Modelling Spatial Distribution of Heavy Metals and their Fluxes in Riverine System of Azad Jammu and Kashmir, Pakistan

Master of Philosophy
in
Environmental Sciences
by

Beenish Malik
Registration No: 02311413010

DEPARTMENT OF ENVIRONMENTAL SCIENCES,
FACULTY OF BIOLOGICAL SCIENCES,
QUAID-I-AZAM UNIVERSITY
ISLAMABAD, PAKISTAN

2014-2017

Modelling Spatial Distribution of Heavy Metals and their Fluxes in Riverine System of Azad Jammu and Kashmir, Pakistan

Master of Philosophy
in
Environmental Sciences
by

Beenish Malik
Registration No: 02311413010

DEPARTMENT OF ENVIRONMENTAL SCIENCES,
FACULTY OF BIOLOGICAL SCIENCES,
QUAID-I-AZAM UNIVERSITY
ISLAMABAD, PAKISTAN

2014-2017

PLAGIARISM CERTIFICATE

It is certified that I, Beenish Malik registration number **02311413010** has completed my M.Phil in Environmental Science (Environmental Biology and Eco-toxicology). The title of my thesis is **"Modelling Spatial Distribution of Heavy Metals and their Fluxes in Riverine System of Azad Jammu and Kashmir, Pakistan."** My thesis has been checked on Turnitin for similarity index and found that it lies in the limit provided by HEC.

DECLARATION

The research work presented in this thesis was carried out by me in the Environmental Biology and Applied Ecotoxicology lab, Department of Environmental Sciences, Quaid-i-Azam University, Islamabad. The results, findings and conclusions were of my own investigation with discussion of my supervisor Dr. Riffat Naseem Malik. No part of this work has been presented for any other degree.

Beenish Malik

APPROVAL CERTIFICATE

This is to certify that the dissertation entitled "Modelling Spatial Distribution of Heavy Metals and their Fluxes in Riverine System of Azad Jammu Kashmir, Pakistan" submitted by Miss. Beenish Malik 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".

Supervisor/Chairperson: _____

Riffat Naseem Malik
Professor,
Department of Environmental Sciences,
Quaid-i-Azam University Islamabad

External Examiner: _____

Dated: 13-02-2017

DEDICATED TO MY BELOVED PARENTS

(LATE)

Acknowledgements

On the foremost, I would like to thank Almighty Allah, The Merciful and The Compassionate for the successful completion of this endeavor. I owe my respect and esteem to Hazrat Muhammad (PBUH) who is forever the light of knowledge for mankind.

I would like to express immense appreciation and deepest gratitude to Dr Riffat Naseem Malik (Research Supervisor) for his support, help, guidance, suggestions and valuable comments that very much benefited in the successful completion of the study.

I would like to pay my earnest thanks to my parents who are a real source of motivation and courage. I can't thank them enough for their unconditional love, prayers and support. Thanks to my siblings Hina Api, Saba, and Haroon for their encouragement and boost.

Thankyou much to Usman Ali and Rahat for their constant support, assistance and advice. I am also very much grateful to Ayesha Butt, Mehreen, Uzma, Maryem Arshad, Summaiya Baji, Sundas Ansari for their motivation and help. I extend my appreciation to my lovely friends (Sadaf, Nisbah, Ayesha, Aqeela, Zainab) for all the fun, amusement, motivation and moral support. We carried it all till the end guys.

A big thankyou to my in-laws (Ami and Abu) who supported me till the end.

Special thanks to my husband Salman Hyder for his moral support and praise.

Beenish Malik

TABLE OF CONTENTS

List of Figures

List of Tables

Abstract

Himalaya region is considered as hotspot for climatic change, ecology and hydrological studies. The cold climatic regime, altitude, remoteness, scarce population and minimum traffic movement has gained very less attention for conducting studies specifically on heavy metal contamination. The present appraisal has investigated heavy metal concentration for AJK riverine system located in Lesser Himalaya Region (LHR) of Pakistan. Statistical modelling techniques were used to evaluate concentration levels, spatial distributio, source identification and contribution factors for metal enrichment. The development of heavy metal mass inventory and annual depositional fluxes calculation were done for sediments of riverine system of this region for the very first time. Thirty two sites from three sampling stations were located for sampling of soil, sediments and water. Pb, Cd, Zn, Cu, Ni, Mn, Cr and Fe concentrations were analyzed in all matrices. Moreover, the burial flux calculations for Black Carbon (BC) and Total Organic Carbon (TOC) levels were made in sediments of all sites. Descriptive stats, multivariate data ordination analysis and HYSPLIT model were employed for delineation of metal profile, spatial distribution and source apportionment. Ecological risk assessment was done using mathematical equations of Enrichment Factor (EF), Geo-accumulation index (I-geo) and Metal pollution index (MPI). Results indicated some natural sources, anthropogenic interference and transboundary movements (LRAT) are playing their role for metal enrichment and flux in the region. The average concentration of Pb and Cd in soils and sediments were found higher than the pre-industiral/crustal values. Their elevated mean concentrations can be attributed to well preserve ore forming topographic feature of limestone as well. The concentrations found in river water of LHR were in compliance with the maximum allowable limit (MAL) in drinking water as per prescribed by NSDWQ Pakistan. BC burial flux showed the human interference especially biomass burning, vehicular emissions and hydropower projects can also be significant for intensifying heavy metals in the region. Since severity of contamination in the entire area is very low but if the current pace of development and human intrusion will remain constant in future then picture will be entirely opposite for LHR. Therefore, the attention of local and regional research institutions is required to investigate the seasonal and temporal trends of heavy metals in LHR and to formulate policies and

strategies to cater heavy metal problems if they are seriously posing threats to the regional ecology.

CHAPTER 1

Introduction

"And among His signs is that He shows you the lightening, for fear and for hope, and He sends down water (rain) from the sky, and therewith revives the earth after its death. Verily, in that are indeed signs for a people who understand."

Al Quran (Surah Ar-Rum, Verse 24).

Without water life cannot be sustained on the planet earth. The significance of water for the health of humans, natural processes, agriculture, and economic progress and for elevated population can never be underestimated. But access to the clean drinking and domestic water has been highlighted globally from the past few decades. Riverine ecosystem possesses versatility as the surface water bodies are important structures carrying fresh water, reviving ground water, and regulating locale climate (Forghani et al., 2009). Over the past century water demand has increased twice the ratio of growing population in the entire world. Consequently, 2/3 of world's population is surviving and struggling with water scarcity and clean water access. It is estimated that by the end of 2025 approximately1800 million people will be living in the areas afflicted by water insufficiency (UNDP, 2005). Out of 2.5 % of freshwater covering surface of earth only 1 % is accessible, most of which is stored in the ice caps and glaciers. To cut the story short only about 0.007% fresh water feeds and fuels 7 billion people globally. Fresh water ecology not only benefiting human race but it is also home to 40% of aquatic life. Regardless of their services and worth, anthropic demands and activities are dejecting this 0.007% freshwater ecosystem including rivers, wetlands and lakes across the globe rapidly (Hu et al., 2012).

Developed country like United States is also suffering with the extreme riverine water pollution problems. Comprehensive assessment revealed that 45% streams, 32% estuaries and 47% lakes in the country are polluted with heavy metals and other toxic chemicals (Bhuiyan et al., 2013)

Global climatic changes have brought spatial hydrological changes like rainfall patterns, glacial melting, flooding and droughts around the world specifically in Asian countries China, India and Pakistan were highlighted because of their

increasing demands for population, geographical extent and irrigation (ESCAP, 2011). Apart from hydrological changes and demands, developmental activities and urbanization has led the pollution of riverine ecosystem around the world. In general water pollution is characterized by the presence of toxic pollutants or microbial bodies exceeding allowable limits for human health and environment (Zhang, et al., 2010).

Among chemical pollutants heavy metal pollution is of global concern because of their non-degradability and persistence in one form or other becoming a serious threat to aquatic life as well (Varol, 2013). Since, heavy metals are ubiquitous, persistent and bio-accumulators, they are posing hazardous impacts on humans and environment therefore this very subject has gained attention of various researchers (Pertsemli and Voutsa, 2007). Rapidly increasing population and industrialization have changed both quantity and quality of fresh water (Arkoosh, et al., 2010). Heavy metal pollution episodes have stressed various rivers around the globe in the few past years (Anh, et al., 2010). In response to these situations there is an imperative need to evaluate and revise the heavy metal contamination profiles spatially and temporally (Varol, 2013).

Statistics showed that China is suffering from severe riverine pollution and about 0.5 billion natives have no access to clean water (Baoxing, 2005). Similarly, 0.7 billion people of India are deprived of lavatory and due to uncleanliness 14 million Indians die every day out of which 0.1 million accounted for children deaths due to shortage of clean drinking water (Reporter , 2008). In Pakistan very limited population has access to unpolluted water. In most areas only a single source (stream, water from catchment basin, natural ponds or river) is being consumed by humans for drinking and domestic use like washing bathing laundering and for animals as well. According to WRI report about 0.25 million children die annually due to no access to clean drinking water and even by 2040 it would be ranked 23rd water scarce country in the world ranking if conservation and management practices would not be renovated (Maddocks et al., 2015).Worldly, numerous studies have assessed the bulk of chemical release in rivers causing constant threats to health of man and riverine environmental regimes (Bush, & Mol, 2010).

1.1. Importance of Riverine System in Pakistan

Allah has blessed Pakistan with freshwater treasuries in the form of glaciers than any other country in the world excluding northern and southern poles. Himalayan mountains have 17% glacial area and Karakorum ranges have 37% glaciers however the in European Alps glacial mountains are spread along 22% land range. The glacial land included in Pakistan territory is stretched over 14,000 $km^{2,}$ which is accounted for an average of 3% covering the upper reaches of mountainous Indus basin system (spread over 2,250 km^2) that is the main water supplying natural resource for the rivers of Pakistan (Khattak et al., 2010). There are 60 large and small rivers in Pakistan among these rivers the Jhelum River makes its way from Azad Kashmir comparatively at lower elevation than that of other Indus River and joins indus river at Mirpur city and become the part of Indus River (Salma et al., 2012).

Being agricultural country with 70% population reliance on irrigated agriculture, water is indispensable resource for fulfilling her needs. Surface water hydrology is the key for planning the water resources particularly for the countries. According to Pakistan Water Strategy report the irrigation system is built around River Indus and its five major tributaries and is called Indus Basin Irrigation System (IBS) (Hazarika and Honda 2001). Pakistan stands first in its irrigation system with well-planned networking working with canal supplying and ground water pumping (Salma et al., 2012).

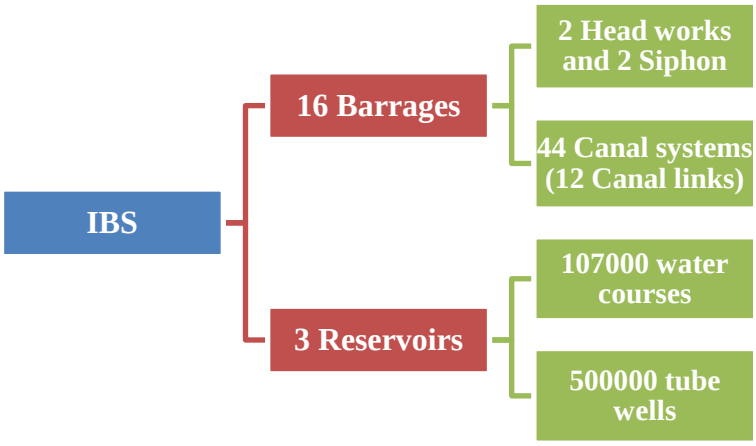

Figure 1.1 Pakistan's IBS networking system

Despite the fact of having best surface water hydrological planning Pakistan is also facing heavy metal pollution problem like other developing world. Speedy industrial sector race, agricultural practices and domestic waste may blow the problem of heavy metal riverine pollution across the country. Few studies from Pakistan (KPK, Sindh, Balochistan, Punjab, AJK and Capital) have been identified which reported anthropogenic inputs of heavy metals to the surface water (Appendix 1).

1.2. Role of sediments in riverine system quality

According to (Langland and Cronin 2003) sediment is referred to the, "Conglomerate material of organic or inorganic origin transported by strong winds, water or through melted ice. The sediments exist in environment may be soil based or mineralogical materials (clay, silt and sand) and organic sediments come from biogenic sources with flux of TOC (Wetzel, 2001). The mineral sediments are resulted from weathering and erosive events of soil (EPA, 2014). These erosive events generate sediments as the consequence of geomorphological interactions among soil surface and wind/precipitation. The surface runoff can move the eroded soil and minerals as sediments to the riverine system (Czuba et al., 2011; Hickin, 1995).

Sedimentation finds its roots principally in slope system of terrain, erosion events and alluvial flood plains. Slope systems generate and transport sediments to the rivers under the influence of independent catchment factors (topography, climatic factors, land use patterns etc.). Laminar erosion is resulted from farming activities. Unmanaged infrastructure (road drainage, sewage system, unplanned agricultural fields etc.) contributes to gully erosion. Alluvial plains remobilize of sediments by lateral erosion during wind storms or flooding. Water reservoirs are considered as final sinks for sediments (Kalbus et al., 2011). In artificial reservoirs sedimentation pose problems like reducing volume of the dams, remobilize and accumulate contaminants (Sawaske and Freyberg, 2010) like heavy metals. Sedimentation in reservoirs can be due to type of vegetation, rate of precipitation and characteristics of the catchment (de Asis and Kenji 2007). 30% of world's sediment inputs in oceans come from Asian rivers. These rivers are considered as principle transporters for sediment loads in oceans. The Indus and tributaries transport 20% of the global

sediment inputs and ranked as the third largest transporting rivers in the world. But the rate of sediment load in oceans is changing due to the construction of dams over large rivers (Butt et al., 2011).

According to statistics reported by (Beskow, et al., 2009) one of the river basins in Norway say that about 49% of the river basin is suffering with great intolerable loss of soil as a result of erosive events due to climate change, poor management areound dam area and aggressive land use pattern. Both climate change patterns and anthropogenic activities trigger sedimentation (Bogen, 2009; Charman and Murphy, 2007; Jacobson et al., 2009). Another study was carried out for the sedimentation problem for the Mangla dam in Pakistan constructed in 1967 for increasing irrigation efficiency and hydropower generation over Jhelum River, which is the 12th largest dam in the world. The study reported 39 years of sedimentation record from 1967 to 2005. The results indicated there is decrease of dam's 20% storage capacity in the aforementioned time period due to sedimentation problem (Butt et al., 2011).

Sediments are the good predictors for the organic matter and metal concentration as and carry them in adjacent water (Pradit et al., 2010). From the past few years examination of sediments from riverine system has gained attention in field of research because they exhibit long residence time and reveal quality status of the riverine system with delivering facts on human interference. Anthropogenic inputs (industrialization, urbanization, artificial reservoir construction) uphold the deposition of contaminated sediments in the nearby river system, as ultimate safe dumping site for dirty sediments. Heavy metal contamination in river system can be investigated by analyzing soil, sediments and water as important sources for the assessment of man-made contamination in rivers (Katiyar et al., 2009).

According to (Guevara et al., 2005) sediments carry nutrients with them and have been proved to be ultimate sink for contaminants (Bai et al., 2011) and provide information on anthropogenic inputs in various sptaio-temporal studies (Appendix 1). Surface water was their primary attention and carried out on the regional level. The contaminated sediments disturb the underlying water quality and aquatic organism thus ultimately food chain disruption makes human health risky (Rodrigues et al., 2010).

