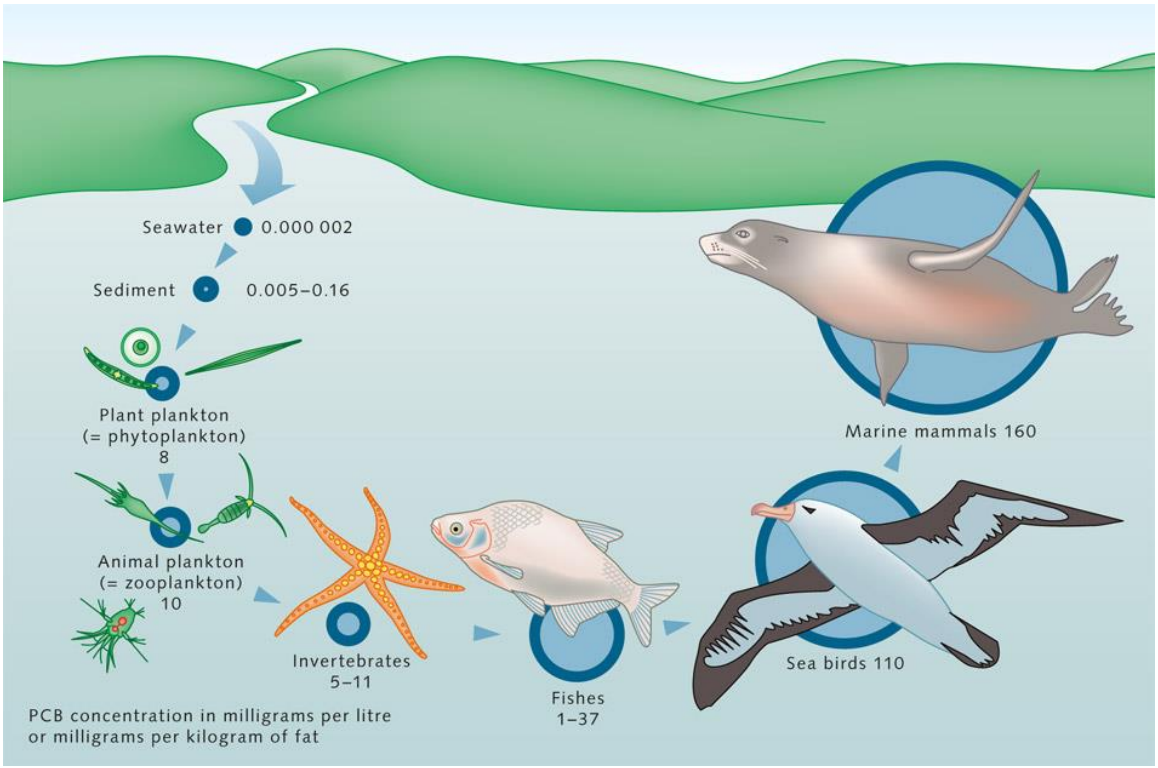


Figure 4.5: PCBs in marine environment and accumulation in Sea life (Adopted from Allsopp et al., 2008)

4.3.2 PBDEs in Sediments (2009)

PBDEs as organo-bromine compounds are composed of two phenyl rings linked by an oxygen bridge (ether linkage). Theoretically, 209 unique PBDE structures (congeners) exist. Congeners with the same number of bromine atoms are referred to as a homologue, and thus, there are ten homologues ranging from mono- to deca BDEs. For example, a PBDE with ten bromines is called deca BDE; and five bromines are known as penta BDE. In 2009, the total concentration of deca-BDEs in sediments ranged from minimum106 ng/g dry weight (dry wt.) at Guddu to maximum 65231 ng/g (dry wt.) at Qadirabad (Table 4.2). At the Ravi River near Indian border, the detected concentration of deca-BDE was 28118 ng/g (dry wt.). Panjnad is a joining point of major rivers, where the third highest concentration of deca-BDE 209 was detected (8618 ng/g dry wt.). Deca-BDE 209 was detected in 16 samples with variable recoveries.

Table 4.2: Concentration (ng/L) of PBDEs in sediment samples

PBDEs in Sediments	Locations	Concentrations (ng/g)
Deca-BDEs	Guddu	106
	Qadirabad	65,231
	Ravi	28,118
	Panjnad	8,618
Penta-BDE	Mangla	500
	Sulemanki	3,834
	Rasool	2,489
Hepta-BDE	Sulemanki	11,345
	Tarimu	76.7
	Mangla	82.6
	Rasool	196

The highest concentration of Penta-BDE was found at Sulemanki (3834 ng/g dry wt.) followed by Rasool (2489 ng/g dry wt.) and Mangla (500 ng/g dry wt.) as given in Table 4.2. The highest concentrations of hepta-BDE was detected at Sulemanki (11345 ng/g, dry wt.), followed by Rasool, Mangla and Traimu. With semi-quantitative analysis, BDE compounds such as mono-BDEs, di-BDEs, hexa-BDEs and hepta-BDEs were detected at 18 sites with various levels, whereas both tri-BDEs and tetra-BDEs were not found at any site.

Overall, deca-BDE-209 was the dominant PBDE contaminant detected in a total of 16 sediment samples. Deca-PBDE (BDE-209) is the only commercial PBDE mixtures still allowed for use and may be the reason for its high concentration (Moon et al., 2012). However, its analysis in samples is tricky because of its complicated nature. Though detection of PBDEs in sediments is not a surprise but a serious concern as POPs have low water solubility but bond strongly to particulate matter in aquatic sediments. Thus, sediments can serve as reservoirs or "sinks" for POPs. When sequestered in these sediments, POPs can be taken out of circulation for long periods of time. If disturbed, however, they can be reintroduced into the ecosystem and food chain, potentially becoming a source of local, and even global, contamination (Chakrabarti, 2011).

4.4 Potential Health Impacts

a. A variety of human health issues including neurological, immunological, and reproductive problems have been reported due to PCB exposure.

b. PCBs are known to cause a variety of types of cancer in rats, mice and other study animals (ATSDR, 2000; Abu-Helil and van der Weyden, 2019).The International Agency for Research on Cancer classify PCBs as a probable

human carcinogen (IARC, 2016). Studies of PCBs in humans have found increased rates of melanomas, liver cancer, gall bladder cancer, biliary tract cancer, gastrointestinal tract cancer and brain cancer and may be linked to breast cancer.

c. Long-term exposure may affect the liver functioning and mutation in DNA leading to developmental defects. PCBs are considered as “endocrine disrupting” chemicals, and their exposure may cause thyroid hormone dysfunctioning by reducing serum concentration (Wang et al., 2016).

4.5 Conclusions

PCBs were detected in 12 (63%) of the 19 water sources with higher levels at Mangla and Tarbela dams and other surface water sources.

Detection of PBDEs in 84% of the sediments samples collected from strategic locations indicate the wastes coming in river system from textiles, furniture, and electronics and fire safety industries.

In conclusion, hydropower, industrial and domestic disposals are the possible causes of the PCBs and PBDEs in water bodies and environment of Pakistan. A continued long-term monitoring of these organic contaminants in environmental matrices is needed in order to assess the potential risk for human health.

Chapter 5: Monitoring of Per-Fluorinated Compounds

5.1 Introduction:

The Perfluorinated compounds (PFCs) are persistent toxic compounds of non-natural origin which were identified in the environment at the end of the 1990s. PFCs are widely used in industrial, agricultural and commercial productions for its unique stabilities. PFCs are a class of chemicals used to repel oil and water from clothing, carpeting, furniture, food packaging and non-stick surfaces on cookware. Locations that may possibly release PFCs in the environment are indicated as Figure 5.1.

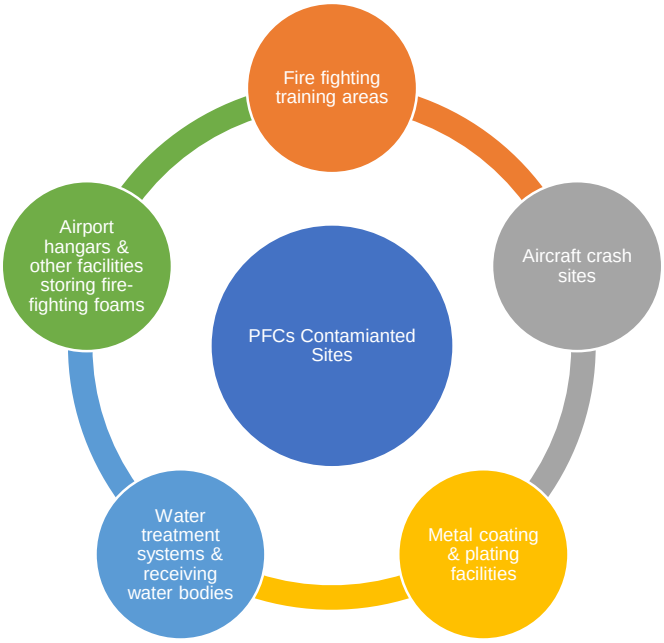


Figure 5.1: Contaminated sites resulting in release of PFCs in the environment

The production and application of PFCs are officially restricted. However, these are still being used for their versatility and hence exist in the global environment, including air, water, sediments, marine, terrestrial life, human plasma and remote polar regions (Zhang et al., 2021). Though major global manufacturers of PFCs were asked to stop production in 2002, however, PFCs were found in surface water of several countries (Zhang et al., 2021).

PFCs are transported through two main pathways such as atmospheric transmission and aquatic transmission. Aquatic transmission is the primary transport/pathway of PFCs in the environment, for its solubility and polarity. In the aquatic environment, sediment plays a vital role in the fate of PFCs, and sediment-adsorbed PFCs are a contamination source to the surrounding water and aquatic biota. Aquatic plants are an essential medium for pollutants from the aquatic environment to the food chain. Attributed to the, characteristics of persistence,

bioaccumulation, and ecotoxicity, PFCs pose potential risk to the human and environmental health. Therefore, it was crucial to monitor the concentration of PFCs in water bodies of Pakistan. Following were the objectives:

a. Determine the current status and extent of PFCs concentrations in surface and groundwater, sediment, and biota.
b. Assess the potential risk of PFC to both humans and wildlife by determining their compositions.
c. Evaluate the impact of seasonal variation on the potential ecological risk of PFCs in water bodies.

5.2 Materials and Methods

5.2.1 Water Sampling (2013-14)

Surface water monitoring for PFCs was undertaken in dry and wet seasons from 2013 and onward. Dry season samples were collected in December-January, 2013 and wet season in July-August, 2014. Sampling sites were almost same as sampled for the past investigation of PCBs and PBDEs (Table 2.1). In total, 24 samples were collected for PFCs separately in dry and wet seasons of 2015 i.e. 19 samples from pre-selected fixed sites, while two samples were collected from the Rawal and Simly reservoirs lakes near the capital territory providing drinking water to Islamabad and Rawalpindi, one sample from river Kabul where it joins river Indus and two additional samples were collected from the Arabian Sea. These water samples were collected each in 1 litre glass bottle and replicate samples were collected from each site to have total volume of 2 litres. Samples were immediately placed in insulated ice boxes kept away from direct sunlight and transported to National Water Quality Laboratory of PCRWR, Islamabad, where these were refrigerated till extraction.

Pre-treatment of Water Samples for PFCs

1. 1000 ml water sample was collected in volumetric cylinder funnel. Surrogate was diluted from 2 mg/L to 50 µg/L and added 1 ml to 1000 ml sample (Figure 5.1).
2. Sample was filtered from 60 micron filter and the filter was washed with methanol.
3. The WAX cartridge was activated by 4 ml of 0.1% NH_4OH, 4 ml of Methyl alcohol and 6 ml of purified water.
4. Samples were then passed through the activated cartridge with 3 ml/minute flow rate.
5. After passing the whole sample through the cartridge, the elution was made with 0.1% NH_4OH in Methanol slowly. The elution was concentrated with nitrogen purging. Volume was reconstituted to 5 ml.

6. Sample extracts were stored in refrigerator and later shifted to Chonnam National University (CNU), Yeosu South Korea for analysis on Liquid Chromatograph Mass Spectrometer-Mass Spectrometer (LC-MS/MS). Figure 5.2 shows a complete process of pre-treatment.

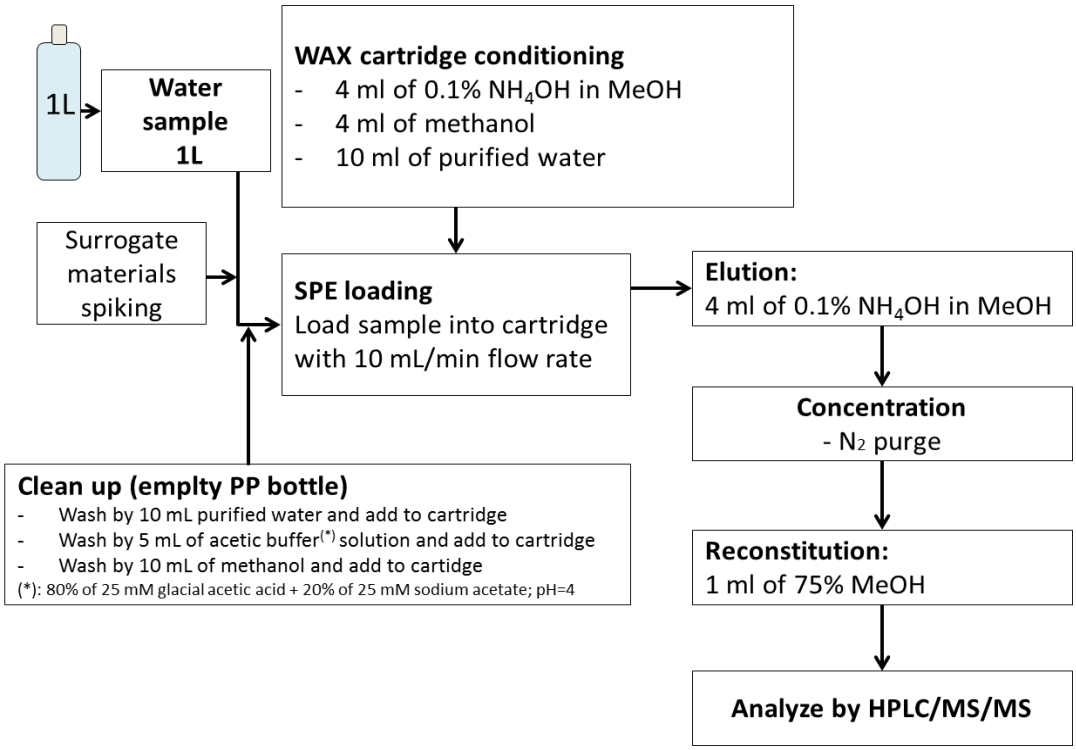


Figure 5.2: Schematic diagram showing the complete process of pre-treatment for PFCs analysis

5.2.2 Sampling of Surface Water, Groundwater and Sediments Samples (2016)

Water and sediment samples from surface water sites and their nearby groundwater sources (mostly hand pumps) were collected in dry season (November to December, 2016). Detail of sampling sites is given at Annexure V. All the samples (total 57 samples19 in each category surface, groundwater and sediments) were collected following the procedure given earlier in Section 5.2.1.

5.2.2.1 Pre-treatment of Sediment and Water Samples (2016)

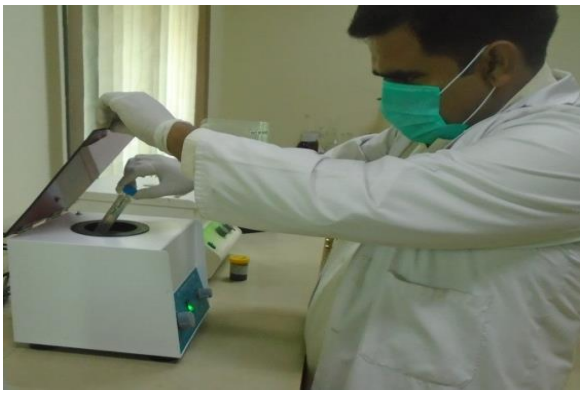
Pre-treatment of sediment samples was undertaken adopting standard procedure provided by the Shimadzu Cooperation, Japan (Pre-Treatment of Sediment Samples, 2015). Sediment samples (1000 g) were collected, sieved through 2 mm sieve, and centrifuged to separate water from sediments, and wet bottom sediments were collected in tubes, weighed and dried. In dried sediments, added the surrogate (1 ml) of 5 µg/L internal standard. Then 10 ml of 20% methanol was added, sonicated and centrifuged. Supernatant was collected repeating the process till final volume made up to 20 ml and the final process was completed using solid phase extraction (Figure 5.3).

One millilitre of 5 µg/L internal standard was added in 1 L of water sample and after solid phase extraction, 500 ml water sample was collected as extract for testing. All the prepared sediments and water samples were transported under controlled conditions to Korea for analysis on Liquid Chromatograph Mass Spectrometer-Mass Spectrometer (LCMS/MS) in Chonnam University, Korea.

