Tracking Persistent Organic Pollutants Signatures in the Pristine Environment of the Mountainous Ranges of Northern Pakistan: The Implication for Long Range Atmospheric Transport and Mountain Cold Trapping along Altitudinal Gradient

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APPROVAL CERTIFICATE

This is to certify that the dissertation entitled **"Tracking Persistent Organic Pollutants Signatures in the pristine Environment of the Mountainous Ranges of Northern Pakistan: The implication for Long Range Atmospheric Transport and Mountain Cold Trapping along Altitudinal Gradient** submitted by **Aqeela Muheen** is accepted in its present form by the Department of Environmental Sciences, Quaid-i-Azam University Islamabad, Pakistan, as satisfying the dissertation requirement for the degree of M.Phil in Environmental Science.

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Dedicated to my Loving and Caring Parents

Without whom I would not have achieved

this Milestone

DECLARATION

The material contained in this thesis is my original work, except where acknowledge. No part of this thesis has been previously presented elsewhere for any other degree.

Aqeela Muheen

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Table of Contents

List of Tables

List of Figures

List of Appendices

List of Abbreviations

Abbreviation	**Word**
POPs	Persistent Organic Pollutants
DDT	Dichlorodiphenyltrichloroethane
DDE	Dichloro diphenyl dichloro ethylene
DDD	Dichloro diphenyl dichloro ethane
HCB	Hexachloro benzene
HCH	Hexachlorocyclohexane
NBFRs	Novel Brominated Flame Retardants
PCBs	Poly Chlorinated Biphenyl
PBDEs	Polybrominated diphenyl ethers
DPs	Dechloran Plus
SVOCs	Semi Volatile Organic Compounds
TP	Tibetan Plateau
PAN	Pesticides Action Network
UNEP	United Nations Environmental Programme
AMAP	Arctic Monitoring and Assessment Programme
CKNP	Central Karakorum National Park

Abstract

High altitude mountain regions are ideal settings to study fate and behavior of Persistent Organic Pollutants (POPs). The pristine region of the mountainous ranges of northern Pakistan is characterized by mountain valley topography and diverse climatic conditions. POPs can be transferred to this region through Long Range Atmospheric Transport (LRAT) from the adjacent densely populated and agricultural countries like India, China and Sothern part of Pakistan. To investigate the signature and implications for LRAT and cold trapping effect along altitude soil and sediment samples were analyzed. Overall detection level of POPs were quite low but were comparable with the background concentrations reported from the various studies around the globe. The general trend of POPs was in this order OCPs>PCBs>PBDEs>NBFRs with average mean concentration of 2.150±1.326, 0.544±0.529, 0.417±1.455and 0.149±0.185 ng/g respectively. Among OCPs, DDTs were the most abundant in the study with an average concentration of 1.77 ng/g followed by Endosulfan and HCH. Hexa and Tetra CBs were more prevalent among PCBs and BDE-209 was more frequent congener found among PBDEs. While NBFRs were detected at very low levels. No significant correlation was found for the concentration of POPs with increasing altitude but steady trend was observed from low to mid altitudes under study. High ratios of DDT/DDE+DDD and low ratio of α/γ-HCH indicated the use of dicofol and Lindane in the adjacent countries. Low ratio of α/β-Endosulfan indicates the absence of technical Endosulfan and low TC/CC ratio suggests the hint of aged chlordane. The air mass back trajectory analysis revealed that the sampling area is mainly influenced by the air currents from North India, China and South part of Pakistan. So it can be assumed that these contaminants have been transported to the area by atmospheric transport from source regions. Further research need to be done to understand the environmental complexities associated with long range transport and cold trapping phenomena of POPs.

Keywords: POPs, Mountain cold trapping, Long range atmospheric transport, northern Pakistan, Altitude, DDT, HCH, PCBs, PBDEs, NBFRs

Chapter 1

Introduction

1.1.The rising concern and awareness about chemical pollution

There was a remarkable evolution in the chemical industry in the initial decades of 20th century (Aichner et al., 2013). So many organic chemicals were produced and brought into global market for the commercial purpose and they have been extensively used without knowing their adverse consequences on environment and human health. By the mid of 20th century the problem was raised by some individuals, then followed by some scientific observations (Tomasic, 2009). The concern about chemical exposure of humans and environment were taken into consideration after the publication of "Silent Spring" by an ecologist, scientist and writer Rachel Carson in 1962. The very first rising concern observed was the thinning of eggshell and reduced bird life expectancy in polar regions of the World (Carson, 1994). These observations were more highlighted under scientific studies in 1970s and 1980s. The concentration of these organic chemicals were found in the tissues of birds and mammals in the pristine regions, where no contamination source of these chemicals were found (Stow, 2005). This observation has led to the new era of research for the environmental scientist. Several studies reported the deterioration of Arctic regions confirm the trans-boundary pollution caused by these chemical industries. Different chemicals have different behavior in the environment depending on their chemical properties. Among the toxic chemicals, Persistent Organic Pollutants (POPs) have been classified as the most toxic and hazardous group of chemicals showing quite unique properties and behavior once released into the environment (El-Shahawi et al., 2010).POPs have been extensively reported in the cold environment of Arctic, so researchers have been looking for more evidences for the presence of airborne organic chemicals in the other colder regions of the globe as well like our mountain environment (Kumar et al., 2005; Zhao et al., 2006).

1.2.Persistent Organic Pollutants, Characteristics and their adverse impacts

Persistent organic pollutants (POPs) are organic chemicals, generally halogen substituted hydrocarbon molecules having cyclic or aromatic structure (Bartrons et al., 2012). They are characterized by their high persistency in the environment having bioaccumulation capacity and potential to cause toxicity. They posed high risk to the humans and environment being exposed to them (Axmon et al., 2008; Chemicals, 2002;

Lunder et al., 2010). They highly resist the biological, chemical and photolytic degradation and thus remain intact with environmental media for a long duration of time (Wang et al., 2006). They are widely distributed in the environment even in those region where they have never been produced or used (Simonich & Hites, 1995; Wania & Mackay, 1993). This wider distribution is due to Long range atmospheric transport (LRAT) where some selected POPs moves with the air currents to the distant places. This phenomena is supported by the physicochemical properties of POPs such as chemical stability and semi volatility from the point of release to the remote regions of the world (Simonich & Hites, 1995). When these contaminate get enter into the food chain, they lead to bioaccumulation and biomagnification processes where the concentration of a contaminant in the organism increases as compared to the environment with the passage of time. As a result different possible harmful effects of these contaminants can be observed, they can be teratogenic, carcinogenic, neurotoxin and endocrine disruptive effects in different organism. These effects are due to their lipophilic property of POPs, they deposit into the fatty tissues of organisms when they become part of the food chain (Jones & De Voogt, 1999).

1.2.1. Sources of POPs

POPs release into the environment from the natural as well as anthropogenic sources (Tomasic, 2009). Natural sources of POPs (PAHS) can be volcanic activity and vegetation fire (El-Shahawi et al., 2010) and anthropogenic activities includes intended application of industrial (PCBs) and agriculture/farming (OCPs) and unintended production as well, such as by-products from combustion like dioxins and furans (Lohmann et al., 2007). The agriculture sources of POPs can be found globally, the places with intensive agriculture. The Organochlorine pesticides (OCPs) such as DDT, Toxaphene, HCH, Chlordane, Aldrin, Mirex and Dieldrin are grouped under this category. They have been extensively used to increase the yield of crops and to control some diseases as well (e.g. DDT to control malaria vector) (Monitoring, 2004).

1.2.2. Fate and distribution of POPs in the environment

If the general distribution of contaminants in the environment is concerned, their concentration decreases with the increasing distance from the source because of different factors that are dilution, degradation and dispersion. While opposite is true for the POPs, their increasing concentrations have been observed in different environmental media taken from the very distant place from the source as compared to the samples taken near the point of source (Wania & Westgate, 2008). Such a case is applicable for the selected POPs which moves towards the northern latitudes and their concentration also increase accordingly. These selected POPs are semi volatile organic compounds (SVOCs) which undergo LRAT to the distant regions far from their source of production (Daly & Wania, 2005). Even the low concentration of POPs can transfer via fresh and marine water and also SVOCs can move through air currents to the long distances, that's why their distribution in the environment is wider global and beyond boundaries. Due to these wider distribution these pollutants have been found in the most remote, pristine and colder regions of the world (El-Shahawi et al., 2010). Such pollutants transfer in the form of vapors or adsorbed onto the atmospheric aerosols through atmospheric circulation on a regional and global scale. When they reach to the remote ecosystem, they deposit on to the surface media via precipitation and air-soil exchange (Hansen 2000; UNEP 2001).

1.2.3. Regulations regarding safety of POPs

In the current era environmental health is an important part of official political agenda of all international organizations (Tomasic, 2009). POPs have been banned and regulated since early 1970s after realizing their adverse impacts on environmental health. The health issues of local populations due to POPs exposure were related to that of Arctic regions (Selin & Selin, 2008). Many of the industrial countries regulated and restricted the usage of certain chemicals after doing chemical risk assessments. In 1980s the trans-boundary nature of POPS were revealed, so it was very important to raise this particular issue beyond the national level. Many of the international organizations did deal with POPs in their agenda with some other hazardous chemicals such as Pesticides Action Network (PAN), United nations environmental program (UNEP), Arctic Monitoring and Assessment Program (AMAP) (Tomasic, 2009). In 2001 Stockholm Convention was signed by 90 countries which came into force in 2004. This convention was all about POPs, it was agreed that 12 POPs and their substances should be eliminated or reduced which were named as "Dirty Dozen". Eight Organo-chlorine pesticides included in the list that are, DDT, dieldrin, endrin, heptachlor, Mirex and Toxaphene, Aldrin, and chlordane; two industrial chemicals hexachlorobenzene (HCB) and the polychlorinated biphenyl (PCB) group; and two industrial by-products: dioxins and furans (El-Shahawi et al., 2010).The developed countries already prohibited these chemicals but still they are being transported to developing countries through illegal marketing. The Stockholm convention also deal with the measures of obsolete stockpiles of POPs that still exist in some third and second world countries (Eqani et al., 2012).

1.3.Cold Trapping Mechanism and its influence on the fate of POPs

1.3.1. Polar Cold Trapping and Mountain Cold Trapping

Polar regions and mountains are considered to be the most clean and pure ecosystems on earth but actually this is not true (Meire et al., 2012). This issue was highlighted in late 1970s when pesticides were reported in the fatty tissues of polar bear in the Arctic region. This evidence led to a new era of research regarding airborne POPs in the colder regions of the world (El-Shahawi et al., 2010). POPs have been reported in the numerous studies in the polar regions of the world, this phenomena is termed as **"Polar Cold Trapping"** and can be explained by **"Global Distillation Model"** proposed by Mackay and Wania. The model suggest that the Semi Volatile organic compounds (SVOCs) undergo repeated cycles of deposition and evaporation at higher latitudes called grass hopper effect (Wania & Westgate, 2008). Temperature is considered as the main driven force in cold trapping mechanism. The distribution can be explained by the cold condensation effect that SVOCs shift their phase equilibria with decreasing temperature from the gas phase in the atmosphere to the earth surface (Wania, 2003). Just like polar regions, mountain regions are also susceptible to POPs contamination due to global fractionation process(Chemicals, 2002). Some studies have witnessed the presence of some selected POPs on higher elevations on mountains and this effect has been termed as **"Orographic or Mountain Cold Trapping".** In early 1990s some comprehensive studies were conducted in North America and Europe regarding the fate and transport of the POPs in the high altitude environment (Calamari et al., 1991; Camarero et al., 1995; Miller et al., 1993; Smith et al., 1993).

1.3.2. The Mechanism of Mountain Cold Trapping

Mountains are characterized by temperature gradient from low to high elevation. Chemical distillation towards cold regions happens in the mountains because of increasing elevation and decreasing temperature(Davidson et al., 2003). Temperature difference in scavenging the precipitation between low land and mountains is the main driven force behind the mountain cold trapping (Wania & Westgate, 2008). Previous studies reported that the atmospheric wash-out of the POPs to the tropical and sub-tropical mountainous regions is due to the precipitation rate (Daly & Wania, 2005).

Snow is the prime form of precipitation in the higher altitude ecosystem. Snow has an important role to deposit and accumulate POPs to the soil and fresh water after being transported to these pristine regions by air circulations (Herbert et al., 2006). The efficiency of snow in mountain cold trapping can be explained by several reasons, firstly it contains a significant fractions of annual precipitation which have better efficiency of scavenging the POPs in atmosphere, secondly the seasonal snow pack act as temporary reservoir of POPs, they release to the soil and fresh water system when it melts (Arellano et al., 2011). The snow melting contributes more towards the accumulation of POPs in the mountain ecosystem along with the direct deposition from atmosphere. So snow deposition and cold temperature both boost up the transfer of POPs from atmosphere to the terrestrial surfaces in the mountain region. Snow has the lower capacity of storage of organic contaminants as a result of the air-surface flux as compared to vegetation and soil. The role of mountain regions in the long range transport of POPs depends on the air-surface exchange including wet and dry deposition and emissions (Wang et al., 2009). The burden of POPs in the mountain soil depends on the physicochemical properties of each pollutant being deposited and this ultimately linked to the temperature factor. Temperature cause partitioning of chemical in the environmental media, when temperature decreases the air-water partition coefficient (K_w) of POPs gets lower and tends to improve air-soil partition coefficient (K_{SA}) and it leads to the deposition of POPs more into the soil and vegetation at higher altitudes (Daly et al., 2007; Hippelein & McLachlan, 1998). POPs in the atmosphere can directly accumulate to the terrestrial surface via exchanges between different environmental media. POPs present in the air go through exchanges between water and soil in the gaseous form and can further deposit in sediments (Bhattacharya et al., 2003).

1.3.3. The Preferential accumulation of POPs at higher altitudes

Polar Regions and high mountain regions have many similarities that they have low temperature, deep snow cover, and both are considered as pristine regions. As far as POPs are concerned even these regions are not left away. In such a consideration there are many differences which count in their accumulation such as closeness to emission sources, different meteorological conditions (wind direction, precipitation gradient, temperature) and dramatic shift in ecological gradient after short distances (Tremolada et al., 2008).The principal of atmospheric long range transport of the POPs to both high altitude regions and arctic regions are the same, however the type of pollutants being transported to these regions and the distance from the source regions make differences (Kallenborn, 2006). The short lived organic compounds which cannot reach to the Arctic by latitudinal atmospheric transport are trapped by the high altitude environment (Daly & Wania, 2005). High volatile organic compounds become more enriched in higher altitude to a larger extent than less volatile organic compounds. The relative composition of the POPs also varies with different altitude. The contaminants which prefer to move towards high altitude regions are more volatile like HCHs and HCBs, while less volatile contaminants like DDT stays in lowlands.

1.4.The altitudinal dependence on mountain cold trapping effect of POPs

The first study was reported in 1998 regarding the altitudinal dependence of organochlorine accumulation in mountain areas (Blais et al., 1998). In general consideration with the increasing altitude the concentration of SVOCs also increase as these pollutants can be directly accumulated from the atmosphere. Other factors like pre-deposition degradation, meteorological conditions, local emission sources, land cover topography etc. can give rise to more complications in the phenomena (Daly & Wania, 2005). An increasing concentrations of some selected contaminants have been observed with the increasing altitudinal gradient (Borghini et al., 2005; Fernández & Grimalt, 2003).The temperature gradient effectively leads to the accumulations of POPs in higher altitude areas. Snow, air, soil and vegetation samples from the mountains region showed increasing concentration with altitude(Demers et al., 2007). POPs relationship to the altitudinal-temperature gradients was reported from the alpine ecosystem of Italian Alps (Nizzetto et al., 2006). The trend of increasing concentration with increasing altitude for DDT and Endosulfan were observed in the western slope of Shergyla mountain (Zhu et al., 2014). Precipitation has a very strong relationship with the increasing trend of POPs along the increasing altitudinal gradient, it boost up the condensation process at higher altitude and reduce summer revolitilization of organic pollutants from the mountain surface. Tremolada suggested a strong precipitation effect with the levels of POPs in the mountain soil of Alps and Andes along altitudinal gradient (Tremolada et al., 2008).