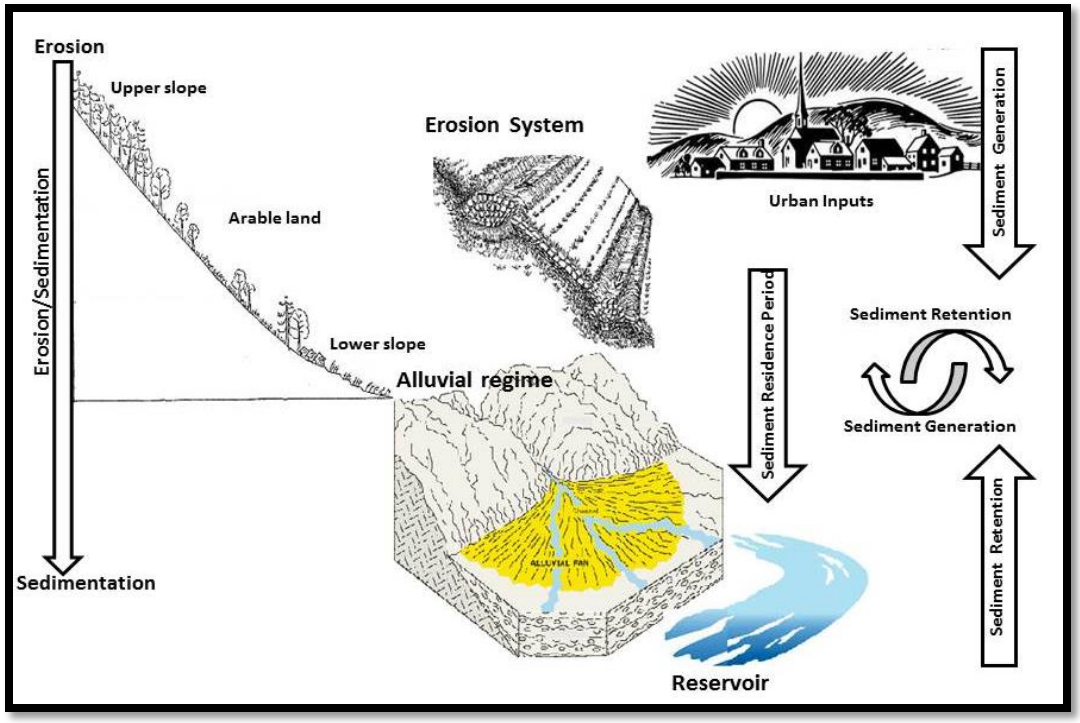

Figure 1.2 Principle of sediment generation

1.3. Sources of heavy metals

Generally, anthropogenic activities are continual source of polluting river ecosystem. However, surface runoff plays an important role for carrying heavy metals along due to heavy rain fall within the environmental compartment. The varying concentrations of heavy metals have been reported in various environmental systems even in pristine ecosystems. The evident variations in composition of parent rocks from which weathered soils are formed and discrepancies in the domain of soil-forming processes decide the concentrations of heavy metals in soils and ultimately in sediments and river water (Alloway 2013).

It is hard to categorize exact source of heavy metal pollution because both natural and/or anthropogenic sources (see Appendix 1) are contributing factors. Some heavy metals including cobalt, iron, copper zinc and manganese come under the umbrella of "essential nutrients" for living entities but their exceeding concentrations can be harmful (Nagajyoti et al., 2010). Heavy metals enter the environment through rain, vaporization or in the form of particulate matter. They are not bound to only one place; therefore take different paths and forms to move across long ranges distant

from their sources (Mostert et al., 2010). Air, water, soil and sediments are increasingly threatened by heavy metal contamination (Özkan, 2012). The concentration of heavy metal in soil, sediment and water depends on the composition of the parent rock because after weathering the broken crystal-like minerals either physically adsorbed on soil or they may move to the adjacent water resource as a result of natural biochemical or physical processes (Salonen and Korkka-Niemi, 2007).

Heavy metals are naturally present in the earth's crust but the human activities are continuously giving boost to load environmental compartments with heavy metals. Anthropogenic sources of heavy metal loads are industries (chemical, smelter, oil, non-ferrous metal industry, pesticide production plants, raw material processing), application of untreated sludge to the soil, mining, incineration, metallic plumbing, combustion processes, vehicular emissions and electronic waste disposal (Li et al., 2000). Disposal of electronic waste is another alarming threat to the planet earth, containing thousands of toxic compounds including heavy metals (UNEP, 2006) Fresh water reservoirs particularly rivers receive heavy metal loading from both point and non-point sources through surface run-off containing wastes of animal farms, agricultural fields, chemical effluents, domestic and urban litter etc. (Singh et al., 2010). Point sources of pollution are easy to be identified and manageable but the non-point sources are challenging to be properly identified because they take unidentifiable ways to get inflow to the river and the catchment areas (Kotti et al., 2005).

1.4. Health impacts of heavy metals

Heavy metals have devastating impacts on living beings (see Appendix 1). They inhibit proper functioning of life running systems and even some of them are carcinogens. Aquatic ecosystems are badly affected by heavy metal loads. According to (Munthe et al., 2001) Scandinavian fish have found to be high in concentration of Hg, it will not only reduce the water quality but can also be devastating for the entire ecosystem with the passage of time (Pekey, 2006).

The significant route of heavy metals to the food chains is their uptake by plants. Metals from plants are moved to the animals whenever they consume those plants

and toxicity of that particular metal goes on increase with the increase of trophic level i.e. from species to the population level. Stunted growth, physical, biochemical and morphological changes have been reported so far for the plants as a result of metal induced stress in many countries. In forests of Central Europe the heavy metals pollution has induced stress over the exuberance of growing tree because of the disturbance in nutrient circulation in soil (Olmo el al, 2015). If such situation prevails in the upcoming years, one can foresee serious threats to food security around the globe (Lee et al., 2006). Accumulation of heavy metals in soils has the potential to inhibit soil functioning, cause toxicity to plants, contaminate the food chain, and promote heavy metal accumulation to rivers through runoff and erosion (He et al., 2005). Traces of heavy metals are found in various birds and animals living in higher altitudes away from urban areas indicating long range transport of heavy metals. Aquatic organisms are more prone to the heavy metal accumulation in their bodies (Waheed et al., 2013) because these free metal ions in water either absorb, adsorb or ingested via water and food into the individual's body. (Flora, 2011) reported the increased level of oxidative stress, inflammation and toxicity of heavy metal in various fish samples.

1.5. Contributing factors for metal enrichment in riverine ecosystem

Long term and excessive transport of heavy metals, retention time and ongoing complex natural biogeochemical processes enhance the concentration in both water bodies (Gavrilescu, 2006).

In surface water the heavy metals are distributed in three zones i.e. the upper most surface water, suspended particles and bed sediment bound metals. Physical or chemical disturbance mobilize heavy metals in riverine system. **pH** is one of the water quality controlling factors, which is measuring the hydrogen ions activity, determines the quality of solution on the basis of acidity or alkalinity (Zdorikov et al., 1998). At low pH metals become mobilized in water. In dissolved form metals are relatively toxic and bioavailable for aquatic organism (Seshadri et al., 2015) whereas, in alkaline conditions the metals are suspended in upper zone of river water or bound to the bed sediments where they remain there for many years, building high concentration (Singh, et al., 2002) before finding their way towards water column

(Singh et al., 2005).The sediment-bound metals impose less toxicity to the aquatic organisms. Precipitation is one the factors which hinders metal mobilization in water the anionic surfaces (SO_4^{-2} or OH^-) on adsorptive surfaces tightly bind metallic cations (Cr^{+3}) (Bolan & Thiagarajan, 2001). **Temperature** also affects the mobility of metals in river water. At high temperature the sediment bound metals unbound themselves and become mobile in water. Increasing temperatures are responsible for the dissolution of (CO_3^{-2}) and (OH^-). Therefore, metallic water soluble fraction and carbonate fraction from the sediment into the overlying water also increased. However, opposite behaviour is observed for heavy metals in area with low (cold) temperature conditions (Gavrilescu, 2006).

The quality of water in rivers is controlled by dynamic nature of existing ecosystem and the climatic factors (Iqbal and Shah, 2014). The cycle of metal flux and their enrichment occurred as a result of heavy **rain fall** near riverine ecosystem. Heavy rainfall and flooding may also contribute towards enrichment of heavy metals in rivers and its tributaries. Land use patterns are significant contributors of metal loading to the rivers due to erosion and runoff (Smith et al., 2007). After leaching or direct discharge in rivers, heavy metals flow into riverine system and stay there as dissolved or suspended particles (Kaizer and Osakwe 2007). Heavy metals are non-biodegradable the **organic content** in the soil, sediments and water bodies may bring about changes in mobility, complexation and speciation of heavy metals due to the structural complexity of organic compounds with variety of functional groups at different pH ranges (Redman et al., 2002). Since heavy metals face diverse and complex environments and may stay for longer period time thus bring change to the quality of water. **Soil erosion** is another significant factor for bringing heavy metals to the adjacent rivers. Surface **runoff** can move heavy metals from eroded soil to the riverine system (Wilcox et al., 2014). The load of metals that moves to the rivers depends upon the type of land through which surface runoff travels (Hickin, 1995). **Slope factor** is one of the topographic features which influence distribution of heavy metal to the rivers. The rivers present at upper slope may have low concentration of heavy metals than those present at lower slope. As water falls from higher slope to lower slope thus enriching metal concentrations downstream water. The

concentration depends upon flow rate of water and physicochemical properties of heavy metal in any underlying system (Sharma and Subramanian, 2010).

1.6. Fate and transport of contaminants in river system

Various processes and mechanisms transport and transform heavy metals in river ecosystem. However, extensive information is required about contaminant's chemical nature and capability for sorption, precipitation, dissolution and degradation if determining the fate of contaminant. Contaminants in water either exist in particulate form or as dissolved entities (Tchobanoglous and Schroeder, 1987).

Heavy metals in the atmosphere can also be transported directly to the surface water bodies through wind or air turbulence. Other means of transportation for contaminants within water are **advection** i.e the transfer of unchanged mass and nature of contaminants from one place to other with moving of water like downstream movement of contaminant in river (Chapra, 1997). Second mode of transportation for contaminants in water is **diffusion**. Due to random turbulence and motion in water due to wind, it is transported from high concentration area to the lower concentration area over time (Wireman, 2012). **Dispersion** mixes contaminants in water due to change in velocity within confined space. The mixing that occurs in rivers where water flow is steady and fast is the result of dispersion (Chapra, 1997). These three modes of transportation are occurred within water to water. However other transportation ways might be from water to solids (sediments/soil). **Sorption** is the mode of transfer of contaminant in which contaminant either adsorb physically on the solid particle of it may absorb chemically inside the solid particle. The sorption (adsorption or absorption) depends mainly on properties of soil/sediment (pH, temperature), properties of inorganic moieties or organic compounds (Baudoin et al., 2003). The reversal of conditions suitable for sorption brings about desorption i.e. releasing the contaminant from the soil back to the water column. **Precipitation** is the significant process which removes contaminants from water column with the formation of solid minerals. The situation occurs when the concentrations of the mineral forming ions exceed like SO_4^{2-}, OH^- etc. helps the precipitate formation with cations (Bolan & Thiagarajan,

2001). However, dissolution is opposite to the precipitation and alkalinity and elevated pH prevent dissolution (Snoeyink and Jenkins, 1980). Moreover, redox reactions may significantly influence the solubility and mobility of heavy metals (Seshadri et al., 2015).

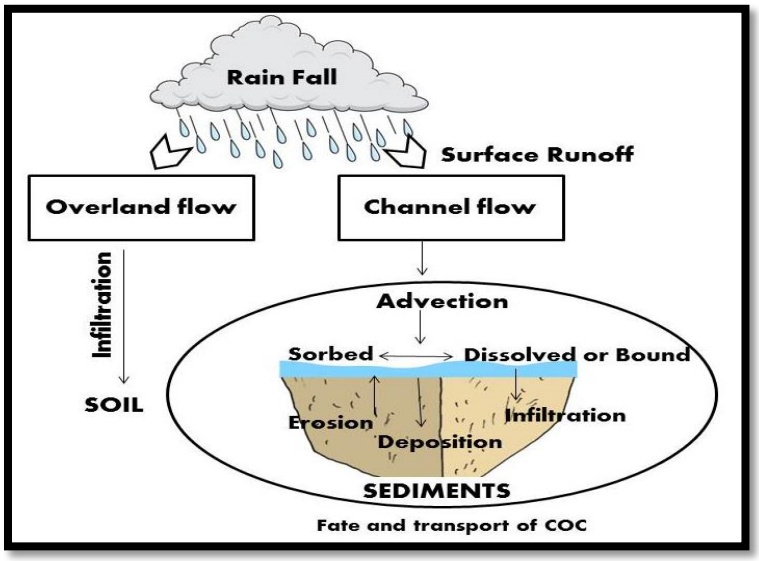

Figure 1.3 Transport of heavy metals in rivers

1.7. Long range atmospheric transport (LRAT) – the possible source of heavy metal distribution

Atmosphere plays significant role for the transportation, diffusion and dispersion of heavy metals in any ecosystem (Cong et al., 2010). Heavy metals are subjected to LRAT under the influence of "grasshopper" or "cold condensation" effect. Long range atmospheric transportation of compounds depends on many factors like climate, precipitation patterns, persistence of the toxic compound, time of release, elevation, area, distance and the wind patterns (Harner, 2006). Depending upon aforementioned factors, the mechanism of LRAT can be along altitudinal gradients and along latitudinal gradients. The difference among latitudinal and altitudinal LRAT seems very little but both can have great impact on the ecosystems. In general if long distance exists among the source of pollution to the area of atmospheric deposition then the LRAT here would be along latitude and vice versa case for the altitudinal LRAT (Guzzella et al., 2011). Therefore, the toxic pollutants having

smaller half-life spend more retention time and mixing up with the atmospheric aerosols in the regions along altitudes (Harner, 2006).

The regions with the warm temperature conditions would have more toxic compounds in the atmosphere while in cold condition they settle down and adsorb over the soil, sediments and other available surfaces and stay there for longer time if the same temperature exists (Sheng et al., 2013). Sometimes high concentrations of toxic and persistent pollutants are found because they have more residence time in soils and sediments in cold weather. Similarly, chemical and biological degradation and evaporation processes slow down or completely stops in low temperature conditions (Petersen, 1998).

Both dry and wet depositions enrich heavy metals in atmosphere, land and water (Cong et al., 2010). When heavy metals in particulate form are transferred directly to the surface of planet earth takes place the phenomenon is known as dry deposition. This kind of deposition takes place with the aid of convection currents of winds which excavate aerosol or particulate metals from the atmosphere and deposit them to the surface of soil or sediments. These newly deposited aerosols may remain there unreactive or produce chemical transformations in the adsorptive surfaces of the adhering matrix. On the other hand, the transmission of particulate metals in aqueous form to the land surface is known as wet deposition. Rain droplets, dew drops, haze and fog are the medium for bringing particulate metals down over the earth surface after the (Petersen, 1998). At cold layer of atmosphere the processes of cloud formation or condensation trapped these metallic particulates on their anionic aerosols and precipitation process further aids them to bring down and deposit on the earth surface (Barrie & Schemenauer, 1989).

1.7.1. Mechanism of LRAT of heavy metals

According to (Petersen, 1998) Initial mixing is the process when toxic metal released into environment and passes through various transformational phases through chemical or physical mechanisms in the tropospheric layer of the atmosphere interacting with the underlying environment. After that the small turbulent waves of gaseous vapors generate which allow metals to diffuse freely here and there. This turbulence and collision between metals and vapors present in the atmosphere make

a very strong association between aerosol-pollutant particles with the simultaneous dispersion of metal in the atmosphere (Hailin et al., 2008). Strong wind and air currents then transport heavy metals under the influence of gravity and the temperature fluctuations. Half-life of the metal specifies the actual residence time in the particular region and distance travel by them (Nicholson et al., 2003). Those metallic particles which are trapped by rain droplets quickly remove from the troposphere the surfaces while those adhere to tiny aerosols or BC (1μm) can travel longer distances and can be found at high altitudinal areas (Petersen, 1998).