Sediments sieved from 2 mm sieve

Weighing of samples

Drying of sediment samples



Centrifugation for extraction

Figure 5.3: Pre-treatment of sediment samples for PFCs

5.2.3 Sampling of Water, Sediment and Biota (2017-18)

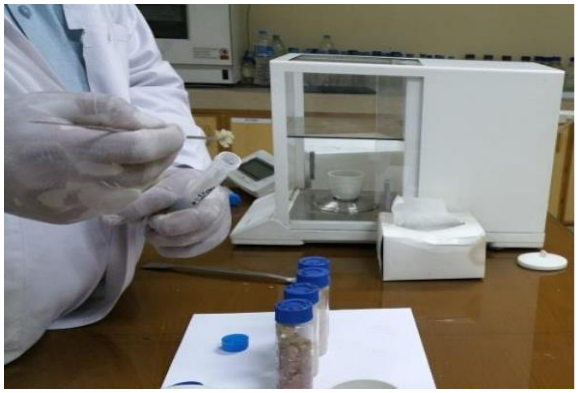
Altogether 67 samples such as; surface water (24 samples in wet and 11 samples in dry season), sediment (15 samples in wet and 11 samples in dry season) and biota (5 samples) were collected from pre-defined sites during dry and wet seasons for the analysis of PFCs.

5.2.3.1 Pre-treatment of Water, Sediment and Biota Samples

Water and sediments samples were prepared as given in the Sections 5.2.1 and 5.2.2. However, the pre-treatment process of fish samples for PFCs comprised homogenization, extraction and centrifugation steps explained below:

- **Homogenization:** Fish sample was cut into small blocks and was homogenized in homogenizer, 10 g of each homogenized sample was weighed in centrifuge bottle and 50 µL of 100 µg/l internal-standard was added.
- **Extraction:** 10 mL of methanol was added as extraction solvent, shaken by hand and ultra-sonicated for 10 minutes. Following sonication, centrifugation was done and the supernatant was collected. 10 mL of methanol was added again to the remaining in centrifuge bottles, supernatant was collected and repeated the steps of sonication and centrifugation.
- **Collection of filtrate and concentrate:** Extracted sample solution was combined (approx. 20 ml), and supernatant was filtered using Wattman filter paper (1 µm). The sample volume was reduced by using rotary evaporator (approx. 5 ml). Finally, volume is made up to 20 ml by adding water sample and further processing by using solid phase extraction.

All samples were processed in National Water Quality Laboratory (NWQL) of PCRWR (Figures 5.4) and analysed on LC-MS/MS available in Shimadzu Asia Pacific Centre Singapore.



Weighing of biota samples

Homogenization process

Centrifugation of biota samples

Extraction with methanol

Figure 5.4: Biota Sample Pre-treatment for PFCs in National Water Quality Laboratory Islamabad

5.2.4 Sampling of Water, Sediment and Biota (2018-19)

Forty-four samples i.e. surface water (16), sediments (16), groundwater (9) and fish (03) were collected from earlier sampled surface water sites during wet season (August-September, 2018). Sediment and fish samples were also collected from close proximity to surface water sites. All samples were collected and processed following the UNU procedures referred earlier in Sections 5.2.1, 5.2.2 and 5.2.3. The auto-sampler was used for the collection of water and sediment samples. Detail of sampling sites is given at Annexure VII. All the samples processed in National Water Quality Laboratory (NWQL) of PCRWR Islamabad were transported to Shimadzu Asia Pacific Centre Singapore for testing on LCMS/MS.

5.3 Results and discussion

5.3.1 PFCs in Surface Water (2013-15)

5.3.1.1 The LOD and LOQ of Test Method

The Limits of Detection (LOD) was calculated as three times of Standard Deviation (SD) for the results of 0.5 µg/L standards of each compound, whereas Limit of Quantification (LOQ) was calculated by ten times of SD for the results of 0.5 µg/L standard of each compound (Table 5.1).

Table 5.1: LOQs & LODs of PFCs determined for surface water samples testing (2015-16)

Names of Compounds of PFCs	Abbreviations	Run-1	Run-2	Run-3	SD	LOD	LOQ
Perfluorobutanoic acid	PFBA	0.50	0.485	0.469	0.016	0.047	0.155
Perfluorohexanoic acid	PFHxA	0.588	0.546	0.548	0.024	0.071	0.237
Perfluorobutanesulfonic acid	PFBS	0.516	0.425	0.42	0.054	0.162	0.540
Perfluoroheptanoic acid	PFHpA	0.475	0.441	0.448	0.018	0.054	0.180
Perfluorooctanoic acid	PFOA	0.491	0.501	0.45	0.027	0.081	0.270
Perfluorohexane sulfonic acid	PFHxS	0.447	0.427	0.39	0.029	0.087	0.289
Perfluorononanoic acid	PFNA	0.466	0.44	0.439	0.015	0.046	0.153
Perfluorodecanoic acid	PFDA	0.414	0.369	0.405	0.024	0.071	0.238
Perfluorooctanesulfonic acid	PFOS	0.417	0.478	0.431	0.032	0.096	0.320
perfluoroundecanoic acid	PFUnDA	0.486	0.452	0.476	0.017	0.052	0.175
Perfluorododecanoic acid	PFDoDA	0.468	0.515	0.554	0.043	0.129	0.431
Perfluorodecyltriethoxysilane	PFDS	0.489	0.521	0.472	0.025	0.075	0.249
Perfluorotridecanoic acid	PFTrDA	0.556	0.563	0.604	0.026	0.078	0.259

5.3.1.2 Recovery Rates (%) of Surrogate

The Chonnam University had only provided the percent recoveries data of per-fluorooctanoic acid (PFOA) and Per-fluorooctane sulfonate (PFOS) for standards of different concentrations (Table 5.2). The data depicted the acceptable percent recoveries in most of the water and sediments samples.

Table 5.2: Percent recovery rates of PFCs standards (2015-16)

Sr #	PFOA Standards Run (codes)	% Recovery	PFOS Standards Run	% Recovery
1	SED-BLANK.1cd	95.92	SED-BLANK.lcd	119.02
2	SED-5ppb.1.1cd	99.86	STD- 5ppb-1.lcd	99.84
3	SED-5ppb.2.1cd	100.35	STD- 5ppb-2.lcd	85.15
4	SED-5ppb.3.1cd	99.79	STD- 5ppb-3.lcd	115.00
5	DW-1.lcd	107.42	DW-1.lcd	133.28
6	DW-9.1cd	95.54	DW-1.lcd	107.42
7	DW-13.1cd	97.47	DW-8.lcd	125.28
8	DW-15.1cd	101.05	DW-9.lcd	68.77
9	DW-19.1cd	83.57	DW-13.lcd	128.39
10	SW-1.1cd	87.73	DW-15.lcd	119.25
11	SW-8.1cd	82.78	DW-19.lcd	107.54
12	SW-9.1cd	85.76	SW-1.lcd	103.09
13	SW-13.1cd	61.60	SW-13.lcd	78.01
14	SW-15.1cd	80.38	SW-15.lcd	116.98
15	SW-19.1cd	89.24	SW-19.lcd	115.59
16	SD-1.1cd	64.74	SD-1.lcd	87.09
17	SD-2.1cd	89.22	SD-2.lcd	123.11
18	SD-3.1cd	88.06	SD-3.lcd	123.82
19	SD-5.lcd	75.76	SD-4.lcd	127.74
20	SD-6.lcd	76.14	SD-5.lcd	98.11
21	SD-7.lcd	80.38	SD-6.lcd	102.41
22	SD-8.lcd	76.09	SD-7.lcd	111.42
23	SD-9.lcd	89.04	SD-8.lcd	90.01
24	SD-10.lcd	92.10	SD-9.lcd	114.85
25	SD-11.lcd	29.80	SD-10.lcd	101.37
26	SD-12.lcd	79.45	SD-12.lcd	105.28
27	SD-13.lcd	70.79	SD-13.lcd	85.94
28	SD-14.lcd	75.92	SD-14.lcd	93.29

Sr #	PFOA Standards Run (codes)	% Recovery	PFOS Standards Run	% Recovery
29	SD-15.lcd	58.77	SD-15.lcd	70.19
30	SD-16.lcd	70.50	SD-16.lcd	96.23
31	SD-17.lcd	70.50	SD-17.lcd	85.77
32	SD-18.lcd	74.33	SD-18.lcd	101.57
33	SD-19.lcd	67.81		

The recoveries in surface and groundwater samples were good. However, some of the water and sediments samples were low in recoveries. The reason was found to be the sediments and water samples preparation by two different analytical methods.

5.3.2 Levels of PFCs in Surface Water (2013-15)

During 2013-2015, 48 surface water samples were collected (24 in dry season and same in wet season of the year 2013 and analyzed for PFCs. Although 12 different compounds were investigated, however the discussion will focus primarily on PFOS and PFOA since these compounds were consistently found at the greatest concentrations and are of toxicity concerns. Comparing with LOQs, analytical results showed the detection of PFOAs in wet and dry seasons ranging from 0.25 to 1.94 ng/L (Figures 5.5 and 5.6). The highest concentration of PFOA was found in Kabul river i.e. 1.94 ng/L in dry season which reduced to 1.26 ng/L during wet season. However, it was still the highest at all sites. PFOA were not detected at Tarbela and Guddu site in both seasons (Figures 5.5 and 5.6). Maximum concentration of PFOS was also detected in the Kabul River (12.15 ng/L) in dry season, which reduced to 5.34 ng/L during wet season probably due to dilution effect (Figure 5.5).

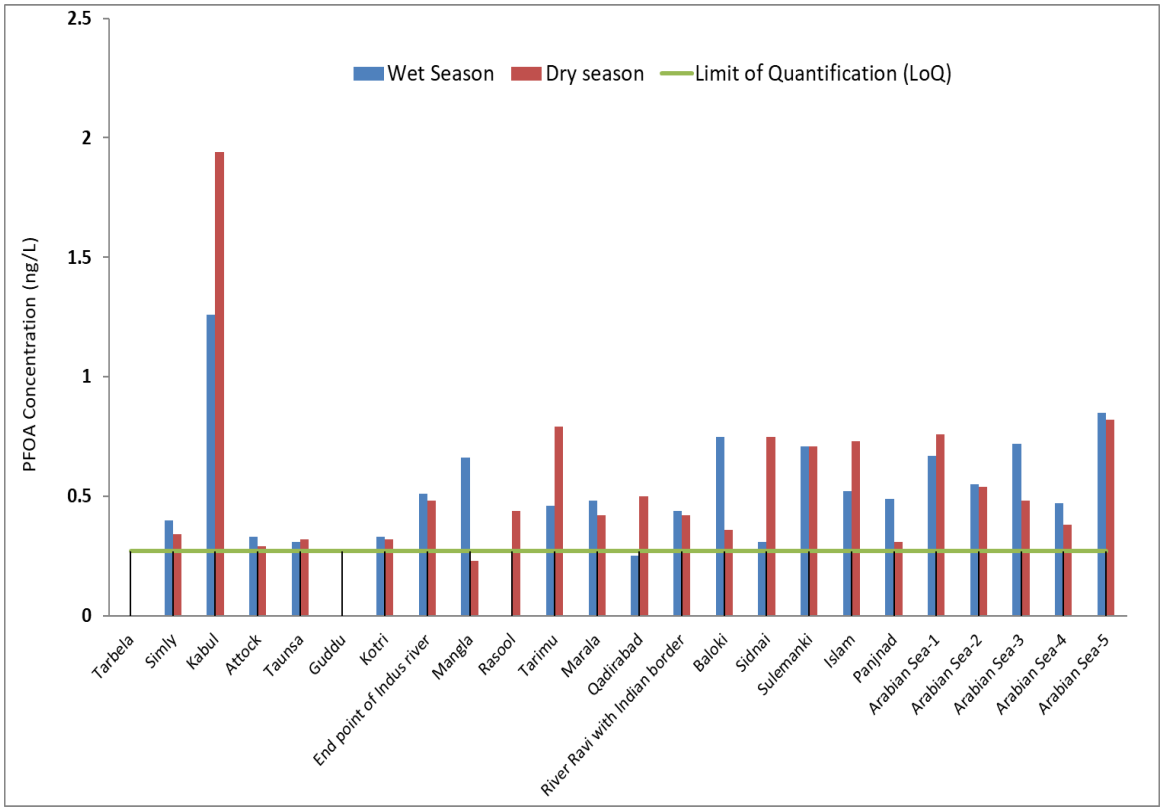


Figure 5.5: Concentration of PFOA (ng/L) in surface water sites (2013-15)

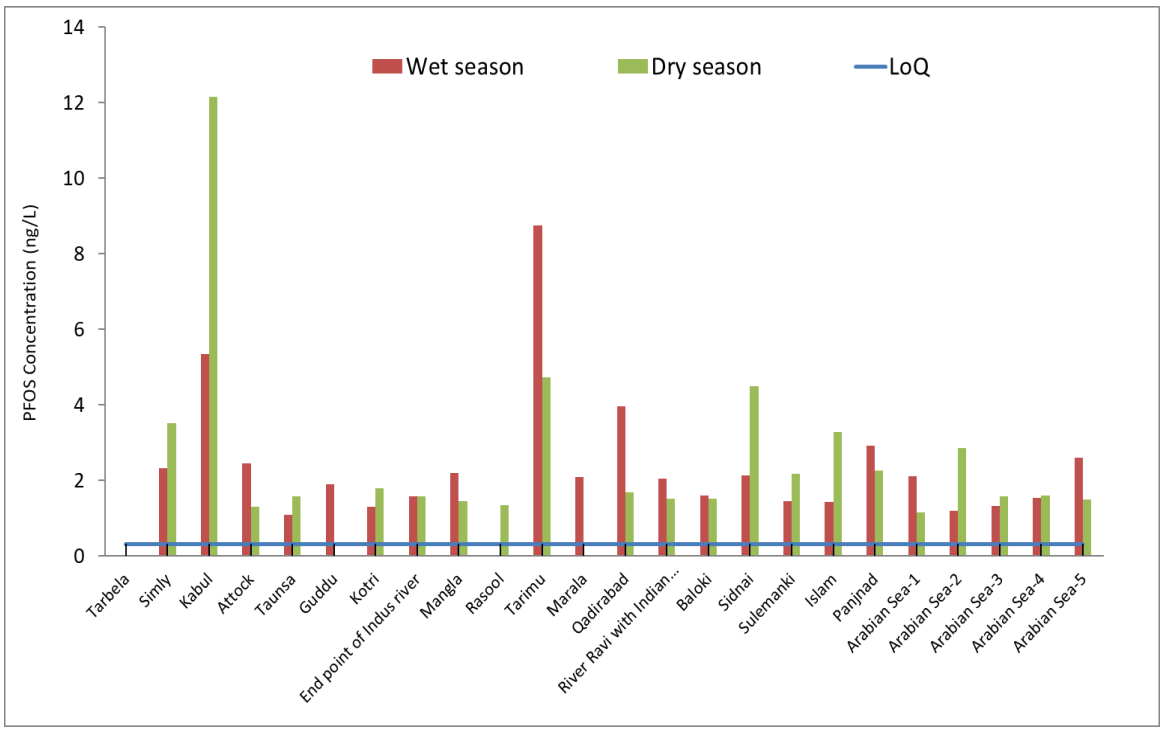


Figure 5.6: Concentration of PFOS (ng/L) in surface water sites (2013-15)

PFOS is used in the semiconductor industry, scotchgard formulation, and fire-fighting foam mixture. Whereas PFOA is used to make fluoro polymers such as Teflon (Lohmann et al., 2020). Kabul River after entering into Pakistan's passes Peshawar and Nowshera and joins the Indus River near Attock. The highest concentrations of PFCs found in the environment may be associated with direct discharge from industries, where PFCs are in use. This region is influenced by a variety of local industries encompassing steel/mechanical, electric/electronic and petro-chemical companies. Thus all of these local activities are thought to be potential sources for PFCs contamination.

During wet season (2014), the highest concentration of PFOS was found at Tarimu (river Chenab) i.e. 8.75 ng/L which reduced to 4.73 ng/L in dry season (Figure 5.6). Overall, the concentrations of PFOAs were comparatively lower than PFOS in both sampling times (Figures 5.5 and 5.6). The sum concentrations of PFOA and PFOS as ΣPFCs were higher in wet season possibly due to surrounding run off (Figures 5.7 & 5.8). The pesticides, chemical fertilizers and industrial waste from surrounding areas may probably be enhancing the level of restricted POPs in the riverine ecosystem.