1.5. Factors controlling the mechanism of Mountain Cold Trapping of POPs

1.5.1. Meteorological factors

Fluctuations in different meteorological factors can alter the pathways of POPs in the air and ultimately influence their fate in the environment and wild life. Monsoon is a climate system operating on seasonal scale, having various wind speed direction an d precipitation pattern. The monsoon driven variability has a strong influence on the transport and fate of POPs in certain regions. The concentrations of POPs change with seasonal variations and current winds (Sheng et al., 2013). Some ice core records studies in different studies evident a good correlation between the pollutants level and their air mass trajectories originating from certain source regions. The air mass trajectories originating from South Asia showed very good correlation with the pollutants levels in the Tibetan Plateau having the same features (Ming et al., 2008). Different air monitoring based studies reported Organochlorine Pesticides (OCPs) and Polychlorinated biphenyls (PCBs) in the air of Tibetan Plateau. An air sampling study near Mount Everest by Ling et al reported that the OCPs found in the air primarily originated from the India-Nepal-Pakistan region. The high level of DDT in the south Tibetan Plateau reported by Gong et al, showed a strong association with the Eastern Asian Monsoon system. An extensive air sampling study across Tibetan Plateau by Wang et al, suggested that the Indian monsoon impacted regions have high POPs levels in the air than the other region which are not influenced by the monsoon. In general these studies suggesting the possibility of monsoon driven atmospheric transport of the organic pollutants to the untouched location of Tibetan Plateau (Sheng et al., 2013). Davidson reported a study "Orographic Cold-Trapping of Persistent Organic Pollutants by Vegetation in Mountains of Western Canada" where back trajectories used to provide the information on the transport pathways (Davidson et al., 2003). The trajectories exposed that the air masses received by these particular sites passes over Asia and Pacific Ocean. The result of this study showed the similar trend of contaminants received by other alpine ecosystems by LRAT. Combining the air mass trajectories with the seasonal variations, the pathways of these organic contaminants can be traced out (Yang et al., 2013). (Ren et al., 2014) reported that higher concentration of DDT in passive air samples from Sygera mountain in Tibetan Plateau have been observed in the monsoon season as compare to non-monsoon season. Beside macro-meteorological patterns, micro-meteorological pattern also influence POPs concentration in soil (Guazzoni et al., 2011). Various features of mountain like aspects, landforms and slopes leads to different meteorological variables like solar radiations, soil and air temperature, precipitation and wind and relative humidity (Barry, 1992). All these factors are responsible for different concentration of POPs accordingly. (Tremolada et al., 2009) reported lower concentration of POPs in the southern slope of Andossi plateau (Central Italian Alps) as compare to the northern slope because of the high solar radiations and lower humidity in the soil. The condition in northern slope favor the more accumulation and retention of POPs in the soil like lower temperature and snow cover.

Vegetation also has a significant role in trapping these organic contaminants from the air to the terrestrial surface in the high altitude regions. A large scale vegetation have major impact on the atmospheric concentrations of POPs during their annual growth (Wania & McLachlan, 2001). Vegetation has high lipid content having high ability to bioaccumulate POPs (Tarcau et al., 2013). Vegetation such as mosses, lichens tree bark, and pine needles have been extensively used as a passive sampler in different studies for monitoring purpose of atmospheric organic contaminants.

1.5.2. Seasonal cycle of POPs transfer in mountain area

Airborne pollutants effectively deposited and retain in the mountain surface during winter season because of efficient snow scavenging and low temperature. The pollutants deposited depend directly on the amount of pollutants present in the air masses. Thus concentration in the air get decreased in winter due to the increased deposition rate to the mountain surface from the air (Guazzoni et al., 2011). In summers, high temperature in low lands leads to the increased emissions fluxes and also the pollutants present in terrestrial surface re-volatilize and this way the concentration becomes more in the air and the anabatic wind (wind blow at day time) blow this contaminated air to the uphill and deposited in the snow (Hoff et al., 1992; Wania et al., 1998).. And in springs when this snow melts, the POPs present in there re-volatilize back to the air or get enter to the water-soil system. And when soil is directly exposed to air again with the rise in temperature, the POPs from soil revolitilize and deposit somewhere else via Grasshopper Effect and thus the cycle carry on and POPs distribute widely in different environmental matrices (Dalla Valle et al., 2005). A study in the air of Shergyla mountain in the southern TP, revealed that most of the targeted

POPs concentration significantly increased in summers as compare to winters (Zhu et al., 2014).

1.6.Indicators of POPs in mountain environment

To investigate the fate and transport of POPs at high altitude environment different environmental matrices have been studied that includes both biological and physical. In different studies higher elevation lakes from different part of the globe, fish samples have been analyzed for the investigation of POPs accumulation in the food web of alpine ecosystems (Kallenborn, 2006). Lakes in remote regions are considered as main trappers of long range atmospheric transported organic contaminants. So the aquatic food web can be sensitive to the accumulation of the long range transported contaminates and can be investigated conveniently because such food chain is simple and short. Fresh water fish and sediments are considered as best indicators for POPs for the assessment of eco-toxicological risks (Kallenborn, 2006). High altitude alpine fauna are the best indicators for the air monitoring for POPs, because they have slower growth rate, longer lives and have more lipid contents comparatively organisms of lower lands (Yang et al., 2010). Pines are the best natural passive air samples of air born organic contaminants because of the potential uptake properties of their waxy layers. In literature Pines have been reported as an efficient matrix for the quantification of semi volatile organic contaminants such a s Polycyclic Aromatic Hydrocarbons (PAHs) (Amigo et al., 2011; Piccardo et al., 2005; Ratola et al., 2010; Tremolada et al., 1996), Polybrominated diphenyl ethers (PBDEs) (Ratola et al., 2011), Polychlorinated diphenyl ethers (PCBs) (Grimalt & Van Drooge, 2006) and Organochlorine pesticides (OCPs) (Hellström et al., 2004). Man-made passive air sampling devices are other best tools to investigate the POPs concentration level in the atmosphere of remote regions of the world. The reason is they don't need electrical power supply for their operation and easy to deploy in the remote sites and they can give the quantitative assessment of the SVOCs concentrations in the atmosphere (Schrlau et al., 2011). Snow is the dominants from of precipitation in most of the high altitude mountain regions and efficiently traps both gaseous form and particulate bounded SVOCs from the atmosphere. The gaseous SVOCs undergo sorption from air to snow surface while particulates are being trapped in the structure of ice core. The historical trends of POPs usage can be reflected by assessment ice cores, glacier ice has been regarded as an important source of POPs. The glacier melting supplies water to the downstream water system, in this way they are contributing enough towards the influx of POPs in the mountain ecosystem. It is revealed that glaciers do contribute 50 - 90% of OCPs to the downstream water bodies stated by (Blais et al., 2001). This way high mountain livestock and vegetation are at greater risks in the mountainous regions. Recently long lived POPs were detected in cow milk in high altitude region of Switzerland showing the significant increase in cold trapping mechanism from air to milk (Shunthirasingham et al., 2013). Concentrations of PCBs and PBDEs in Tibetan butter and the highest values were reported from the butter samples from Siachin province (Wang, et al. 2009). Soil is the ultimate sink for POPs in the environment, so soil samples have been extensively used for the analysis purpose. Extensive studies have been reported regarding POPs concentrations in the soil and its relation to the altitudinal gradient (Gong et al., 2014; Pan et al., 2013; Tremolada et al., 2008; Wang et al., 2007). For POPs soil has been considered as an important sink and carrying the majority burden of environmental pollutants (Mackay, 2001; Meijer et al., 2003). Special properties of mountain soil like high organic content, efficient snow scavenging (Lei & Wania, 2004), low temperature, and particular wind directions which moves the pollutants along the mountain slopes from the source. And all these characteristics favor the accumulation of POPs in the mountain soil and increase their retention time in the soil (Guazzoni et al., 2011). So soil has been used as an important and most frequently used indicator in most of the relevant studies.

1.7.Problem statement

It is evident from the literature review that POPs experience long range atmospheric transport and deposit to the colder environment far away from their source of production. Northern part of Pakistan is home to three of the world famous ranges that are Karakoram, Himalayas and Hindukush. The region has extensive network of fresh water system and narrow mountain valleys. The sparse human population, minimal to nonexistent industrial activities and no identified reported sources of POPs in this region set an ideal setting for researching environmental fate and distribution plus the potential of LRAT of these organic pollutants. The region is considered as third pole of the world, because these all ranges are concentrated with glaciers outside the polar region but this region is adjacent to the most populous and rapidly industrializing countries including China, India and southern part of Pakistan. POPs from distant source regions can be transported via air currents to this pristine environment. High elevations and low temperature in the area may play important role in trapping organic contaminants from atmosphere due to cold condensation effect called as "orographic cold trapping effect". According to (Blais et al., 2001) glacier melting supplies water to the downstream water system, in this way they are contributing enough towards the influx of POPs in the mountain ecosystem. Low temperature, snow cover and remote ecological similarities with the Arctic regions make it an ideal place to provide more evidences of mountain cold trapping phenomena. Several studies have been reported in Tibetan Plateau China regarding the existence of POPs, implication of long range atmospheric transport and their fate and distribution with mountain cold trapping effect (Liu et al., 2010; Zheng et al., 2012; Zhu et al., 2015). Some studies in the same region focused the altitudinal distribution of POPs that their concentration increase with the increasing altitude (Wang et al., 2009; Yang et al., 2013). The northern part of Pakistan lies quite near to Tibetan Plateau and share almost same geographical characteristics. The longest river of Pakistan (Indus) originated in the highlands of Tibetan Plateau and enters to the northern Pakistan and then running to whole length of the country. The above mentioned studies, reported in Tibetan Plateau also provide an indication of the existence of POPs in the northern mountain region of Pakistan as well. Furthermore these mountainous regions got less attention regarding monitoring of POPs. No relevant study has been reported so far from the northern mountain regions of Pakistan, while some studies have been reported from Himalayan regions from Nepal and China (Gong et al., 2014; Guzzella et al., 2011; Kang et al., 2009; Lee et al., 2008; Wang et al., 2007; Wang et al., 2006).

1.8. Objectives of the study

- Tracking signature and potential sources of POPs in the pristine environment of the mountainous ranges of Northern Pakistan.
- To highlight the potential of pristine environment as sink of the POPs as a result of Long range atmospheric transport and cold trapping effect.
- Assessing different factors responsible for Mountain cold trapping of POPs along the altitudinal gradient
- To provide a baseline study for the further research opportunities in the area to study the global fate of POPS and their adverse effect.

Chapter 2

Methodology

2.1. Study area description

For the study purpose Gilgit district was chosen, this is the central district of Gilgit Baltistan province located in the Northern part of Pakistan. The district covers an area of 16, 300 Km^2 lies between 35° 31́ to 36° 09́ N and 73° 24́ to 74° 54́ E. It borders with Hunza-Nagar to the North, Astore and Diamer to the south, Skardu to the north east and district Ghizer to the west. The study area map is given in (Fig 2.1). The area is characterized by mountain valley topography and fed by Hunza River, Ghizer River and Indus River along with several other tributaries. The area is surrounded by several glaciated ranges which feed water to these rivers in the form of fresh water streams. Gilgit is surrounded by famous mountain ranges of the world that are Karakoram, Himalayas and Hindukush (Fig 2.2) The junction of these glorious ranges, at the convergence of Indus and Gilgit rivers near a small town Jaglot which is 40Km away from Gilgit city creates a distinctive geographical feature(Geographic, 2015). The area have distinctive ecological zones due to its vast altitudinal range and the climatic conditions, low precipitation and the effects of westerly humid winds (CKNP, 2015).

2.1.1. Climate and Topography

Due to diverse topography the climate of the study area varies from subtropical temperate to dry alpine (Alam et al., 2012). The minimum average temperature reaches -15 to -20 °C in winters and in summers the average temperature is moderate with average maximum temperature 35°C and minimum 16 °C (PMD, 2015). In the study area the local climate is characterized by greater precipitation in winter and spring season, in summer's arid continental climate is dominant and sudden start of cold weather in early autumn. Karakoram and Himalayan mountains in northern Pakistan are greatly influenced by the diverse trend of precipitation during summer, the maximum rainfall in winters and spring by the limited influence of south monsoon system. The snowfall is more concentrated in the January and February in high altitude valleys and stays for a long time and in lower altitude snow fall is not very strong (CKNP, 2015).