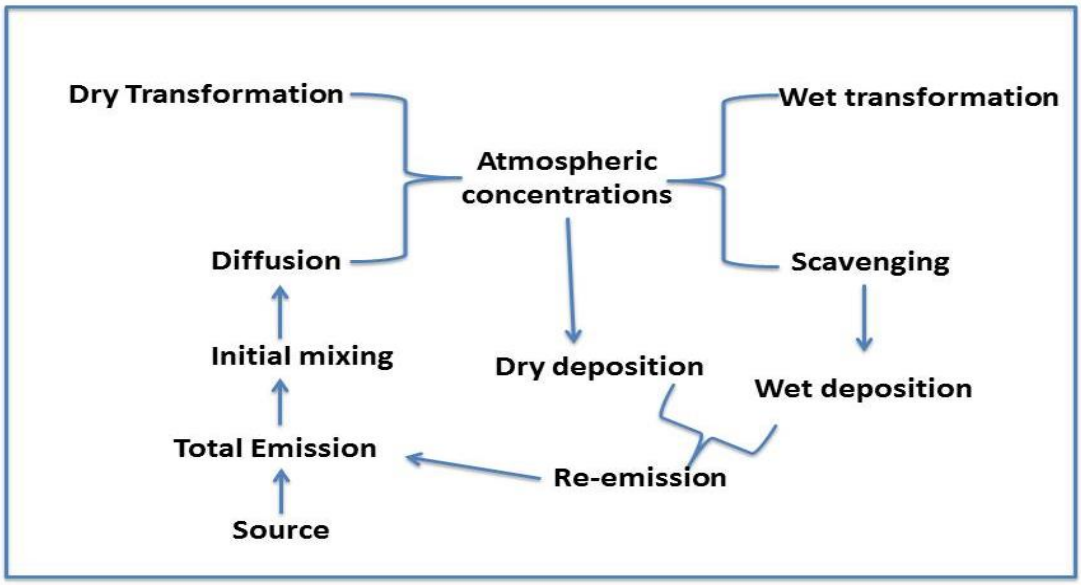

Figure 1.4 Mechanism of LRAT for heavy metal

1.8. Black carbon-Missing carbon finds human intrusion for heavy metal transportation

Together with mineral dust and water-soluble inorganic salts, carbonaceous particles are a major component of the overall aerosol burden of the lower atmosphere. Carbonaceous compounds are produced from both natural and anthropogenic sources (Jacobson et al., 2000). Black Carbon (BC) is considered as the anthropogenic aerosol produced in the atmosphere either suspended in liquids, in atmosphere as aerosols or adsorbed on sediments and soils (Rehman et al., 2011). The term "Missing Carbon" is also used for BC and many studies reported these are tools for providing carbon sequestration in soils and sediments (Luo et al., 2010).

Black Carbon (BC) is also known as hard carbon produced as char or soot as a result of incomplete combustion processes including burning of biomass, fossil fuels, wood burning and forest fires (Genilas et al., 2001). There is not clear understanding of significant role char or soot in atmospheric processes but the impacts of BC in atmospheric carbon circulation has been recognized by scientists (Hsieh and Bugna, 2008; Genilas et al., 2001; Muri et al., 2002). Biomass burning is thought to be sustainable substitute of coal and fossil fuel as an energy source because it addresses environmental concerns of waste generation using fossil fuels (Bessou et al., 2011). Domestic cooking relies mainly on biomass burning in rural areas. In spite of several benefits of using biomass energy for domestic use it comes under the umbrella of one of the manmade sources of organic compounds including BC and heavy metals in various regions including Asia (Gatari, 2003). Pb, Cd and Cr have been found during biomass burning along with BC (Wierzbicka, 2005). Since BC itself is non-reactive, having high surface to volume ratio and resistant to heat, high stability against gravity with the particle size less than 1μm (Poot et al., 2009). These properties make BC as a facilitator or ultimate sink for the transfer of enormous environmental pollutants like heavy metals from atmosphere to the terrestrial and aquatic ecosystem (Middelburg et al., 1999). BC particles have a three-dimensional structure, are composed of stacked sheets (Fernandes et al., 2003).

Industrialized of North America, Europe and Asia depend on fossil-fuel burning. These industrial activities annually produce tonnes of BC and heavy metals which are then subjected to local or transboundary transport. As a result of emission by incomplete combustion of fossil fuel soot particles are released, soot is the form of BC with high porosity and globular structured in grape-like aggregates. These are light weight particles with size of 0.1-1μm. Soot particles are mostly subjected to long range atmospheric transportation due to their light weight. The specific surface area is 10-63m^2 /g. However, high temperature combustion of biomass resulted in production of char the less structured, low porosity, carbonized residues form parent material with of 1-100μm. The specific surface area is 100-200 m^2 /g. These particles are subjected to local deposition (Schmidt and Noack, 2000).

TOC and BC are ubiquitous in soils and sediments (Schmidt and Noack, 2000). However BC has accounted for median of 9% and 4% of the total organic carbon (TOC) in sediments and soils of 300 worldwide samples. TOC is often considered as tracer of the primary productivity of an aquatic ecosystem (Meyers 1994). BC presence n sediments may serve as proxy for other air-borne contaminants like heavy metals (Goldbery et al., 1981) However, allowable limit has not been set uptil now for BC because uncertainty exists in the quantitative analysis of BC in various studies (Gustafsson et al., 2001). Recently, it has been reported that melting alpine glaciers incorporate various aerosols such as BC. In alpine glacier lake sedimentary BC was found with other aerosols.The only source of BC in remote alpine region is atmospheric deposition either wet or dry (Kestelec, 1999). BC is considered as anthropogenic aerosols which might be behaving exactly like gas vapours and may transfer number of heavy metals and organic pollutants to the environment (Jurado et al., 2008). They may not only contaminate soil and sediments but also the quality of adjacent rivers and fresh water resources (Shotyk et al., 2015). The high stability makes BC to transport heavy metals over long range and deposit them in higher altitudes under the effect of cold trapping (Yang et al., 2008). Several researchers have reported the presence of carbonaceous particulate matter with the increased concentrations of heavy metals in high mountainous regions like TP as a result of LRAT and precipitation (Lee et al., 2008; Bing et al., 2016).

1.9. Rationale of the study

Ecology of Lesser Himalayan is of great importance as it is connected to the urban cities, the industrialized and densely populated countries like India and China (Loewen et al. 2005). Riverine system of AJK is originating and merging with Indus River from Himalayan ranges as tributaries (Valdiya et al., 2001). Mostly the area's landscape is remote with beautiful natural setting of riverine freshwater networking and the green mountainous vales where 88% population relies on biomass burning as a source of fuel (Saleem et al., 2013). Few studies have reported existence of heavy metals in Pakistan including rivers of the study area too. No study has highlighted anthropic invasions (biomass burning, tourism, hydropower project and artificial dam construction) or long range atmospheric transport as contributors of heavy

metal fluxes and enrichment in this remote area (Saleem et al., 2013; Bing et al., 2016). Soil erosion, rainfall pattern, transboundary sources and local activities might be adding heavy metals to the soil, water and ultimately sunk to the sediments of riverine system of AJK (Qiu, 2008). Therefore present study will provide current status of spatially distributed heavy metal, anthropic factors and their depositional fluxes in the riverine system of AJK.

1.10. Objectives

- To trace the spatial distribution and possible sources of heavy metals in the selected matrices.
- Evaluation of contributing factors for the enrichment of heavy metals in the soil, sediment and water.
- To highlight the potential of natural ecosystem as a sink of heavy metals due to long range transport and sedimentation.
- Providing the baseline study for further research opportunities in the study area in order to frame out strategies for tracking the sources of heavy metals

CHAPTER 2

2. Materials and Methods

2.1. Area Description

Beautiful Himalayan range is the leeway of great Tibet Plateau covering an area of approximately 2 x10^5 km^2. It is divided into Higher Himalaya, Sub Himalaya and Lesser Himalaya, based on tectonics and structural data (Khattak et al., 2010). Expanding from the Indus River to the northern Pakistan eastward, the territories of Jammu and Kashmir, northern India, southern Tibet and some areas of Nepal are surrounded by Himalaya glaciers (Sheng et al., 2013). Ecology of this very region is of great importance as it is connected to the industrialized and densely populated countries Pakistan, India and China (Loewen et al. 2007). Approximately 33,000 km^3 of fresh water source for locals is fetched by these glacial mountains. It is estimated that around 0.5 billion of population living around the Asian rivers including Indus, Yellow river, Ganges, Yangtze and Brahmaputra rely upon the water coming from this glacial range (Huang et al., 2008; Kang et al., 2010). In Pakistan, the Lesser Himalaya comprised of Azad Jammu & Kashmir (AJK), Rawalpindi-Islamabad districts and the entire Hazara division with an estimated area of 23295 km^2 (Hussain and Ilahi, 1991). Hazara and Kalachitta are the two major geological zones of the Lesser Himalaya (Champion et al., 1965).

2.2. Study Area

2.2.1 Geography and Topography

The part of Himalayan range that stretches along Rawalpindi, Islamabad, Haripur, Mansehra, Batagram and Pakistan Administered Azad Kashmir is known as *Lesser Himalaya*. Riverine system expanded in lesser Himalaya region is of particular importance as act as catchment basin for Indus Waters System. **Azad Jammu and Kashmir (AJK)** is Pakistan administrated state of Kashmir with approximate elevation ranges between 360-6325 meters. AJK have total population of four million people over an area of 1.33 million ha stretches along Line of Control (LOC) in northern part of the Lesser Himalayan range of Pakistan (Lat: 33^o – 36^o ′N, Long: 73^o – 75^o′E). Administratively, Azad Kashmir is divided into three divisions (Muzaffarabad, Mirpur

and Poonch) and ten districts with Muzaffrabad district as capital of the state (Nawaz and Shafique, 2003).

Territory of AJK comprised of three major rivers, several perianal water tributaries and one water reservoir. Major rivers included Neelum River, Jhelum River and Poonch River and Mangla Dam is only multipurpose water reservoir of this region. This whole water system of this region is collectively known as **Jhelum River System.** The riverine system shows tremendous topographic variation owing to its altitudinal aspects, with approximate elevation ranges between 300-3000 meters. Neelum River enters into AJK at Taobat from India and with total length of about 190 km flows along LOC in Neelum and Muzaffarabad districts.

On the other hand, Jhelum River enters into AJK at Chakothi (Hattian District) from India and have total span of about 56 km and meets Neelum River in Muzaffarabad district at site of Domail. After junction with Neelum River, Jhelum River flows southwardly, passing through Muzaffarabad, Bagh, Haveli, Poonch, Sudhnoti and Mirpur. Districts (total stretch after junction is about 160 km) finally discharge in Mangla Water Reservoir. This reservoir is expanding over an area of about 250 km^2 with storage capacity of about 9.12 km^3. By conserving massive amount of surplus water especially during monsoon period, Mangla Dam fortifying irrigation system of country as part of (**Indus Basin Project)** under Indus Waters Treaty 1960. Besides supportive to irrigation system, Dam has hydropower generating capacity of about 969 MW, thus further strengthening the economy of country. Orogenic Himalayan belt along Jhelum Riverine System is characterized by hilly and mountainous belt in north (Neelum, Muzaffarabad, Hattian, Bagh, Haveli, Poonch, and Sudhnoti), while plain areas in south (Kotli, Mirpur, and Bhimber) (Akram et al., 2011). Alpine biomes, temperate forest, mountainous ecotones and monsoon systems made this region ecologically unique. Eighteen protected areas (6 national parks and 12 game reserve) over an area of 1133.5 Km2 have been designated to protect and conserve its unique flora and fauna. This region is major hub of tourism in northern Pakistan owing to its distinctive ecological and topographical features (Khattak et al., 2010).

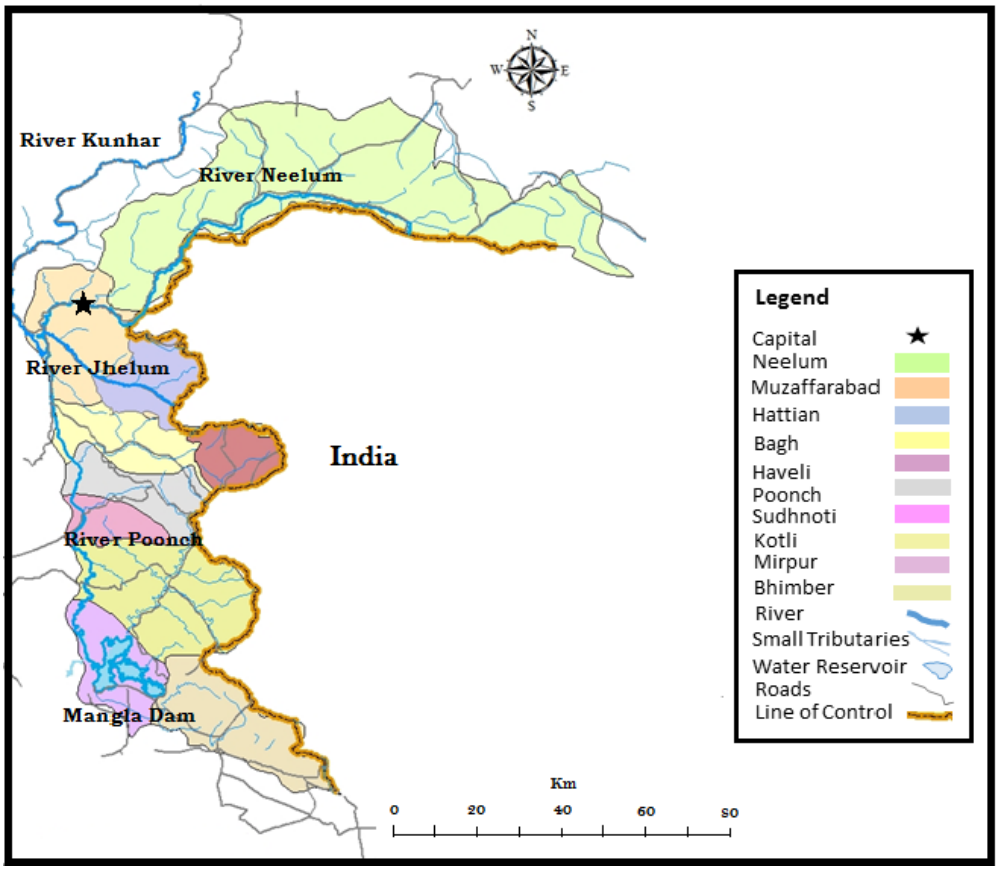

Figure 2.1 Map of the rivers along study area

The soil of area is deep, gravelly loam with relatively low infiltration and frequent surface runoff takes place whereas steep sloped alluvial valleys are present in the heart of these mountains which are suitable for agricultural practices. The mountains are basically made up of sedimentary rocks containing clay-stones and sand stones with the beautiful water channels are coming downwards from high elevation of Himalayan ranges (Akram et al., 2011).

2.2.2. Climate

Owing to the variation in altitudinal aspect, topography and vegetation cover, AJK shows wide range of climatic conditions. Climatically, this region is categorized as moist temperate in north and dry sub-tropical in south with average maximum and minimum temperature ranges from 20-30 ^{o}C and 04 - 07 ^{o}C respectively. Mean annual precipitation is 1000-2000 mm, while in northern part 30-60% of precipitation is in the form of snow and hail storming (Abbasi et al., 2010).

2.2.3 Occupation

90% of total population of AJK is living in rural area, but unlike Pakistan, only 13% (194191 ha) of total land is not very fertile. The reason for less agricultural land is the unique formation of land and rocks of lesser Himalayan region. The terrace farming is under fruit farming and livestock contributes 30-40% of domestic earning. Forests covers 770,000 ha (43% of total area) and have diverse forests network ranges from coniferous in north to temperate in southern region. Major part of population (88% of total) directly or indirectly depends upon forest practices not only for their life sustenance but also meet energy demands. Total dependence of most of population on forests results into massive deforestation (16% of forest cover as compared 47% in 1950s) and other associated problems, such as pollution (by biomass combustion) and land slide. Confluence of mountain ecosystem, monsoon climate and topographic variation of AJK, made this bionetwork as center for tourist. Increasing tourism, high growth rate (2.3%), urbanization, local scale industrialization and developing activities put pressure on natural resources as well as results into high road density and may potentially act as native source of pollution (Saleem et al, 2013).

2.3. Sampling Strategy

To pursue defined objectives, sampling strategy was designed accordingly. Based upon elevation gradient and direction of discharge 3 sampling stations were designed and within these station thirty two sampling sites were further identified for detailed sampling of environmental matrices i.e. soil, water and sediment along with meteorological parameters from each site.

2.3.1 Sampling Stations

Station 1

First station is Neelum River that enters into Kashmir from India at Taobat. The total length of about 190 km flow from east to westwards. A total of seven sites were identified on this river at different elevation aspect using portable GPS system.