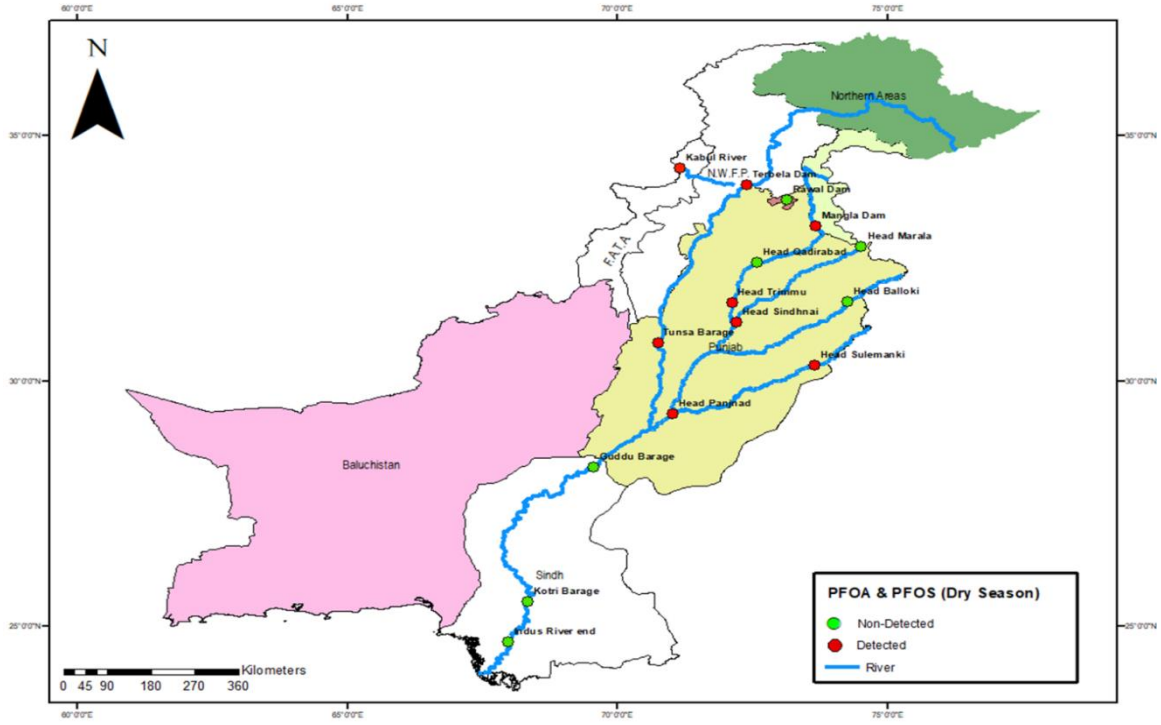


Figure 5.7: Characterisation of distribution of ΣPFCs (ng/L) in surface water sites during dry season (2013-15)

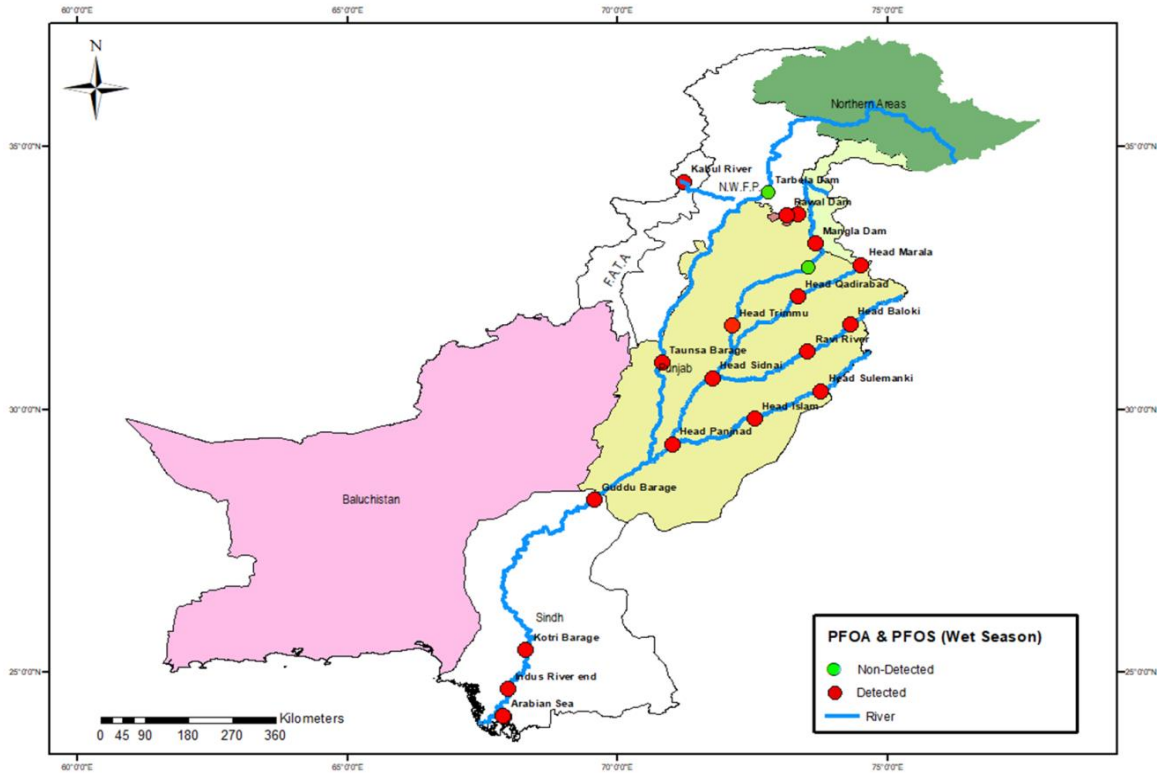


Figure 5.8: Characterisation of distribution of ΣPFCs (ng/L) in surface water sites during wet season (2013-15)

5.3.3 PFCs in Groundwater Sources (2015-16)

Closer to the surface water sites, groundwater sources mainly used for drinking purpose were also monitored for PFCs. Besides the PFOA and PFOS, significant concentrations of PFBAs and PFHxA were detected in the groundwater. When compared with the LOQs of these compounds given in Table 5.1, the maximum concentration of PFBA (1.24 ng/L) was detected at Head Sulemanki followed by 0.82 ng/L at Tarimu (Jhelum river), PFHxA (0.86 ng/L) at Panjnad (Sutlej river), PFOA (0.39 ng/L) at Sulemanki, and PFOS (0.30 ng/L) at Sulemanki (Sutlej river) as shown in Figure 5.9.

Other PFCs such as PFBS (0.27 ng/L) at Sidhnai (Ravi River), PFHpA (0.08 ng/L) at Sulemanki (Sutlej river), PFNA (0.07 ng/L) and PFDA (0.12 ng/L) at Panjnad (Sutlej river) were below the LOQ values of these compounds.

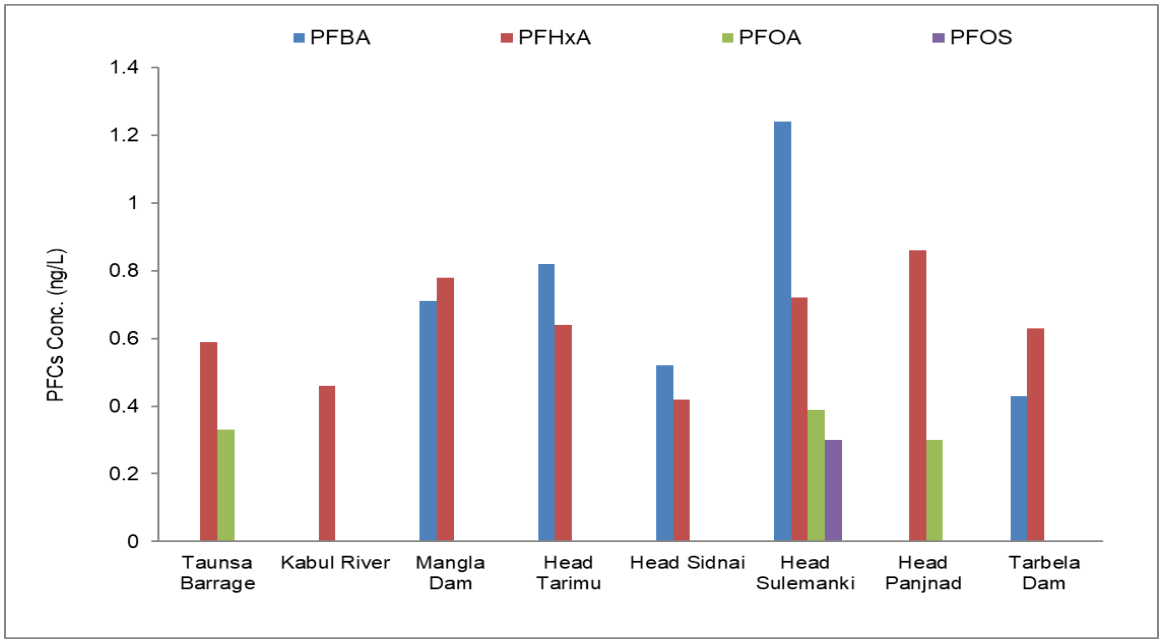


Figure 5.9: Concentration of PFCS (ng/L) above LOQs in groundwater (2015-16)

Based on the sum concentrations of PFCs as ΣPFCs detected at 8 of 15 sources are indicated in Figure 5.10.

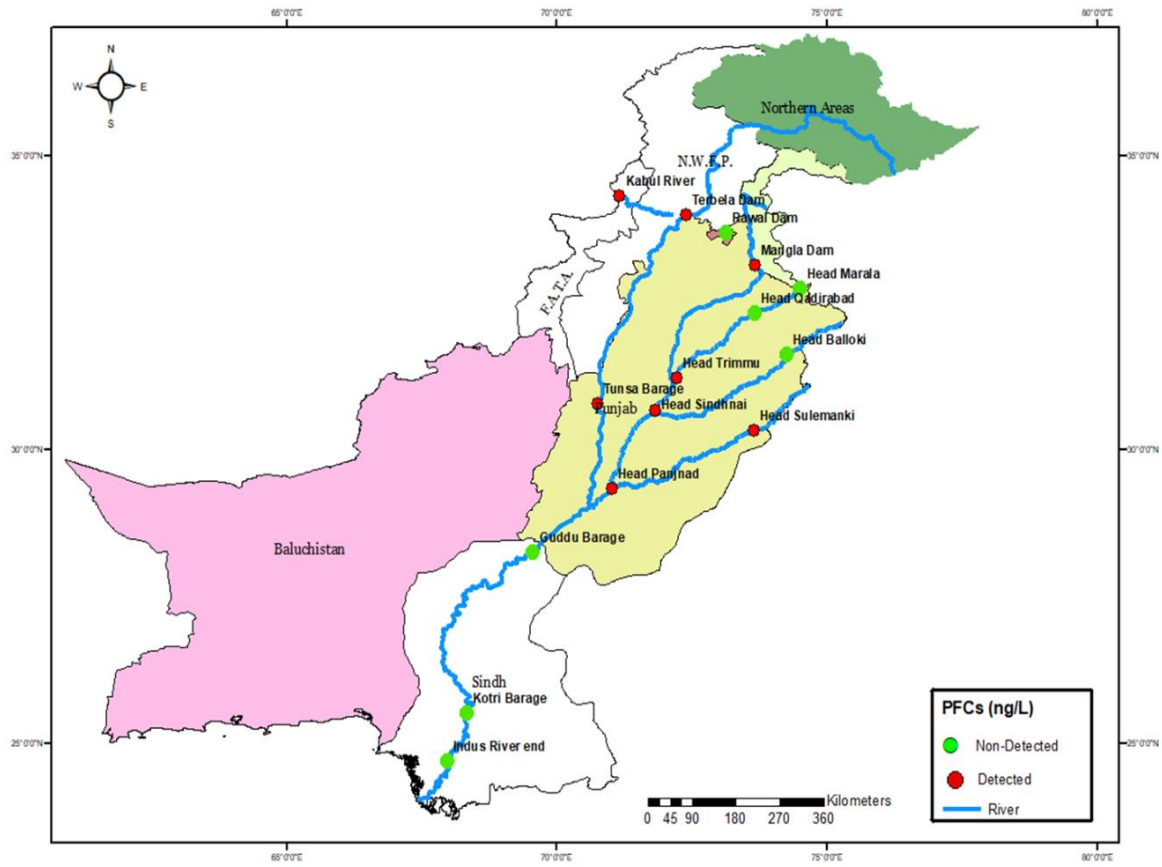


Figure 5.10: Characterisation of distribution of ΣPFCs (ng/L) in groundwater sources (2015-16)

The hydrogeological conditions have an important influence on the concentrations of PFAS in groundwater. Comparatively, the concentration of PFAS in groundwater in the study area is not very high, but it reflects that the groundwater in this region is affected by industrial sources to some extent. Provincial and local governments need to pay more attention on industrial pollution control and groundwater protection.

5.3.4 PFCs in Surface Water and Sediments (2015-16)

5.3.4.1 Levels of PFCs in Surface Water (2015-16)

The surface water samples collected in the year 2015 showed the levels of some PFCs above the LOQs (Table 5.1). The maximum concentration of PFBA (1.53 ng/L) was found at Tarbela dam in river Indus followed by PFHxA (1.56 ng/L) at Sidhnai in Ravi river, PFOA (0.59 ng/L) at Sidhnai in Ravi river, and PFBS (0.56 ng/L) at Tarbela dam in river Indus (Figure 5.11). These levels were higher as compared to concentration of same compounds in groundwater samples.

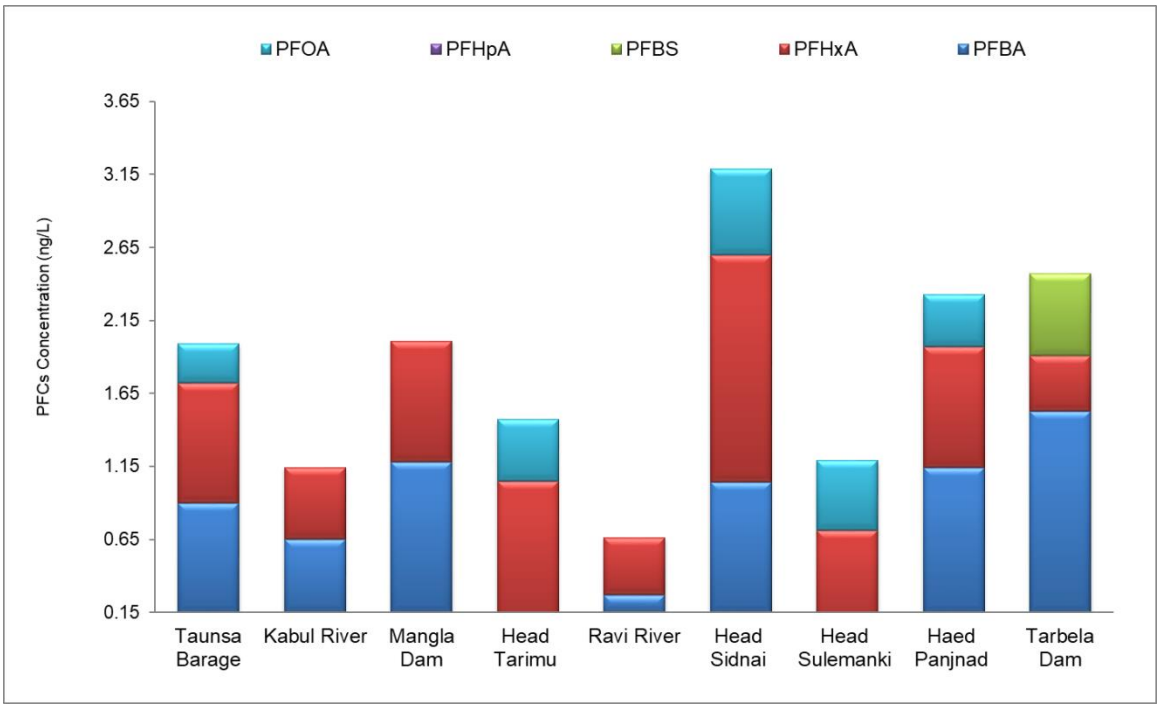


Figure 5.11: Concentration of PFCS (ng/L) above LOQs in surface water sites (2015-16)

The other PFCs such as PFHpA (0.13 ng/L), PFHxS (0.17 ng/L), and PFNA (0.12 ng/L) at Sidhnai in Ravi river, PFDA (0.07 ng/L) at Sulemanki in Sutlej river, PFOS (0.25 ng/L) at Panjnad in Sutlej river were detected below the LOQs. However, summing up the detected PFCs indicated 11 of 19 sites with presence of ΣPFCs (Figure 5.12). PFCs are present in the environment primarily in the form of the most

stable PFOS and PFOA, which are the final degradation products of various per fluorooctyl compounds. With phasing out of PFOS uses, the environmental concentrations of other related substances such as PFBS, PFHxS and PFNA were reported to be increasing (McCleaf et al., 2017).