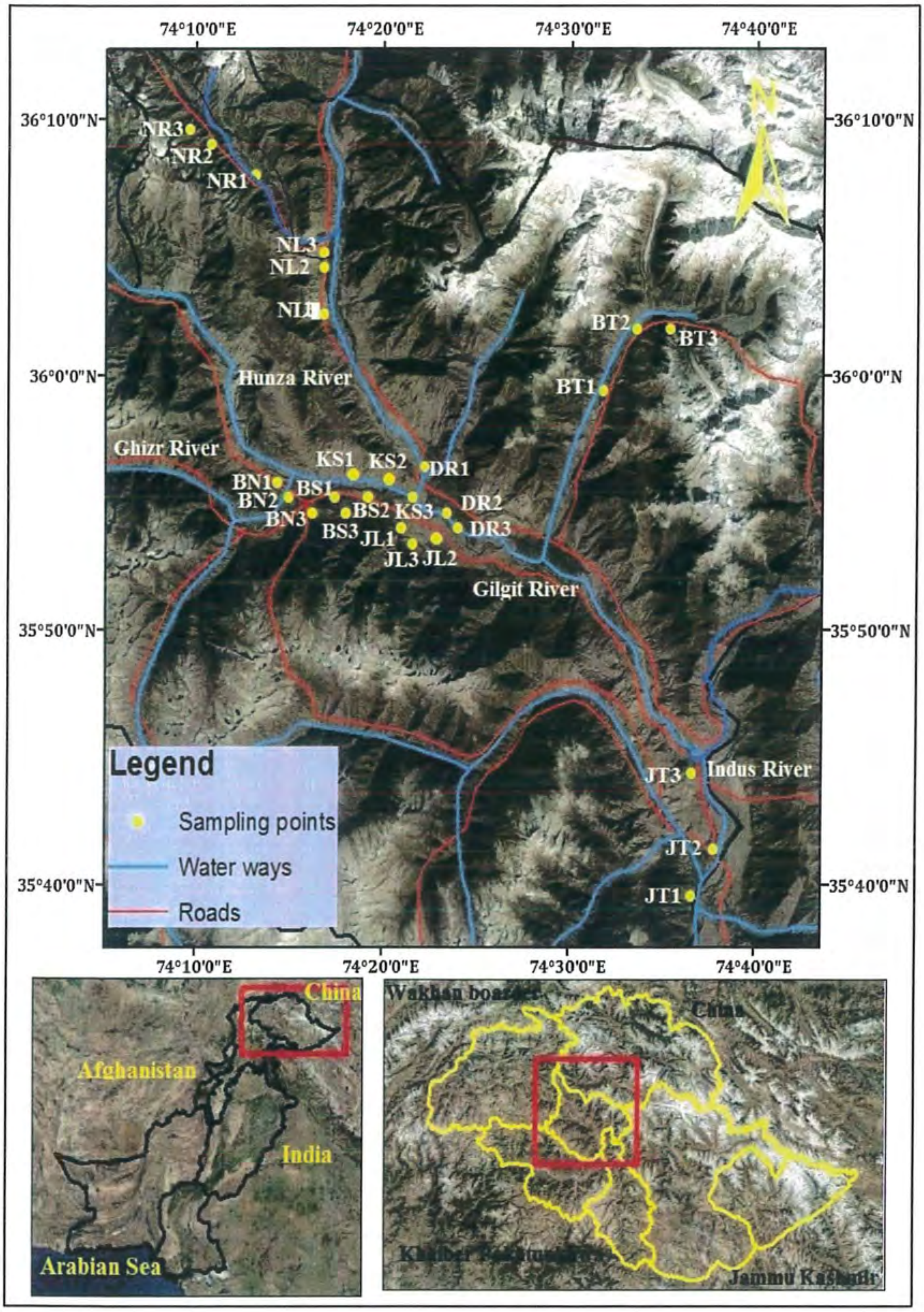


Figure2.1: Map of study area

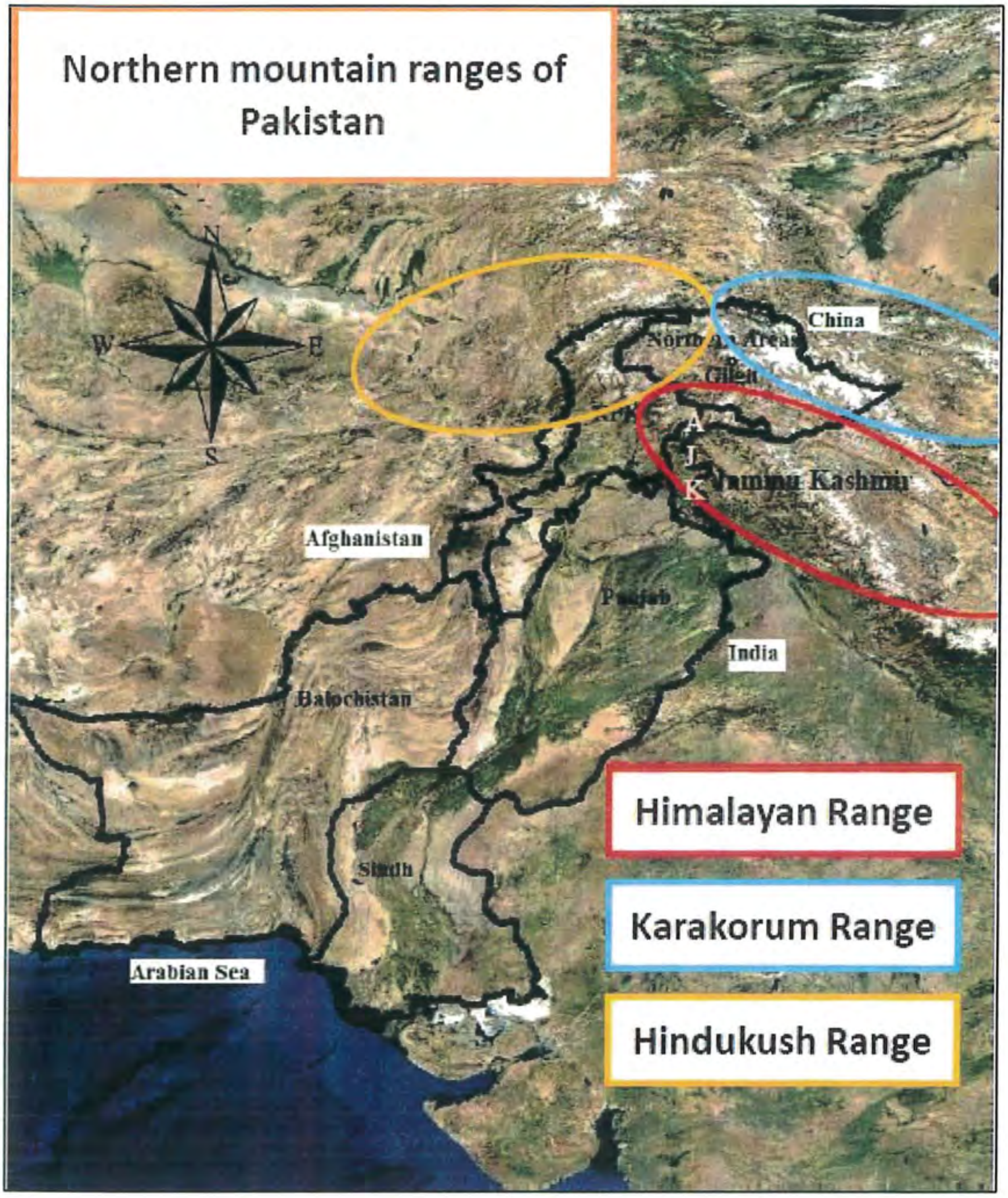


Figure 2.2: The northern mountain ranges of Pakistan

2.1.2. Sampling sites

The sampling points are shown in the study area map in (Fig 2.1) and some information is given in (Table 2.1). The following sampling locations were selected for the study purpose.

1-Konodas 2-Danyore 3-Jutial 4-Baseen 5-Barmas 6-Nomal 7-Naltar 8-Bagrot 9-Jiglot

The first four sites represent the central part of District Gilgit and considered as main towns. This part longitudinally spread along the north and south bank of the Gilgit River. Kondas and Danyore lies in the north bank of the river while Jutial, Baseen and Barmas lies in the south bank of the river.

Bagrot Valley

Bagrot valley located at 36°1'4" N 74°33'19" E encircled by high Karakoram mountains. Wonderful physical features in the locality of the valley include the Rakaposhi, Diran peaks in the northwest and northeast respectively and Dubani peak in the east. Bagrot valley is one of the important valley in National Karakorum Central Park (CKNP) which has summer pastures, glaciers and possess faunal and floral variety (Hussain et al., 2012).

Naltar

The Naltar Valley is situated at 36°9'34.14 N and 74°11'20.29 E covering a total area of 27,206 ha situated within the Karakoram highlands. It lies very close to the Hunza Valley in the Karakorum range and 40 km from the Gilgit city. From the Hunza River a narrow steep area starts, which ends up in the rocky terrain of Naltar. The valley comprises a range of habitats from snow zone to alpine grassy meadows and pastures, forest, stony and rocky vertical cliffs. This is beautiful valley covered with snow peaks and glacial lakes at the altitude ranging between (1700-5000 m) (Abbas et al., 2013).

Nomal

Nomal Valley is located in district of Gilgit on the left of River Hunza about 25 km from Gilgit town and has a covered area of 9 miles. Agricultural land of this valley is mostly plain fertile and suitable for all kind of crops, vegetables and fruits.

Jaglot

Jaglot situated 45 km from central Gilgit lies along Karakoram highway. Jaglot is very important spot located at the junction of three important mountain ranges that are Karakoram, Himalayas and Hindukush and two rivers that are Hunza River and Gilgit River.

Table 2.1: Information about sampling sites

Sites	Code	Latitude(N)	Longitude(E)	Altitude (m)
Jaglot	JT	35°41'52.35"	74°37'56.66"	1350
Konodas	KS	35°55'33.26"	74°19'46.51"	1487
Danyore	DR	35°55'0.74"	74°23'29.35"E	1504
Baseen	BS	35°55'24.38"	74°15'26.68"	1546
Jutial	JL	35°54'32.68"	74°20'56.12"E	1555
Barmas	BS	35°54'48.60"	74°18'11.19"E	1587
Nomal	NL	36° 4'0.18"	74°17'5.74"E	1700
Bagrot	BT	36° 1'40.00"	74°33'39.71"E	2450
Naltar	NR	36° 9'34.66"	74°11'48.35"E	3000

2.1.3. Sampling strategy

The selected sampling points represent different altitudinal gradients with different topography and climatic conditions. One of the important considerations was accessibility to the points with respect to various altitudes to fulfill the objectives of the study. The altitude of the sampling sites ranged from 1300-3000 m above sea level. The sampling was carried out to explore the possible signature of POPs in the study area and to assess their implication for mountain cold trapping effect along altitudinal gradient.

2.2. Sample collection

2.2.1. Soil sampling

A total of 27 surface soil (n=27) were collected at the depth of (0-10cm) from the 9 sampling sites. From each site 3 samples were taken and each sample was combination of 3 sub samples. Samples were taken using a stainless steel spade and reserved in plastic zippers and transferred to the laboratory. The samples were sieved through 2mm sieve, freeze dried and transported to Guangzhou and were stored frozen at -20°C until further laboratory analysis.

2.2.2. Sediment sampling

Same number of surface sediment samples (n=27) were collected from the Gilgit River and available fresh water streams from each site. Each sample was composite of 3 sub samples collected (0-5cm) from the upstream, downstream and from the deposition zone along the river and streams. The samples were taken with hand trowel and sealed in polyethylene zippers and then transferred to laboratory. The samples were air dried, grind and sieved through 2mm sieve and transported to Guangzhou laboratory and reserved frozen at -20°C until further analysis.

2.3. Extraction and clean up

OCPs

Sediment and soil samples (20gram each) were Soxhlet-extracted with DCM (Merck and Co., Inc.) for 24 hr. Before extraction a mixture of surrogate standardsof2, 4, 5, 6-tetrachloro-*m*-xylene (TC*m*X), PCB 30, PCB 198, and PCB 209 were added to samples. Then samples both soil and sediments (20g) each were Soxhlet-extracted with DCM (Merck and Co., Inc). Activated copper granules were added into the collection flask to remove elemental. Then this extract was exchanged into hexane by concentrating it (Merck and Co., Inc.). An alumina/silica gel column extracted for 48 hours with DCM then at 250, 180 and 450°C baked for 12 hours. It was then followed by the clean up by using extracted alumina/silica column packed with neutral alumina neutral silica gel sulphuric acid silica, and anhydrous sodium sulphate. The column was eluted with 50 ml of DCM/hexane (1:1). By adding 25 μL of dodecane, the fraction was concentrated to 0.2 ml under a gentle high-purity nitrogen stream. Prior to the analysis a known quantity of PCB-54 was added to the sample as an internal standard.

PBDEs/NBFRs

After drying and homogenization samples (20 gram) were spiked with 20ng of PCB 198 and PCB 209 as surrogate recovery standards. The extraction was done using with dichloromethane (DCM) for 36 hr. For removing elemental sulphur, activated copper granules were added to the collection flask. The sample extract was concentrated and solvent-exchanged into hexane and further reduce by a rotary evaporator. Extracts were purified through an 8 mm i.d. alumina/silica column packed as follows (from top to bottom): anhydrous sodium sulphate (1cm), 50% sulfuric acid silica (3cm), neutral silica gel (3cm, 3% deactivated) and neutral alumina (1cm, 3% deactivated). FRs were eluted with 20ml of a mixture of dichloromethane:hexane (1:1, V/V), and concentrated to 0.5 ml under a gentle stream of nitrogen. For the final cleanup step a GPC column was used. In a 15cm glass column (id=2 cm) 6.5g of Bio-Beads S-X3 were used. The concentrated samples were loaded and eluted with 55mL of a mixture hexane:DCM (1:1, V/V). The first fraction (15mL) was discarded, FRs and the recovery standard was collected the following fraction (40ml). As "keeper"30μL of dodecane containing 10 ng 13C-PCB 141 were added as internal standards. Under a gentle nitrogen stream samples were concentrated to the final volume of 30 μL and then stored for injection.

PCBs

Sediment and soil (20g) were spiked with 20 ng PCB 30 and PCB 198 as surrogate standards, Soxhlet extracted with dichloromethane (DCM) or mixture of acetone and hexane (1:3), respectively for 48 h. Activated copper pieces were added in flasks of Soxhlet extraction apparatus to remove elemental sulfur. The extracts were solvent exchanged into hexane, volume reduced to approximately 1 mL using a rotary evaporator, and cleaned on a 7 mm i.d. acidic silica gel-alumina column containing anhydrous sodium sulphate (1 cm), 50% sulfuric acid silica (3 cm), neutral silica gel (1 cm, 3% deactivated) and neutral alumina (3 cm, 3% deactivated) from top to bottom. The column was eluted with 40 mL hexane/DCM (1:1) to yield PCB fractions. For soil and moss samples, they were further purified by concentrated sulphuric acid and gel permeation chromatography (GPC). A GPC column was filled with 6 g of Bio-Beads S-X3 in a 15 cm glass column (2 cm i.d.). S4 PCB fractions were loaded and eluted with 45 mL DCM/hexane (1:1). The first 15 mL were discarded and the next 30 mL fraction, containing the PCBs, was collected and concentrated under a gentle N2 flow. PUF disk extracts were only purified with the multilayer column and N2 concentrated. Prior to instrumental analysis, 10 ng 13C labeled PCB 141 was injected into each sample as an internal standard.

2.4. Instrumental analysis

OCPs

Agilent GC-ECDHP-6890 series system with a CP-Sil 8 CB capillary column (50 m, 0.25 mm, 0.25 µm) was used for the analysis of OCPs. As a carrier gas Helium was used at a flow rate of 1.1 ml/min under a constant-flow mode. The oven temperature started at 60 °C for 1 min, increased to 295 °C at a rate of 4 °C/min and held for 28 min. Split/Splitless injection with temperature 250°C of 1 µl sample was analyzed with a 5 min solvent delay time. Prior injecting and analyzing the samples an inlet DDT degradation was checked and controlled on daily basis. Then detected OCPs in samples were quantified.

PCBs

PCBs concentrations were measured using GC-EI-MS applied with a 50 m capillary column (Varian, CP-Sil 8 CB, 50 m, 0.25 mm, 0.25 µm). The temperature of ion source, injector inter-surface and transfer line were 230, 250 and 280°C. Oven temperatures started at 150 °C for 3 min, and increased to 290 °C at a rate of 4 °C/min, and held for 10 min.. For the monitoring of each target compound group in a specific window, MS was used in the SIM mode with two ions. Quantification of PCBs were performed using a HP-Chemstation by con- firming their peaks and retention times.

PBDEs

The analysis of PBDEs was performed on GC-ECNI-MS (Agilent GC7890 coupled with 5975C MSD) with a DB5-MS capillary column (15 m × 0.25 mm i.d. × 0.25 µm film thickness). Helium was used as carrier gas at the flow rate of 1 mL min-1 and methane was used as chemical ionization moderating gas. The injection of 1 µL of sample done in a split less mode. The temperature of transfer line was 280°C and ion source was maintained at 280 °C and 230°C. The initial temperature of GC oven set at

110°C for 1 min, raised up to 200°C at a rate of 20°Cmin-1 (held for 1 min), then to 310°C at a rate of 10°Cmin-1 (held for 12 min).

2.5. Quality assurance and quality control

To evaluate potential sample contamination and the repeatability of analysis a procedural blank, a spiked blank consisting of all chemicals and a duplicated sample were run after every batch of 10 samples. Strict quality assurance and control measures were followed for the monitoring purpose of all analytical procedures. Average surrogate recoveries for TC*m*X and PCB-209 were calculated to be 73±6% and 81±5 % for the sediment samples, 57±4% and 71±11% for soil samples. Estimating the corresponding amount of analytes that would generate a signal-to-noise ratio of 3:1, the instrumental detection limit (IDL) values from the lowest standards were calculated. The compounds were measured as not detected (ND) below IDLs. The method detection limits (MDLs) were calculated as average values of blanks, with 3 standard deviations of blank values. A standard of 3 times the IDLs was used for calculating the MDLs for the compounds which were not detected in the blanks. According to recovery ratios and blanks values, reported values were corrected.

2.6. Statistical analysis

Statistical tests were performed using SPSS (Statistical Product and Service Solutions, V. 16.0, SPSS Inc., CHI, USA) and XLSTAT. Principle component analysis (PCA) was performedto evaluate sources, similarities and differences among the distribution of all targeted compounds during sampling period as well with different factors. Satellite imagery maps were developed using Arc GIS version 9.3.

Chapter 3

Results and Discussion

3.1. Concentration profile and spatial distribution of POPs in soil and sediments

The overall POPs concentrations trend in soil and sediment samples followed the same order that is OCPs>PCBs>NBFRs>PBDEs but the concentrations were higher in soil samples as compare to sediment samples shown in (Fig 3.1 and 3.2). Comparison of this study with many other similar studies from worldwide in soil is compiled in (Table 3.4) and in sediment samples in (Table 3.5).

3.1.1.Organochlorine pesticides (OCPs)

The mean concentration of all OCPs in both soil and sediments are summarized in (Table 3.1). OCPs concentrations were found in all soil and sediment samples and bearing the highest concentration values among all POPs. In general, trend for OCPs concentration in soil samples follows the order as ΣDDTs> Endosulfan (*α*-Endosulfan+ *β*-Endosulfan)> ΣHCH> Chlordane (*trans*-Chlordane (TC)+*cis*-Chlordane (CC)>Heptachlor>HCB. The average concentration of $\sum_7$OCPs was 2.150±1.326 ng/g and 1.016±0.266 ng/g in soil and sediment samples respectively. The concentration of DDTs was most abundant in this study. The mean concentration of ΣDDTs (*o,p'* DDE+ *p,p'*-DDE+ *o,p'*-DDD+ *p,p'*-DDD+ *o,p'*-DDT+ *p,p'*-DDT) was 1.772±1.955 in soil samples. DDT concentration was highest accounted for 47% with the mean value of 1.016±0.753ng/g followed by its metabolites DDD and DDE contributing 21% and 14% with mean values of 0.458±0.860 and 0.298±0.393 ng/g respectively. Then mean concentration of $\sum_6$DDTs found in this study was less than many other relevant studies from Everest area China, Italy Andes, China and much less than North Eastern Romania that was reported as 19.9 ng/g and South East region Tibet (Tarcau et al., 2013; Tremolada et al., 2008; Wang et al., 2007a; Yang et al., 2013). ∑DDTs concentration from this study was greater than the study reported from Peru Alps, another study from South East Tibetan Plateau (Tremolada et al., 2008; Zhu et al., 2015) and comparable with South slope of Himalaya Nepal (Gong et al., 2014). ∑Endosulfan, ΣHCHs (*α*-HCH+ *β*-HCH+ *γ* HCH+ *δ*-HCH, *ε*-HCH) and ∑Chlordane contributing 6%, 5% and 4 % with mean values of 0.133±0.075, 0.116±0.123 and 0.087±0.117 ng/g respectively. HCB and Heptachlor contributed lowest concentration