Station 2

Jhelum River is flowing in a beautiful 'V' shape flow. One arm of river was considered as side "A" which enters into Territory of AJK at Chakoti from India and direction of flow is also from east to westward. Six sites were further identified on this river stretch of

56 km. The second arm or "B" side of Jhelum river starts at junction point of station 1 and "A" arm od station 2 flowing north to south. Total stretch of this station is about 160 km and eleven sites were located as sampling points.

Station 3

Last sampling station was Mangla Dam which covers an area of about 250km^2 and eight sampling points were sampled along its lobes.

2.3.2. Altitudinal zones

The systematic sampling strategy was further modified by dividing whole study area to zones on the basis of elevation because at the time of sampling river flow direction and altitudinal gradient were expected. Zone 1 was defined within the altitudinal range of (2374 to 1301 m.a.s.l), Zone 2 with altitudinal range of (1300 to 951 m.a.s.l), Zone 3 having altitudinal range of (950 to 751 m.a.s.l), Zone 4 with altitudinal range (750 to 376 m.a.s.l) and finally Zone 5 with altitudinal range (375 to 300 m.a.s.l). The number of sites from each zone were 5, 4, 7, 8 and 8 respectively.

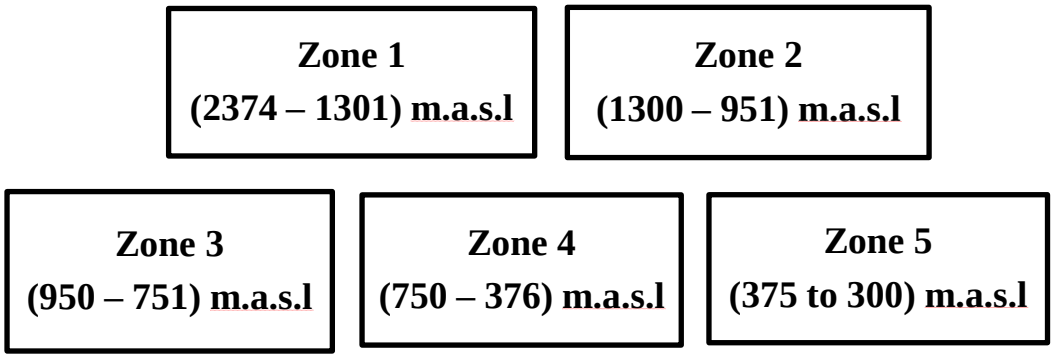

Figure. 2.2. Altitudinal zones

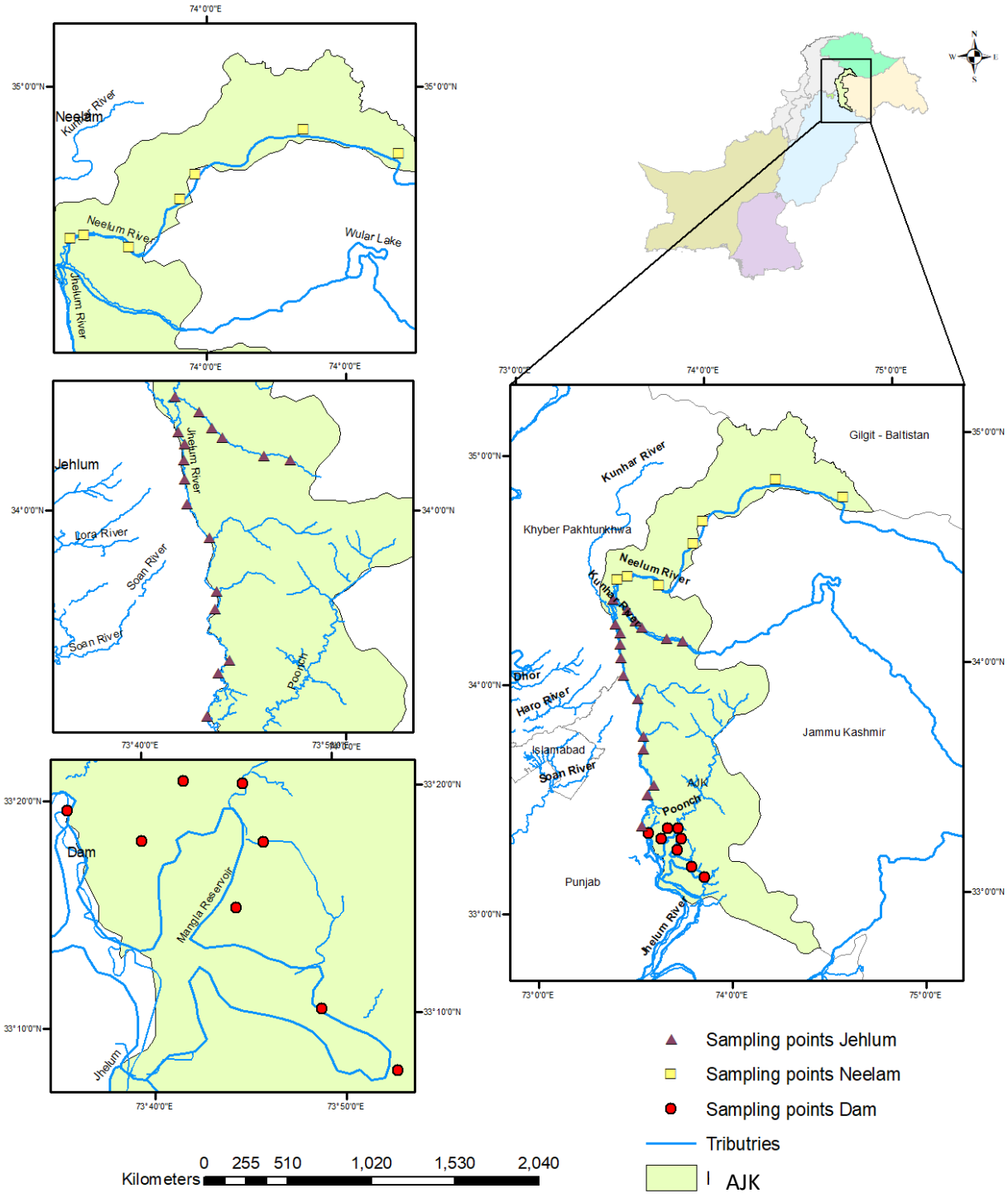

Figure 2.3. Map of Study Area showing sampling points

2.4. Sample Collection

2.4.1. Soil Sampling

Total thirty two surface soil samples were collected from three sampling station including. Soil core samples (5-20 cm depth) consist composite of 3 sub-samples collected from the radius of one kilometer from each sites. All soil samples were collected using stainless steel ladle and soil core sampler, kept in glass containers and brought to the laboratory where after preliminary treatment stored at − 4 ℃ until analysis.

2.4.2. Sediment Sampling

Hand trowel was used for sediment sampling from 32 sites of selected sampling stations. Each sample was a composite of three sub-samples. The samples were brought to laboratory in polythene bags (cleaned with 10 % HNO_3 prior to use), and then air dried at room temperature. After drying, the samples were crushed and passed through 2-mm-mesh sieve. The sieved samples were then kept in prewashed metal free glass containers and stored at 4 °C till further analyses.

2.4.3 Water Sampling

Surface water samples were collected by using the hand with grab method in plastic bottles. The bottles cleaned, bottles were soaked in 5M analytical grade nitric acid and then rinsed with deionized water. The bottles were kept filled for a whole week with high purity 1.4 M nitric acid following rinsing with deionized water.

2.5 Pretreatment and sample analysis

2.5.1. Physico-chemical analysis

Physicochemical parameters were calculated for each sample of three matrices. The texture was determined using dry sieve shaker method for particle size distribution based on USDA particle size distribution and % sand, % silts and % clay were recorded. Soil and sediment moisture were calculated by weighing sample before and after drying in a drying oven set at 105 °C following ASTM (American Society for Testing and Materials) standard method (Standard, 2010). Crison pH meter calibrated at pH 4.01, 7 and 9.21 by standard solutions and PCS testr 35 multi parameter EC meter were used for EC. Slurry of soil and sediment samples was prepared with de ionized water in a ratio of 5:1 and stirred for about 3 to 10 minutes.

2.5.2. Soil analysis

Soil sampling was performed along with the recording of geographical coordinates of sampling points with GPS (Geko 301). After taking soil samples they were left for air drying at room temperature and 2mm sieve was used for the removal of coarse material present at the time of sampling. After that particle size analysis was done with sieving method. For further analysis first the soil pH and EC were measured by using probe. Following standard USEPA 1998 (Method 3051A) the samples were subjected to acid digestion in microwave digester CEM 630W (Bettinelli, 2000). 5g of soil sample was weighed and were stored in Teflon vessels. Microwave assisted acid digestion was then performed with 3:1 ml of HCL: HNO_3 (USEPA 1998 Method 3051A). After digestion the samples were filtered using Whattman filter paper no.42 and dilutions were made upto 50 ml volume. Fe, Cd, Co, Cu, Ni, Pb, and Zn concentrations in each sample were determined using atomic absorption spectrometer (Model GBC Avanta Ver 1.33).

2.5.3. Sediment analysis

1 g of each sample was taken up and subjected to acid digestion in total of 15 ml aqua regia (3 parts of HCl and 1 part of HNO_3) and it was left for a whole night after that the mixture was heated at about 150 °C when the brown fumes came out of the mixture it was removed from flame and 5 ml $HClO_4$ was added and again heating was performed till near dryness. Whattman filter paper no.42 was used for the mixture filtration. In the filtrate distilled water was added for the purpose of raising volume up to 50 ml (Malik et al. 2010). Flame atomic absorption spectrophotometer (Model GBC Avanta Ver 1.33) was used for the analysis of selected heavy-metals.

2.5.4. Water analysis

The water samples were analyzed for Cd, Cr, Cu, Fe, Mn, Ni, Pb, and Zn under standard analytical condition. Standard reference material (SRM-1643d) was also used for the calibration and quality assurance of the metal data. The reagents were of best analytical grade (certified purity > 99.99% from BDH, UK). For sample preparation and dilution double distilled water was used (Sadeghi et al., 2012). Stock solution of 1000 mg/L was used for the preparation of metal standards. Atomic adsorption spectrometer (Model GBC Avanta Ver 1.33) was used for the analysis of metal concentration.

2.6. Black carbon (CTO-375) and Total organic carbon (TOC) analysis

For analysis of Black Carbon and TOC 3g of air dried and homogenized soil and sediments samples were taken. For black carbon analysis the samples were treated with 1N solution of HCL. For TOC analysis acid digestion was performed by using 10% HCL solution in order to completely remove inorganic carbon. After acid digestion, samples for TOC were washed many times with deionized water and were placed in microwave oven for drying atleat for 24hours at 60 °C temperature. For oxidation of the acidified pretreated BC samples (CTO-375 protocol) was followed. 3 grams of soil samples was taken out and subjected to oxidation in a muffle furnace at 375 °C for 17-18 hour under constricted air flux. After above mentioned treatments both BC and TOC were calculated by TOC analyzer (Ali et al., 2014a).

2.7. Model Based Data Analysis

Statistical modelling techniques were used to generate the hypothesis for main contributing sources of heavy metal pollution in soil sediment and water of the study area. Statistical tests were performed using SPSS, MVSP and XLSTAT. Principle component analysis (PCA) was performed to evaluate similarities, sources and differences among the distribution of all targeted compounds during sampling period as well with different factors.

2.7.1. PCA-MLR model for source apportionment

With the spatial variation source identification is also important in order to assess the contributing factors for heavy metals enrichment in soil sediment and water. For Source identification PCA and the subsequent statistical technique MLR (Multiple Linear Regression) was employed for all sampling stations (Neelum, Jhelum and Mangla Dam). XLSTAT was used for this purpose in order to evaluate the variance among the factors following commutative variability in terms of percentage for the contributing factors. The varimax rotation method is the regression method that reduces the covariance among orthogonally related factors and gives the Z score (Alleman et al., 2010). The Z scores were then employed to the aforementioned MLR technique based of model (equation 1) to get the combined contribution of the PCA factor loading scores for the source identification (Sofowote et al., 2008).

Mean i source contribution =Bi / ΣBi × 100 Equation …… (2.1)

2.7.2. Evaluation of heavy metal contamination level

2.7.2.1. Enrichment factor

Enrichment factor (EF) is a worldwide acceptable indicator for the calculations of heavy metal enriched concentration under the influence of anthropic activities in aquatic sediments (Saleem et al., 2013; Siddique et al., 2009). The indicator value shows the current status of the environment under observation.

Equation used for EF calculation is

EF= (Ms/Fes) / (Mcr/Fecr) Equation…… (2.2)

Here (Ms/Fes) is ratio of metal of interest to iron in sample of interest while (Mcr/Fecr) is the background value of metal to iron ratio. In our study, we used values of average crust abundances adopted from Taylor (1964) as we do not have natural background metal values for the Lesser Himalayan Region of Pakistan. For evaluating metallic ratio Fe was used as a predictor because it is naturally present in sediments due to erosion and weathering events (Zhang et al. 2007). The EF scale used by (Saleem et al., 2013) was used in the study (Appendix 2.1)

2.7.2.2. Geo accumulation index for heavy metals in soil and sediments

For the quantification of heavy metals enrichment level in the soil and sediments above background values, different indices are being used throughout the world. One of the widely accepted indexes is "Geo-accumulation index" or (Igeo). This method assesses the quality of sediments and soil in terms of grades based on classification level (Muller, 1981). Earlier this index was only used for the evaluation of sediment pollution in coastal areas (Dou et al. 2013) but later it was employed for both soil and sediments distant from coastal areas as well (Zhiyuan et al., 2011)

Igeo is quantified as;

$$\mathbf{I\ geo = \log_2 (C_n / 1.5 \times B_n)}$$ Equation…… (2.3)

n= Element (heavy metal)

Cn= concentration of heavy metal measured in the soil

Bn= Shale or background values of the element (n) of interest

(1.5) = Background matrix correction factor (Turekian & Wedepohl, 1961)

The (Appendix 2.2) shows grading system used for assessing heavy metals pollution based on (Taylor, 1964) background values and classification scale of (Muller, 1981).

2.7.2.3. Metal Pollution Index (MPI) for river water

According to (Reza and Singh, 2010) qualitative analysis of flowing water is important to rate the influence of each variable on overall quality of water used for various purposes. Internationally accepted index for metal contamination assessment in surface water is calculated using Metal Pollution Index (MPI). The MPI rating classes are from 1 to 6 which are used for classifying degree of contamination of particular metal in the water (Appendix 2.2 b). The MPI is based on equation as a below;

MPI=Σ Ci/ MAC Equation……. (2.4)

Ci: mean concentration of ith parameter.

MAC: maximum allowable concentration (NEQS, 2008).

If the measured concentration of a metal is higher than its maximum allowable concentration, then it will be an indication of bad water quality (Amadi, 2011).

2.7.3. Backward trajectory HYSPLIT Model

Precipitation and temperature data was extracted by Hybrid Single Particle Lagrangian Integrated Trajectory Model (HYSPLIT) endpoint files after running backward trajectories for February and March, 2015. Similarly, for tracing the possible direction for heavy metals coming to the study area back which are arriving at the coordinates for the sampling tenure (February-March, 2015) were computed using HYSPLIT (Hybrid Single Particle Lagrangian Integrated Trajectory Model) model. HYSPLIT is developed and run by NOAA (National Oceanic and Atmospheric Administration) working under the United States Air Resource Laboratory (Draxler & Rolph, 2003). The map was generated for the two consecutive months of February and March 2015 in order to evaluate the actual movements of air currents circulating around the study area.

2.7.4. TOC and BC burial flux

Sediments are considered as the final sink for the accumulation of various compounds as they spend long time along the rivers as suspended particles, in depth bound sediments or in compacted form. Similarly, sediments accumulate more organic matter as compared to the other matrices. The organic entities can be influential for enrichment of heavy metals due to their absorptive capacities. Therefore TOC and man-made released carbon BC were calculated after that their concentrations were subjected to the following equation (2.3) in order to calculate their burial flux in sediments (Hu et al., 2016).