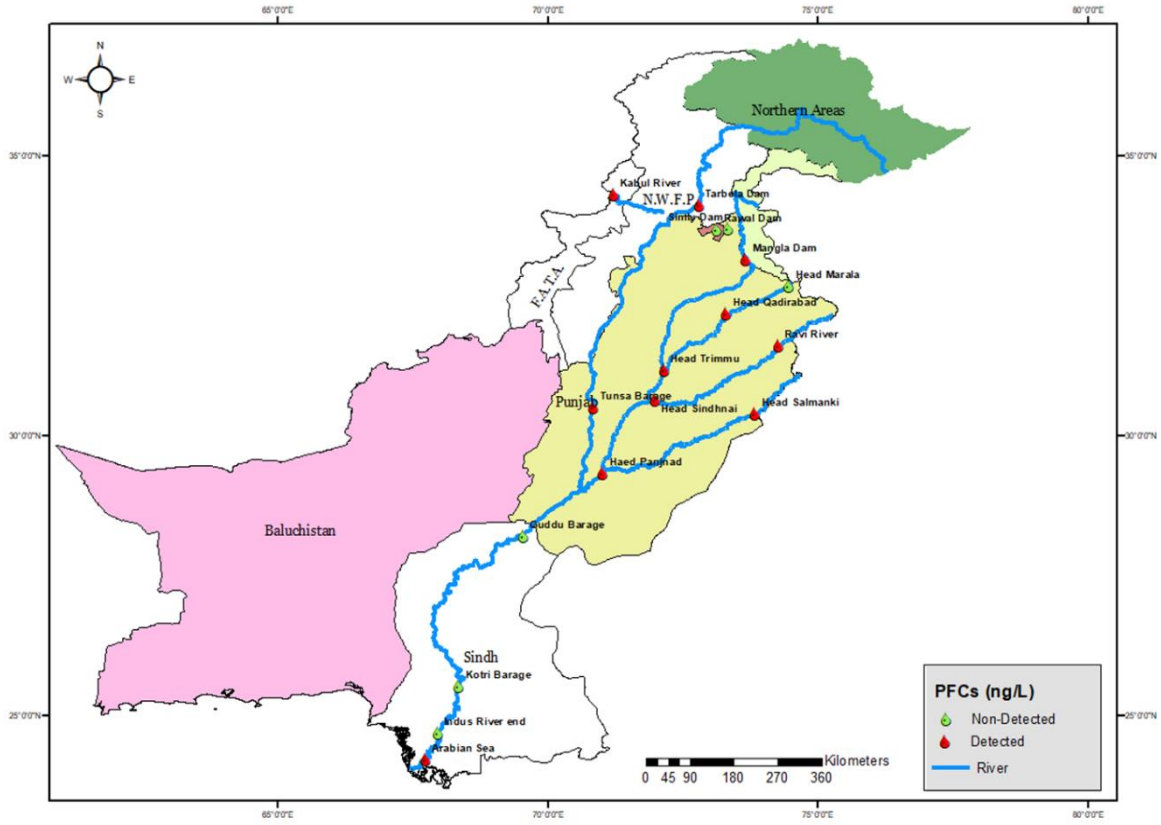


Figure 5.12: Characterisation of distribution of ΣPFCs (ng/L) in surface water sources (2015-16)

In this phase, PFCs were not considerably detected in sediment samples. The maximum concentrations of PFBA (0.08 ng/L) and PFHxA (0.09 ng/L) were found at Panjnad in Sutlej river, however these levels were below LOQs.

5.3.5 PFCs in Surface Water, Sediments and Fish (2017-18)

All the surface water sites were again sampled in 2017 for PFCs to see the trend. In addition sediment and fish samples were also collected from close proximity to surface water sites. Thus, 65 samples comprising surface water (34 No.), sediments (26 No.) and fish (5 No.) were collected and extracted as per UNU protocols in PCRWR's National Water Quality Laboratory Islamabad and then analysed on LCMS/MS in Shimadzu Asia Pacific Centre Singapore.

5.3.5.1 The LOD and LOQ of Methods

Mixed standard of 0.5 ng/L having nine compounds of PFCs was run twice and the obtained data were used for the calculation of the Limit of Detection (LOD) and Limit of Quantifications (LOQ) of the method. The LOD was calculated as three times of Standard Deviation (SD) for the results of 0.5 ng/L standards of each compound, whereas the LOQ was calculated as ten times of SD of values obtained by running 0.5 ng/L standard of each compound (Table 5.3).

Table 5.3: LOQs & LODs of PFCs in surface water samples (2017-18)

Compounds Abbreviation	Run-1	Run-2	Run-3	SD	LODs	LOQs
PFOS	1.061	0.976	1.052	0.047	0.140	0.467
PFHxsS	1.074	1.025	0.932	0.072	0.216	0.721
PFOA	0.99	1.012	1.003	0.011	0.033	0.111
PFBA	1.05	0.981	0.877	0.087	0.261	0.871
PFNA	1.005	0.999	0.983	0.011	0.034	0.114
PFDA	0.982	1.011	0.946	0.033	0.098	0.326
PFUnA	0.927	0.988	0.82	0.085	0.255	0.850
PFDoA	0.886	0.868	0.94	0.037	0.112	0.375
PFHxA	1.031	1.034	1.089	0.033	0.098	0.327

5.3.5.2 Levels of PFCs in Surface Water (2017-18)

Twenty four surface waters samples were collected and analyzed for PFCs in wet season. The maximum concentration of PFHxs (1.20 ng/L) PFOA (2.14 ng/L), PFBA (16.30 ng/L) and PFNA (1.32 ng/L) were found above LOQs at Panjnad. All the five rivers (Indus, Jhelum, Chanab, Sutlaj and Ravi) joining at Panjnad may be the reason of higher concentration of different type of PFC's compound accumulating at this point due to industrial and agricultural wastes (Figure 5.13).

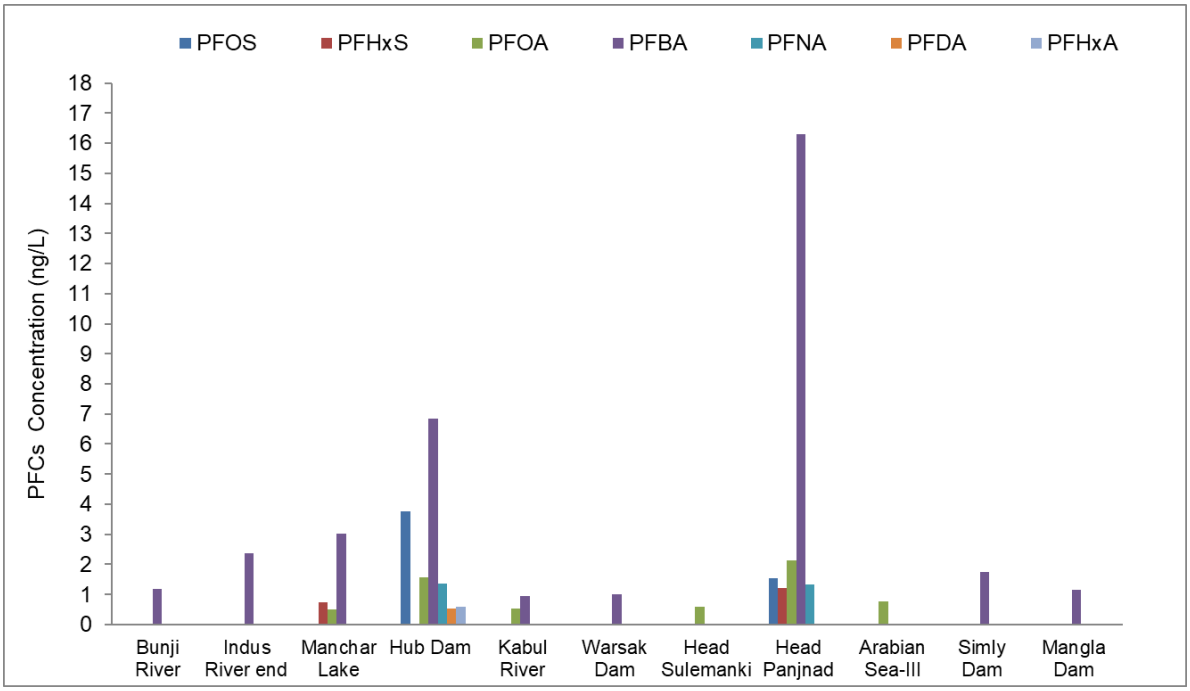


Figure 5.13: Concentration of PFCS (ng/L) in surface water during wet season (2017-18)

Considerable concentrations of these compounds were also detected at Hub Dam and Manchar Lake. Drainage water is being discharged into the Manchar Lake through Main Nara Valley Drain since many years. Consequently, concern has grown regarding the quality of lake water. Decades of draining untreated agricultural and industrial waste into the lake as well as lack of management have converted this fresh water reservoir into a pool of toxins destroying its natural aquatic flora and fauna and endangering the lives and livelihoods of its inhabitants (Soomro et al., 2017). Consequently, about 20,000 fishermen were relocated to different cities in the past three to four decades in search of livelihood because of depleting fish stocks. Sum of all PFCs as ΣPFCs shows 15 sites with the presence of PFCs (Figure 5.14).

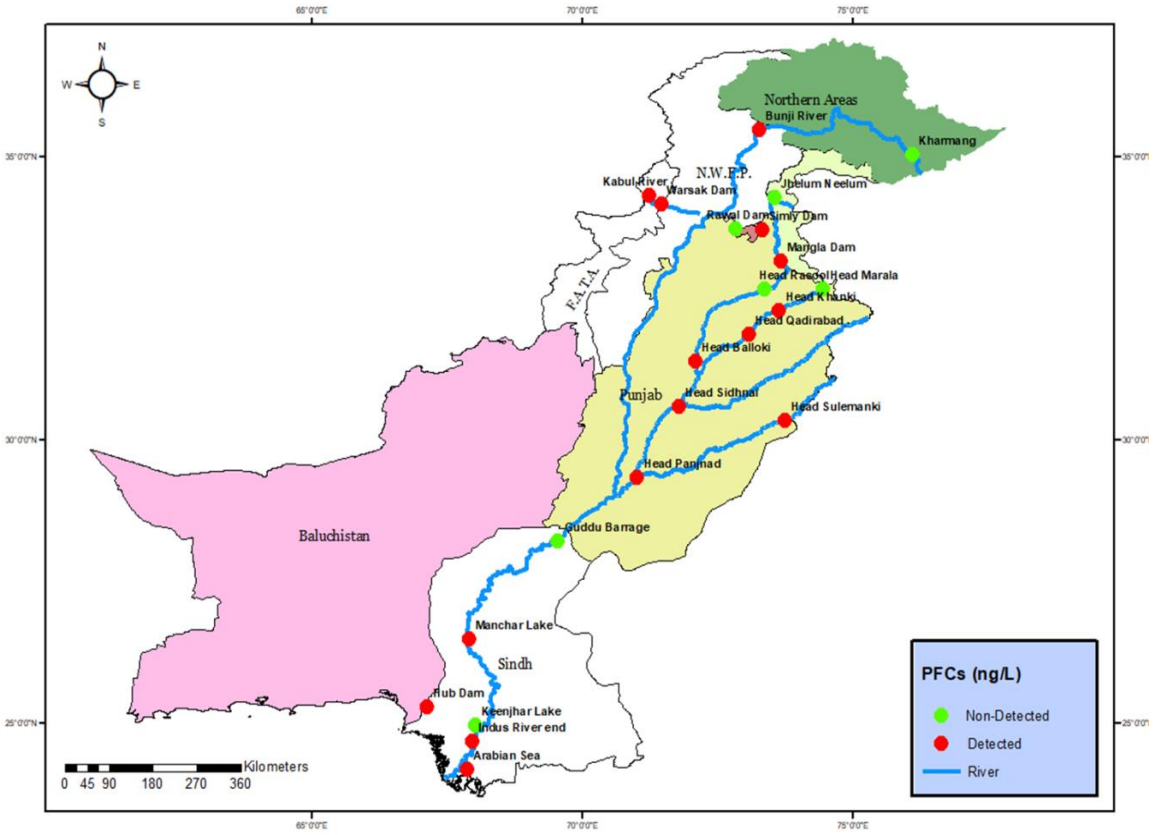


Figure 5.14: Characterisation of distribution of ΣPFCs (ng/L) in surface water sources in wet season (2017-18)

During dry season (2017-18), surface water samples from 11 selected sites were analyzed for PFCs. Out of these, 10 were detected with PFBA at maximum concentration of 1.688 ng/L near the entry point of River Indus in Pakistan (Kharmang). The PFOS was detected at 5 locations. However, only one site at Panjnad exceeded the LOQ level with maximum concentration of 0.66 ng/L (Figure 5.15). PFCs i.e. PFHxS, PFOA, PFNA, PFDA, PFUnA, PFHxA were not detected at any site.

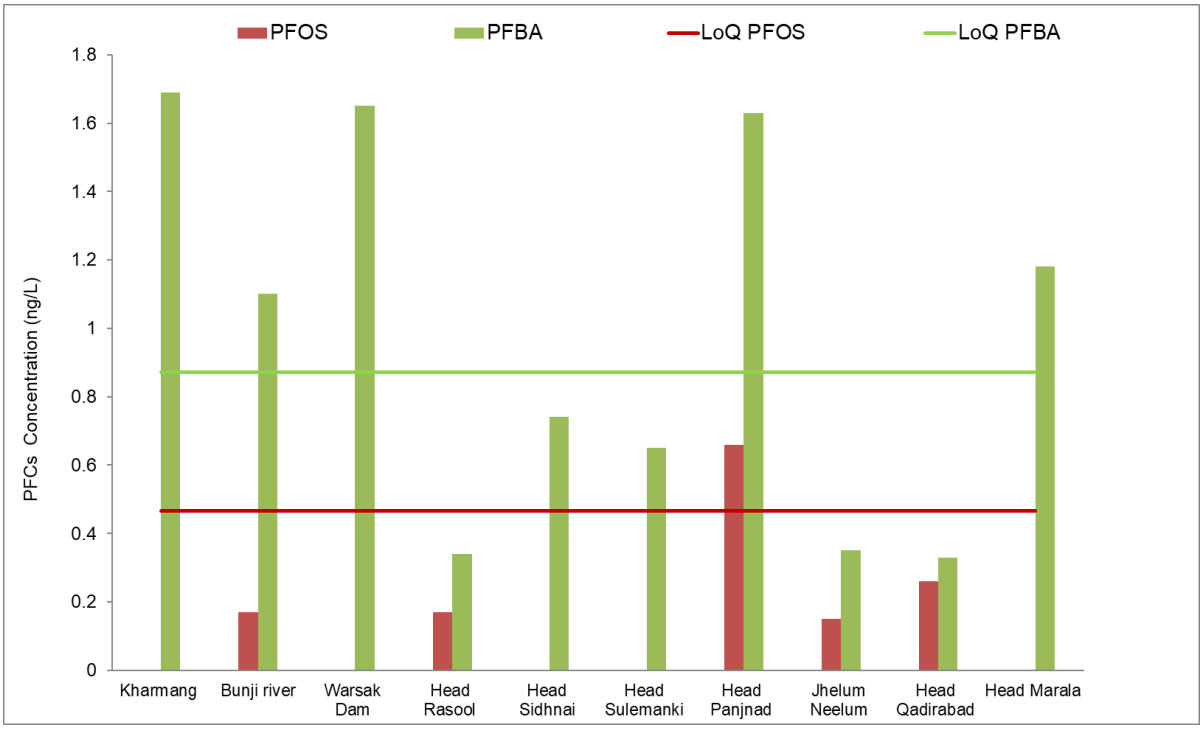


Figure 5.15: Concentration of PFCS (ng/L) in surface water sites in dry season (2017-18)

Ten of 11 sites showed presence of ΣPFCs (Figure 5.16). The concentrations of PFCs at such points though at lower level are considered to be highly influenced by distribution of untreated wastewater.