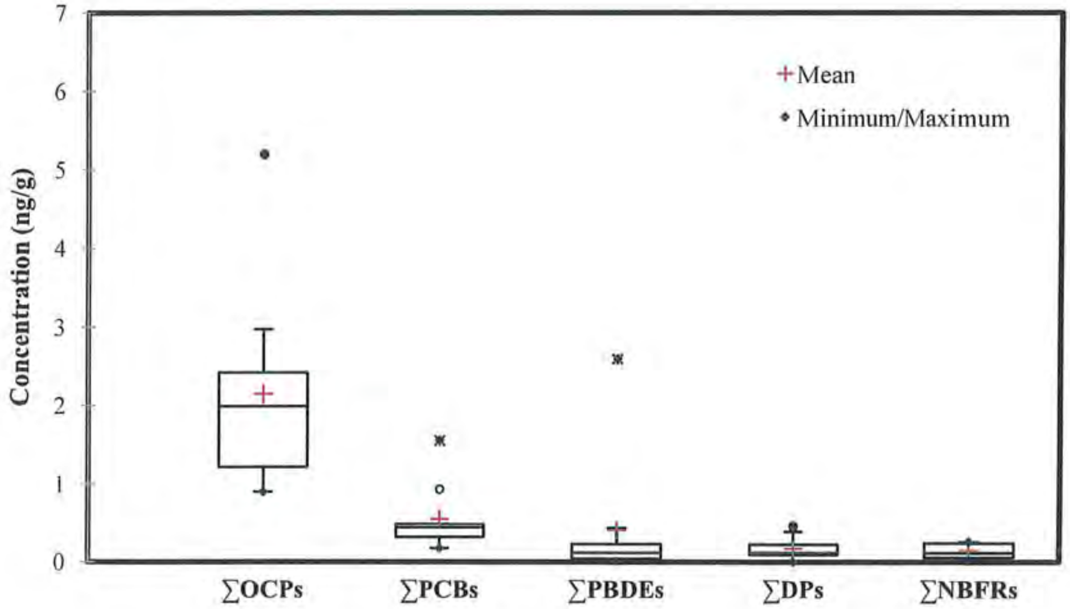


Fig 3.1: Concentration of POPs in soil samples

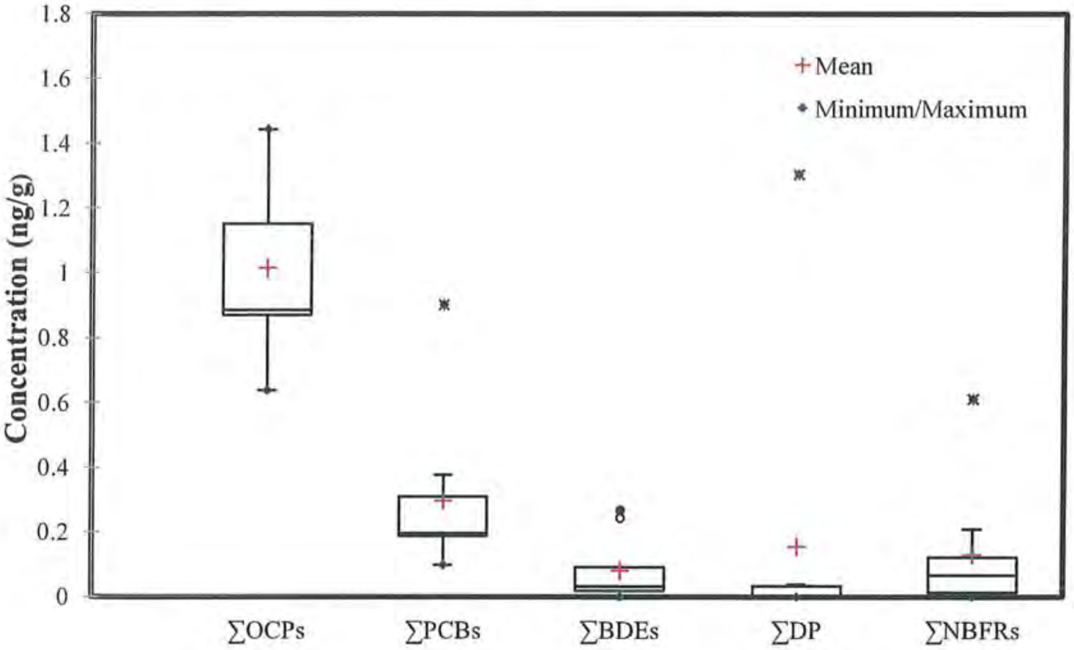


Fig 3.2: Concentration of POPs in sediments

with the mean values of 0.029±0.041 and 0.016±0.017 ng/g respectively accounted for 2% collectively to the whole OCPs.

The mean concentration of Endosulfan was comparable with (Zhu et al., 2015) and mean concentration of ∑HCH was about the same level as documented by (Yang et al., 2013; Zhu et al., 2015) and much lower than concentrations reported from European mountain regions that are Andossi plateau Italy and North-Eastern Romania (3.1 ng/g each) (Tarcau et al., 2013; Tremolada et al., 2009). The mean concentration of Chlordane in this study was similar with Italy Andes but greater than Peru Alps (Tremolada et al., 2008). HCB concentration reported in this study was comparable with (Gong et al., 2014; Tarcau et al., 2013; Tremolada et al., 2008) and less than reported by (Tremolada et al., 2009).The mean concentration values of OCPs in sediment samples were lower as compare to soil samples. The overall trend follows this order: ∑DDT>∑Endosulfan>∑HCH>∑Chlordane>Heptachlor>Mirex>HCB. The mean concentration value of ∑DDT in sediments was 0.790±0.359 ng/g. DDT was again the most abundant in sediments accounted for 63 % with the mean value of 0.643±0.120 ng/g followed by Endosulfan, DDE and ∑HCH contributing 13%, 8% and 7% with mean value of 0.130±0.115, 0.079±0.158 and 0.069±0.093 ng/g respectively. Chlordane and Heptachlor both accounted for 4% with mean value of 0.040±0.033 ng/g each. In sediments samples the average concentration of ∑DDT was comparable with lake Star sea TP (Cheng et al., 2014), greater than reported by (Borghini et al., 2005) and much less than the concentration values reported by (Grimalt et al., 2004) and three lakes studied by (Cheng et al., 2014). ∑HCH mean concentration from the current study was less than in studies reported by (Cheng et al., 2014; Grimalt et al., 2004). The lowest mean concentrations were of Mirex and HCB (0.008±0.024, 0.006±0.007 ng/g) respectively. The mean concentration of HCB was less than which reported by (Borghini et al., 2005; Grimalt et al., 2004).

Table 3.1: Descriptive statistics of OCPs in soil and sediment (ng/g) samples.

POPs	Soil			Sediments		
	D.F(%)	**Mean±SD**	**Range**	**D.F (%)**	**Mean±SD**	**Range**
o,p'-DDT	100	0.256±0.3	0.013-1.543	88	0.061±0.08	ND-0.367
o,p'-DDD	100	0.041±0.06	0.003-0.255	100	0.007±0.009	0.001-0.043
o,p' DDE	100	0.013±0.02	0.001-0.096	100	0.002±0.003	0.001-0.016
p,p'-DDT	100	0.759±0.4	0.529-2.689	100	0.580±0.04	0.530-0.693
p,p'-DDD	100	0.255±0.3	0.012-1.543	88	0.060±0.08	ND-0.367
p,p'-DDE	100	0.444±0.8	0.015-3.817	100	0.076±0.15	8.2E-04-0.780
∑DDT		**1.772±1.9**	**0.592-9.946**		**1.016±0.26**	**0.638-1.440**
α-Endosulfan	100	0.025±0.02	ND-0.100	100	0.025±0.04	0.001-0.197
β-Endosulfan	85	0.106±0.06	ND-0.229	88	0.104±0.08	ND-0.332
∑Endosulfan		**0.133±0.07**	**0.001-0.330**		**0.130±0.11**	**0.003-0.530**
α-HCH	100	0.022±0.02	1.6E-04-0.07	100	0.009±0.01	1.6E-04-0.056
β-HCH	100	0.050±0.09	1.1E-03-0.499	100	0.006±0.008	1.1E-04-0.039
γ HCH	100	0.032±0.03	1.2E-03-0.125	100	0.014±0.01	5.1E-04-0.052
δ-HCH	100	0.007±0.008	3.8E-04-0.009	100	0.006±0.01	3.2E-04-0.052
ε-HCH	100	0.002-0.002	1.2E-04-0.009	100	0.003±0.003	1.9E-05-0.009
∑HCH		**0.116±0.1**	**0.008-0.593**		**0.040±0.03**	**0.005-0.139**
Trans-Chlordane	100	0.065±0.07	0.003-0.433	100	0.029±0.02	3.6E-04-0.036
Cis-Chlordane	92	0.021±0.03	ND-0.200	100	0.011±0.01	1.1E-04-0.036
∑TC/CC		**0.087±0.11**	**0.004-0.634**		**0.042±0.03**	**4.8E-04-0.150**
Heptachlor	100	0.029±0.04	0.003-0.191	96	0.009±0.008	ND-0.034
HCB	100	0.016±0.01	0.001-0.056	100	0.006±0.007	2.3E-04-0.034
Mirex	88	0.002±0.00	ND-0.019	96	0.008±0.02	ND-0.117
$\sum_7$OCPs		**2.15±1.32**	**0.906-5.197**		**1.016±0.26**	**0.638-1.440**

D.F: Detection frequency
N.D: Not Detected

3.1.2.Polychlorinated biphenyls (PCBs)

The mean concentration of the PCBs congeners in soil and sediment are given in (Table 3.2) and their site wise percent composition in soil is shown in (Fig 3.3) and sediments in (Fig 3.4). The average concentration of $\sum_{32}$PCBs in soil samples was 0.544±0.529 ng/g which is almost 4 times lower than that of OCPs. The mean concentrations $\sum_{32}$PCBs detected in soil samples ranged from 0.085-2.358 and 0.007-1.591ng/g in sediments. The mean concentration of $\sum_{32}$PCBs in soil from this study are comparable with (Tremolada et al., 2009; Zhu et al., 2014) and slightly higher than (Zheng et al., 2012; Zhu et al., 2015; Zhu et al., 2014) and Peru Alps (Tremolada et al., 2008). While the mean concentrations of PCBs reported by Andes Italy (Tremolada et al., 2008) and in Andossi Plateau Italy (14 ng/g) by (Tremolada et al., 2009) were much higher as compare to the mean concentration reported in this study. The most abundant congener found was PCB-169 contributing 23 % to the total PCBs followed by PCB-28 (13%), PCB-158, PCB-138 and PCB-153 accounted for almost 5 % each. The trend of homologues of all PCBs in soils and sediments followed the same order follows: Hexa-CBs>Tetra-CBs> Penta CBs>Tri-CBs>Hepta-CBs> Di-CBs. Hexa-CBs were more abundant (42%) followed by Tetra-CBs (23%), Penta-CBs (16%), Tri-CBs (14%) Hepta-CBs (4%) and Di-CBs (2%) with mean values 0.225±0.223, 0.124±0.103, 0.087±0.182, 0.074±0.058, 0.020±0.021 and 0.014±0.011 ng/g respectively. While in sediment samples the average concentration of $\sum_{32}$PCBs was 0.302±0.327 ng/g. PCB-169 was the dominant congener in sediment samples as well, accounted for 33% followed by PCB-138, PCB-158 (10%) each, PCB-28 (9%), PCB-153 (7%) and 128 (6%) of the total PCBs congeners. The trend of homologues PCBs was very much similar in sediments as of in soil samples. Hexa-CBs are leading with 49%, Tetra (19%), Penta-(13%), Tri-(9%), Hepta-(8%), and Di-CBs (2%) with mean values 0.148±0.148, 0.058±0.061, 0.039±0.078, 0.026±0.033, 0.025±0.031, and 0.006±0.005 ng/g respectively. PCBs in both soil and sediments were mainly consist of Hexa, Penta and Tetra-CBs in agreement with the studies reported in soil from Mt. Sagarmatha, Himalayas, Nepal (Guzzella et al., 2011)and such a trend were also observed from Italian Alps and Andes Peru (Tremolada et al., 2008) and in sediments (Pozo et al., 2007). And the same proportion of congener was found in a global survey conducted by (Meijer et al., 2003). The abundance of medium level chlorinated congeners in the current study suggest the accumulation of these organic contaminants in the cold environment at higher altitude driven by the process of cold condensation (Lei & Wania, 2004). The low detected concentration of PCBs in both soil and sediment in the current study can be considered as the background levels in Karakoram and Himalayan region.

Table 3.2: Descriptive statistics of PCBs congeners in soil and sediment (ng/g) samples.

POPs	Soil			Sediments		
	D.F(%)	**Mean±SD**	**Range**	**D.F (%)**	**Mean±SD**	**Range**
PCB-8 (Di)	100	0.014±0.011	0.001-0.034	100	0.006±0.005	0.001-0.022
PCB-28(Tri)	100	0.074±0.058	0.006-0.197	96	0.026±0.033	ND-0.113
PCB-37	100	0.009±0.007	0.001-0.025	100	0.007±0.006	3.1E-04-0.02
PCB-44	100	0.015±0.016	0.001-0.075	100	0.007±0.008	1.0E-04-0.03
PCB-49	100	0.011±0.010	0.001-0.051	100	0.005±0.005	1.4E-04-0.02
PCB-52	100	0.021±0.021	0.001-0.093	100	0.007±0.008	1.4E-04-0.03
PCB-60	100	0.011±0.010	0.001-0.041	85	0.005±0.005	ND-0.018
PCB-66	100	0.016±0.015	0.001-0.069	100	0.007±0.008	4.4E-05-0.03
PCB-70	100	0.018±0.014	0.001-0.060	100	0.010±0.011	4.2E-04-0.04
PCB-74	100	0.013±0.012	5.4E-04-0.04	100	0.005±0.005	3.2E-05-0.02
PCB-77	89	0.003±0.003	ND-0.013	81	0.002±0.002	ND-0.011
∑Tetra-CBs		0.124±0.103	0.012-0.450		0.058±0.061	0.004-0.256
PCB-82	89	0.017±0.054	ND-0.277	58	0.006±0.012	ND-0.045
PCB-87	100	0.004±0.011	1.2E-04-0.05	100	0.001±0.003	2.4E-05-0.01
PCB-99	100	0.008±0.016	6.5E-05-0.05	100	0.002±0.005	3.1E-05-0.02
PCB-101	96	0.013±0.021	ND-0.090	96	0.007±0.016	ND-0.078
PCB-105	69	0.007±0.017	ND-0.086	58	0.003±0.008	ND-0.041
PCB-114	92	0.014±0.032	ND-0.156	62	0.006±0.013	ND-0.056
PCB-118	92	0.014±0.030	ND-0.141	58	0.008±0.019	ND-0.095
PCB-126	81	0.003±0.003	ND-0.017	62	0.002±0.002	ND-0.013
∑Penta-CBs		0.087±0.182	0.002-0.869		0.039±0.078	0.001-0.349
PCB-128	54	0.007±0.017	ND-0.075	31	0.005±0.017	ND-0.075
PCB-138	87	0.025±0.054	ND-0.238	42	0.012±0.035	ND-0.159
PCB-153	88	0.027±0.058	ND-0.250	54	0.011±0.028	ND-0.129
PCB-156	56	0.013±0.049	ND-0.254	46	0.001±0.004	ND-0.020
PCB-158	85	0.025±0.055	ND-0.237	42	0.012±0.035	ND-0.158
PCB-166	78	0.005±0.012	ND-0.055	31	0.004±0.012	ND-0.056
PCB-169	96	0.125±0.065	ND-0.276	96	0.099±0.066	ND-0.274
∑Hexa-CBs		0.225±0.223	0.002-0.960		0.148±0.148	ND-0.707
PCB-170	70	0.007±0.009	ND-0.039	62	0.006±0.009	ND-0.042
PCB-179	19	0.000±0.001	ND-0.004	15	0.000±0.001	ND-0.007
PCB-180	81	0.007±0.009	ND-0.039	62	0.006±0.009	ND-0.042
PCB-183	67	0.003±0.004	ND-0.016	62	0.004±0.006	ND-0.022
PCB-187	78	0.005±0.004	ND-0.016	69	0.005±0.007	ND-0.026
PCB-189	59	0.003±0.004	ND-0.013	62	0.002±0.006	ND-0.145
∑Hepta-CBs		0.028±0.033	ND-0.130		0.025±0.031	ND-0.146
$\sum_{32}$PCBs		**0.544±0.529**	**0.085-2.358**		**0.302±0.327**	**0.007-1.591**

D.F: Detection Frequency
ND: Not Detected

3.1.3.Polybrominated Diphenyl Ethers (PBDEs) and Dechlorane Plus (DPs)

Summarized mean concentration of PBDEs congeners are given in (Table 3.3) and their site wise percent composition in soil and sediments are shown in the (Fig 3.3 and 3.4). Seven congeners of PBDEs (BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, BDE-183, and BDE-209) were detected both in soil and sediment samples. The mean concentration of $\sum_7$PBDEs in soils was 0.417±1.455 ng/g which was lower but closer enough to the average concentration of PCBs. The average concentration of $\sum_7$PBDEs in this study was considerably higher than the studies reported by (Tarcau et al., 2013; Wang et al., 2009; Zheng et al., 2012; Zhu et al., 2015) and much lower than the background soil concentrations from Europe (Cetin & Odabasi, 2007; Hassanin et al., 2004).The most abundant congener was BDE-209 in most of the samples contributing 87% of the total PBDEs with mean concentration 0.368±1.447 ng/g followed by The same concentration trend of congeners was also observed by (Guzzella et al., 2011; Jiao et al., 2009) at higher altitude lake sediments from Norway and Himalaya Nepal and (Zheng et al., 2015) in Chinese Forest soil. BDE-99 and BDE-47 contributed 7% and 3% with mean concentration values 0.028±0.101 and 0.011±0.036 ng/g respectively. (Zheng et al., 2012) reported abundance of lower brominated congeners that are BDE-28 and BDE-47 from the Balang mountain Tibetan Plateau, while in current study BDE-47 was least abundant and BDE-28 was not detected in any of samples. In sediment samples $\sum_7$PBDEs mean concentration was 0.076±0.163 ng/g which was almost 5 times less than that of the soil samples. BDE-209 was again the most dominant congener accounted for 94%, while rest of them was not detected in 99% of the samples. The presence of penta BDE-99 was again the indication of the cold condensation phenomena in the study area for highly volatile organic compounds (Jiao et al., 2009). On the other hand the presence of BDE-209, deca brominated compound might be due to the usage of technical formulation of BDE-209 in nearby countries and other reason may be the octa and penta BDEs have been banned but deca BDE-209 is still being used. PBDEs are flame retardants widely used in plastics and textiles (Guzzella et al., 2011) so their usage in China, India and Pakistan is possible.