TOC and BC burial fluxes were estimated with following equation (Hu et al., 2016);

$$F_{burial} = C.\ M$$ Equation…… (2.5)

Where Fburial (g/cm^2 .yr) is the burial flux, C is the concentration of TOC/BC (g/g), M is the mass sediment accumulation rate (g/cm^2.yr) from each sampling site. The mass sediment accumulation rate (g/m^2.yr) was deduced using sedimentation rate (m/yr) and density at each site (g/cm^3). The sedimentation rate (ω = cm/yr) was computed by following depth dependent empirical relationship (Middelburg et al., 1997)

$$\omega = 10^{(a+bZ)}.CF$$ Equation…… (2.6)

a and b are constant values known as predictive relationship with values of −0.875 and −0.00044 respectively. Z is the depth (m) from where the sediment sample was taken and CF is the correction factor with value of 3.3.

2.7.5. Annual Depositional Flux and Mass Inventory of heavy metals

For evaluation of annual sedimentary deposition flux of selected heavy metals (Cu, Mn, Cr, Cd, Pb, Zn and Ni) in study area following relation was used for calculations:

$$\mathbf{HMD} = \frac{\sum_{i=1}^{n} \mathbf{AR} \times [\mathbf{HM}]\mathbf{i}}{\mathbf{n}}\ \mathbf{x\ S}$$ Equation…… (2.7)

Where HMD is depositional flux of heavy metal, AR is mass accumulation rate at the site from where sample i was taken, [HM] is the mean concentration of heavy metal at the selected site, n is the total number of sites in each zone and S is the surface area of each zones from where sediment samples were collected. Similarly, In order to develop mass inventory for heavy metals found in sediments of Lesser Himalaya Region "Mass Inventory" was also calculated by the following equation (Middelburg et al., 1997).

$$I=C.A.d.\rho$$ Equation…… (2.8)

Where, C is the average concentration of heavy metal in sediments, A is the surface area, d is density (1.5 g cm-^{3}) and ρ is depth of the sediments (7cm).

CHAPTER 3

3. Results and Discussion

3.1. Contaminants profile and spatial distribution of heavy metals

Finding the loads of heavy metals in riverine ecosystems present at higher altitudes is thought to be originated from underlying parent rock material, sediment composition, physico-chemical processes and through atmospheric deposition (Nagajyoti et al., 2010). Anthropogenic interference may also add in the bulk of heavy metals in rivers, adjacent soils and the underlying sediments to the areas where there are no industrial units working. Remoteness, cold climatic conditions, unique rain fall patterns and altitudinal gradient may also become triggering factors for scavenging heavy metals from distant areas (Qiu, 2008).

3.1.1. Delineation of contaminants profile in soil

In an attempt to delineate heavy metals profiles and to gauge spatial trends for 8 metals including (Mn Cu, Cr, Zn, Pb, Cd and Fe) of interest in soils of the selected five zones of study area the statistical analysis was performed. The concentrations were recorded in mg/kg for Mn, Cu, Cr, Ni, Cd, Pb and Zn except for Fe (%). The concentration of Fe in the present study was recorded very high in mg/kg so it was also converted to percentage unit to report them easily according to previous literature in (Ikenaka et al., 2010).

Mean order of individual metal level was; **Cd** (1.37±0.97mg/kg) < **Cu** (10.08±6mg/kg) < **Mn**(14.7±8.0mg/kg) < **Cr**(14.41±7mg/kg) < **Pb**(22.9±7.1mg/kg) < **Ni**(24.51±9.3mg/kg) < **Zn**(33.1±22mg/kg) < **Fe** (64.6±0.5%).

The sum of average concentration of all metals in all zones was calculated approximately 649981.4 (mg/kg).

The output of statistical analysis revealed that Fe, Zn, Ni and Pb were abundant in all zones while Cd, Cu, Mn and Cr were less abundant in soils of study area. Fe was highly abundant in all of the zones. The presence of such high concentration of Fe because of its natural abundant occurrence in earth crust and due to weathering processes soils become enriched with Fe (Zhang et al. 2007). Prior works confirm the abundance and constant uniformity of Fe in different soils sediments and waters across different continents (Siddique et al. 2009). Due to natural abundance in the earth crust Fe rarely poses harm to

the soils and related biotic components if exceeds the shale value (Pagotto et al., 2001). According to (Schiff and Weisberg, 1999) Fe shows constant behavior in relation to other metals under anoxic and oxic conditions. Fe values are comparable to the values reported by (Tüzen, 2003; Pagotto et al., 2001).

Zone 4 zone of the study area were present at medium elevation gradient and abundance of heavy metals was observed in this zone located at middle elevation of the study area (950 to 1058 m.a.s.l). The catchment area of Jhelum River above Mangla covers about 12,870 sq. miles of which 44% comes under the territory of AJK, Pakistan. Rest of the areas is under roads, colonies, or forest lands. This very zone lies within the area where busy roads and land construction is prominent along. The traffic emissions, generators and construction operations are might be responsible for heavy metal loadings (Cheng and Hu, 2010).

The mean concentrations of all metals were comparable to the Chinese screening values (GB15618-1995 Standards) as per reported by (Wang and Sham, 2013) can be seen in (Appendix 3.1) The mean higher concentrations for Pb and Cd were observed higher than background values and also above standard values in the soils as of all selected zones can be attributed to the geological sources like weathering or soil erosion events, traffic emissions, local and transboundary pollution through Long Range Atmospheric Transport (LRAT) or precipitation (Cheng and Hu, 2010). Same observations were recorded for the metal enrichment in soils at medium elevation of Mountain Gonga located at the eastern slope of Tibetan Plateau (Bing et al. 2016). (Reiners et al., 1975) has been reported high concentration of Pb at elevation 1300 to 1400 (m.a.s.l). The mean concentration of Cd observed here was (1.37mg/kg) which was less than observed for (2.47 mg/kg) in soil of Yuanyang county, Ailao Mountain (Zhang et al, 2012), Tehran–Karaj soil, Iran (3.9 mg/kg) by (Saeedi et al, 2009) and calculated for the soil of Heihe River TP, China (2.93 mg/kg) by (Bu et al., 2016). The concentration of Cd was far greater than reported for soil of Beijing, China (Zheng et al 2010), Khathmando Nepal (F. Zhang et al., 2012) and for soil of Yanqi, Xinjiang China (Mamat et al, 2014). The recorded mean concentration of Pb in study area was (22. 9 mg/kg) which is much less than recorded for Tehran–Karaj soil, Iran (669.3 mg/kg) and Shanghai, China (70.96 mg/kg). Less urbanization is the

reason for finding comparatively low concentration of metals in areas with high elevation (Bu et al., 2016).

3.1.2. Delineation of contaminants profile in sediments

Delineation of heavy metals profiles and to gauge spatial trends for 8 metals (Mn Cu, Cr, Zn, Pb, Cd and Fe) in the sediments of selected five zones of study area the statistical analysis was performed. The concentrations were recorded in mg/kg for Mn, Cu, Cr, Ni, Cd, Pb and Zn except for Fe (%). The concentration of Fe in the present study was recorded very high in mg/kg so it was also converted to percentage unit to report them easily according to previous literature in (Ikenaka et al., 2010).

The concentrations were reported in mg/kg except for the Fe. It was reported in both mg/kg and percentage for the purpose of having ease during calculations because Fe is naturally abundant metal in the earth crust as a main constituent of clay particles due to weathering processes (Zhang et al. 2007. The cumulative average concentration found in sediments of all sampling stations was 714437 mg/kg. Fe being the main constituent of crustal minerals was found high. The average concentrations for metals of interest found at all sampling sites were;

Cd (1.01±0.97mg/kg) < **Cr**(14.9±7.4mg/kg) < **Ni**(19.83±8.2mg/kg) < **Cu**(22.6±21mg/kg) **Mn** (26.6±14.1mg/kg)< **Pb** (27.34±11.09mg/kg) < **Zn**(49.5±25.6mg/kg) < **Fe** (2.2±1.1%)

Overall the trend shows high concentration of metals in sediments of Zone 5 (low elevation zone) as compared to other zones. Sedimentation can be the reason for finding the gradual flux of heavy metals in the reservoir (Sawaske and Freyberg, 2010).

The overall concentrations of metals in sediments were higher than observed for soil and river water of the present study area. This might be due to sedimentation or variation in water capacity of the river where low water flow in winter takes place and the precipitation of the metals in sediment thereby increasing their concentration (Islam et al., 2014). Change in average concentration can be due to the effect from point and non-point sources gasoline, municipal runoffs and atmospheric deposition (Shikazono et al., 2012). Higher mean concentration of Cd than crustal value indicates it can be some non-crustal sources (Siddique et al., 2009). Such high concentration of Cadmium recorded at these sites is similar to the concentrations reported by (Bing et al, 2016). Beside from anthropogenic sources the atmospheric deposition can also contribute for distribution of

some metals metals. At neutral pH the formation of CdCO3 takes place the pH of study area was neutral to the alkaline thus facilitating the sediment binding of cations to the available anionic surfaces on sediments (Balistrieri et al, 2007).

All metals were in line with worldwide accepted Canadian SQG's values for metals in sediments (CCME, 1995) in fresh water except for mean concentration of Cd. The average concentration of Pb can be compared to the observations made by (Bastami et al., 2012; Ali et al., 2015). The concentration of Zn (49.5 mg/kg) observed was far less than observed for Almemdares River, Cuba (Rieumount et al., 2005) with concentration (262mg/kg), Aswan and Beni Suef, River Nile, Egypt with concentrations (101.1 mg/kg) and (126.6 mg/kg) respectively (Osman and Kloas, 2010), Zhu River, China with reported concentration (192mg/kg) (Tang et al., 2014) and higher than (32mg/kg) reported for Tembi River, Iran (Shanbehzadeh et al., 2014). The observed mean concentration of Pb in present study was (27.34mg/kg) was much less than reported by (Akcay et al., 2003) for Gediz River Turkey (105- 140 mg/kg), Almemdares River, Cuba (Rieumount et al., 2005) with (93mg/kg), Tembi River, Iran (151 mg/kg), (Islam et al., 2015) recorded concentration as (58mg/kg) for Korotoa River, Bangladesh and Zhu River, China with reported concentration of (61.9 mg/kg) (Tang et al., 2014). However, the concentration of Pb was higher than recorded for River Ganges (Gupta el al., 2009), Aswan and Beni Suef, River Nile, Egypt (Osman and Kloas, 2010).

3.1.3. Delineation of contaminants profile in rivers

Delineation of heavy metals profiles and to gauge spatial trends for 8 metals (Mn Cu, Cr, Zn, Pb, Cd and Fe) in river water of selected five zones of study area were statistically analyzed. The concentrations were recorded in mg/L for Mn, Cu, Cr, Ni, Cd, Pb Zn and Fe. The mean concentration recorded in water for metals was;

Cu (0.03±0.03) < **Cr** (0.04±0.024) < **Cd** (0.05±0.039) < **Mn** (0.080±0.059) < **Ni** (0.13±0.10) < **Fe** (0.142±0.073) < **Zn** (0.16±0.23) < **Pb** (0.3±0.468)

The average concentrations for all metals observed were within permissible limit of drinking water guidelines of Pakistan (NSDWQ, 2008) but the concentrations for Pb (0.3mg/L), Ni (0.13mg/L) and Cd (0.05mg/L) were higher than the recommended concentrations for these metals by (WHO, 2006) and (Pak-EPA, 2009) while other metals were found in compliance with the prescribed limits (see Appendix 3.4).

Metal concentrations in Zone 5, Zone 3 and Zone 4 were found high can be due to the urbanization, farming and tourism (Nazeer et al, 2014). As these metals are naturally occurring in parent rocks, precipitation may also be responsible for bringing these metals to the river water through runoff or erosive processes at relatively low pH (Nazeer et al. 2014). Finding low concentrations of metals in water may be attributable to their strong affinity for soil, sediment particles and aquatic biology (Censi et al. 2006). It can also be due to dilution characteristic of rivers which is successful in rivers having less anthropogenic inputs (Caruso et al., 2012). However, higher concentrations of metals were found near urban sector of study area revealing that their concentrations had been strongly affected by anthropogenic influences. Earth moving activities might also be responsible for mobilizing metals in water. Pollution increases downstream the gradient as the river passes through different land uses. The rivers present at high altitudes would have low contamination as compared to the rivers present downstream (Kotti et al. 2005; Wang et al. 2015).Thus, it can also be logical to conclude that the elevated concentrations of metals in water were considerably due to direct or indirect discharge of untreated municipal wastes into water either from point source or from diffused sources (Bai et al., 2011; Saleem et al., 2015). The concentrations observed for all metals in water Jhelum river station were much lower than observed for Jhelum River, (AJK) Pakistan (Khan et al., 2004). The difference in concentration might be due to seasonal variation. Whereas, the concentration observed for Zone 5 are comparable to the concentrations calculated for temporal trends of heavy metals in Mangla Lake, Pakistan (Saleem et al., 2014; Saleem et al., 2015). The mean concentrations of the metals were much less than the concentrations reported for Domimickie Lake Poland (Szymanowska et al., 1999), Wetland of Wadi Gaza (Shomar et al., 2005), Manchar Lake Pakistan (Mastoi et al., 2008). The concentrations computed for the study area were higher than calculated for Northern Delta Lakes Egypt (Saaed and Shakir, 2008), Lake Gilow Poland (Cymerman and Kempers 2004), Kanyaboli Lake Kenya (Ochieng et al., 2008), Manchar Lake Pakistan (Kazi et al., 2009), Kralkızı Dam Reservoir, Dicle Dam Reservoir, Batman Dam Reservoir, Turkey (Varol 2013), Danjiangkou Reservoir, China (Li et al., 2008), Lalbagh Tank, India (Lokeshwari and Chandrappa, 2006), Sapanca Lake Turkey (Duman et al., 2007).

3.2. Spatial and altitudinal associations

For evaluation of spatial and altitudinal associations among metals and environmental parameters, ANOVA and Pearson's correlation statistical analysis were performed for all zones in soils, sediments and river water. Metals had shown altitudinal variation in soils and sediments but metals in river water did not show significant variations along altitudinal zones.

3.2.1. Spatial and altitudinal associations among metals in soil and ecological factors

Appendix 3.3 provides information on zone wise altitudinal association among metals and selected ecological parameters in the soils of the study area. ANOVA was employed for finding altitudinal relationship of metals among all 5 zones of the study area. Pb, Cu, Cd and Ni came out with ($p < 0.05$) showing their spatial variation. Fe, Cr, Mn and Zn did not show spatial variation among altitudinal zones. This might be because of having same parent rock material throughout the all zones (Li et al., 2008). The similar interrelationships and distributed patterns among these metals were also presented in the study by (Bu et al., 2016) conducted along the soils from upper reach of Heihe River present in northeast Tibetan Plateau, China the part of Himalaya region which further supports the relationships with geological mineralization processes. Researchers of Pearl River Delta, China found enriched soils with heavy metals Cd, Zn, Cu, Pb, and Cr can be from both natural and anthropogenic sources (Cheng and Hu, 2010). The high concentration of Cd was recorded and confirmed in another study conducted at Himalaya region. They found Cd on top soils at the high elevation is because of natural sources (Wu et al., 2011; Bing et al., 2016). The maximum mean values of Pb and Cd found in the present study were also reported by (Patel et al. 2009) and found that high concentrations of these metals in soil is due to coal burning activities and the traffic emissions. The trend found in the present study with in line with trend of metals (Pb, Cu and Zn) found in the soils of French Alps (Hernandez et al., 2003), Heihe river, China (Bu et al., 2016), Central Pyrenees (Bacardit et al., 2012), Mt. Gonga (Bing et al., 2016) and Mt. Everest (Zhang et al., 2007). The observed mean concentrations for these metals are comparable to the concentrations measured in several other studies such as

(Hjortenkrans et al., 2006), (Zheng et al., 2008). However (H.M. Zhang et al., 2012) measured very high concentrations for these metals in soils of Qing yuan China.

Overall trend shown by heavy metals along the altitude in soils of study area was quite clear. The concentration of metals was high at the highest elevation Zone 1 and concentration was comparatively low at the low elevation Zone 5. Finding these metals at such high elevations can also be attributed to the atmospheric deposition, traffic emission, soil erosion or LRAT (Liu et al. 2014). Some metals have shown strong correlation with each other and with environmental factors. Observable positive correlation with precipitation is attributed to the wet deposition of heavy metals to the study area (Liu et al. 2014). Whereas fluxing concentrations for Pb, Cu, Zn and Ni were observed for the mid elevation zones (Zone 3 to its extension Zone 4) of the study area. This might be because of dense automobile movements in this zone. According to (Christoforidis & Stamatis, 2009) these metals are associated with vehicular machineries, tire scrape and greases.