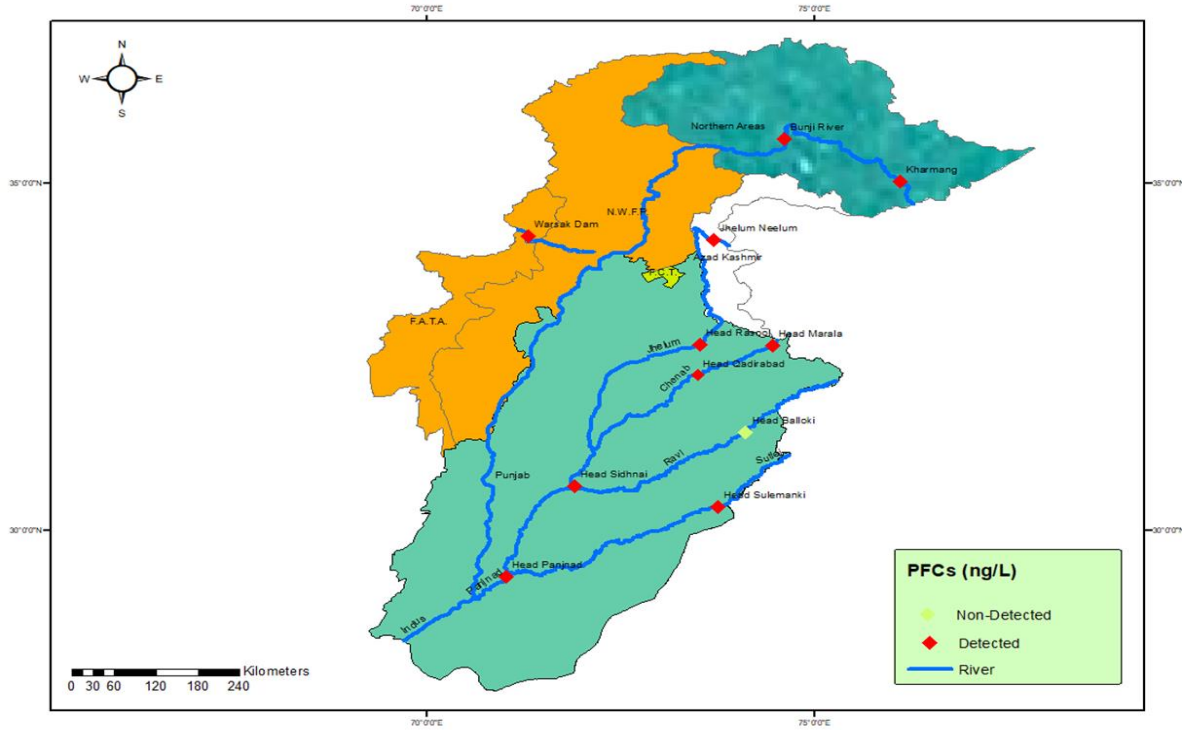


Figure 5.16: Characterisation of distribution of ΣPFCs (ng/L) in surface water sources in dry season (2017-18)

5.3.5.3 PFCs in Sediment (2017-18)

Fifteen sediment samples were analyzed in wet season. Nine out of fifteen samples were detected to have PFCs. However, PFCs were found below the LOQs (Table 5.3) in all of the sediment samples with maximum concentration of PFOA detected at Rawal Dam (0.11 ng/g). The levels of other compounds i.e. PFBA at Head Khanki (0.10 ng/g), PFNA at Warsik Dam (0.09 ng/g) were detected below the LOQs listed in Table 5.3. Overall sum of all compounds as ΣPFCs is shown in Figure 5.17.

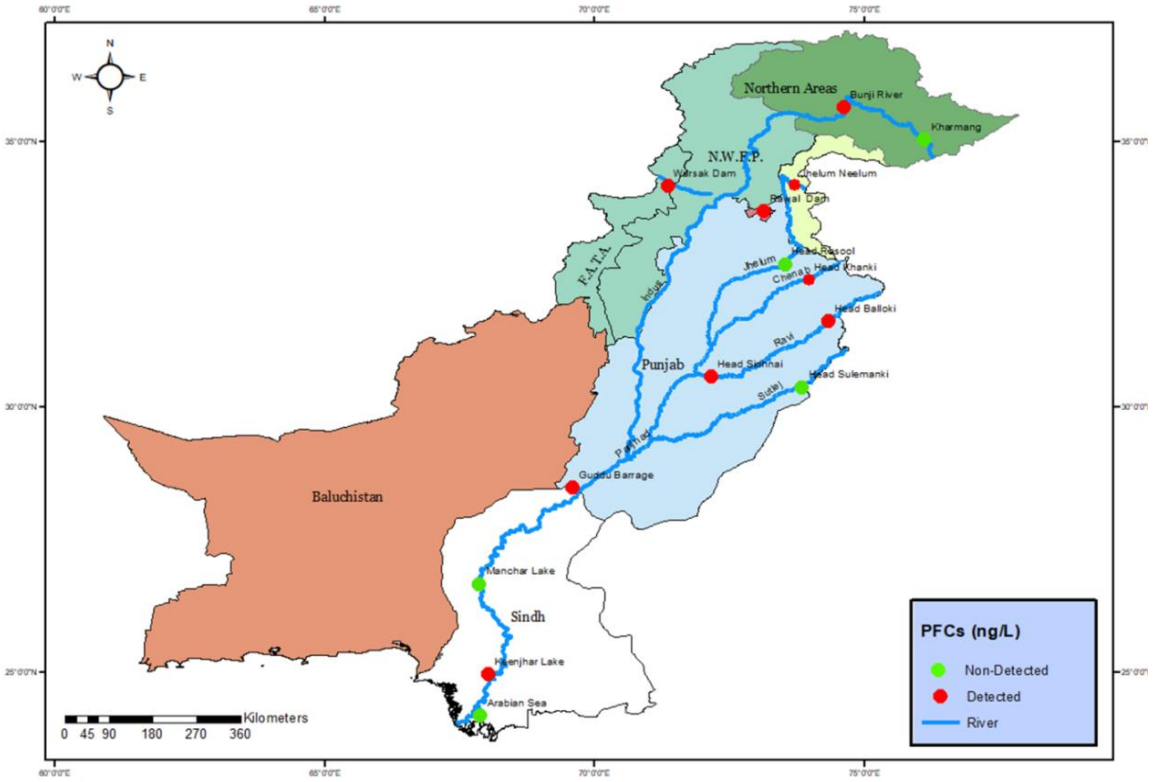


Figure 5.17: Characterisation of distribution of ΣPFCs (ng/L) in sediments in wet season (2017-18)

During dry season (2017-18), 3 out of total 11 sediments samples were detected with PFOA i.e. 2 samples with PFHxA, and one sample each with PFBA and PFDA (Figure 5.17). At lower concentrations, sum of PFCs indicated the detection of PFCs compounds at five sites (Figure 5.19).

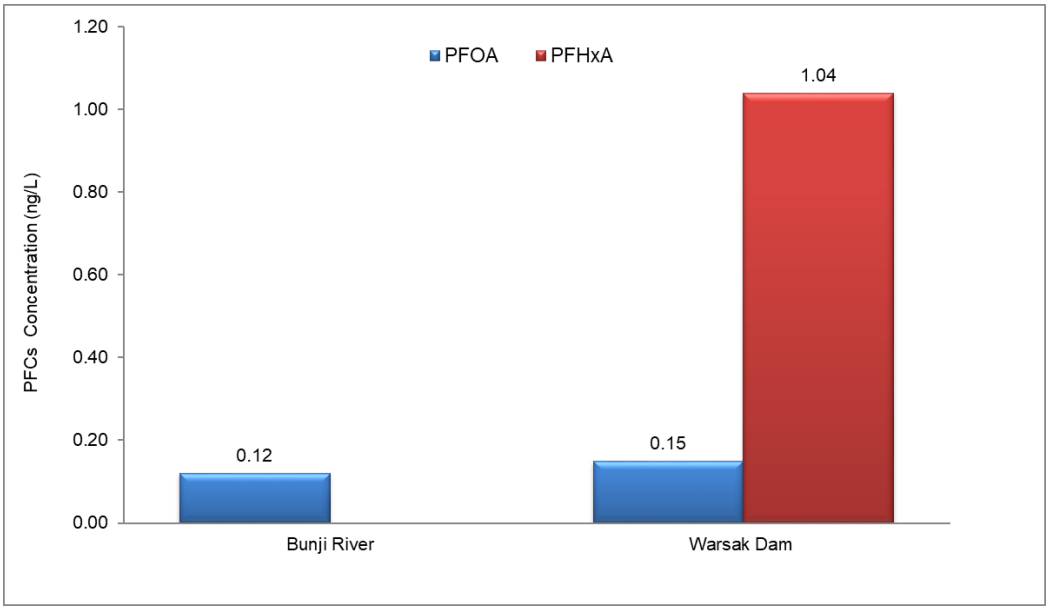


Figure 5.18: Concentration of PFC (ng/L) in sediments during dry season (2017-18)

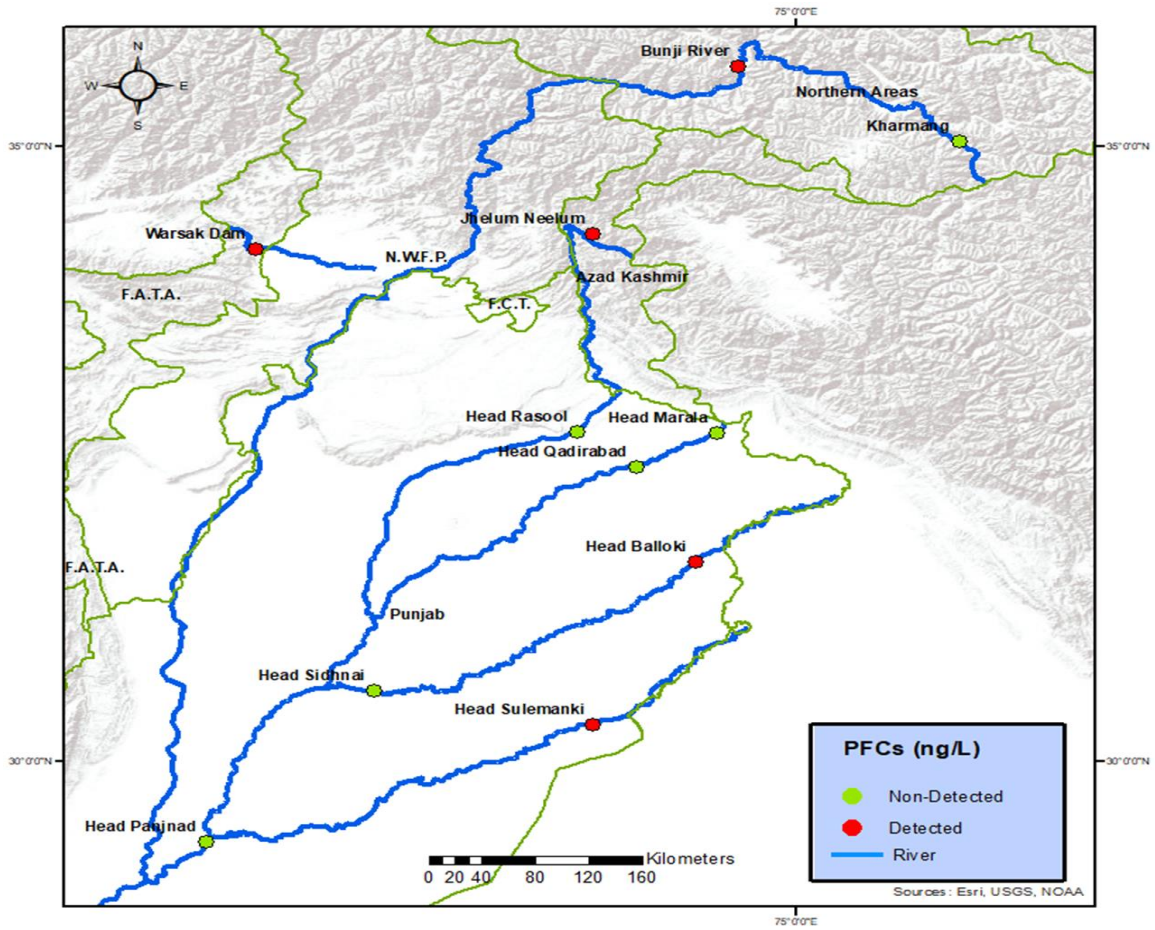


Figure 5.19: Characterisation of distribution of ΣPFCs (ng/L) in sediments in dry season (2017-18)

5.3.5.4 PFCs in Biota (2017-18)

Five fish samples collected from different sources i.e. Indus River, Mancher Lake, Keenjhar Lake, Clifton and Rawal Dam were analysed for PFCs. Analytical results showed that PFOA was the only compound detected in fish collected from Rawal Lake (1.49 ng/g). This is a matter of serious concern as Rawal lake water is used for drinking after treatment. Sewage waste from Bhara Kahu, Bani Gala, Muslim Colony, Barri Imam is discharge into freshwater streams of Rawal Lake and is a possible source of organic pollution in biota and water.

5.3.6 PFCs in Water, Sediments and Fish (2018-19)

5.3.6.1 LOD and LOQ of Methods (2018-19)

Limit of Detection (LOD) and Limit of Quantifications (LOQ) of the test method was determined (Table 5.4).

Table 5.4: LOQ & LOD of PFCs in surface water samples (2018-19)

PFC Compounds	Test run 1	Test run 2	Mean	SD	LOD	LOQ
	0.5 ng/L	0.5 ng/L				
PFOS	0.89	0.80	0.85	0.04	0.13	0.42
PFHxsS	0.77	1.06	0.92	0.26	0.62	2.06
PFOA	0.62	0.58	0.60	0.026	0.078	0.26
PFBA	0.49	0.50	0.50	0.006	0.019	0.06
PFNA	0.49	0.56	0.52	0.05	0.15	0.49
PFDA	0.70	0.63	0.67	0.05	0.15	0.48
PFUnA	0.47	0.53	0.50	0.04	0.12	0.41
PFDoA	0.63	0.75	0.69	0.086	0.26	0.86
PFHxA	0.67	0.60	0.64	0.051	0.15	0.51

All test results of water samples were evaluated in comparison to LOQs.

5.3.6.2 PFCs in Groundwater Sources (2018-19)

Nine water samples were collected in wet season from the groundwater sources used for drinking purpose in major cities and analyzed for PFCs. Three samples (Thatta, Karachi and Hyderabad cities) were detected with PFOA and PFBA, and one sample (Karachi city) with PFNA (Figure 5.20).

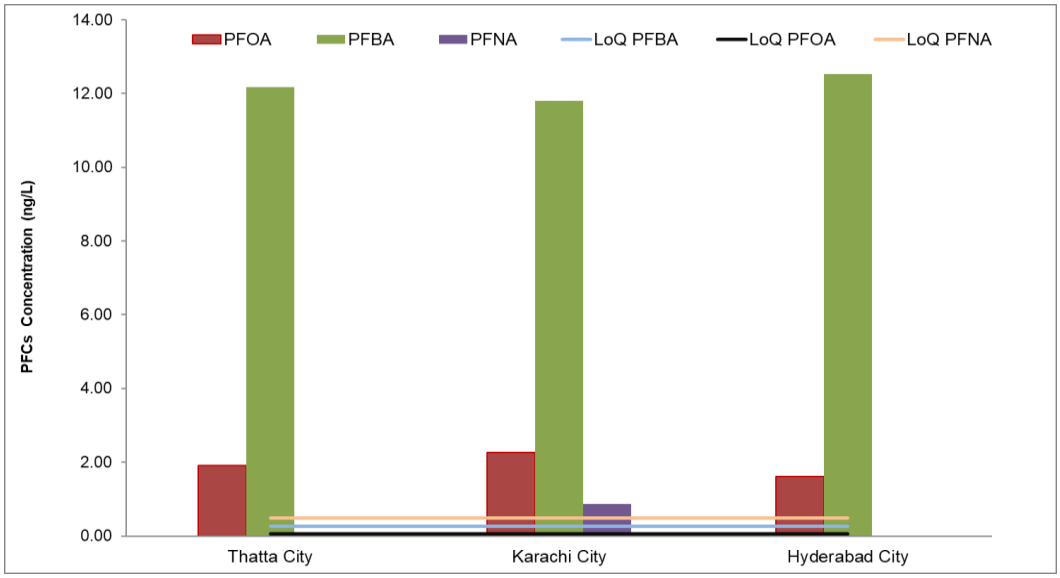


Figure 5.20: Concentration of PFCS (ng/L) in groundwater (2018-19)

Figure 5.21 shows the locations reflecting sum of PFCs (ΣPFCs) in drinking water sources.