Table 3.3: Descriptive statistics of PBDEs congeners and NBFRs in soil and sediment (ng/g) samples.

POPs	Soil			Sediments		
	D.F (%)	**Mean±SD**	**Range**	**D.F (%)**	**Mean±SD**	**Range**
BDE-47	15	0.011±0.036	ND-0.178	4	0.002±0.009	ND-0.045
BDE-100	4	0.004±0.020	ND-0.102		ND	ND
BDE-99	19	0.028±0.101	ND-0.513	4	0.001±0.006	ND-0.032
BDE-154	4	0.002±0.010	ND-0.054		ND	ND
BDE-153	4	0.002±0.012	ND-0.059		ND	ND
BDE-183	54	0.001±0.008	ND-0.039	4	0.002±0.011	ND-0.055
BDE-209	46	0.368±1.447	ND-7.431	23	0.070±0.155	ND-0.657
$\sum_7$PBDEs		**0.417±1.455**	**ND-7.431**		**0.076±0.163**	**ND-0.702**
anti-DP	46	0.065±0.086	ND-0.321	19	0.078±0.363	ND-1.818
syn-DP	58	0.114±0.181	ND-0.628	46	0.089±0.408	ND-2.045
PBEB	58	0.017±0.068	ND-0.342	38	0.000±0.001	ND-0.005
HBB	42	0.008±0.025	ND-0.127	38	0.001±0.001	ND-0.003
TBB	54	0.002±0.010	ND-0.050	42	0.001±0.004	ND-0.020
TBE	58	0.016±0.026	ND-0.111	50	0.026±0.055	ND-0.206
TBPH	58	0.027±0.056	ND-0.260	50	0.015±0.026	ND-0.096
DBDPE	58	0.079±0.121	ND-0.365	46	0.089±0.199	ND-0.835
$\sum_6$NBFRs		**0.149±0.185**	**ND-0.654**		**0.132±0.274**	**ND-1.032**

ND: Not Detected

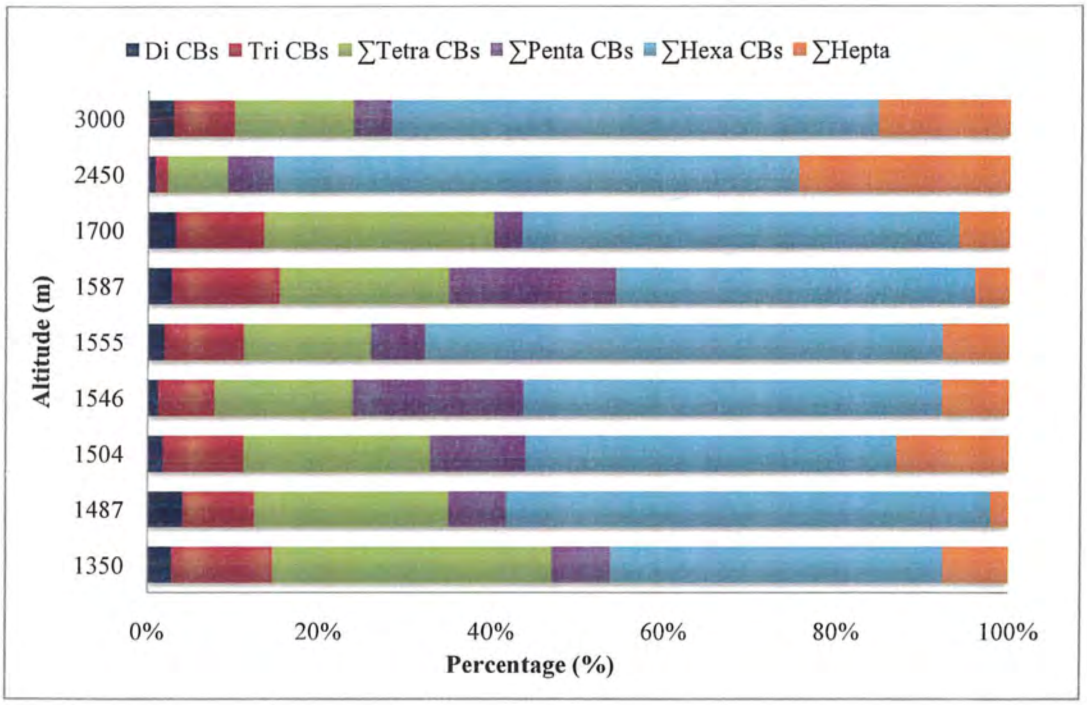
Dechlorane Plus (DPs) individual isomers (anti-DP and syn-DP) were also analyzed and their average concentrations in soils are 0.065±0.086 and 0.114±0.181 ng/g respectively, while in sediment samples their concentrations were 0.078±0.363 and 0.089±0.408 ng/g respectively. The data regarding DPs is very limited in the pristine regions of the world. Their concentration can be related to the available literature. The average concentration of ∑DPs in this study was lower than all available literature and these reported studies were conducted in urban, industrial and e-waste recycling sites (Ma et al., 2011; Yu et al., 2010) and also lower than the remote surface soil of Northern China (Ma et al., 2014) and forest soil of China (Zheng et al., 2015).

Table 3.4: Mean concentrations (ng/g) of POPs in soil from this study and other mountainous regions worldwide

Location	Altitude (m)	DDT	Endosulfan	HCH	Chlordane	HCB	PCBs	PBDEs	References
Southeastern Tibetan Plateau, China	2596-4144	$\sum_{6}$DDT 0.65	$\sum_{2}$Endo 0.067	$\sum_{5}$HCH 0.14	-	0.20	$\sum_{18}$PCBs 0.057	$\sum_{13}$PBDEs 0.024	**Zhu et al, 2015**
30 mountains across China	1320-3830	-	-	-	-	-	$\sum_{29}$PCBs 0.5 1	-	**Zheng et al, 2014**
Balang mountain, east edge, TP	1439-4479	-	-	-	-	-	$\sum_{25}$PCBs 0.163	$\sum_{13}$PBDEs 0.026	**Zheng et al, 2012**
South East Tibetan Plateau	2000-5000	2.85		0.40		0.17			**Yang et al, 2013**
Mt.Qomolangma,EverestChina	4700-5620	0.385–6.06*	ND	ND	-	-	-	-	**Wang et al, 2007**
Tibetan Plateau	3000-6000						0.186	0.011	**Wang et al, 2009**
Andossi plateau, Italian Alps	1900			3.1		2.1	14		**Trmolada et al, 2009**
South Tibetan Plateau	3500 - 5000						0.016		**Tian et al, 2014**
North-Eastern Romaina	-	19.9		3.1	ND	0.03	-		**Tarcau et al, 2013**
Central Tibetan Plateau	4824							0.080	**Yuan et al, 2012**
Andossi plateau central Italian Alps	1930						0.5-5		**Guazzoni et al, 2011**
Southern Himalaya Nepal	135-5100	0.067-1.151*				0.008-0.018*			**Gong et al, 2014**
Peru Alps	3710- 4790	0.51		<0.01	<0.01	0.02	0.08		**Tremolada et al, 2008**
Italy Andes	245-2600	2.2		0.51	0.016	0.24	3.6		**Tremolada et al, 2008**
Mt. Gongga, Eastern Tibetan Plateau	2060-4167						Σ_{24}PCBs 0.04-0.5*		**Liu,X et al, 2014**
Mt.Sagarmatha, Himalayas, Nepal	4893-5293						0.01	0.01	**Guzzella et al, 2011**
Gilgit, northern Pakistan	1300-3000	$\sum_{6}$DDTs 1.77	$\sum_{2}$Enosulfan 0.133	$\sum_{5}$HCH 0.11	$\sum$TC/CC 0.08	0.016	$\sum_{32}$PCBs 0.55	$\sum_{7}$PBDEs 0.41	**This study**

Table 3.5: Mean concentrations (ng/g) of POPs in sediments from this study and other mountainous regions worldwide.

Location	Altitude (m)	DDT	HCH	Endosulfan	Chlordane	HCB	PCBs	PBDEs	References
YamzhoYumco TP	4500	3.4($\sum_4$DDT)	3.5($\sum_4$HCH)						**Cheng et al, 2014**
Nam Co TP	4800	1.8	1.5($\sum_4$HCH)						**Cheng et al, 2014**
Co Ngoin TP	4700	1.8($\sum_4$DDT)	0.99($\sum_4$HCH)						**Cheng et al, 2014**
Star Sea TP	4300	0.26($\sum_4$DDT)	0.60($\sum_4$HCH)						**Cheng et al, 2014**
Zoige TP	3600	1.78($\sum_4$DDT)	3.87($\sum_4$HCH)						**Cheng et al, 2014**
DugliStaw (Europe)	1516	25	-			1.6	10		**Grimaltetal, 2004**
Ladove (Europe)	2068	12	-			1.3	9.2		**Grimalt et al,2004**
Chungara (Chile)	4500	0.55(p-p' DDE)	0.068			0.055	2.2		**Borghini et al, 2005**
Cotacotani (Chile)	4400	0.023	0.27			0.065	2.3		**Borghini et al, 2005**
Mt.Sagarmatha, Himalayas, Nepal	4893-5293						0.3	0.3	**Guzzella et al, 2011**
Gilgit, Northern Pakistan	1300-3000	0.79($\sum_6$DDT)	0.040($\sum_5$HCH)	0.130	0.042	0.006	0.3	0.09	**This study**



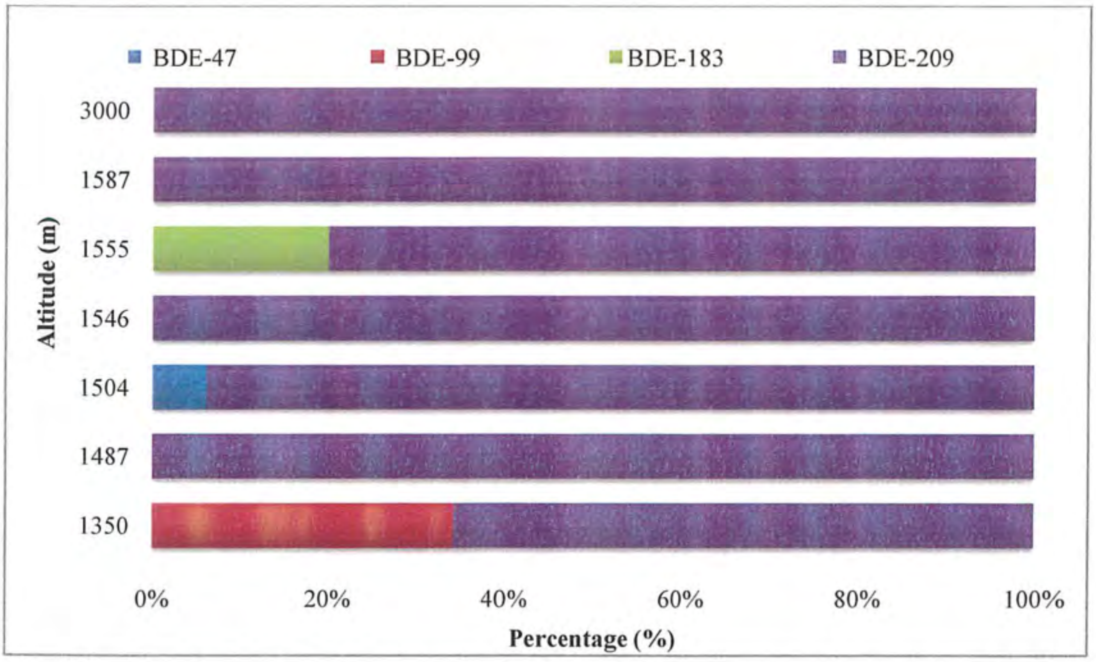
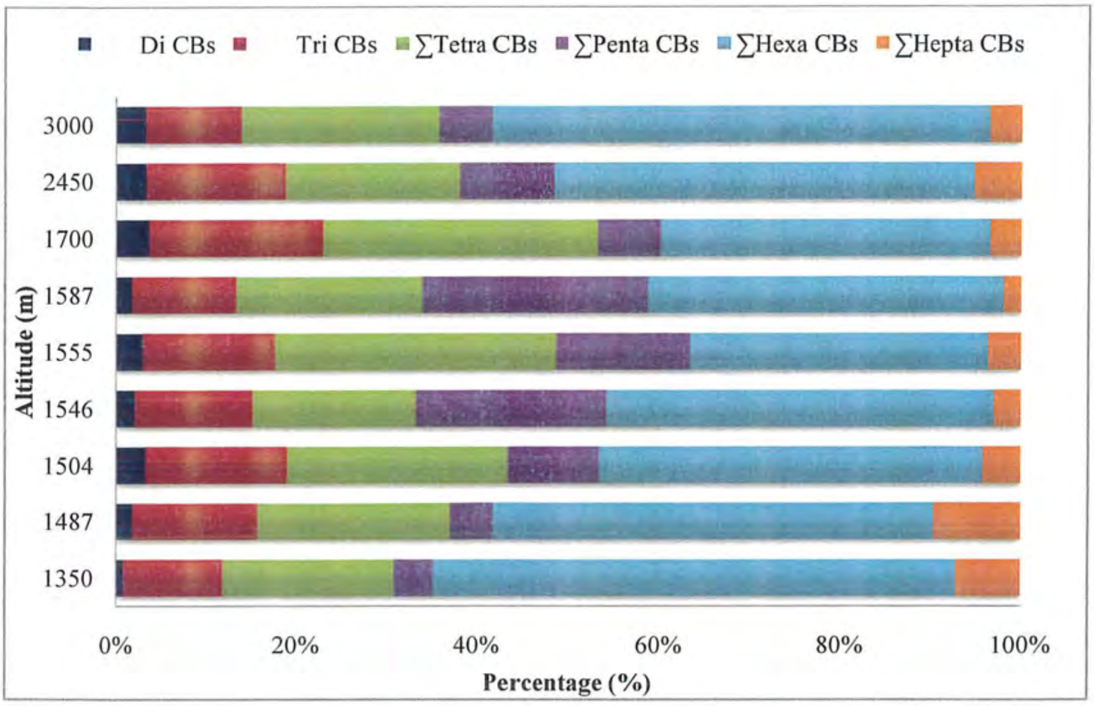


Fig 3.3: Percent composition of the homologous PCBs and congeners of PBDEs in sediments.