3.2.2. Spatial and altitudinal associations among metals in sediments and ecological factors

All metals have shown significant variation with p value ($p < 0.05$) in sediments except Fe. This is because of the consistent naturally higher abundance of Fe in sediments of the area sharing same geological conditions (Siddique et al. 2009). The abundance of Fe (2.2%), Zn (49.5mg/kg), Pb (27.3mg/kg) and Mn (26.68mg/kg) can be attributed to sedimentation, atmospheric deposition, LRAT and the neighboring industrial regions might be responsible for their accumulation in such areas with little or no industrial activities (Yang et al., 2009). All metals have shown significant variation along all altitudinal zones. The similar trend was observed in Kor river sediments (Sheykhi et al., 2015) and (Elghobashy et al., 2001). The average concentration recorded for Ni was similar to the mean calculated for sediments of Bohai lake, China (Lu et al, 2005) and even along coastal belt of Pakistan (Ali et al., 2015).

Metals have shown positive correlation among each other and with environmental factors. 90% metals have shown negative correlation with precipitation. This indicates that other independent catchment factors and independent channel factors are taking part for the enrichment of heavy metals in sediment regimes of the study area like

sedimentation (Dollar et al. 2007). Metals have shown their positive correlation with (TOC). The comparative study of concentrations for heavy metals in sediments in the present study area revealed that sediments act as the ultimate sink for heavy metals and presence of high organic matter provides more sites for cations exchange thus high concentrations are observable in sediment (Hamed, 1998; Nguyena et al., 2005; Saeed and Shaker, 2008) especially in Dam area. Clastic sediments are well preserved in our study area, so they can contain relatively high level of Fe and Mn (Sheng et al., 2012). Similarly, the presence of reasonable percentage of clay and other fine particles further actively adsorb heavy metals due to the presence of associated sedimentary organic carbon and oxides of Fe or Mn (Liaghati et al., 2005).

3.2.3. Spatial and altitudinal associations among metals in water and ecological factors

Significantly very few metals have shown altitudinal relationship with environmental parameters. Only Pb and Zn have shown significance ($p > 0.05$) along altitude. The least variation is attributed to less urbanization in the catchment areas across the study zones. Pollution increases downstream the gradient as the river passes through different land uses. The rivers present at high altitudes would have low contamination as compared to the rivers present downstream (Kotti et al. 2005; Yang et al. 2006). Poultry farming, tourism, grazing, and deforestation are major environmental threats for river streams (Nazeer et al., 2014). Cu and Zn has shown weak positive correlation with precipitation. Shales, limestones and mudstones from the bedrocks potentially contain relatively high concentrations of Mn and Cu (Zhang, 2005). The solubility of these metals is generally lowered by elevating pH and increased by lowering pH, discharging free metal ions into the overlying water (Zhang, 2005).

Overall metals have shown least significant correlation among each other and the other parameters. The low mobility might be the reason for low variance and correlation. Since pH observed at all sampling points in all stations was high 7.1 to 8.5. Consequently, the water samples were slightly alkaline in nature which possesses their binding ability with carbonate species as HCO_3^{1-} (Adams et al. 2001). Such high pH value accelerates the formation of cationic complexes thus hinders the release of free metal ions in water (Sakan et al., 2011). However, slight difference in pH due to human activities such as use

of fertilizer and timber harvesting (Bellos and Sawdis 2005) can cause release of metals in river water. The enrichment of metals in such areas through anthropogenic inputs is less as compared to the areas surrounded by industrial sectors (Farkas et al., 2007).

The ANOVA (see Appendix 3.2) indicated the variation for Zn and Pb among altitudinal zones. That is due to the difference in concentrations in the zones located at higher altitudes and those located near urban areas. High precipitation and large water inputs can be reasonable explanations for the lowest total concentrations in river water. Heavy rain mixes large volumes of uncontaminated runoff water with contaminated water which resulted in dilution of total metal concentrations in water (Varol. 2013).

3.3. PCA for ordination of metals and ecological variables

Principle component analysis is used to ordinate variables/gradients along the axis with defined position and distance according to their characteristic properties (Lambert and Dale, 1964; Lu et al. 2005). PCA abolishes the redundant variation (Jeffers, 1988). It is the technique used for classification or clustering of data on the basis of similarities and differences between different samples. In ordination techniques, units are arranged in one dimension as close as possible, with accurately extracting information from the data while the data is arranged in groups, sharing common characteristics (Kent and Coker 1992; Lambert and Dale, 1964).

3.3.1. Data ordination in Soil

PCA has initially elucidated seven components with cumulative variance of 75%. Euclidean biplots for soil data (Figure 3.2 a) were drawn for the purpose of visual interpretation based on the PCA scores. The length of the arrow and distance from origin aids in interpreting the correlation among variables. The larger the distance from origin the weaker will be the similarity and vice versa. The grouping of metals was along the higher altitudinal zones and the zones with heavy traffic roads. Mn Ni, Cd, Cu with TOC and elevation can be seen with strong correlation. Finding such metals with altitudinal gradient can be ascribed to number of reasons. Heavy traffic loads can be reason for the classification of these metals together (Christoforidis & Stamatis, 2009; Divrikli et al., 2003). TOC concentration might be impacting the concentration of Ni in soils, especially in wet or nutrition-enriched areas (Sheng et al., 2012). Furthermore, the drastic dredging activities of bedrocks resulting from the exploitation of mineral resources may impact

the soil Cd concentration by accelerating the weathering processing. Similarly, higher levels of dry deposition of Cu, Mn and Ni occurred due to stronger winds (Gerdol et al., 2002). Ni and Cu from multiple deposition surveys showed that the soil contaminated and deposited by them is in the vicinity of point source mainly (Steinnes & Friedland, 2006). Soil organic matter may actively chelate some of the Ni in specific environment.

Soils developed on limestone, shale and clastic sedimentary rocks have high concentrations of Fe, Zn, Pb and sometimes Ni indicating inheritance from parent rocks. It was reported that lime stone and different kinds of clay minerals have high sorption capacity for heavy metals (Sdiri et al., 2012).

Although Pb is found related to the geology of the area it has also shown correlation with Fe and Zn with EC. Similar findings were reported by (Cheng and Tian, 1993). The ore formation and minerology justified this finding as the aforementioned metals share similar bed rocks geochemical behaviors and properties. The type of bedrock like sandstones, sedimentary rocks and limestone facilitate polymetallic ore formation and their deposition in Himalayan region (Bu et al., 2016). Several activities in the region may also contribute to heavy pollution such as fossil fuel burning, biomass burning, vehicle emissions and development of mega projects like Neelum Jhelum Hydropower Project extended from Nausada to Thota sites of the study area (WAPDA, 2016).

3.3.2. Data ordination in sediments

Principle component analysis has extracted six component factors with cumulative percentage 70%. Euclidean biplots for sediment data (Figure 3.2 b) were drawn for visual interpretation of PCA. The short length of arrows from origin indicates the close association among the labelled variables and vice versa. Fe and Ni are grouped along with TOC at few sites of Zone 3 showing their crustal origin (Bu et al., 2016). TOC concentration might be impacting the concentration of Ni in soils, especially in wet or nutrition-enriched areas. Similarly, soil organic matter may actively chelate some of the Ni in specific environment (Sheng et al., 2012).

However, all other metals are classified along Zone 5 (dam) with close association of sediment EC and clay particles. Limestone and different kinds of clay minerals have high sorption capacity for heavy metals (Sdiri et al., 2012). Finding these metals in sediments can be attributed to traffic loads. Precipitation may be one of the factors which transport

heavy metals to the sediments (Christoforidis & Stamatis, 2009). Moreover the area is already prone to soil erosion therefore soil erosion may plays major role for transporting heavy metals loads towards sediments. The high sediment amplification of metals might be because of limestone ($CaCO_3$), clastic sedimentary rocks and shale rocks of the Lesser Himalaya region. During soil erosion or weathering processes the carbonate ions react with metal ions making metallic carbonates there after precipitation (Cheng and Tian, 1993). The climatic factors are grouped in opposite axis points showing these are not closely associated much especially in case of sedimentary heavy metal loading.

The clustering of heavy metals along dam area can be a depiction of sedimentation problem. These man-made artificial reservoirs become aged with the passage of time so that natural stream and sediment loads are transformed which can affect river quality and hydrologic processes (Sawaske and Freyberg, 2010).

Therefore, sediment bound heavy metals become enriched because of their long residence time (Ulbrich et al., 1997). During impoundment sediments from soil erosion are mobilized towards dam in the course of high streaming in river water. The Government of Pakistan has declared Himalayan and Karakorum mountain ranges significant with respect to sediment loads towards Indus River system and its tributaries. When sediments are transported from soil to reservoir a sediment delta is usually formed at the mouth of reservoir (Meynell at al., 2014). According to a report Mangla Dam efficiency is declining due to sedimentation loadings in reservoir which may result in rise of bed and flooding may occur. From the time when it was constructed the water storing capability of Mangla Dam has been reduced upto 1500 million cubic meters. The reason is the high sedimentation loads from the adjoining ranges (Butt et al., 2011). The loading of sediments might be responsible for enrichment and high concentration of heavy metal in the dam area. Similarly, the removal of sediments from river is responsible for causing "famine river" syndrome, in which the river after the power house tries to pick up the sediment that it has lost from the bed and banks, causing erosive problems. One of the major impacts from soil erosion occurs when the eroded soils reach the river and increase the sediments. Excessive sediments in the river can extend for many kilometers downstream, and tend to cover gravel beds that are important for the river health (Meynell et al., 2014). The serious erosive condition can pose a great threat not only to

the useful life of the dam but also to the rivers and canals by way of raising their beds and causing floods (WAPDA, 2016).

3.3.3. Data ordination in water

Principal component analysis (PCA) is a widely used ordination technique for unfolding the ecological gradients and to explore spatiotemporal trends in limnological studies (Perona et al. 1999). Data transformation is performed to reduce the set of interrelated variables to the set of uncorrelated (orthogonal) variables (Yusuf et al. 2013; Retnam et al. 2013). Factor analysis is designed to reduce the contribution of less significant variables to decrease the complication in data that have passed through PCA (Shrestha and Kazama 2007; Chen et al., 2015).

Data ordination (Figure 3.2 c) has grouped Zn, Ni, Cd and pH in a group along sampling points of Zone 5 (the dam area) sites. This grouping shows the role of pH for mobilizing metals in water according to the chemical nature of the metal. pH is the factor which is quite sensitive to the water pollution hence greatly vary under the influence of other environmental factors (Wang et al., 2007). The reservoir water is also used for domestic purpose by the residents. Untreated domestic waste, industrial discharge or agricultural runoff from nearby villages and towns may create reducing conditions with low pH enhancing metal solubility in river water Various streams also carry the pollutants into the reservoirs during the high flow period (Nazeer et al., 2014). pH plays significant role for metal solubility in water, in alkaline conditions it forms nickelous hydroxide, $Ni(OH)_2$, which is a stable compound. In very alkaline conditions; it forms nickelite ion, ($HNiO_2$) that is also soluble in water (Raymond and Okieimen, 2011). Cu, Fe, Mn, and precipitation were syndicated in another group with elevation. According to (Daly and Wania, 2005) the amount of precipitation increases with elevation and occurred mostly in the form of snow owing to lower temperatures at higher elevations. According to (Lenntech, 2004) Cu released in the environment through biomass burning and remains in atmosphere for eminent time until dry or wet deposition occurs. This explanation validates the results. According to (Chang, 2008) heavy rainfall and runoff become influential cause of mobilizing toxic compounds from elevated lands to the rivers. During industrial activities Pb and Cd can also volatilize during high-temperature conditions and become oxidize as fine particles unless reducing atmosphere is maintained and until dry

and/or wet precipitation mechanisms remove them and transported in various environmental compartments. Moreover, biomass burning, traffic emissions and various projects are under the process of completion near and within the vicinity of study area may be contributing for heavy metal contamination. Because fugitive emissions are often distributed over a much smaller area and emissions are made near the ground. The type and concentration of metals emitted from both types of sources will depend on site-specific conditions. All solid particles in smoke from fires and in other emissions from factory chimneys are eventually deposited on soils and rivers (Raymond and Okieimen, 2011).

Overland flow and soil erosion are increasingly recognized as important in the transfer of heavy metals from soils to surface waters. Heavy metal contamination can not only affect soil ecology, agricultural production, and underground quality but also influence aquatic ecosystems (Heredia and Cirelli, 2009). Severe soil erosion caused by high sand content in the soils and steep slopes in Himalayan region (Xu et al., 2009) may contribute to increase sediment loads (He et al., 2007; Le et al., 2007; Miao et al., 2010) with heavy metal contamination in the areas's riverine system (Cenci and Martin, 2004; Fu et al., 2012). Hydropower exploitation via the proposed reservoir system in the Neelum-Jhelum River (Zhai et al., 2010) may submerge parts of the Hiamalayan region, making this region a potential source of heavy metal pollution in downstream agricultural products, fisheries, and river ecosystems (Phan et al., 2013; Steininger, 2003).

3.4. Tracking possible source of metals using PCA-MLR (Principle Component Analysis-Multiple Linear Regression)

3.4.1. Source apportionment of metals in soil

For source apportionment of metals adding in the soil of the study area MLR extracted the three main components which accounts for the cumulative variance of 20%, 31% and 43% respectively. Factor 1 (F1) accounted 20% of variance with the strong positive factor loadings of Fe, Ni, TOC and elevation whereas, for Mn, Zn and Cr it showed strongly negative factor loadings. Natural source like rock outcropping or wet deposition are eminent from the factor loadings for the concentration of heavy metals at higher elevation (Li et al., 2008; Bing et al., 2016). Fe is found with high positive loading in the factor is due to its natural abundance in the soils (Zhang, 2007). Heavy metals found at

higher altitudinal soils and snows come from weathering of parent material or via atmospheric deposition (Nagajyoti et al., 2010). This correlation indicates that the TOC concentration may, to some extent, impact the concentration of Ni in soils, especially in wet or nutrition-enriched areas (Sheng et al., 2004). Soil organic matter may actively chelate some of the Ni in specific environment. F4 So the F1 identifies geochemical features of natural processes as the contributors for metal loadings with percentage contribution of 68%.

Percentage contribution from each factor is shown in (Figure 3.3a). Strong positive relation of Cd, Cu and Pb with BC were identified by the second factor F2 having factor loading of 31% cumulatively. The high factor loadings explain the source must be from some anthropogenic activities like vehicular emission, burning of coal or biomass for cooking or natural forest fires from the local areas (OECD, 1994). F2 accounted only for 2% contribution. Last component explained 43% of total variance with high factor loadings values for Cu, Ni with elevation and negative factor loading for EC of soil. If negatively charged surface of soil clay particles is available for cations adsorption then this cation-soil interaction causes the lowering of EC (Ouhadi and Goodarzi, 2007). At high elevations the positive correlation with aforementioned metals along with precipitation was executed by this factor. According to (Daly and Wania, 2005), the amount of precipitation increases with elevation and occurred mostly in the form of snow owing to lower temperatures at higher elevations in this factor are from miscellaneous sources it can be from natural or anthropogenic processes like soil erosion, change in CEC of soil, atmospheric deposition, change in pH, vehicular emission or LRAT (Elik, 2003; Bing et al., 2016). The recorded contribution of F3 is 23%.

3.4.2. Source apportionment of metals in river sediments

For maximizing the total variance of factor loadings varimax rotation was employed. This makes results more meaningful in terms of interpretation (Acosta, 2011). Those components were taken under consideration with eigen value more than 1(Kaiser, 1960). For sediment data first three factors were considered significant each having eigen value more than 1 and explaining 51 % cumulative variance in the data set. Factor 1 (F1) showed 21% cumulative variance with significant contribution of Cd and Zn with high positive loading for elevation. It represented long range transport or any other

atmospheric deposition contributing for the metal enrichment as reported by various authors previously for lesser Himalayan region (Bing et al., 2016). Percentage Contribution of F1 is 73% computed as the highest contribution source of metals towards sediments (Figure 3.3b).