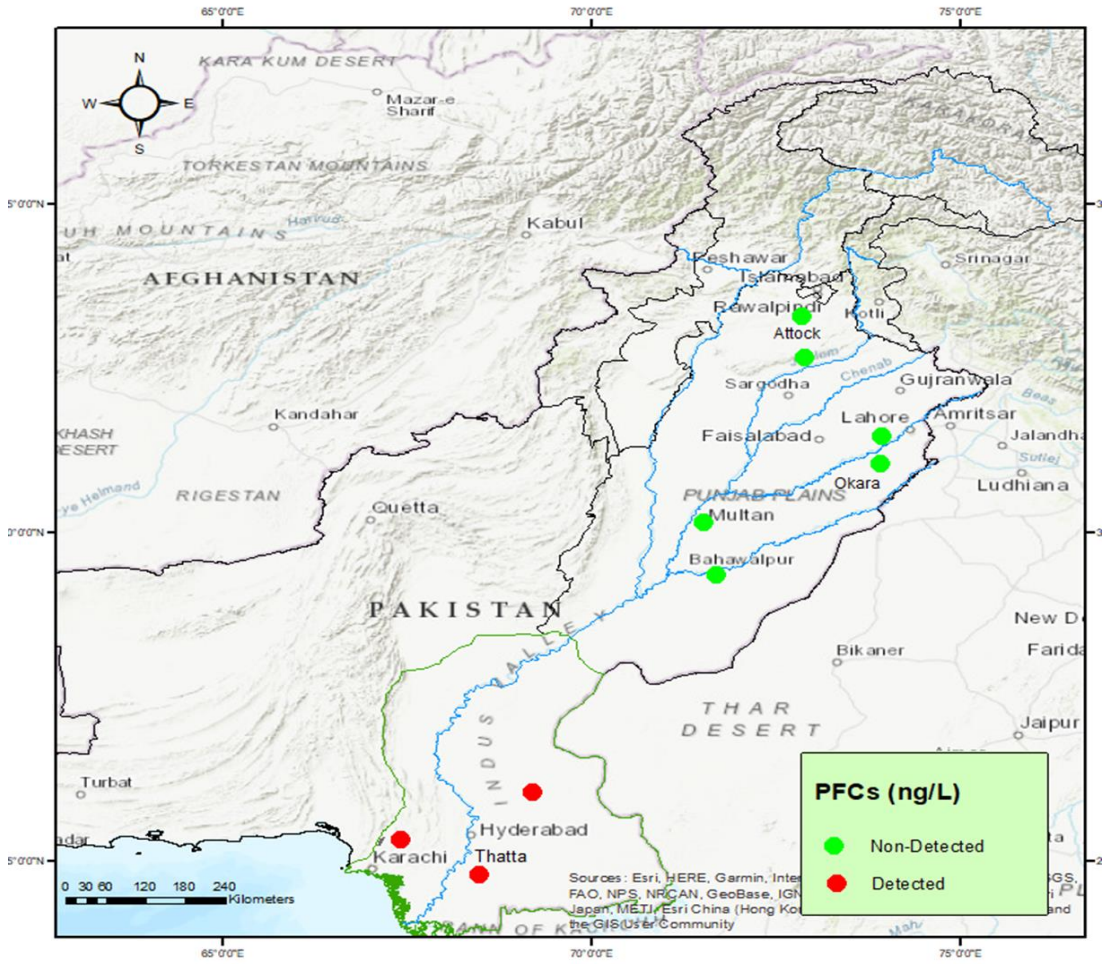


Figure 5.21: Characterisation of distribution of ΣPFCs (ng/L) in groundwater sources in wet season (2018-19)

5.3.6.3 PFCs in Surface Water Sources (2018-19)

Sixteen water samples during wet season of 2018-19 were collected from surface water sites and analyzed for PFCs and were found to have PFOA (12 sites) & PFBA (16 sites). The maximum concentrations were found as; PFBA (13 ng/L) at Indus river at Thatta, PFDoA (4 ng/L) at Sutlej River Bahawalpur, PFOA (2 ng/L) at Arabian Sea sites and Rawal dam; and PFNA (2.2 ng/L) at Arabian Sea site III (Figure 5.22).

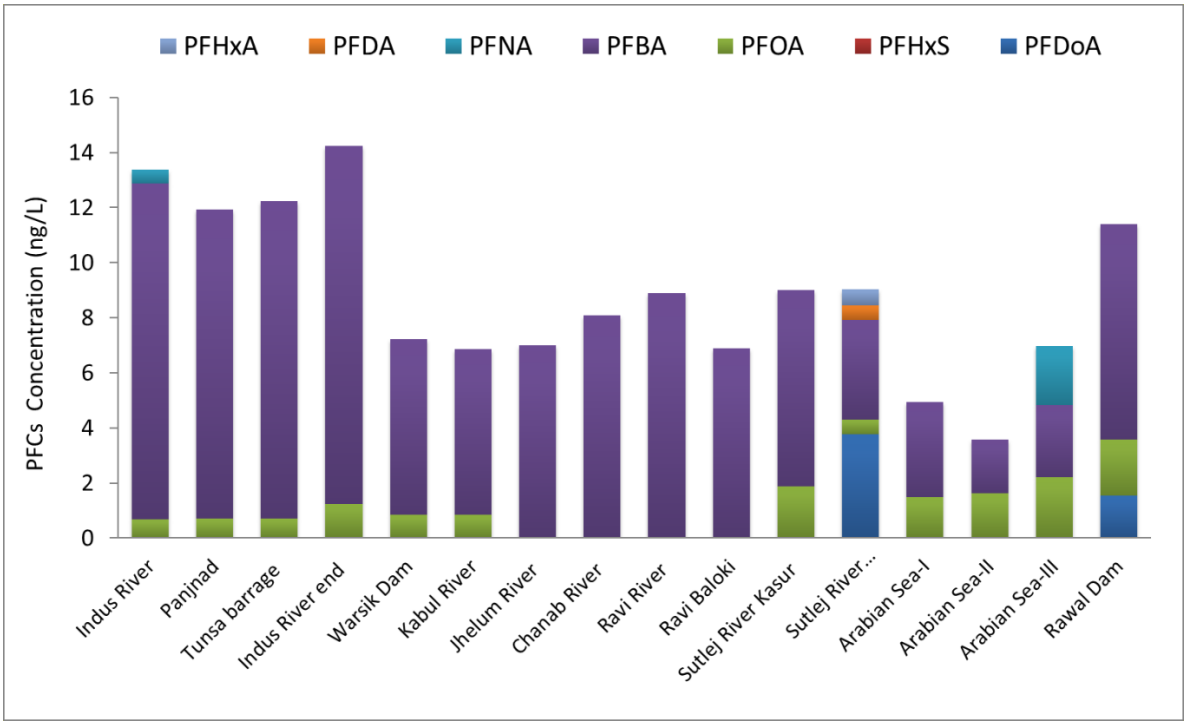


Figure 5.22: Concentration of PFCs (ng/L) in surface water sites in wet season (2018-19)

PFCs can deposit in marine and freshwater ecosystems through effluent releases, atmospheric deposition, runoff, and other means. In addition to pollutants being transported to Arabian Sea through Indus River, PFCs are expected to be entering the sea from other sources, including waste sites, river runoff, and atmospheric deposition. Around 580 million gallons of sewage is disposed in Karachi into the sea every day, of which 10 million gallons is disposed of through Sea View point. The entire sewage, which is mostly untreated, after going through different drainage channels fall in six nallahs/rivers such as Lyari, Malir, Frere, Kalri, Railway and Nehr Khayyam. There are more than 10,000 registered industrial units in Karachi manufacturing food, chemical, textile, paints, paper and pulp products. Moreover, there are thousands of cottage industries operating in informal sectors. Although there are few industries who have established waste treatment facilities, but a majority of the industrial units are throwing their waste directly into the Arabian Sea through Malir and Lyari channels. These two major drains carry the entire waste of Karachi city and discharge into Arabian Sea.

Industries in Karachi generate approximately 100 million gallons of industrial effluents per day, of which 90% goes into the Arabian sea without any treatment (Alamgir et al., 2019). Three wastewater treatment plants operated through Karachi Water and Sewerage Board (TP-1 at Sher Shah; TP-2 at Mahmoodabad and TP-3 at Mauripur) are not functioning properly, and the wastewater only receives the preliminary treatment after which it is discharged into the sea with heavy pollution load. Such wastes are expected to be the major source of POPs in the Arabian Sea. The effluents from wastewater treatment plants and urban runoff were found to be significant nonpoint sources of PFCs to water (Xiao et al., 2012). The detection of POPs raise serious concerns regarding the impacts on human health and aquatic life, including several species of fish and shellfish, and other birds of prey, and fish-eating mammals.

The sum of PFCs compounds (ΣPFCs) indicated 13 sites with presence of PFCs compounds (Figure 5.23). The higher level of PFCs during wet season compared to the dry season is attributed to increased surface run-off with contaminants into the water bodies.

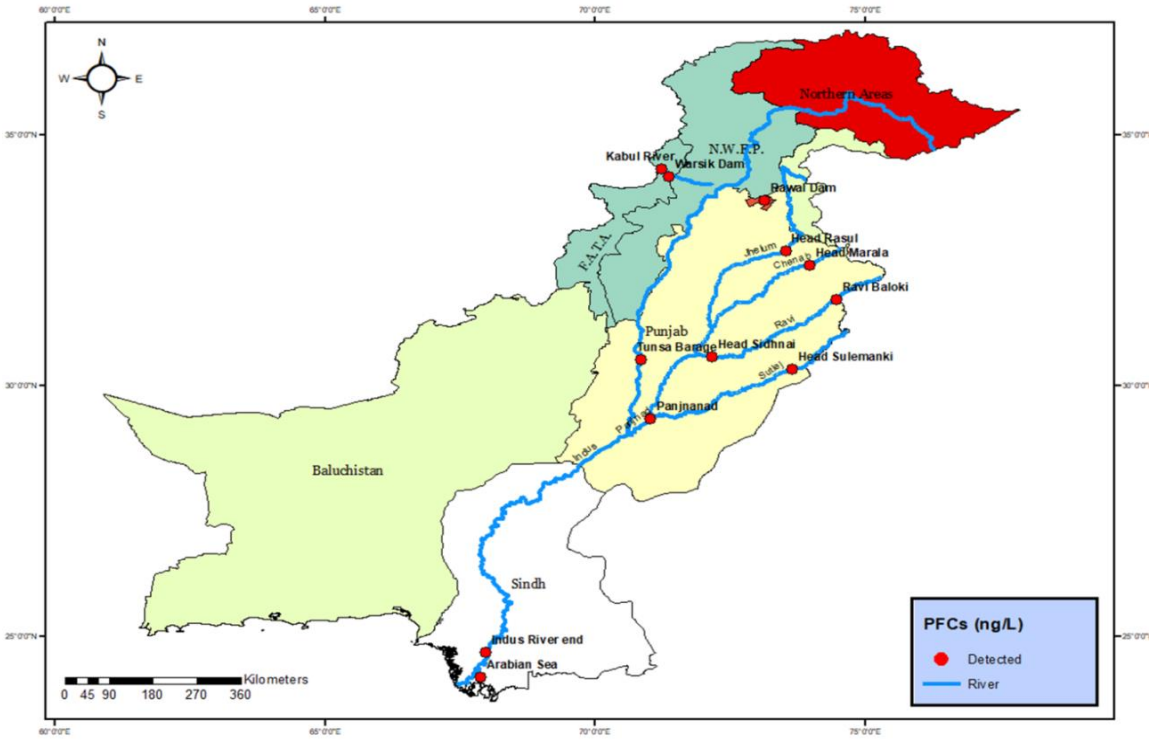


Figure 5.23: Characterisation of distribution of ΣPFCs (ng/L) in surface water sites in wet season (2018-19).

5.3.6.4 PFCs in Sediments and Biota (2018-19)

PFCs were not detected in 16 sediment samples collected during wet season. Only 1 out of 3 fish samples collected from Indus River before Panjnad was detected with PFDA (0.39 ng/L).

5.4 Potential Health Effects

Humans are likely exposed by consuming PFC contaminated water or food. PFOS are known to bio-accumulate and persist in the environment. Animal studies have also shown that they are toxic, affecting reproduction and development. For humans, these are carcinogenic due to their accumulation in water and food (Coperchini et al., 2017). PFOAs are persistent, bio-accumulative and known to be contaminants in waterways and can bio-accumulate within fish.

Studies have found PFOS and PFOA in the blood samples of the U.S population, indicating that exposure to these chemicals is widespread (Andrews and Naidenko, 2020).

Epidemiologic studies have also found associations between kidney, testicular, ovarian, prostate, and non-Hodgkin lymphoma with PFOA exposure (Barry et al., 2013).

PFCs have the potential to affect human health linked with neurological disorders and immunosuppressive responses. Studies of laboratory animals given large amounts of PFCs have found that some PFCs may affect growth and development, reproduction and injure the liver.

5.5 Conclusions

Perfluorooctanoic acid (PFOA) was found to be dominant PFCs followed by Perfluorooctane sulfonate (PFOS) in water and sediment samples. The highest concentrations found in the environment, may be associated with direct discharge from industries where PFCs are in use.

The PFCs vary geographically and also seem to be affected by the hydrogeological conditions. The differences in human and industrial activities in different parts of the country and the discharged wastewater from the urban settlements are expected to be the major contributors for these geographical differences.

Concentrations of PFOS or PFOA found at some locations were sufficient to potentially cause adverse effects to some human and aquatic life, thus monitoring effort of such PFCs should be of great attention.

Chapter 6: Overall Conclusions and the Way Forward

6.1 Overall Conclusions

Several POPs, some of them considered at high risk, were found in water, sediments and biota in Pakistan. This report have revealed the occurrence of POPs at higher levels than those found in other regions of the world. The presence of OCPs, PCBs, PBDEs, and PFCs in water, sediments and biota, even though at low levels, might be harmful and should not be neglected due to their persistence and toxic effects. The impact on human health after long-time exposure cannot be ignored. Thus, their presence should be monitored in the future studies. Even compounds already banned in the world such as Dieldrine, Aldrin and DDT are still found in water, sediments and biota.

This study demonstrated the extensive use of POPs in Pakistan and probably in neighbouring countries, their transboundary movement, and their transportation as hazardous waste. Additional studies concerning sediments and biota should be encouraged to provide valuable information for assessing the fate of these pollutants in the environment. Studies concerning bioaccumulation and toxicological effects as an integrative measure of a water body quality should be also stimulated. Key species and standardized biological samples should be used to allow a more reliable and comparable data. Some POPs, such as alkylphenols, bisphenol and estrogens (e.g., ethynylestradiol) included in the list of the Stockholm Convention, were never investigated in these matrices and required to be monitored.

Though the National Implementation Plan (NIP) on management of POPs is already developed by the Ministry of Climate Change, however it is yet to be implemented through development of actionable plans and strategies. To develop such strategies, the commitment of different stakeholders to the Stockholm Convention and Convention on Long-range Transboundary Water Pollution is required to protect water resources and aquatic life in the region and ultimately to avert hostile impacts of POPs pollution on human health.

6.2 The Way Forward

There is need for sustained efforts of all stakeholders for managing POPs, at the local, national, and regional levels by undertaking appropriate initiatives:

6.2.1 Monitoring

There is need to establish local, provincial, national and regional inventories of POPs, monitoring networks, shared technical capacity and data repositories. As the testing facilities of POPs are cost intensive, therefore centralized testing facilities at local and/or national level may also be established for continuous monitoring of POPs in different matrices. Moreover, transboundary POPs transport should also be monitored through establishing monitoring mechanism with neighbouring countries and between provinces.

POPs exposure assessment of susceptible human groups, including children should be conducted and should be shared with the health care agencies specifically in rural areas for understanding the potential threats. It is suggested that the annual monitoring of the organic pollutants should be done so that regulatory bodies can control the organic pollutants being added in surface water bodies directly and in groundwater indirectly.

6.2.2 Regulatory

Strong coordination and partnership between local, national and international stakeholders should be developed to enforce mechanism to restrict use, import, export, and safe disposal of stockpiles/waste of banned chemicals, to advocate the elimination of POPs, implementation of integrated pests management (IPM) and organic farming in the country.

Governments and stakeholders should understand the risk associated with exposure to POPs and to ensure the response to international agreements and implement policies and take protective actions to completely phase out POPs. In this context, POPs monitoring data should be intelligently used by concerned agencies to develop risk management strategies for phasing out the use and release of POPs through power generation, industrial productions and wastes, municipal and medical wastes, waste incineration, safe agricultural practices in the use and disposal of pesticides.

6.2.3 Awareness and Behaviour Change

National protocols on fish cleaning and cooking methods should also be developed and publicized by the concerned departments. Awareness programme should be launched for professionals working in hydropower generation sector, farmers, pesticide companies and industries using the POPs/pesticides directly or indirectly. A strong coordination mechanism between public and private sector stakeholders should be established to foster integrated approaches and sustainable solutions for the management of POPs.