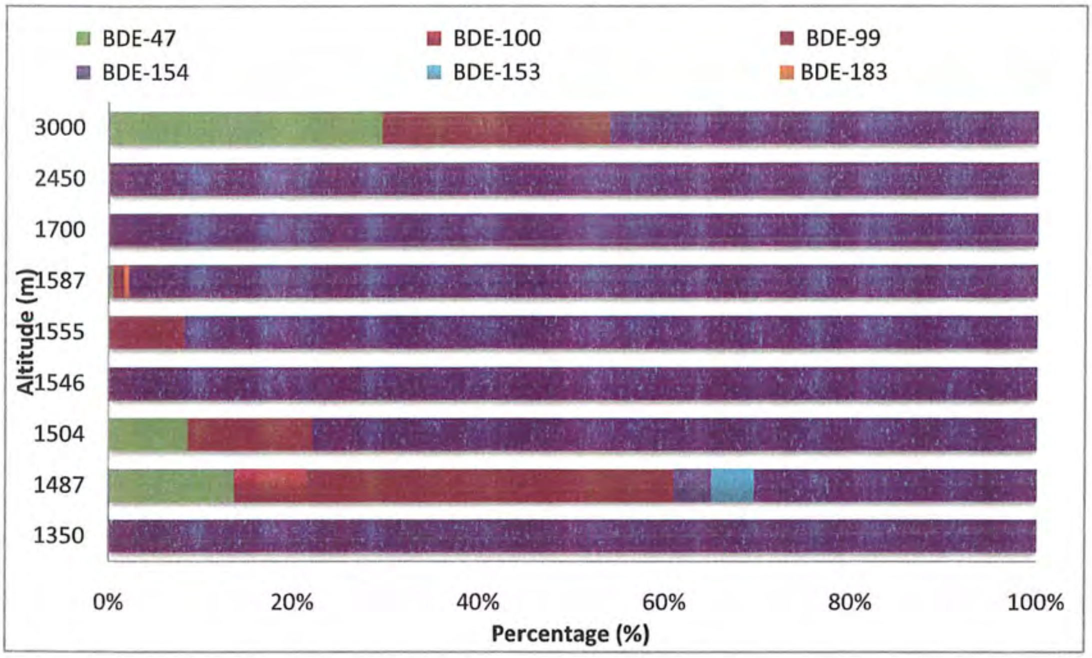


Fig 3.4: Percent composition of the homologous PCBs and congeners of PBDEs in soil.

3.1.4. Novel brominated flame retardants (NBFRs)

The average concentration of $\sum_6$NBFRs is given in (Table 3.3). In soil sample the mean concentration was 0.149±0.185 ng/g, almost 14 times less than that of OCPs but they were found in most of the samples. DBDPE were dominant contributing 53% followed by TPBH (18%), PBEB and TBE (11%) each, HBB (5%), TBB (2%) with mean values of 0.079±0.121, 0.027±0.056, 0.017±0.068 each, 0.008±0.025, 0.002±0.010 ng/g respectively. While in sediment samples the average concentration of $\sum_6$NBFRs was 0.132±0.274 ng/g. DBDPE accounted for 68% with mean concentration value 0.089±0.199 ng/g, TBE (19%), TBPH (11%) with mean concentration values of 0.026±0.055 and 0.015±0.02 ng/g respectively. The data set regarding NBFRs in soil and sediments was also very limited. Among NBFRs, DBDPE was found as the most abundant compound in the current study in agreement with (Zheng et al., 2015) but the concentration in the current study (0.078 ng/g) was much lower than reported by (Zheng et al., 2015)Chinese forest soil (2.64 ng/g). And all other NBFRs were also found in much lower concentration reported by (Zheng et al., 2015). DBDPE high proportion in the environment was also witnessed by (Tian et al., 2011) in the air sample of rural China.

3.1.5. General comment about overall level and trend of POPs in the current study

From these results it can be stated that POPs level investigated in this study were quite low but were comparable with many studies of same nature from many other remote mountainous regions of the world. The northern part of Pakistan which is considered as the pristine region and not influenced by any point source of these organic contaminants. Their detected concentration level in this study revealed the phenomena of long range atmospheric transport of these contaminates from the surrounding countries like India, China as well as the southern part of Pakistan. The highest level of $\sum$DDT among all POPs revealed the usage of parent DDT in adjacent regions or may be locally. The lower concentrations of lighter compounds like HCH and HCB in this study may be due to the rapid evaporation from soil because of the increasing temperature in the sampling period in summer in the month of July. The low levels of OCPs, PCBs, PBDEs/DPs and NBFRs reported in this study can be used as representative of the background levels both in soil and sediment in mid latitude Northern hemisphere and suggesting stronger contribution of long range atmospheric transport and mountain cold trapping effect in the high altitude regions of Karakoram and Himalayas.

3.2. Diagnostic ratios of OCPs for potential source identification

3.2.1.Dichlorodiphenyltrichloroethane(DDT)

DDT/DDE+DDD ratio was widely used in different studies to identify its potential source either from fresh application or aged one ((Yang et al., 2013; Zhu et al., 2015; Zhu et al., 2014). The ratios of DDT/DDE+DDD>1 indicate the fresh input of DDT while DDT/DDE+DDD< 1 suggest that the parent DDT gradually degrade or transformed into more persistent and stable metabolite that are DDE and DDD (Willett et al., 1998). In this study the average ratios of *o,p'*-DDT/*o,p'*-DDE+*o,p'*-DDD and *p,p'*-DDT/*p,p'*-DDE+*p,p'*-DDT in soil are 7.4 and 6.9 and in sediments and 9.1 and 13.91 respectively. The higher ratios indicate fresh application of parent DDT containing DDT-dicofol and re-emission of industrial DDT from the historic residues from the adjacent source regions like India and China. Another reason can be low temperature in the area which prevents the microbial degradation and transformation of parent DDT into its metabolites DDE and DDD. Technical DDT has been banned in 1970s but in several countries, for example in India it is still used for the purpose of disease control such as malaria (Bedi et al., 2013). The occurrence of DDT in the environment may come from the technical DDT and DDT-containing dicofol pesticides. The *o,p'*-DDT/*p,p'*-DDT ratios can be used to differentiate these two sources (Qiu et al., 2005). In this study the average *o,p'*-DDT/*p,p'*-DDT ratio in soil is 0.752 which lies between the ratio values of both technical (0.2) and dicofol (7) suggesting their joint influence on the occurrence of DDT in the study area. These ratio observations in this study are in comparison with (Zhu et al., 2015) and in the air of Shergyla Mountain, China (Zhu et al., 2015). While in sediments the *o,p'*-DDT/*p,p'*-DDT ratio is 0.10 less but in comparison with the ratio value of technical DDT which also strongly suggest the long range atmospheric transport of residues of technical DDT from the adjacent countries like China and India because no source of technical DDT has been observed in the study area.

3.2.2. Hexachlorocyclohexane (HCH)

The occurrence of HCHs in the environment is mainly due to use of technical HCHs and the mixture of it contains 60–70% of α-HCH, 5–12% of β-HCH, 10–15% of

γ-HCH, 6–10% of δ-HCH and 3–4% of ε-HCH(Zhu et al., 2014). In this study the mixture contains α-HCH (20%) β-HCH (44%), γ-HCH (28%), δ-HCH (6%) and ε-HCH (2%) showed no indication of technical HCHs in study area. Furthermore α/γ-HCH ratio is used to find the potential source of HCHs in the environment either technical HCH or Lindane (insecticide). The ratio values of α/γ-HCH in the technical HCH range from 3-7 but increases with the passage of time due to the lower air-water partitioning coefficient (K_{AW}) of γ -HCH compared to α -HCH (Walker et al., 1999). While the ratio value decreases due to the continuous application of Lindane in the environment (Zhu et al., 2014). The average α/γ-HCH ratio in the current study is 0.65 in soil and 1.26 in sediments, and these low ratio values indicate the influence of the application of Lindane in the study area. It may use locally for the agricultural purpose or may be result of the long range atmospheric transport from the adjacent source regions like India, China or Southern part of Pakistan where agriculture is practiced at a very larger scale. The α/γ-HCH ratio in this study were less as compare to reported by (Yang et al., 2013; Zhu et al., 2014). But the higher ratio was observed in the sediments of Bagrot (BT) which is a very remote site with higher altitude, suggest the transfer of technical HCH through long range atmospheric transport from source regions and potential cold trapping in the area. In addition if the ratio of α/γ-HCH>4, it indicate the fresh input of technical HCH while the higher percentage of γ-HCH suggesting the contamination source as Lindane(Kalantzi et al., 2001), so the present study is very much in agreement with this justification that the ratios are less than 4 and the percentage of γ-HCH is dominating in sediments (36%). In soil sample the percentage of β-HCH is the highest (44%) which is because of the its lowest pressure among all the HCH isomers, become more resistant in the environment and tends to accumulate in the soil (Li, 1999).β-HCH/(α-HCH + γ-HCH) ratio can be used to indicate the fresh input or aged HCH, if the ration is higher than 0.5, suggest no fresh input of HCH otherwise indicate the fresh application of HCH (ZHANG et al., 2007). In this study the average of β-HCH/(α-HCH + γ-HCH) in soil and sediments was and 0.48 respectively 1.20 in which suggesting both aged and fresh input of HCH in the study area. Furthermore the significant correlation between α-HCH and γ-HCH both in sediments and soil (Fig 3.5 & 3.6) also suggesting common sources of HCH in the area comparable with the study reported by (Gai et al., 2014).

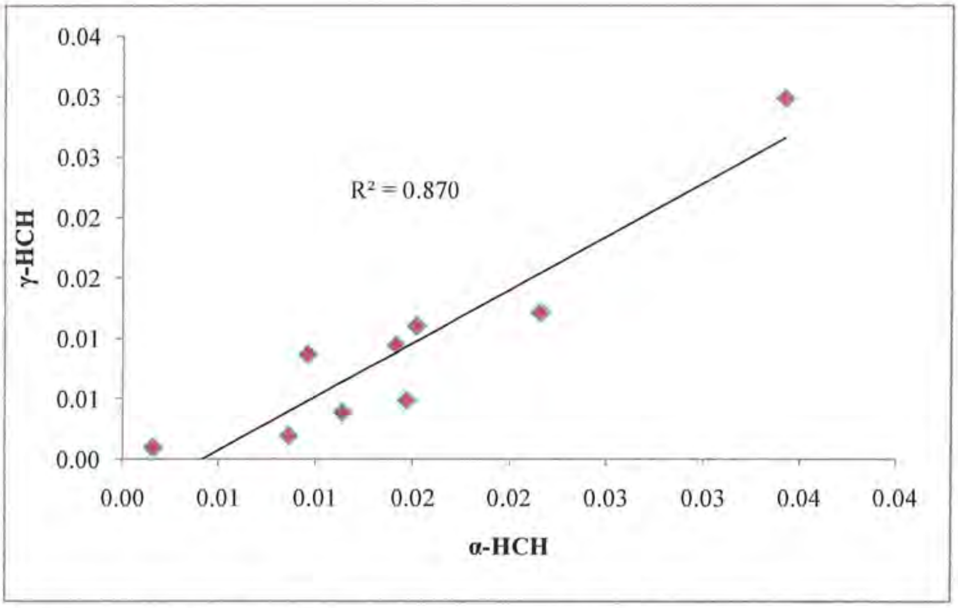


Fig 3.5: Correlations between α-HCH and γ-HCH in sediments of northern Pakistan

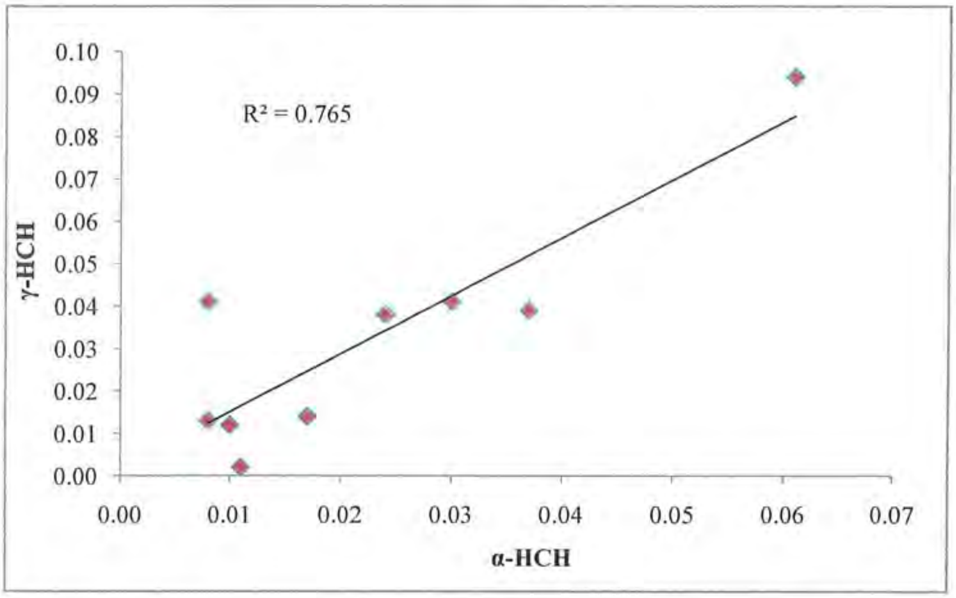


Fig 3.6: Correlations between α-HCH and γ-HCH in soil of northern Pakistan

3.3.3 Endosulfan

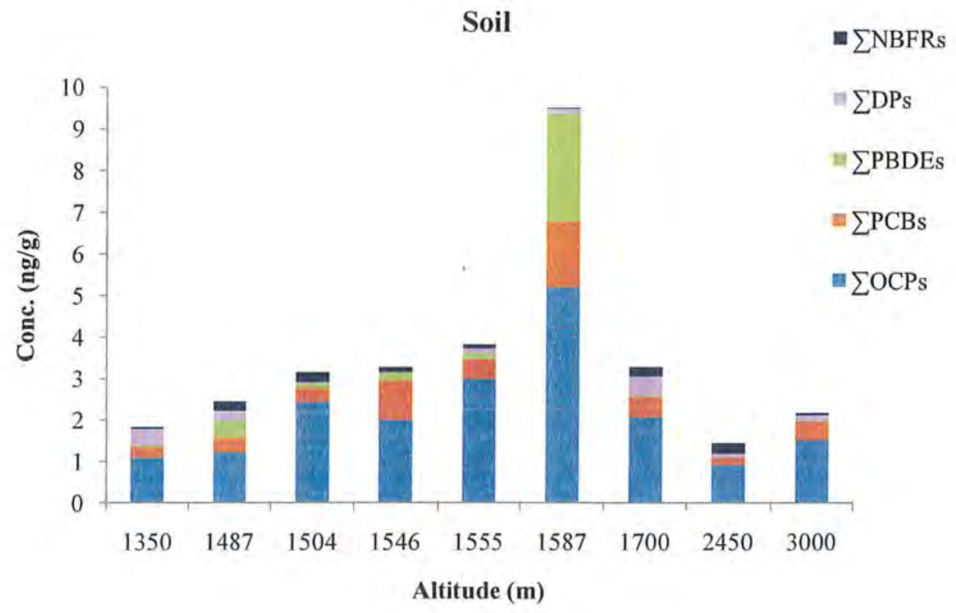
Endosulfan is a pesticide used throughout the world to control variety of insects and mites. The ratio of α/β-Endosulfan in the industrial mixture is 2.0-2.3 (Estellano et al., 2008). In this study the average α/β-Endosulfan ratio in soil and sediments were 0.24 and 0.17 respectively indicate the absence of the commercial Endosulfan in the study area. α/β-Endosulfan ratio <2.3 can be used to assess the age of Endosulfan in the soil based on the fact that β-Endosulfan gradually convert into α- Endosulfan in soil (Schmidt et al., 2001). The lower ratios in this study suggest the decomposed Endosulfan in the area. Though there are no reported sources of Endosulfan, so it's small but detectable concentrations suggesting the long range atmospheric transport from the surrounding regions through monsoon and winds.

3.2.4.Chlordane

Chlordane production started in 1948 and it was then used worldwide as a pesticide the next 50 years (Bidleman et al., 2002). In North America technical chlordane was manufactured and used as an insecticide. herbicide and termiticide in early 1980s, then it was restricted and banned in 1988 (Shen et al., 2005). Technical chlordane is a complex mixture of over 140 different structurally related compounds but the most abundant are trans-chlordane (TC, 13%), cis-chlordane (CC, 11%), heptachlor (5%) and Trans nonachlor (5%).Chlordane presence have been also reported in different environmental compartment of the environment. The chlordane components were found at very low concentrations in this study. The ratio of TC/CC is frequently used to differentiate between fresh chlordane and aged one. TC/CC ratio less than 1 suggest a hint of aged chlordane (Bidleman et al., 2002). In this study the average TC/CC ration values for soil and sediments are 4.5 and 12.32 suggesting the fresh input of chlordane in the area and the higher ratios were in comparison with the study in air sample from the alpine site of Manipur, India (Devi et al., 2011). Furthermore the TC/CC ratio is used to identify the closeness of source because Trans-chlordane degraded more rapidly than cis-isomers (Shen et al., 2005). Locally agriculture is practiced at a very smaller scale but it may contribute to the occurrence of chlordane in the environment, though the presence of chlordane is not reported from the sampling area. The ratio of TC/CC in commercial chlordane is 1.17 and lower ratios are sign of greater distance from the source (Shen et al., 2005). Higher ratios reported in these studies are indication of proximity of emission source and contamination of fresh application of chlordane as pesticide. The air mass back trajectory analysis also showed the air currents coming from China, India and south Pakistan, so chlordane usage as a pesticide in these countries is possible.