Factor 2 (F2) accounted for 37% cumulative variance with the high positive loadings for Cr, Pb and BC. This factor F2 represented contribution through anthropogenic sources. The high concentrations of Pb, Cr and Cu were also reported in Antarctic along with the fine aerosol particles (Barbante et al., 1998) where these metals are adding up due to human activities carried out in other continents (Planchon et al., 2002). Hence intracontinental pollution emissions can be reached to such altitudes with the aid of BC or other fine aerosols. As BC is considered as aerosol with the particle size less than 1μm released due to man-made activities it acts as vapor in the atmosphere and easily transport toxic compounds including heavy metals to the riverine ecosystems located comparatively at higher altitudes (Shotyk et al., 2001). Percentage contribution recorded for the F2 is 9% only. The last factor F3 accounted for 51% of the cumulative variations having high loadings of Fe, Mn and Ni. This factor represented the natural sources like weathering of parent rock material or erosion of sedimentary bed rocks. The naturally abundant Fe has been found along with the minute quantities of heavy metals in sedimentary rock studies (McLean and Bledsoe, 1996). Percentage contribution of F3 is 18%.

3.4.3. Source apportionment of metals in water

For the purpose of sketching the spatial distribution and source identification in limnological studies PCA-MLR (Principal Component Analysis) is worldwide acceptable technique (Perona et al. 1999; Ghrefat et al., 2012). The orthogonal transformations reduce complexity in data and sort out the significant factors known as varifactors (Shi et al. 2008; Murillo et al. 2013). PC-MLR explicated the significant contributions of first three factors with the cumulative variance of 70%. The first factor has cumulative variance of 20% and showed the strong percentage contribution around 40% for the variables Fe, Mn, Zn, elevation and negative factor loading of pH. This factor must be contribution of some natural processes like weathering of underlying parent rock, soil erosion, precipitation or runoff (Huaxing et al., 2009). According to (Nazeer et al., 2014;

Chang 2008) heavy precipitation and runoff becomes the cause of mobilizing toxic compounds from land to rivers with lowering pH values pH is the factor which is quite sensitive to the water pollution hence greatly vary under the influence of other environmental factors (Wang et al. 2007). Hence the factor F1 is contribution of natural geochemical processes with the 40% percentage contribution (Figure 3.3c). The dominant positive factor loadings from second factor F2 are for Pb, Cu, Cr, Ni and Cd. This factor has input of 40% cumulative variability among variables and elucidated the strong contribution of anthropogenic sources taking place in the neighboring ranges to the river water through various means (Saleem at el., 2014). F2 contributed 37% in overall factor contribution. Third factor F3 has 57% total variance with the significant loadings for positive EC and negative factor loading for TDS but no significant factor loadings for metals is observed. These two parameters are reciprocal to each other. This factor identifies the miscellaneous sources and explains that there must be some activity which is adding higher amount of TDS to the river water hence increasing metal concentration in riverine system. The activities performing around study area for the completion of Neelum-Jhelum hydropower project can be considered important factors for this disturbance in selected riverine system.

Similarly, non-point sources play their active role for adding up heavy amount of TDS in water bodies through atmospheric inputs or soil erosion (Bing et al., 2016; Pandey et al., 2016; Kotti et al., 2005). F3 is contributing 23% for among the overall contributions. F3 has high loadings of Zn. Galvanizing units operating in the region most likely attributed for release of Zn in the air, which entered freshwaters through atmospheric deposition (Pak EPA, 2006).

3.5. Transboundary turbulence of heavy metals using HYSPLIT-Backward Trajectories

For tracing the possible direction for heavy metals coming to the study area back which are arriving at the coordinates for the sampling tenure (February-March, 2015) were computed using HYSPLIT (Hybrid Single Particle Lagrangian Integrated Trajectory Model) model. HYSPLIT is developed and run by NOAA (National Oceanic and Atmospheric Administration) working under the United States Air Resource Laboratory (Draxler & Rolph, 2003). The maps were generated for the two consecutive months of

February and March 2015 in order to evaluate the actual movements of air currents circulating around the study area (Figure 3.4a and 3.4b respectively). Three different altitudinal heights from low to high elevation covering the 5 zones of study area i.e. 500, 1500 and 2500 (m.a.s.l) respectively, were used for generating these maps for 24hrs duration time. It can be predicted from back trajectory maps that the study area is subjected to LRAT of metals via air fluxes from local region coming from Pakistan and through transboundary turbulence coming from India. Many studies have highlighted the local and transboundary turbulence owing to bringing toxic compounds from India, China and other parts of Pakistan to the neighboring regions located at higher altitudes (Eqani et al., 2012; Ali et al., 2014). The study area shares its boundaries to the industrialized countries like North part of India, Southern Tibet and China. According to (Li et al., 2014) southern part of China has mines of Pb-Zn ores and frequent mining processes and smelters emit ample chunk of heavy metals which are tracked to the localized and transboundary pollution. At such high altitudes (Yang et al., 2007) has reported the presence of aerosols adsorbed with heavy metals like Pb, Cu, Zn etc at 1600m elevation of Mount Gonga located in Sichuan province, China due to LRAT.

HYSPLIT model was also used to study the possible source of aerosols and heavy metals are coming to the Tibet by (Cong et al., 2010). Similarly, from the south Asian regions agricultural activities and industrial units have been reported to release toxic compounds as the result of wet deposition and LRAT (Devi et al., 2011). One of the emerging issues growing in South Asian countries including Pakistan. Pakistan is transportation and illegal dumping of e-waste containing Cd, Pb, Mn and Zn etc (Iqbal et al., 2015; Chakraborty et al., 2013). Therefore, elevated concentrations of metals influx can be found in these regions due to Indian monsoon patterns contributes to the transfer of toxic compounds to the areas located at heights (Guzzella et al., 2011). The air mass circulations can be one of the reasons responsible for bringing the traces of heavy metals from one place to the other.

3.6. Determining the severity of contamination in soil, sediments and water

Enrichment factor and Geo-accumulation index (I-geo) have found to be used by various researchers in order to evaluate the extent of heavy metals enrichment and contamination in soils and sediments of any area. Same method was employed for the quantification of

heavy metal pollution levels in the soil and sediments of the present study area. For the evaluation of quality of river water in numeric terms MPI (Metal Pollution Index) was employed for the purpose. I-geo and MPI give general picture of contamination level of heavy metals in different matrices.

3.6.1. Metal Enrichment in soil and sediments

The calculated enrichment factor revealed that there is no anthropogenic enrichment observed for Cu and Cr in both matrices. The range of enrichment factor observed for these metals was EF>1. However, EF ranged between 5-10 for the metals Pb, Cd and Zn in soil and sediments indicating that some natural as well as anthropogenic sources are involved for the enrichment of these metals (Saleem et al., 2013).

3.6.2. Severity of contamination in soil

For the assessment of soil and sediments heavy metals pollution level geo accumulation index was adopted for all three sampling stations. The results suggest the level of pollution in the study area is very low. The index was calculated for Pb, Mn, Cu, Zn, Cd, Ni and Fe. All values of I-geo for Mn, Cu, Ni, Zn and Fe fall in Class- 1 indicating the zero level of their pollution in soil sites of all zones LHS to MD whereas, the index has computed zero to moderate pollution Class-2 for Pb and Cd in all sampling zones. Cd was found high and also reported by (Zhiyuan et al. 2011) under the category of Class-2 in soils of Jhiangxi, China (Bing et al., 2016) also found high concentrations for Pb and Cd in the south eastern part of Himalaya sharing boundaries to the lesser Himalaya region which the present study are of interest.

3.6.3. Severity of contamination in sediments

I-geo for Pb in sediments of Zone 1 to Zone 5 falls under Class-2 as I-geo>1. Similarly, I-geo for Cd for all zones from Zone 1 to Zone 5 was also found I-geo> 0 with Classification 2. Cadmium in sediments of all sites falls under the Class-1 exhibiting zero level of contamination. Sediments of one of the coastal areas of Pakistan were also found moderately polluted with Pb and Cd (Ali et al., 2014). At neutral pH the formation of $CdCO_3$ takes place the pH of the area was neutral to the alkaline and a very little disturbance to the pH can release Cd to the environment (Balistrieri et al., 2007). Same category of Pb pollution was found by (Bastami et al., 2014). However Igeo < 0 was recorded for Mn, Cu, Cr, Zn, Fe and Ni.

3.6.4. Severity of contamination in water

The MPI values found for Cd revealed the pure quality status of river water whereas MPI values for rest of the metals suggest that water of LHR is very pure and fit for various purposes. However, for getting clear picture of water quality there is need to access temporal trends as well. The results found in water of LHR suggest that the water quality is good according to MPI and grading system (Caerio et al., 2005). The results found for heavy metals can be compared with the results found by (Abdullah, 2013) for the Shatt Al Arab River. The values found in current study are far less than the values calculated by (Al Hejuje, 2015) for Shatt Al Arab River.

3.7. Black carbon (BC/TOC) - the lost carbon finds human intrusion in area's contamination

Interestingly some metals have shown weak positive correlation with BC (Black Carbon) (Appendix 3.3) the responsible co-factor can also be BC which enters in the environment through in complete combustion of coal, domestic burning, traffic emission, industrial activities and wood burning. This Missing carbon may be playing its role to some extent for enriching heavy metals in soils and sediments as it acts as an excellent adsorbent for heavy metal and other toxic compounds, changing CEC of soil and sediment affects their quality (Hany et al., 2014). BC itself is inert but the finesse with high affinity and surface area makes it a good adsorbent for organic pollutants and heavy metals to the soils of distant areas through LRAT, rain and runoff (Patel et al., 2013). Constructive projects and domestic activities may influentially increase BC pollution like fossil fuel burning, biomass burning, vehicle emissions and development of mega projects like 969 MW Neelum–Jhelum Hydropower Plant (Meynell et al., 2014).

It can be hypothesized that the carbon entities (TOC and BC) in soil and sediments contribute heavy metals enrichment. The substantial role of BC over TOC can be due to its higher sorption capacity (Accardi-Dey and Gschwend, 2002). Higher TOC content in soil and sediments of Zone 5 might be due to slope factor, sedimentation; runoff and waste water discharge (Saleem et al., 2013). Aged sediments which are compactly bound at the bottom of the river are only mobilized at very high flow velocities, can adsorb more organic compounds than the new ones (Ulbrich et al., 1997). The constant TOC in

deep sediment layers, represent the fraction of organic matter that is decomposition refractory.

BC is considered as conservative species that has been reported for the proglacial Lake Oberaar where the melted glaciers bring these temporarily stored entities to the lake is (Bogdal et al., 2011). Nutrients are adding up from various sources which may contribute to increased primary production of the region along with the higher levels of TOC (Chuan et al., 1996). Good correlation is lost might be the presence of only an appreciable fraction of BC that is resistant to the CTO-375 method applied in this study. Although BC is largely resistant to environmental degradation, in CTO-375 quantification method, an oxidation of the less condensed forms of the BC band (char BC) takes place, resulting in neglecting the total BC present in the sediment (Nguyen et al. 2004). However, the more lighter and inert fractions of the BC (soots), were well caught.

On average concentration of BC found in sediments along altitudinal zone:

Zone 3 (18.6 mg/g) > Zone 1(17.8 mg/g) > Zone 2 (16.1 mg/g) > Zone 4 (9.5 mg/g)Zone 5 (3 mg/g).

Mean concentration of BC was observed high in zone. It is evident from the result that anthropogenic inputs are high in this very zone. Neelum-Jhelum Hydropower plant project and activities (generator emission, traffic emission, exhaust driven emissions, dust particles) might be responsible for adding this much concentration of BC here. (Ali et al., 2014) has been used BC/TOC ratio as an indicator of BC pollution source from various burning activities. BC/TOC < 0.11 has been the indication of incomplete biomass burning as source of BC while a value of 0.5 and above indicated the industrial activities, fossil fuels burning and traffic emissions as BC source (Ali et al., 2014; Liu et al., 2011). Results revealed the miscellaneous activities as source of BC as BC/TOC. For sediments the range of BC/TOC was (0.008-58).

Zone 3 is present in the area having busy roads and heavy traffic emissions that might be responsible for finding this much high percentage ratio. Moreover, transboundary pollution movement and neighboring regions might also be responsible for bringing BC to area because the form of BC measured could be resistant to CTO-375 method thereby primarily determined in the form of small and light BC particles i.e. soot (Hammes et al.,

2007). The light soot particles have higher mobility and can, therefore, be efficiently transported in remote regions (Bogdal et al., 2011). Since sediments are ultimate sink for organic compounds and give more details upon burial flux of organic moieties therefore, only sedimentary BC and TOC were further analyzed and reported for extraction of more details.

Burial flux of TOC and BC in sediments of study area's zones. Sedimentary level burial flux of BC and TOC were determined in study area, ranged between (0.12−30.1 mg/g) (0.3−50.7 mg/g) respectively. Burial flux of TOC was minimum (25.7 g/cm^2.yr) at Zone 2 and maximum (275.7 g/cm^2.yr) at Zone 5. The burial flux for BC was least at Zone 1 (14.9 g/cm^2.yr) and maximum at Zone 4 (167.1 g/cm^2.yr).

3.8. Depositional flux and Mass inventory of heavy metals in sediments of LHR

Concentrations of seven selected metals (Pb, Cd, Cu, Mn, Zn, Ni, Cr) were used for calculation of mass burden and to record mass inventory of metals in sediments of AJK river system of Pakistan. Mass transportation of sediments is hard to estimate and often produces unreliable results (Jacobson, 2009). The estimation of depositional fluxes of heavy metals in sediments is based on the concentration (mg/kg) and mass accumulation rate. Mass accumulation rate was calculated by the evident sedimentation rate (g cm^{-2}yr^{-1}) using the mean bulk density (g cm^{-3}) of dry sediment samples.

For the current calculations study area was divided in five zones on the basis of altitude and then from each zone heavy metal depositional flux was calculated. For each zone the depositional flux in sediments was calculated by the following formula (Ali et al., 2015; Bouloubassi et al., 2012). 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 of heavy metals in sediments were also reported by (Ali et al, 2015). The fluxes found were much higher than reported for heavy metals in coastal sediments from Pakistan (Ali et al., 2015).

The mass inventories also showed the potential of fresh water ecosystem to accumulate heavy metals due to number of reasons. The mass inventory of the studied heavy metals was developed for the very first time which may serve as the baseline inventory for further investigations and to find the contamination impacts in Lesser Himalaya Region of Pakistan. The developed inventory estimates the highest burden of Zn (2 x 10^2 metric

tons), Mn ($1.1x10^4$), Pb (1.1×10^4), Cu (9.7×10^3), Ni (8.7×10^3), Cr (6.5×10^3) and Cd (4.4×10^2). The burden of heavy metals found in LHR is far less than the load found in along coastal belt of Pakistan (Ali et al. 2015) because of less urbanization, no industrialization and minimal human interference comparable to coastal belt of Pakistan.

Conclusions

Generally, no source of industrial pollution is found within the vicinity of study area but other regional and transboundary pollution can be significant factors for bringing heavy metals to the area from distant regions. Overall metal concentrations found here are not alarming for metals except for Cd and Pb. Topography and climatic factors may also lift up heavy metal loads in the area. Landscape beauty and the presence of tourist spots gain attention of tourists to visit the places frequently all across the country and globally too. Traffic emissions in the valleys might be another source of heavy metal pollution. Various mega projects are under the process of completion here like Neelum-Jhelum 969MW Hydropower project and other small projects near study area. These projects demand earthmoving and road construction activities which further exacerbate erosive conditions (area is already prone to erosion). Moreover, 88% people rely on biomass burning for their domestic needs in the area. It might be another source of polluting environment with soot or biochar (BC) carrying heavy metals and other toxic organic pollutants. The catchment area around Mangla dam is erosion prone, so rate of sedimentation may also contribute for TOC and metal enrichment therefore sedimentary burial fluxes show the intrusion of human activities contribute in the area landscape. Anthropic activities are significant here in increasing soil erosion, river water contamination, sedimentation, water resource depletion, fugitive emissions, biomass, vehicular and generator exhaust emissions etc. However, the overall water quality of riverine system of AJK is pure thus it is fit for drinking and other domestic uses.