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Annexures

Annexure-I

Table-1A: Surface Water Field Sampling Data for OCPs (Wet season, 2007)

Sr. No.	Location	Pre-monsoon (May)		Post-monsoon (July)		Lat. Long.	Surrounding
		Sampling date	Temperature	Sampling date	Temperature		
1	Head Marala	16/5/2007	37 ^{o}C	3/7/2007	34 ^{o}C	32° 40’ 04” E 74° 28’ 06" N	Agriculture
2	Sidhnai Head	13/5/2007	38 ^{o}C	5/7/2007	34 ^{o}C	32° 40’ 04” E 74° 28’ 06" N	Agriculture
3	Head Islam	12/5/2007	37 ^{o}C	4/7/2007	36 ^{o}C	29° 49’ 43” E 72° 32’ 57" N	Agriculture
4	Head Panjnad	12/5/2007	38 ^{o}C	7/7/2007	36 ^{o}C	29° 20’ 36” E 71° 01’ 25" N	Agriculture
5	Taunsa Barage	12/5/2007	38 ^{o}C	6/7/2007	36 ^{o}C	30° 30’ 41” E 70^{0} 51’ 07" N	Agriculture
6	Head Tarrimu	16/5/2007	37 ^{o}C	3/7/2007	35 ^{o}C	31° 41’ 02” E 71° 51’ 11" N	Agriculture
7	Tarbela Dam	14/5/2007	35 ^{o}C	4/7/2007	32 ^{o}C	34° 07’ 52” E 72° 48’ 08" N	Agriculture
8	Mangla Dam	14/5/2007	34 ^{o}C	4/7/2007	28 ^{o}C	33° 09’ 18” E 73° 40’ 02" N	Agriculture
9	Guddu Barrage	13/5/2007	43 ^{o}C	1/7/2007	48 ^{o}C	28° 58’ 27” E 68^{0}51’ 38" N	Agriculture
10	Kotri Barrage	12/5/2007	40 ^{o}C	2/7/2007	38 ^{o}C	25° 26’ 22’’ E 68° 08’ 35" N	Agriculture
11	Rasol Barage	16/5/2007	34 ^{o}C	3/7/2007	30 ^{o}C	32° 41’ 07’’ E 73° 31’ 27" N	Agriculture
12	Ravi River Indian border	16/5/2007	35 ^{o}C	3/7/2007	30 ^{o}C	31° 36’ 53" E 74°16’ 08" N	Agriculture
13	Qadrabad Head	16/5/2007	36 ^{o}C	3/7/2007	34 ^{o}C	32° 19’ 00" E 72° 41’ 14" N	Agriculture
14	Sulmanki Head	15/5/2007	35 ^{o}C	4/7/2007	31°C	30° 41’ 43" E 72° 31’57" N	Agriculture
15	Head Baloki	15/5/2007	36 ^{o}C	4/7/2007	34 ^{o}C	31° 13’ 12’’ E 71° 51’ 40" N	Agriculture
16	Thatta end of Indus River	15/5/2007	39 ^{o}C	1/7/2007	32 ^{o}C	24° 41’ 04" E 67° 58’ 26" N	Agriculture
17	Arabian Sea Near Coast Guard Post Shah Bunder	14/5/2007	35 ^{o}C	2/7/2007	39°C	24° 09" E 67° 53’ 56" N	Agriculture
18	Arabian Sea Near Zaman Jat village	14/5/2007	35 ^{o}C	2/7/2007	38 ^{o}C	24° 10’ 29” E 67° 53’ 05" N	Agriculture
19	Arabian Sea Near Allah WarayoBhatti Village	14/5/2007	35 ^{o}C	2/7/2007	38 ^{o}C	24° 10’ 29” E 67° 53’ 05” N	

Annexure-II

Table-2A: Surface Water Field Sampling Data for OCPs (Dry season, 2008)

Sr. No.	Location	Pre-monsoon (April-May)		Post-monsoon (November)		Lat. Long.	Surrounding
		Sampling date	Temperature	Sampling date	Temperature		
1	Head Marala	7/5/2008	40 ^{o}C	13.11.2008	27 °C		Agriculture
2	Sidhnai Head	9/5/2008	40 ^{o}C	15.11.2008	30 ^{o}C	32° 40’ 04’’ E 74° 28’ 06" N	Agriculture
3	Head Islam	10/5/2008	40 ^{o}C	17.11.2008	29 ^{o}C	29° 49’ 43” E 72°32’ 57" N	Agriculture
4	Head Panjnad	12/5/2008	39 ^{o}C	17.11.2008	28 ^{o}C	29° 20’ 36” E 71° 01’ 25" N	Agriculture
5	Taunsa Barage	13/5/2008	40°C	18.11.2008	29°C	30° 30’ 41” E 70° 51’ 07" N	Agriculture
6	Head Tarrimu	14/5/2008	38 ^{o}C	17.11.2008	27 ^{o}C	31° 41’ 02” E 71° 51' 11" N	Agriculture
7	Tarbela Dam	28/4/2008	30 ^{o}C	9.11.2008	24 ^{o}C	34° 07’ 52” E 72° 48’ 08"N	Agriculture
8	Mangla Dam	28/4/2008	34 ^{o}C	10.11.2008	25 ^{o}C	33° 09’ 18” E 73° 40’ 02" N	Agriculture
9	Guddu Barrage	29/4/2008	37 ^{o}C	12.11.2008	29 ^{o}C	28° 58’ 27” E 68° 51’ 38" N	Agriculture
10	Kotri Barrage	30/4/2008	38 ^{o}C	13.11.2008	27 ^{o}C	25° 26’ 22” E 68° 08’ 35” N	Agriculture
11	Rasol Barrage	30/4/2008	38 ^{o}C	10.11.2008	28 ^{o}C	32° 41’ 07” E 73 ^{o} 31’ 27” N	Agriculture
12	Ravi River Indian border	2/5/2008	39 ^{o}C	12.11.2008	30 ^{o}C	31° 36’ 53” E 74° 16’ 08” N	Agriculture
13	Qadrabad Head	5/5/2008	38 ^{o}C	11.11.2008	29 ^{o}C	32° 19’ 00” E 72° 41’ 14” N	Agriculture
14	Sulmanki Head	6/5/2008	38 ^{o}C	12.11.2008	27 ^{o}C	30° 41’ 43” E 72 ^{o} 31’ 57” N	Agriculture
15	Head Baloki	7/5/2008	39 ^{o}C	13.11.2008	28 ^{o}C	31° 13’ 12” E 71° 51’ 40” N	Agriculture
16	Thattaendof Indus River	6/5/2008	38 ^{o}C	10.11.2008	38 ^{o}C	24° 41’ 04” E 67° 58’ 26” N	Agriculture
17	Arabian Sea Near Coast Guard Post Shah Bunder	27/4/2008	35 ^{o}C	10.11.2008	35 ^{o}C	24° 09’ 35” E 67° 53’ 56” N	Agriculture
18	Arabian Sea Near Zaman Jat Village	27/4/2008	35 ^{o}C	10.11.2008	35 ^{o}C	24° 10’ 29” E 67° 53’ 05” N	Agriculture
19	Arabian Sea Near Allah Warayo Bhatti Village	27/4/2008	35 ^{o}C	10.11.2008	35 ^{o}C	24° 10’ 29” E 67° 53’ 05” N	Agriculture

Annexure-III

Table-3A: Surface Water Sampling Data for PCBs (Dry season, 2009)

Sr. No	Location	Sampling date	Temperature	Lat. Long.	Surroundings
1	Head Marala	12/11/2009	25 ^{o}C	32° 40' 04" E 74° 28' 06" N	Agriculture
2	Sidhnai Head	7/12/2009	15 ^{o}C	32° 40' 04" E 74° 28' 06" N	Agriculture
3	Head Islam	9/12/2009	22 ^{o}C	32° 40' 04" E 74° 28' 06" N	Agriculture
4	Head Panjnad	7/12/2009	15 ^{o}C	32° 40' 04" E 74° 28' 06" N	Agriculture
5	TaunsaBarage	8/12/2009	14°C	29° 49' 43" E 72° 32' 57" N	Agriculture
6	Head Tarrimu	7/12/2009	19 ^{o}C	29° 20' 36" E 71° 01' 25" N	Agriculture
7	Tarbela Dam	10/11/2009	23 ^{o}C	30° 30' 41" E 70° 51' 07" N	Agriculture
8	Mangla Dam	11/11/2009	25 ^{o}C	31° 41' 02" E 71° 51' 11" N	Agriculture
9	Guddu Barrage	25-11-2009	32 ^{o}C	34° 07' 52" E 72° 48' 08" N	Agriculture
10	Kotri Barrage	26-11-2009	27 ^{o}C	33° 09' 18" E 73° 40' 02" N	Agriculture
11	RasolBarage	15-11-2009	26 ^{o}C	28° 58' 27" E 68° 51' 38" N	Agriculture
12	Ravi River Indian border	12/11/2009	28 ^{o}C	25° 26' 22" E 68° 08' 35" N	Agriculture
13	Qadrabad Head	14-11-2009	25 ^{o}C	32° 41' 07" E 73° 31' 27" N	Agriculture
14	Sulmanki Head	13-11-2009	22 ^{o}C	31° 36' 53" E 74° 16' 08" N	Agriculture
15	Head Baloki	13-11-2009	26 ^{o}C	32° 19' 00" E 72° 41' 14" N	Agriculture
16	Thatta end of Indus River	24-11-2009	34°C	30° 41' 43" E 72° 31' 57" N	Agriculture
17	Arabian Sea Near Coast Guard Post Shah Bunder	23-11-2009	30 ^{o}C	31° 13' 12" E 71° 51' 40" N	Agriculture
18	Arabian Sea Near ZamanJ at Village	23-11-2009	31 ^{o}C	24° 41' 04" E 67° 58' 26" N	Agriculture
19	Arabian Sea Near Allah Warayo Bhatti Village	23-11-2009	32 ^{o}C	24° 09' 35" E 67° 53' 56" N	Agriculture

Annexure-IV

Table-4A: Selected Sampling Sites for Sediments Sampling for PBDEs (2011)

Sr.#	Source	Site	No. Samples	Description
1.	Indus River	Tarbela Dam	01	Electric power generation
2.	Jhelum River	Mangla Dam	01	Agriculture waste
3.	Chenab River	Head Marala	01	Agricultural & Industrial waste
4.	Jhelum River	Head Rasool	01	Agricultural waste
5.	Chenab River	Head Qadirabad	01	Industrial and Domestic wastes
6.	Chenab River	Head Tarimu	01	Agricultural and Industrial wastes
7.	Ravi River	On Indian border	01	River entering point to from
8.	Ravi River	Head Baloki	01	Domestic, Industrial and Agricultural waste
9.	Sutlej River	Head Sulemanki	01	Agrochemical Industrial wastes
10.	Ravi River	Sidhnai	01	Industrial, Agricultural and Domestic waste
11.	Indus River	Taunsa Barrage	01	Industrial & Agricultural wastes.
12.	Sutlej River	Head Islam	01	Agrochemical and textile Industries waste
13.	Sutlaj River	Panjnad	01	Merging point rivers
14.	Indus River	Guddu Barrage	01	Industrial, Agricultural and Domestic wastes.
15.	Indus River	Kotri Barrage	01	River +tributaries carrying Domestic, Industrial and Agricultural wastes
16.	Indus River	Endpoint of river	01	Entering point of River Indus to
17.	Arabian Sea		03 (at 3 Km distance)	Domestic, Agricultural and Industrial wastes
Total Number of Samples			19	

Annexure-V

Table-5A: Sampling Sites for the Monitoring of PFC's (Dry season, 2016)

Sr. #	Source	Site	Date of Sample Collection	GPS Locations		Samples			No. of Samples Collected
				Latitude	Longitude	Drinking Water ID	Surface Water	Sediment ID	
1	Indus River	Tunsa	11/11/2016	30.512043	70.849669	DW-1	SW-1	SD-1	3
		Guddu	19/11/2016	28.419535	69.712828	DW-2	SW-2	SD-2	3
		Kotri	19/11/2016	25.442080	68.316600	DW-3	SW-3	SD-3	3
		Endpoint of river	18/11/2016	24.986111	68.314722	DW-4	SW-4	SD-4	3
2	Dame (Reservoir)	Simly Dam	27/11/2016	33.721409	73.335190	DW-5	SW-5	SD-5	3
3	Dame (Reservoir)	Rawal Dam	27/11/2016	33.706493	73.112781	DW-6	SW-6	SD-6	3
4	Kabul River	Attock	25/11/2016	33.916399	72.231943	DW-7	SW-7	SD-7	3
5	Jhelum River	Mangla	25/11/2016	33.130303	73.816325	DW-8	SW-8	SD-8	3
		Tarimu	11/12/2016	31.149253	72.144550	DW-9	SW-9	SD-9	3
6	Chenab River	Marala	15/11/2016	32.668758	74.468776	DW-10	SW-10	SD-10	3
		Qadirabad	14/11/2016	32.319729	73.692939	DW-11	SW-11	SD-11	3
7	Ravi River	Lahore border	14/11/2016	32.669444	74.473056	DW-12	SW-12	SD-12	3
		Sidhnai	11/12/2016	30.571214	72.159577	DW-13	SW-13	SD-13	3
8	Sutlej River	Salmanki	13/11/2016	30.378577	73.870871	DW-14	DW-14	SD-14	3
		Panjnad	11/11/2016	29.344444	71.021111	DW-15	SW-15	SD-15	3
9	Arabian Sea	Karachi 1	18/11/2016	40.775833	68.054722	DW-16	SW-16	SD-16	3
		Karachi 2	18/11/2016	24.793056	67.041667	DW-17	SW-17	SD-17	3
		Karachi 3	18/11/2016	24.800556	67.025833	DW-18	SW-18	SD-18	3
10	Dame (Reservoir)	Tarbela	20/11/2016	34.054632	72.895516	DW-19	SW-19	SD-19	3
Total						19	19	19	57

Annexure-VI

Table-6A: Sampling Sites for the Monitoring of PFC's (2017-18)

Sr. No	Source	Site	Latitude	Longitude	Surface Water		Sediment		Biota	Sample no
					Wet	Dry	Wet	Dry		
1	Indus River	Kharmang	3444.293	07610.550	01 W	01D	01 W	01D	-	04
		Bunni	3339.995	7437.653	02 W	02D	02 W	02D	-	04
		Guddu Barrage	2829,09	6942,50	03 W	-	03	-	-	04
		End of River	35^{0}26.060	7528.2090	04 W	-	-	-	01F	02
2	Lake/Reservoir	Manchar Lake	264409	6769,90	05W	-	04 W	-	02F	03
3	Lake/Reservoir	Keenjhar Lake	2491,48	6807,27	06W	-	05 W	-	03F	03
4	Dam/Reservoir	Hub Dam	2524,84	6712,51	07W	-	-	-	-	01
5	River	Kabul River	3405,742	7144.426	08W	-	-	-	-	02
6	Dam/Reservoir	Warsak Dam	3410,311	7125.975	09W	03 D	06 W	03 D	-	05
7	Jhelum River	Head Rasool	3240,752	7331,437	10W	04 D	07W	04 D	-	04
8	Chenab River	Head Khanki	3224,283	7358,147	11W		08W		-	02
9	Ravi River	Head Balloki	3143,17	7428,06	12W	05 D	09W	05 D	-	04
		Head Sidhnai	3034,350	7209.350	13W	06 D	10W	06 D	-	04
10	Sutlej River	Head Sulemanki	3022,683	7351.749	14W	07 D	11W	07 D	-	04
11	Five Rivers Confluence	Panjnad	2920,588	7101.438	24W	08 D	-	08 D	-	02
12	Three sites of sea	Arabian Sea I	2479,71	6701,14	15W	-	-	-	-	01
		Arabian Sea II	2478,52	6704,39	16W	-	12W	-	06F	03
		Arabian Sea III	247575	6706,47	17W	-	13W	-		02
13	Dam/Reservoir	Rawal Dam	3342.630	7307.502	18W	-	14W	-	07F	03
14	Dam/Reservoir	Simly Dam	3442.885	7319.955	19W	-	-	-	-	01
15	Dam/Reservoir	Mangla Dam	3308.910	9342.267	20W	-	-	-	-	01
16	River	Jhelum Neelum	3428,13	7049'36	21W	09 D	15W	09 D	-	04
17	Chenab River	Head Qadirabad	3219,032	7341,168	22W	10 D	-	10 D	-	03
		Head Marala	3240,046	7428'046	23W	11 D	-	11 D	-	03
Total					24	11	15	11	5	66

Annexure-VII

Table-7A: Sampling Sites for the Monitoring of PFC's (2018-19)

Sr.#	Source	Site	Sample Collection Date	Latitude	Longitude	Wet Season			Sample No.
						Surface Water	Sediment	Biota	
1.	Indus River	Before Joining with Kabul river (Attock)	09/09/2018	33.8999183	72.248691	SW-1	S-1	-	02
		Before Panjnanad	19/08/2018	29.31825	70.7126	SW-2	S-2	B-1	03
		Before Tunsa barrage	19/08/2018	30.504458	70.856177	SW-3	S-3	B-2	03
		End point (Thatta)	20/08/2018	24.690051	67.979726	SW-4	S-4	-	02
2.	Kabul River	Warsik Dam	09/10/2018	34.162885	71.351356	SW-5	S-5	-	02
		Before joining Indus river	09/09/2018	33.934125	72.230112	SW-6	S-6	-	02
3.	Jhelum River	After Jhelum City	15/08/2018	32.933132	73.741688	SW-7	S-7	-	02
4	Chenab River	Multan	18/08/2018	30.073829	71.280852	SW-8	S-8	-	02
5	Ravi River	Below syphon	17/08/2018	31.70386	74.470189	SW-9	S-9	-	-
		After Lahore City Baloki	18/08/2018	31.220156	73.861901	SW-10	S-10	-	-
6	Sutlej River	Badian Usman wala	16/08/2018	30.970736	74.442083	SW-11	S-11	-	-
7	Arabian Sea	Before Panjnad Bahalpur	20/08/2018	29.343447	71.023924	SW-12	S-12	-	-
		Clifton Karachi	22/08/2018	24.805012	67.005845	SW-13	S-13	-	-