3.3. Distribution of POPs along the altitudinal gradient and Cold Trapping

The concentration of different group of POPs showed different trends at different altitude in soil and sediments. Considerably higher concentrations in soil and sediments were observed in valleys with mid altitude as compare to the valleys with higher altitudes and some significant increasing trends can be seen from low to mid altitude (Fig 3.7). In soil samples the highest concentration of all ∑OCPS, ∑PCBs, ∑PBDEs were consistently observed at Barmas site (BS) with altitude of 1587(m) except ∑NBFRs. In sediments the highest concentration of POPs were observed in Danyore (DR) site with an altitude 1504 (m) (Annexure Fig 1 and 2).The overall concentration trends of ∑OCPS, ∑PCBs, ∑PBDEs and ∑NBFRs did not significantly correlate with increasing altitude both in soil and sediment samples (Fig 3.8) in comparison with the study reported for soil by (Wang et al., 2007a; Yang et al., 2013) and in contradiction with (Borghini et al., 2005; Chen et al., 2008). Study reported by (Guzzella et al., 2011) also showed no significance correlation between altitude and POPs concentration is in comparison with this study except PCBs which showed positive correlation with increasing altitude. In general consideration the concentration of these organic contaminants increases with increasing elevation due to the direct contribution from atmosphere and decreasing temperature, but complications arises due to the many other factors like topography, land cover, meteorological conditions, distance from the source and local emission sources as well (Daly & Wania, 2005). The current study area is also characterized by diverse topography and climatic conditions and source proximity which may be the reason behind the uneven distribution of POPs along altitudinal gradient. In most of the studies reported regarding the altitudinal dependence of POPs, the increase concentration trend is more significant above 3000 meter above sea level (Wang et al., 2007a) while this study was conducted in the range of 1300-3000 m.a.s.l. In comparison with soil, POPs concentrations in vegetation shown significant correlation with increasing altitude in many of the reported studies in lichens and pine needles (Yang et al., 2013), in grass (Wang et al., 2007a), and in lichen and mosses (Zhu et al., 2015), while in soil samples the increasing trend of POPs was not consistent. The reason may be the revolitilization of lighter POPs from soil and deposit on vegetation (Wang et al., 2007a) because of the high affinity for organic content in foliage (Jones et al., 1992; Liu et al., 2014). The current study was carried out in July (summer season), so the seasonal pattern also count in this regard, in summer the evaporation rate increases and emission fluxes of POPs also increased in the atmosphere, so higher concentration is expected in the air as compare to the soil (Tremolada et al., 2009). Overall concentration of POPs in sediments show increasing trend with altitude in comparison with (Blais et al., 1998; Borghini et al., 2005) but not consistent. A considerable concentration of POPs in fresh water sediments at higher altitudes in this study suggested mountain cold trapping effect. POPs present in atmosphere are trapped by the surrounding snow covered mountains which on melting contribute fresh water to down streams (Arellano et al., 2011) which may deposit in sediments.



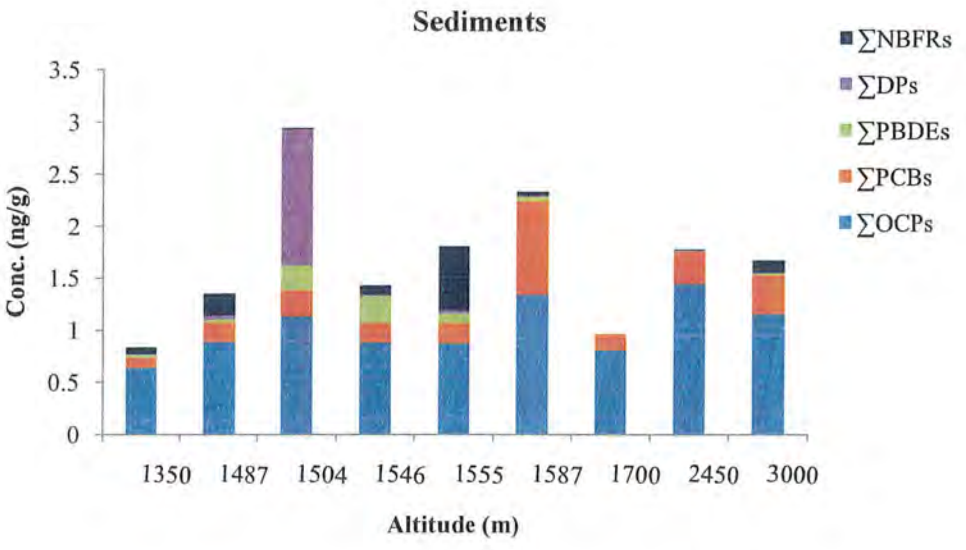


Fig 7: The altitudinal trend of POPs concentration in soil and sediments

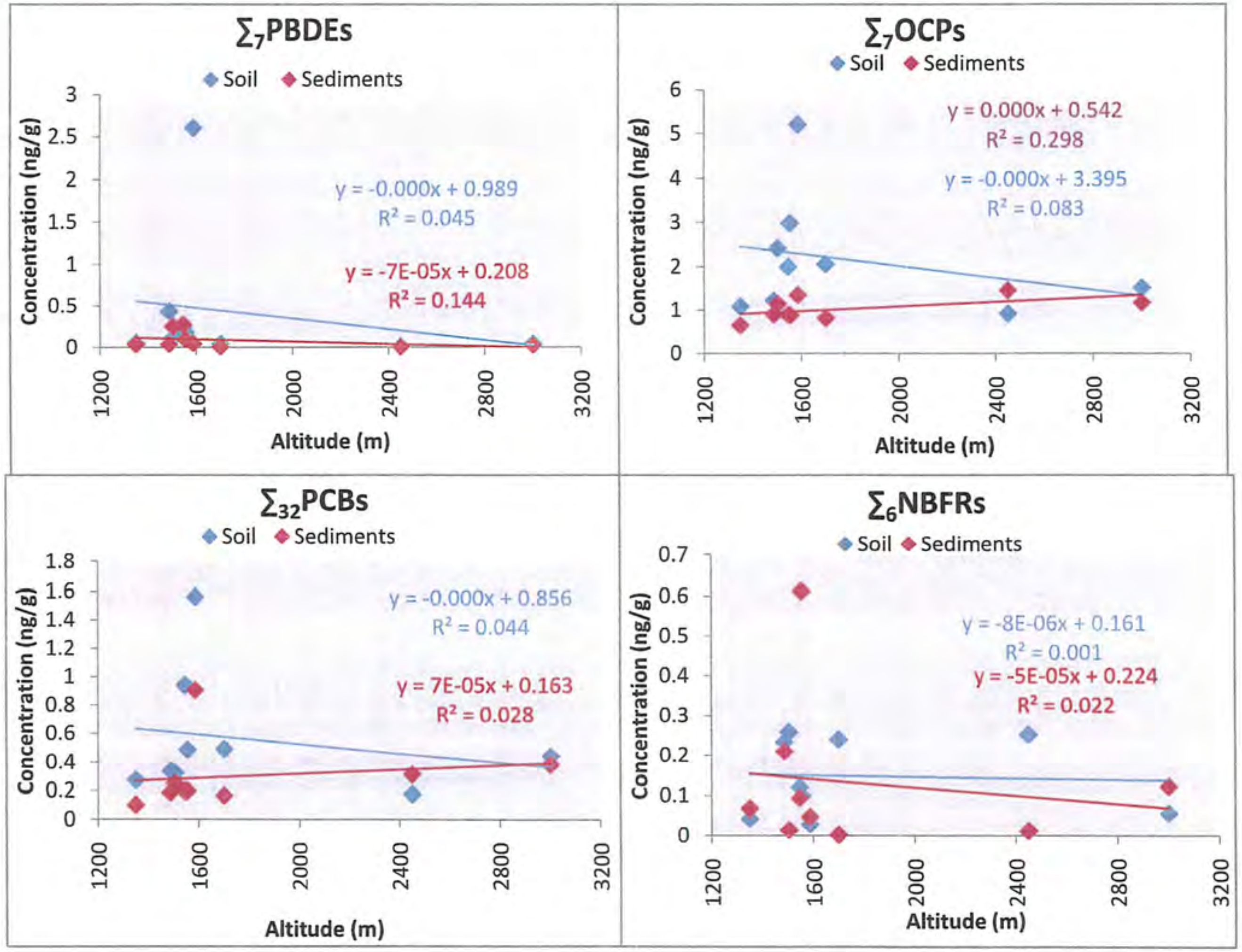
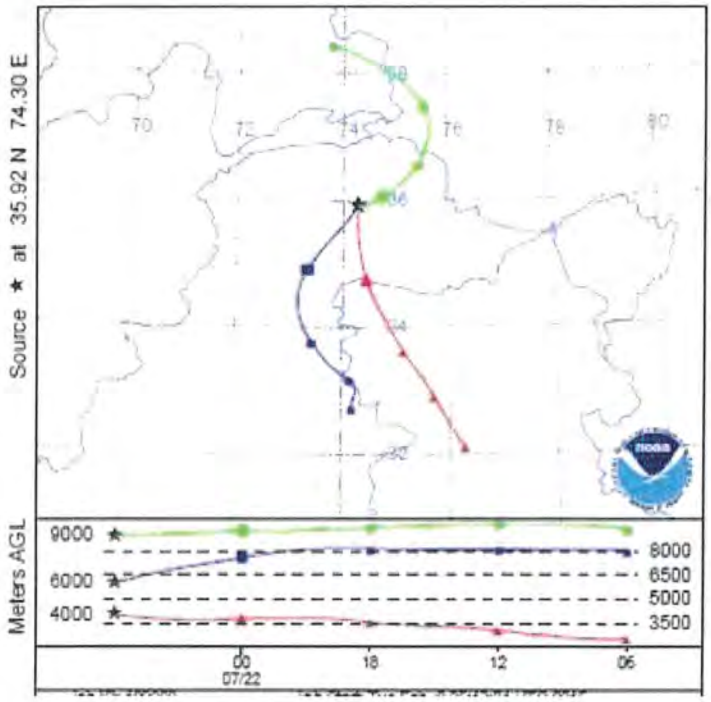


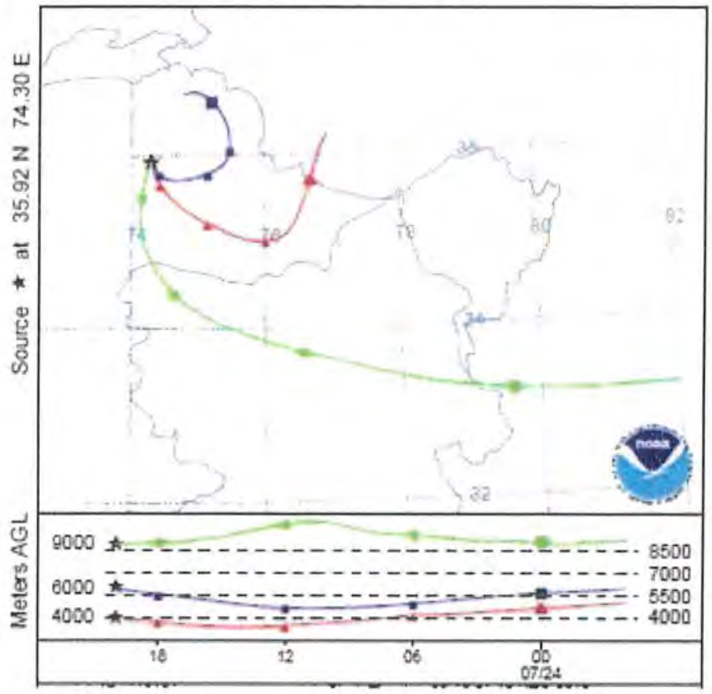
Fig 3.8: Correlation between POPs concentrations in soil and sediment samples with altitude of all sampling sites.

3.4.Backward air mass trajectory analysis and implication for long range atmospheric transport

To investigate the possible sources of POPs, back trajectories arriving at the coordinates of the sampling area were calculated for the sampling period in summer July, 2015. The model was based on the Hybrid Single Particle Lagrangian Integrated Trajectory Model (HYSPLIT) of National Oceanic and Atmospheric Administration of the United States (NOVAA)Air resource laboratory (Draxler & Rolph, 2003). The overall back trajectory map at three different heights 4000, 6000 and 9000 m.a.s.l for the duration of 24 hours a day is given in (Fig 3.7). It's evident from the backward trajectory maps that the sampling area in summers is mainly influenced by the air currents coming from south Pakistan, north east India and from China as well. Though the usage of OCPs has been banned but they still have been used in developing countries. From Pakistan for example, the high input of DDT has been constantly reported (Alamdar et al., 2014; Eqani et al., 2012; Syed et al., 2014). High level of OCPs have been reported in the north east part of India (Chakraborty et al., 2010). The high level of OCPs may be as a result of the long range atmospheric transport from India as a result of extensive agriculture practices and also from the vector control program (Devi et al., 2011).PCBs can be contributed by electronic waste, solid waste dumpling and ship breaking activities in south Asian countries (Chakraborty et al., 2013). High level of PBDEs has also been detected in China, India and Pakistan comparatively in other parts of the world. A huge amount of electronic waste is transported to these countries for the sake of recycling purpose because of cheap labor and poor environmental regulations (Syed et al., 2013; Wang et al., 2007b). So these countries are very major source of POPs at very high levels. Monsoon system has a strong influence for the POPs influx in the high elevated environment (Sheng et al., 2013). On a larger scale South Asia is influenced by the Indian monsoon system in summers and it undergoes an orographic uplift, thus transferring POPs to the high altitude regions in the vicinity. So that in the high altitude regions of Himalayas, POPs have been reported (Guzzella et al., 2011). The detectable levels of all these POPs in the study area also revealed that they are might have been transferred to the region by the air circulation from the surrounding countries and accumulated in the surface matrices due to the cold condensation effect.



NOAA HYSPLIT MODEL
Backward trajectories ending at 0600 UTC 22 Jul 15
GDAS Meteorological Data



NOAA HYSPLIT MODEL
Backward trajectories ending at 2000 UTC 24 Jul 15
GDAS Meteorological Data

Fig 3.9: Backward air mass trajectory analysis

3.5.Depositional Fluxes and Mass Inventory of POPs in Sediments

The estimation of depositional fluxes of POPs in sediments isbased on the concentration (ng/g) and mass accumulation rate. Mass accumulation rate was calculated by the evident sedimentation rate (g $cm^{-2}year^{-1}$) using the mean bulk density (g cm^{-3}) of dry sediment samples. In this study four transects were defined on the basis of different altitudes and water bodies for estimating deposition fluxes. First was five sampling points along Gilgit river, second was of two sampling points along same transect of fresh water stream and with higher altitudes, third transect was defined also with higher altitude and drained by extensive channel of fresh water streams, and fourth one is the transact with lowest altitude and point of junction for Gilgit and Indus river. For each zone the depositional flux in sediments was calculated by the following formula (Ali et al., 2014; Bouloubassi et al., 2012).

$$D = \frac{\sum_{i=1}^{n} ARi \times [OCs]_i}{n} \text{ x S} \quad \textbf{Eq. 1}$$

Where D is depositional flux, AR is mass accumulation rate at the site from where sample i was taken, OCs are the mean concentration of POPs, n is the total number of sites from each zone and S is the surface area of each zones from where sediment samples were collected.

In order to evaluate potential of sediments as a contamination source of high altitude environment "Mass Inventory" was also calculated by the following formula:

I=C.A.d.p **Eq. 2**

Where C is the average concentration of POPs in sediments, A is the surface area, d is density (1.5 g cm^{-3}) and p is depth of the sediments (5cm).

The deposition fluxes (D) and Mass Inventory (I) are given in (Table 3.5 & 3.6). In table average values are given and number of samples (n)is also repressing triplicates for each site. In this study the calculated fluxes were very low. The reported literature for the deposition fluxes in sediments is very limited for remote sites. Depositional fluxes were also reported by (Barra et al., 2006) for PAHs in mountain lakes sediments in Central south Chile. Higher levels of fluxes have been reported for OCPs and PCBs in coastal sediments from Pakistan (Ali et al., 2014), while the one reported in this study are much lower. The mass inventories also show the potential of fresh water sediments for the POPs contamination at higher altitude ecosystem. The depositional fluxes values were more at higher altitude sites for OCPs and PCBs as compare to low altitudes sites in the study area also give the clue of cold trapping effect. The fluxes along the transect of Gilgit river were dominant showed the prime zone of the POPs contamination. Gilgit River is the catchment of the several tributaries can be the reason of being potential zone of POPs contamination.