		Sea view apartments Karachi	22/08/2018	24.791654	67.039908	SW-14	S-14	-	-
		Village Restaurant Karachi	22/08/2018	24.777939	67.053641	SW-15	S-15	-	-
8	Rawal Lake	Middle of Rawal Lake	10/09/2018	33.704978	73.126207	SW-16	S-16	-	-
9	Thatta City		20/08/2018	24.748058	67.927541	-	DW-1	-	-
10	Karachi City		22/08/2018	24.93159	67.125499	-	DW-2	-	-
11	Hyderabad City		23/08/2018	33.67379	73.0655021	-	DW-3	-	-
12	Attock City		09/09/2018	33.790956	72.358133	-	DW-4	-	-
13	Bahawalpur City		20/08/2018	29.39347	71.709138	-	DW-5	-	01
14	Lahore City		17/08/2018	31.591888	74.459051	-	DW-6	-	01
15	Multan City		18/08/2018	30.156523	71.571379	-	DW-7	-	01
16	Jhelum City		15/08/2018	32.924865	73.720097	-	DW-8	-	01
17	Kasur City		16/08/2018	31.133101	74.45989	-	DW-9	-	01

Annexure-VIII

Table-8A: Concentration of PFCs (ng/L) in surface water samples during wet and dry seasons (2013-15)

Sr #	Sampling Sites	Wet Season		Dry Season	
		PFOA (ng/L)	PFOS (ng/L)	PFOA (ng/L)	PFOS (ng/L)
1	Tarbela	ND*	ND	ND	ND
2	Simly	0.4	2.33	0.34	3.52
3	Kabul	1.26	5.34	1.94	12.15
4	Attock	0.33	2.44	0.29	1.29
5	Taunsa	0.31	1.09	0.32	1.58
6	Guddu	ND	1.90	ND	ND
7	Kotri	0.33	1.30	0.32	1.79
8	End point of Indus river	0.51	1.57	0.48	1.58
9	Mangla	0.66	2.19	0.23	1.45
10	Rasool	ND	ND	0.44	1.34
11	Tarimu	0.46	8.75	0.79	4.73
12	Marala	0.48	2.08	0.42	ND
13	Qadirabad	0.25	3.97	0.50	1.69
14	River Ravi with Indian border	0.44	2.05	0.42	1.52
15	Baloki	0.75	1.60	0.36	1.52
16	Sidhnai	0.31	2.13	0.75	4.49
17	Sulemanki	0.71	1.44	0.71	2.17
18	Islam	0.52	1.43	0.73	3.27
19	Panjnad	0.49	2.91	0.31	2.25
20	Arabian Sea-I	0.67	2.10	0.76	1.15
21	Arabian Sea-II	0.55	1.20	0.54	2.86
22	Arabian Sea-III	0.72	1.32	0.48	1.58
23	Arabian Sea-IV	0.47	1.54	0.38	1.59
24	Arabian Sea-V	0.85	2.59	0.82	1.49

*ND: Not Detected

Annexure-IX

Table-9A: Concentration of PFCs (ng/L) in surface water sources (2015-16)

Sample ID	PFBA	PFHxA	PFBS	PFHpA	PFOA	PFHxS	PFNA	PFDA	PFOS
SW-1.1cd	0.90	0.82	ND	ND	0.27	ND	0.05	ND	0.19
SW-7.lcd	0.65	0.49	0.29	ND	0.14	ND	ND	ND	0.24
SW-8.lcd	1.18	0.83	ND	ND	0.14	ND	ND	ND	ND
SW-11.lcd	ND	0.12	ND	ND	ND	ND	ND	ND	ND
SW-12.lcd	0.27	0.39	ND	ND	0.11	ND	ND	ND	0.11
SW-13.lcd	1.04	1.56	0.19	0.13	0.59	0.17	0.12	ND	ND
SW-14.lcd	ND	0.71	0.38	0.08	0.48	ND	0.11	0.07	0.23
SW-15.lcd	1.14	0.83	ND	ND	0.36	ND	ND	ND	0.25
SW-16.lcd	ND	0.11	ND	ND	ND	ND	ND	ND	ND
SW-17.lcd	ND	0.09	ND	ND	ND	ND	ND	ND	ND
SW-18.lcd	ND	0.12	ND	ND	ND	ND	ND	ND	ND
SW-19.lcd	1.53	0.38	0.56	ND	ND	ND	ND	ND	0.15

Annexure-X

Table-10A: Concentration of PFCs (ng/L) in surface water sources in wet season (July-September, 2017-18)

Sr. No	Source	Site	Sample ID (Wet Season)	PFOS	PFHxS	PFOA	PFBA	PFNA	PFDA	PFUnA	PFHxA
1	Indus River	Kharmang	01W	ND	ND	ND	ND	ND	ND	ND	ND
		Bunji	02W	ND	ND	0.20	1.18	0.13	0.17	ND	ND
		Guddu Barrage	03W	ND	ND	ND	ND	ND	ND	ND	ND
		End of River	04W	ND	ND	0.41	2.36	ND	ND	ND	ND
2	Lake/Reservoir	Manchar Lake	05W	0.44	0.73	0.51	3.03	0.25	ND	ND	ND
3	Lake/Reservoir	Keenjhar Lake	06W	ND	ND	ND	ND	ND	ND	ND	ND
4	Dam/Reservoir	Hub Dam	07W	3.76	ND	1.56	6.84	1.37	0.53	ND	0.59
5	River	Kabul River	08W	ND	ND	0.54	0.96	0.18	0.30	ND	ND
6	Dam/Reservoir	Warsak Dam	09W	ND	ND	0.20	1.02	0.13	ND	ND	ND
7	Jhelum River	Head Rasool	10W	ND	ND	ND	ND	ND	ND	ND	ND
8	Chenab River	Head Khanki	11W	0.47	ND	0.24	0.55	ND	ND	ND	ND
9	Ravi River	Head Balloki	12W	ND	ND	0.37	0.63	0.14	0.17	ND	ND
		Head Sidhnai	13W	ND	ND	0.38	0.49	ND	0.32	ND	ND
10	Sutlej River	Head Sulemanki	14W	0.49	0.25	0.60	0.81	0.19	0.21	ND	ND
	Five Rivers Confluence	Panjnad	24W	1.53	1.20	2.14	16.30	1.32	ND	0.19	ND
11	Three sites of the Sea	Arabian Sea I	15W	ND	ND	0.35	ND	ND	ND	ND	ND
		Arabian Sea II	16W	ND	ND	0.36	ND	ND	ND	ND	ND
		Arabian Sea III	17W	ND	ND	0.77	0.31	ND	ND	ND	ND
12	Dam/Reservoir	Rawal Dam	18W	ND	ND	ND	ND	ND	ND	ND	ND
13	Dam/Reservoir	Simly Dam	19W	ND	0.57	0.42	1.76	0.29	ND	ND	ND
14	Dam/Reservoir	Mangla Dam	20W	ND	ND	0.18	1.16	ND	ND	ND	ND
15	River	Jhelum Neelum	21W	ND	ND	0.13	ND	ND	ND	ND	ND
16	Chenab River	Head Qadirabad	22W	ND	ND	0.41	0.67	0.20	ND	ND	ND
17	Chenab River	Head Marala	23W	ND	ND	0.18	0.26	ND	ND	ND	ND

ND: Not Detected

Annexure-XI

Table-11A: Concentration of PFCs in Surface Water Sources in Dry Season (December-February, 2018)

Sr. No	Sources	Site	Sample ID (Dry Season)	PFOS	PFHxS	PFOA	PFBA	PFNA	PFDA	PFUnA	PFHxA
1	Indus River	Kharmang	01D	ND	ND	ND	1.69	ND	ND	ND	ND
		Bunji	02D	0.17	ND	ND	1.10	ND	ND	ND	ND
2	Dam/Reservoir	Warsak Dam	03D	ND	ND	ND	1.65	ND	ND	ND	ND
3	Jhelum River	Head Rasool	04D	0.17	ND	ND	0.34	ND	ND	ND	ND
4	Ravi River	Head Balloki	05D	ND	ND	ND	ND	ND	ND	ND	ND
		Head Sidhnai	06D	ND	ND	ND	0.74	ND	ND	ND	ND
5	Sutlej River (Five Rivers Confluence)	Head Sulemanki	07D	ND	ND	ND	0.65	ND	ND	ND	ND
		Panjnad	08D	0.66	ND	ND	1.63	ND	ND	ND	ND
6	River	Jhelum Neelum	09D	0.15	ND	ND	0.35	ND	ND	ND	ND
7	Chenab River	Head Qadirabad	10D	0.26	ND	ND	0.33	ND	ND	ND	ND
8	Chenab River	Head Marala	11D	ND	ND	ND	1.18	ND	ND	ND	ND

ND: Not Detected

Annexure-XII

Table-12A: Concentration of PFCs (ng/L) in Sediments in Wet Season (July-September, 2017-18)

Sr. No	Source	Site	Sample ID (Wet Season)	PFOS	PFHxS	PFOA	PFBA	PFNA	PFDA	PFUnA	PFHxA
1	Indus River	Bunji	02W	ND	ND	0.04	ND	ND	ND	ND	ND
		Gudd Barrage	03W	ND	ND	ND	ND	0.06	ND	ND	ND
2	Lake/Reservoir	Keenjhar Lake	05W	ND	ND	0.09	ND	ND	ND	ND	ND
3	Dam/Reservoir	Warsak Dam	06W	ND	ND	ND	ND	0.09	ND	ND	ND
4	Chenab River	Head Khanki	08W	ND	ND	0.05	0.10	0.03	0.04	ND	0.04
5	Dam/Reservoir	Warsak Dam	09W	=D	ND	0.20	1.02	0.13	ND	ND	ND
6	Chenab River	Head Khanki	11W	0.47	ND	0.24	0.55	ND	ND	ND	ND
7	Ravi River	Head Balloki	09W	ND	ND	0.04	ND	0.04	ND	ND	ND
		Head Sidhnai	10W	ND	ND	0.04	ND	ND	ND	ND	ND
8	Dam/Reservoir	Rawal Dam	14W	ND	ND	0.11	ND	ND	ND	ND	ND
9	River	Jhelum Neelum	15W	ND	ND	ND	ND	0.03	ND	ND	ND
10	Blank	Sediment Blank	04BS	ND	ND	ND	ND	ND	ND	ND	ND

ND: Not Detected

Annexure-XIII

Table-13A: Concentration of PFCs (ng/L) in Sediments in Dry Season (July-September, 2017-18)

Sr. No	Source	Site	Sample ID (Wet Season)	PFOS	PFHxS	PFOA	PFBA	PFNA	PFDA	PFUnA	PFHxA
1	Indus River	Bunji	02D	ND	ND	0.12	ND	ND	ND	ND	ND
2	Dam/Reservoir	Warsak Dam	03D	ND	ND	0.15	ND	ND	ND	ND	1.04
3	Ravi River	Head Balloki	05D	ND	ND	0.06	ND	ND	ND	ND	0.03
4	Sutlej River	Head Sulemanki	07D	ND	ND	ND	ND	ND	0.06	ND	ND
5	Jhelum River	Neelum	09D	ND	ND	0.03	ND	ND	ND	ND	ND
6	Blank	Sediment Blank	04BS	ND	ND	ND	ND	ND	ND	ND	ND

ND: Not Detected

Annexure-XIV

Table-14A: Concentration of PFCs (ng/L) in Surface Water Sources in Wet Season (2018-2019)

Sr. No	Source	Sample Code	PFDoA	PFHxS	PFOA	PFBA	PFNA	PFDA	PFUnA	PFHxA
1	Indus River Before Joining with Kabul river (Attock)	SW1	ND	ND	0.69	12.19	0.50	ND	ND	ND
2	Indus River Before Panjnanad	SW2	ND	ND	0.71	11.22	ND	0.30	ND	ND
3	Indus River Before Tunsa barage	SW3	ND	ND	0.70	11.53	ND	0.17	ND	ND
4	Indus River End point (Thatta)	SW4	ND	0.571	1.24	13.00	ND	ND	ND	ND
5	Kabul River (Warsik Dam)	SW5	ND	ND	0.84	6.38	ND	ND	ND	ND
6	Kabul River Before joining Indus river	SW6	ND	ND	0.86	5.99	ND	0.17	ND	ND
7	Jhelum River After passing Jhelum city	SW7	ND	ND	ND	6.99	ND	ND	ND	ND
8	Chanab River Multan	SW8	ND	ND	ND	8.10	ND	ND	ND	ND
9	Ravi River Below Syphon	SW9	ND	ND	ND	8.89	ND	ND	ND	ND
10	Ravi River After Lahore City Baloki	SW10	ND	ND	ND	6.88	ND	ND	ND	ND
11	Sutlej River Badian Usmanwala	SW11	0.44	0.73	1.89	7.12	ND	ND	ND	ND
12	Sutlej River Before Panjnad Bahawalpur	SW12	3.76	ND	0.54	3.61	ND	0.53	ND	0.59
13	Arabian Sea Clifton Karachi	SW13	ND	ND	1.50	3.44	ND	ND	ND	ND
14	Arabian Sea Seaview Karachi	SW14	ND	ND	1.64	1.93	ND	ND	ND	ND
15	Arabian Sea Village Restaurant Karachi	SW15	ND	ND	2.20	2.62	2.16	ND	ND	ND
16	Rawal Lake Middle of Rawal lake	SW16	1.53	1.20	2.04	7.82	ND	ND	0.19	ND

ND: Not Detected

Annexure-XV

Table 15A: Overall summary of POPs monitoring (2005-19) in water, sediments and biota samples

UNU Phase	Year	Target compounds	Types of samples	Total samples collected	No of samples detected with POPs	%age	Total # of samples collected
Phase IV (2005-2008)	2007	OCPs	Surface water	19 (pre-monsoon)	9	24	38
				19 (post monsoon)			
	2007-2008	OCPs	Surface water	19 (pre-monsoon)	3	16	60
				19 (post monsoon)	2	11	
			Shrimps	10	5	50	
			Squids	10	10	100	
			Sea bass	4 sea bass samples collected and were analyzed as duplicate	4	100	
Phase-V (2008-2011)	2009	PCB	Water samples	19	7	37	19
	2011	PBDEs	Sediments	19	18	95	19
Phase-VI (2012-2015)	2013-2015	PFC's	Surface water	24 (Dry season)	23	96	48
				24 (Wet season)	23	96	
Phase-VII (2016-2019)	2015-2016	PFCs	Surface water	Dry season (Nov-Dec) 19	13	68	57
			Ground water	19	8	42	
			Sediment	19	0	0	
	2017-18	PFCs	Surface water	Wet season (24)	19	79	66
				Dry season (11)	10	91	
			Sediments	Wet season (15)	9	60	
				Dry season (11)	5	46	
			Biota	5	1	20	
	2018-19	PFCs	Surface water	16	16	100	44
			Sediments	16	0	0	
			Drinking water	9	3	33	
			fish	3	1	33	
Total				332	181	64	353

The compound specific inferences of 15 years long POPs monitoring are given as below:

About PCRWR

PCRWR is an apex body of the Ministry of Science and Technology and is mandated to conduct, organize, coordinate and promote research on all aspects of water resources including irrigation (surface and groundwater), drainage, soil reclamation, drinking water and wastewater. It has eight regional offices located at different agro-ecological zones and each centre conducts research on water-related issues of the respective zones. These Regional Offices are located at Lahore, Bahawalpur, Tandojam, Quetta, Peshawar, Karachi, Gilgit and Muzaffarabad. Besides these eight Regional Offices, PCRWR has a setup of 24 water quality testing and research laboratories in major cities of the country. This includes ISO-17025 accredited National Water Quality Laboratory having its own Laboratory Information Management System (LIMS). PCRWR has all types of infrastructure such as soil and water testing laboratories, groundwater assessment equipment, research farms to conduct and disseminate the research. It is the only organization in Pakistan that owns drainage type lysimeters in Lahore, Tandojam, Quetta and Peshawar. PCRWR has done considerable work on crop water requirements, tile drainage, soil reclamation, on-farm water management technologies, rainwater harvesting, artificial recharge, groundwater assessment and management, skimming wells, drinking water, and indigenous development of water testing and treatment tools, salinity and moisture sensors. To help in developing the capacity of in-service professionals and fresh graduates, PCRWR has also a well-equipped National Capacity Building Institute in Islamabad to provide short and long term trainings on all aspects of water.

PAKISTAN COUNCIL OF RESEARCH IN WATER RESOURCES

PCRWR

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