Table 3.6: Depositional Fluxes (D) in fresh water sediments

Transects	Altitude range	Surface area Km^2	OCPs $ng\ cm^{-2}\ y^{-1}$	PCBs $ng\ cm^{-2}\ y^{-1}$	PBDEs $ng\ cm^{-2}\ y^{-1}$	NBFRs $ng\ cm^{-2}\ y^{-1}$
Along Gilgit River (n=5)	1400-1600	1600	215.77	72.82	28.54	41.09
Naltar and Nomal (n=2)	1600-3000	676	218	60	1.95	13.57
Bagrot (n=1)	2200-2800	324	309	66	0	2.35
Jaglot (n=1)	1300-1400	324	136.5	20.82	6.6	14.25

Table 3.7: Mass inventory (I) for fresh water sediments

Transects	Altitude range	Surface area Km^2	OCPs $\mu g\ cm^{-2}\ y^{-1}$	PCBs $\mu g\ cm^{-2}\ y^{-1}$	PBDEs $\mu g\ cm^{-2}\ y^{-1}$	NBFRs $\mu gcm^{-2}\ y^{-1}$
Along Gilgit River (n=5)	1400-1600	1600	12.26	4.13	1.62	2.33
Naltar and Nomal (n=2)	1600-3000	676	4.95	1.37	0.044	0.3
Bagrot (n=1)	2200-2800	324	3.5	0.75	0	0.026
Jaglot (n=1)	1300-1400	324	1.5	0.23	0.076	0.16

Conclusion

Pristine mountain regions are ideal settings for studying the fate, transportation and distribution of POPs. The detection level of POPs in the sampling area suggest that the phenomena of long range atmospheric transport was mainly responsible for their existence in the region. The variation in distribution of different POPs in soil and sediments shows complexity of environmental behavior influencing the distribution of these contaminants. The air mass back trajectory analysis showed that the sampling area is mainly influenced by the air currents from northern India, China and southern part of Pakistan. Despite of minimal to nonexistent of POPs sources, the presence of these organic contaminants provide the hint that major contribution is from atmospheric deposition to the surface by cold trapping effect. Further research work is needed in the area to further investigate the long range transport of these organic contaminants on a global scale. POPs must be investigated in different environmental matrices at higher altitudes to better understand the cold trapping mechanism of POPs and associated environmental complexities.

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Appendix I

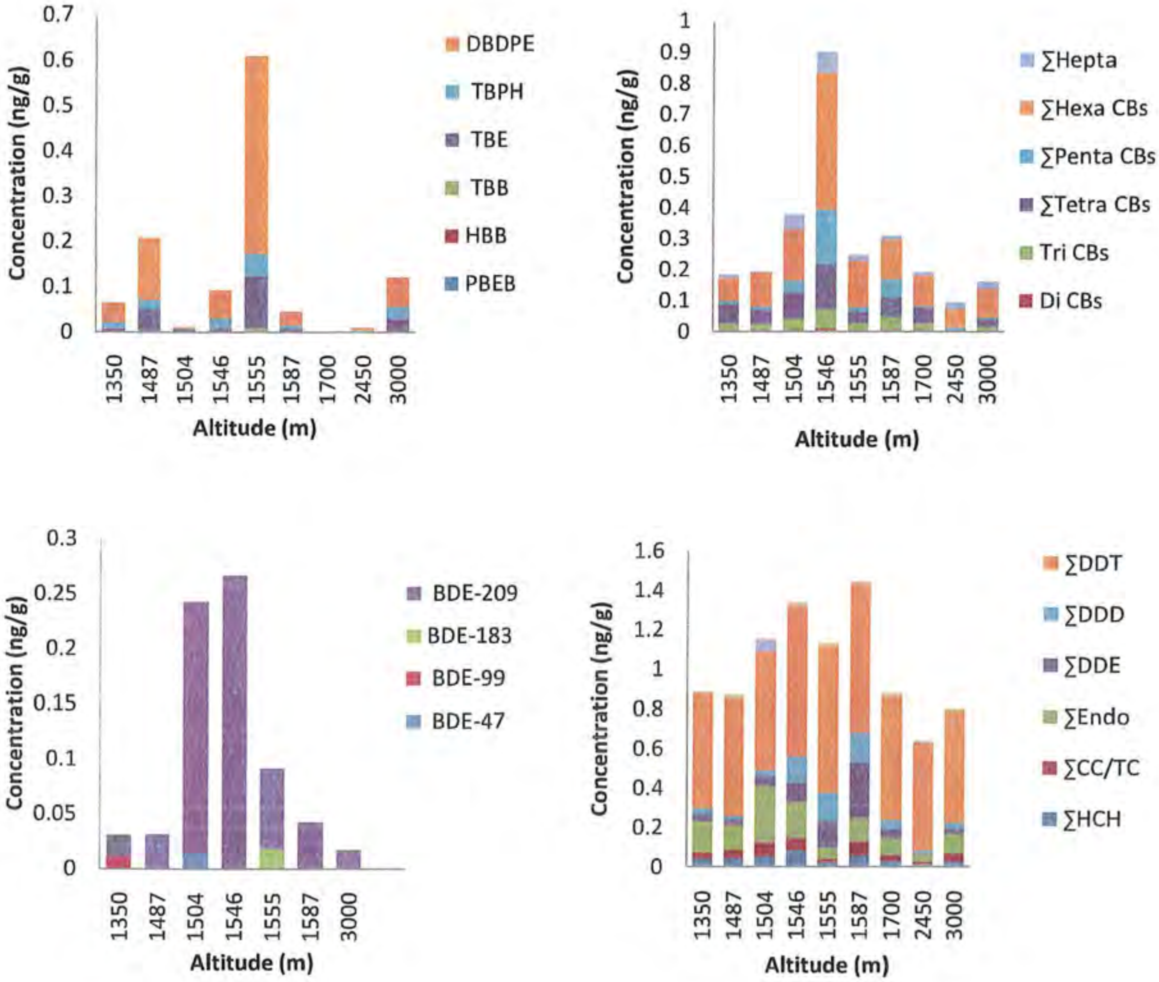

Fig1: Concentration and percentage (%) composition of OCPs, PCBs, PBDEs and NBFRs in sediment samples.

Appendix II

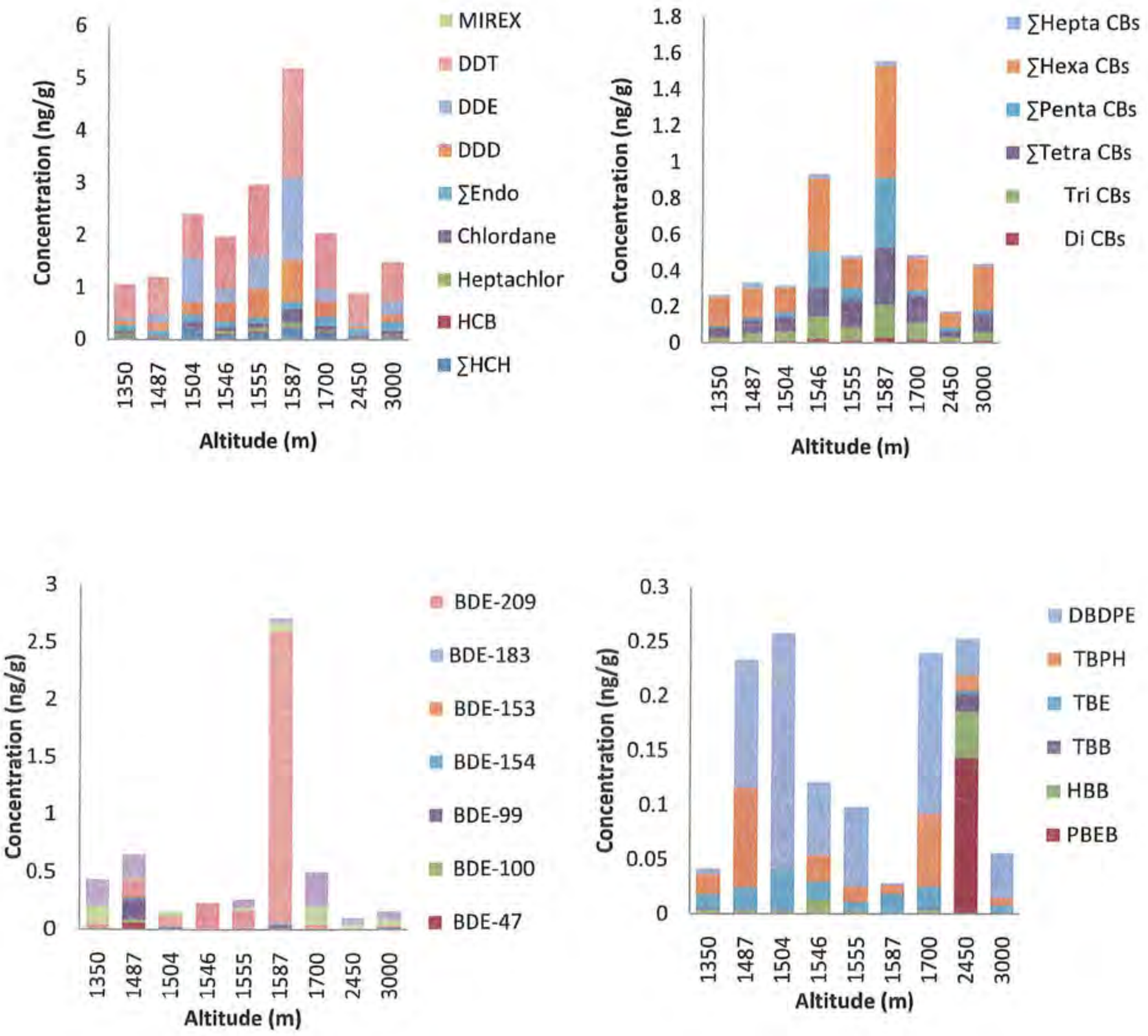

Fig2: Concentration and percentage (%) composition of OCPs, PCBs, PBDEs and NBFRs in soil samples.

Appendix III

Table 1: Diagnostic ratios for POPs in soil samples

Sites	***o,p'*-DDT/*o,p'*-DDE+*o,p'*-DDD**	***p,p'*-DDT/*p,p'*-DDE+*p,p'*-DDT**	***o,p'*-DDT/*p,p'*-DDT**	***α/γ*-HCH**	***α/β*-endosulfan**	**TC/CC**
JT	6.82	3.66	0.21	0.62	0.15	3.34
KS	6.62	1.44	0.47	0.83	0.18	10.7
BS	4.27	3.79	0.17	0.65	0.16	2.47
JL	5.09	0.88	0.45	0.73	0.19	4.92
DR	4.41	1.72	0.30	0.20	0.36	3.78
BN	6.67	6.77	0.11	0.63	0.29	4.60
NL	4.97	3.19	0.25	0.95	0.26	1.53
BT	3.53	6.53	0.12	5.50	0.29	5.59
NR	7.4	2.70	0.30	1.21	0.24	3.48

Table2: Diagnostic ratios for POPs in sediments

Sites	***o,p'*-DDT/*o,p'*-DDE+*o,p'*-DDD**	***p,p'*-DDT/*p,p'*-DDE+*p,p'*-DDT**	***o,p'*-DDT/*p,p'*-DDT**	***α/γ*-HCH**	***α/β*-endosulfan**	**TC/CC**
JT	3.35	15	0.22	0.63	0.27	42
KS	2.95	15	0.20	1.30	0.17	20
BS	3.06	10	0.31	0.41	0.32	10
JL	9.01	3.4	2.64	1	0.08	19
DR	7.74	4.2	1.83	0.35	0.07	6.2
BN	6.03	12.6	0.48	0.33	0.26	4.3
NL	16	16.2	1.03	1	0.04	2
BT	22	37	0.60	0.47	0.02	3.6
NR	11	10.2	1.07	0.37	0.3	2

Appendix IV

Table: Correlation among POPs, altitude and soil Physico-chemical properties in sediments.

	Altitude	pH	EC	∑HCH	∑Chlordane	∑Endo	∑DDT	MIREX	HCB	Heptachlor	DiCB	∑TriCB	∑TetraCB	∑PentaCB	∑HexaCBs	∑HeptaCBs	∑PBDEs	∑NBFRs	∑DP
Altitude	1																		
pH	-.344	1																	
EC	-.266	.082	1																
∑HCH	-.299	.074	.614**	1															
∑Chlordane	-.221	-.089	.347	.744**	1														
∑Endo	-.321	.144	.184	.628**	.494*	1													
∑DDT	-.233	-.008	.243	.676**	.629**	.238	1												
MIREX	-.172	.122	.166	.352	.196	.774**	-.049	1											
HCB	-.236	.024	.226	.782**	.809**	.477*	.737**	.224	1										
Heptachlor	.091	.007	.339	.281	.108	-.070	.283	-.156	.220	1									
DiCBs	-.312	.181	.505**	.683**	.600**	.314	.635**	.085	.607**	.205	1								
∑TriCBs	-.315	.056	.642**	.850**	.683**	.470*	.671**	.282	.633**	.181	.856**	1							
∑TetraCBs	-.355	.105	.682**	.788**	.582**	.502**	.517**	.315	.502**	.170	.869**	.947**	1						
∑PentaCBs	-.165	.045	.740**	.716**	.523**	.208	.519**	.092	.452*	.350	.759**	.869**	.866**	1					
∑HexaCBs	-.230	.113	.620**	.501**	.387	.122	.424*	-.032	.194	.231	.720**	.716**	.771**	.860**	1				
∑HeptaCBs	-.042	.198	.610**	.284	.222	.152	.147	.126	-.010	.179	.545**	.568**	.652**	.725**	.813**	1			
∑PBDEs	-.219	.096	.267	.384	.021	.693**	.077	.751**	.083	.093	.056	.206	.270	.104	.099	.105	1		
∑NBFRs	-.141	.031	-.142	-.199	-.278	-.167	.249	-.120	-.113	.419*	.088	-.163	-.115	-.103	.110	-.015	.166	1	
∑DP	-.055	-.297	-.078	-.075	-.179	-.127	-.048	-.070	-.067	-.177	-.209	.010	-.101	-.095	-.090	-.173	-.108	-.112	1

*****. Correlation is significant at the 0.01 level (2-tailed).***

****. Correlation is significant at the 0.05 level (2-tailed).***

Table: Correlation among POPs, altitude and soil Physico-chemical properties in soil.

	Altitude	pH	EC	∑HCH	∑Chlordane	∑Endo	∑DDT	MIREX	HCB	Heptachlor	DiCB	∑TriCB	∑TetraCB	∑PentaCB	∑HexaCB	∑HeptaCB	∑PBDE	∑NBFR	∑DP
Altitude	1																		
pH	-.242	1																	
EC	.320	.033	1																
∑HCH	-.271	.218	-.073	1															
∑Chlordane	-.122	.092	.100	.110	1														
∑Endo	.171	-.076	.021	.070	.052	1													
∑DDT	-.172	.006	-.070	.542**	.063	-.248	1												
MIREX	-.031	-.314	.066	-.035	.142	.089	-.082	1											
HCB	.024	-.471*	-.034	.044	-.020	.012	.366	.557**	1										
Heptachlor	-.212	-.077	.097	-.024	.834**	-.015	.060	.472*	.233	1									
DiCBs	-.083	-.194	.078	.344	.376	.062	.372	.160	.482*	.406*	1								
∑TriCBs	-.274	-.133	.011	.233	.488*	-.004	.374	.139	.406*	.550**	.904**	1							
∑TetraCBs	-.223	-.142	.004	.217	.697**	.081	.221	.371	.350	.769**	.801**	.901**	1						
∑PentaCBs	-.136	-.197	-.079	.276	.088	-.276	.791**	.058	.484*	.148	.596**	.661**	.466*	1					
∑HexaCBs	-.082	-.174	-.159	.258	.167	-.277	.607**	.120	.369	.228	.584**	.693**	.584**	.885**	1				
∑HeptaCBs	-.174	-.180	-.231	-.051	-.124	-.264	.490*	.265	.477*	.057	.291	.326	.179	.720**	.651**	1			
∑PBDEs	-.102	-.114	-.153	.224	.014	-.290	.844**	-.021	.448*	-.009	.374	.414*	.228	.910**	.713**	.740**	1		
∑NBFRs	-.022	.217	.055	-.221	-.238	.047	-.160	.132	.205	-.127	.035	.018	-.059	-.084	-.106	.208	-.018	1	
∑DP	-.179	-.007	-.138	-.106	-.041	-.023	-.037	.069	.100	.034	-.169	-.039	-.007	-.079	.064	.024	-.024	.047	1

. Correlation is significant at the 0.05 level (2-tailed).

****. Correlation is significant at the 0.01 level (2-tailed).***

Thesis

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