Table 3.1 (a) Descriptive statistical summaries of metals (mg/kg) in soil

	Pb	Zn	Cu	Mn	Cr	Fe %	Cd	Ni
Zone 1								
Max	40	87.53	23	27	15	2.58	2.5	37.5
Min	17	18.7	2.05	14.8	4.87	1.2	0.01	14.5
Mean	25.4±8.8	38.6±27	15.4±8	21±5.3	10±4	2.13±0.54	1.09±1.05	29.2±9
Zone 2								
Max	27.5	28.46	18	28.9	13	2.77	3.5	41.02
Min	6.62	5.575	3	13.33	5	1.192	1	12.55
Mean	19.03±10	15.07±9.8	9.19±6.5	21.9±7.5	9.25±3.5	2.06±0.6	1.98±1.13	22.5±12
Zone 3								
Max	31	77.44	13	18	19	2.71	3.4	34.05
Min	12.5	20	1.67	5	5.97	2.024	0.02	11.5
Mean	21±7	42±20	7.2±4.6	13.17±4.4	12.05±4.2	2.3±0.29	1.4±1.05	25±8.09
Zone 4								
Max	35	78.96	19.55	25.29	20	2.59	3.08	37.75
Min	12.5	12	0.05	1.32	2.11	1.8952	0.05	10.96
Mean	23.6±7	42.3±25.7	9.8±7.01	13.42±8.7	13.4±6.45	2.2±0.2	1.12±1.04	22.8±9.3
Zone 5								
Max	30	33.2	25	23	27.6	2.2	2.5	39.86
Min	15	10.84	3	0.8	17.15	0.77	0.05	13.67
Mean	24.25±4.9	22.26±6.8	10±7.1	9.63±8	22.8±4.21	1.7±0.47	1.47±0.79	23.7±9.9
LHR								
Max	40	87.53	25	28.9	27.63	2.77	3.5	41.02
Min	6.62	5.575	0.05	0.8	2.11	0.77	0.01	10.96
Mean	22.9±7.1	33.1±22	10.08±6	14.7±8.0	14.41±7	64.6±0.5	1.37±0.97	24.51±9.3

Table 3.1 (b) Descriptive statistical summaries of metals (mg/kg) in sediments

	Pb	Zn	Cu	Mn	Cr	Fe %	Cd	Ni
Zone 1								
Min	3.7	10	3	13	3	1.05	0.05	5
Max	36	55.83	45	30	21	3.13	2	35
Mean	23.3±14	29±17.4	16.±16.8	21.2±7	13.8±7.5	1.82±0.8	0.72±0.8	18.8±10
Zone 2								
Min	18	13	1	12.55	2	1.268	0.05	18
Max	43	47	15	25	27	3.979	1.1	30
Mean	28±10.5	26.7±14	6.87±6.6	18.1±5	13.25±10	2.58±1.3	0.7±0.4	23.8±5.3
Zone 3								
Max	44	87	40	47	20	4.79	3	30
Min	14.64	12	1.78	8	2	1.0767	0.09	8
Mean	26.3±9.6	55±30.20	15.±17.3	22.2±12	11.2±6.6	1.9±1.3	0.84±1.0	18.9±8.0
Zone 4								
Max	33	77	64	40	20	4.16	1.5	20.5
Min	5	15	2.1	10	7	1	0.05	1
Mean	21±10.6	48.8±25	17.06±2	24±10.6	12±4	1.89±1.2	0.56±0.5	13.7±6.3
Zone 5								
Max	45	87	63	71	27.57	4.184	3.5	34
Min	27	55	19	22	17	2.0008	0.4	17
Mean	36.6±6.2	69.±10.8	46±16.3	40.5±17	22±3.5	2.82±0.8	1.9±1.08	25.3±5.9
LHR								
Max	45	87	64	71	27.57	4.797	3.5	35
Min	3.7	10	1	8	2	1	0.05	1
Mean	27.3±11	49.5±25	22.8±21	26.8±14	14.9±7.4	2.2±1.1	1.0±0.97	19.8±8.2

Table 3.1 (c) Descriptive statistical summaries of metals (mg/L) in water

	Pb	Zn	Cu	Mn	Cr	Fe	Cd	Ni
Zone 1								
Mean	0.33±0.4	0.08±0.03	0.034±0.03	0.04±0.03	0.04±0.03	0.08±0.01	0.04±0.034	0.07±0.06
Min	0.09	0.045	0.015	0.02	0.01	0.071	0.008	0.041
Max	1.11	0.14	0.09	0.1	0.08	0.11	0.09	0.19
Zone 2								
Mean	0.14±0.08	0.06±0.02	0.02±0.009	0.044±0.02	0.049±0.04	0.11±0.04	0.05±0.045	0.09±0.09
Min	0.0289	0.03	0.011	0.02	0.01	0.084	0.003	0.013
Max	0.237	0.088	0.03	0.055	0.09	0.17	0.11	0.188
Zone 3								
Mean	0.32±0.4	0.08±0.02	0.019±0.005	0.02±0.02	0.08±0.06	0.13±0.05	0.04±0.04	0.11±0.09
Min	0.09	0.052	0.0133	0.01	0.0135	0.062	0.009	0.01
Max	1.3	0.12	0.029	0.06	0.18	0.2	0.12	0.27
Zone 4								
Mean	0.34±0.52	0.13±0.11	0.034±0.04	0.04±0.022	0.08±0.06	0.14±0.07	0.03±0.04	0.16±0.14
Min	0.019	0.065	0.011	0.027	0.0162	0.06	0.004	0.02
Max	1.27	0.37	0.15	0.09	0.19	0.275	0.13	0.38
Zone 5								
Mean	0.51±0.61	0.36±0.41	0.04±0.05	0.050±0.02	0.11±0.06	0.18±0.10	0.05±0.03	0.18±0.10
Min	0.02	0.02	0.0179	0.01	0.016	0.052	0.005	0.06
Max	1.7	1.07	0.18	0.093	0.2	0.31	0.11	0.35
LHR								
Mean	0.3±0.47	0.16±0.23	0.032±0.03	0.043±0.02	0.080±0.06	0.14±0.07	0.04±0.04	0.13±0.10
Min	0.019	0.02	0.011	0.01	0.01	0.052	0.003	0.013
Max	1.7	1.07	0.18	0.1	0.2	0.31	0.13	0.38

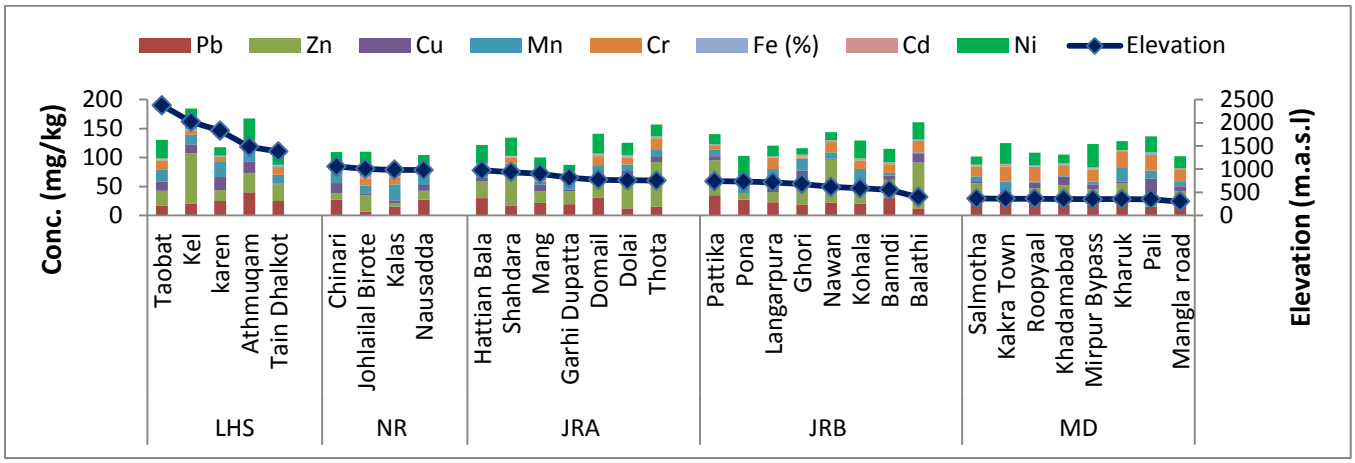

Figure 3.1(a) Concentration (mg/kg) of metals in soils along altitudinal zones

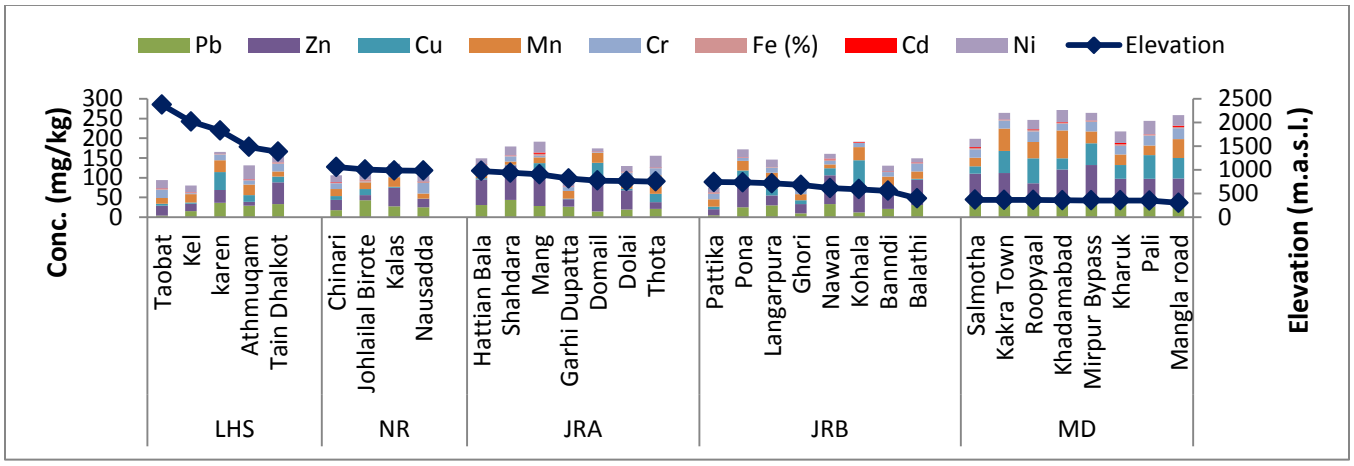

Figure 3.1 (b) Concentration (mg/kg) of metals in sediments along altitudinal zones

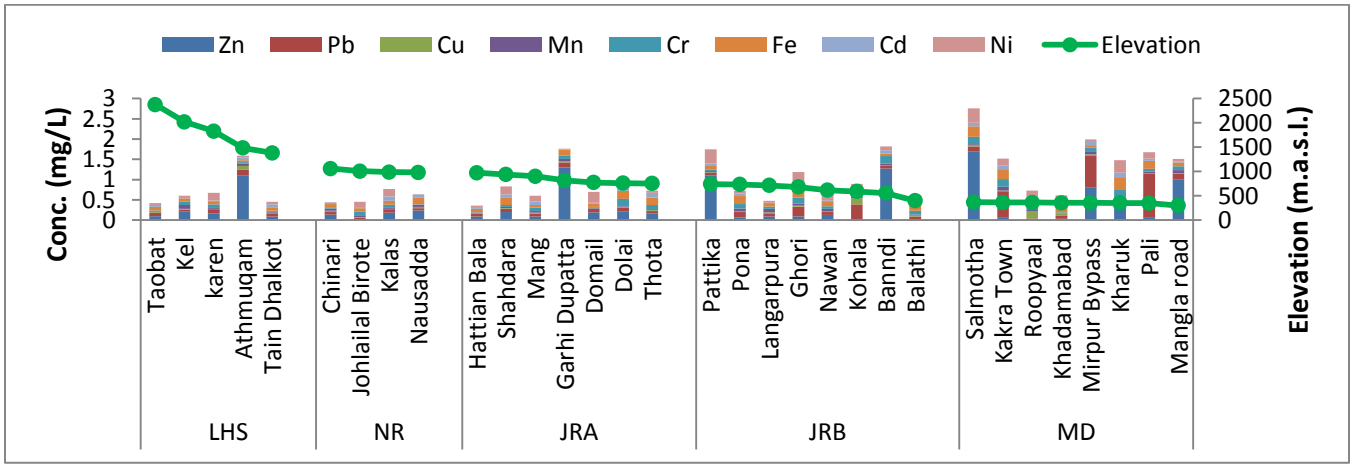

Figure 3.1 (c) Concentration (mg/L) of metals in water along altitudinal zones

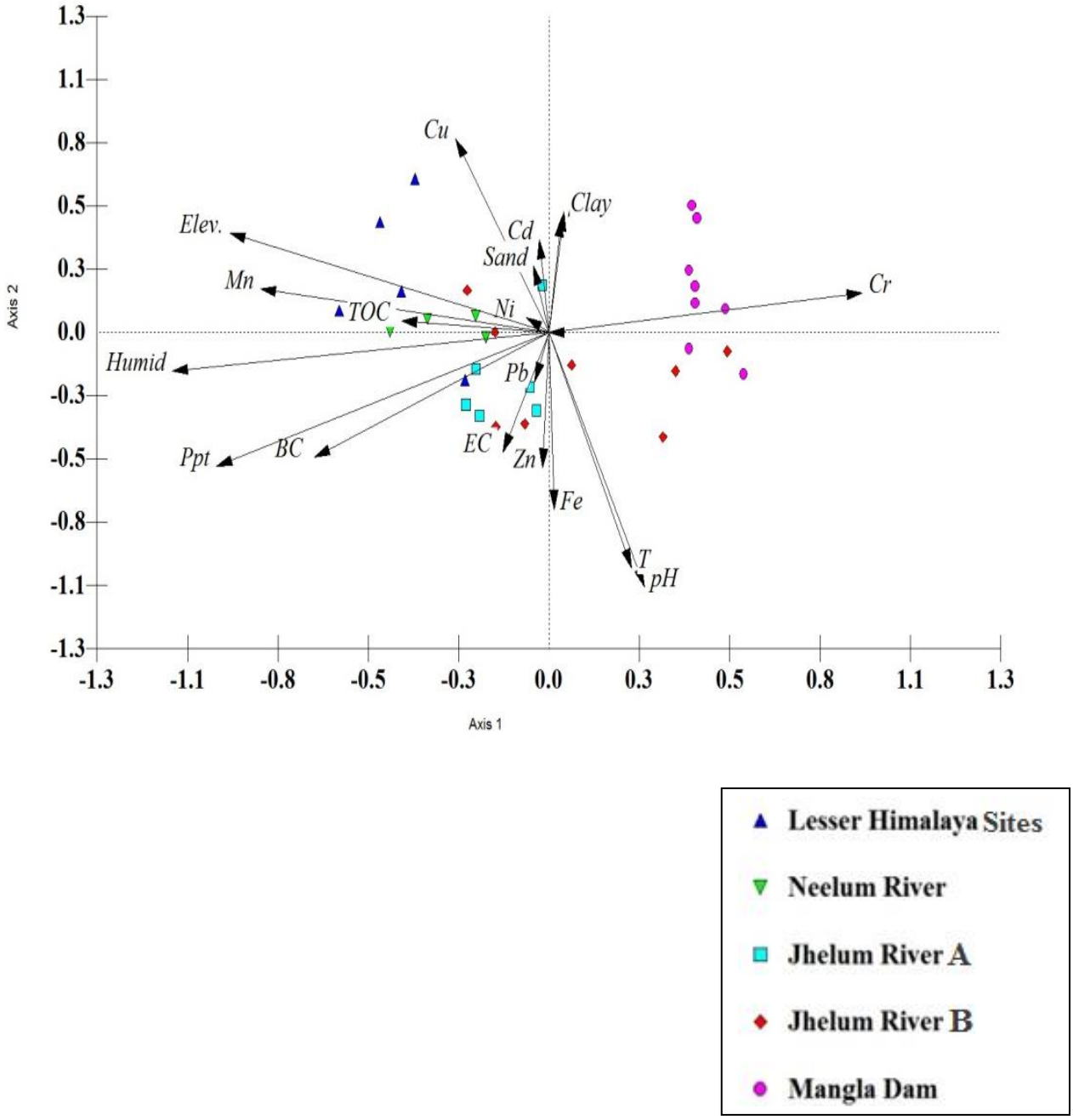

Figure 3.2 (a) Biplot for grouping of data in soil

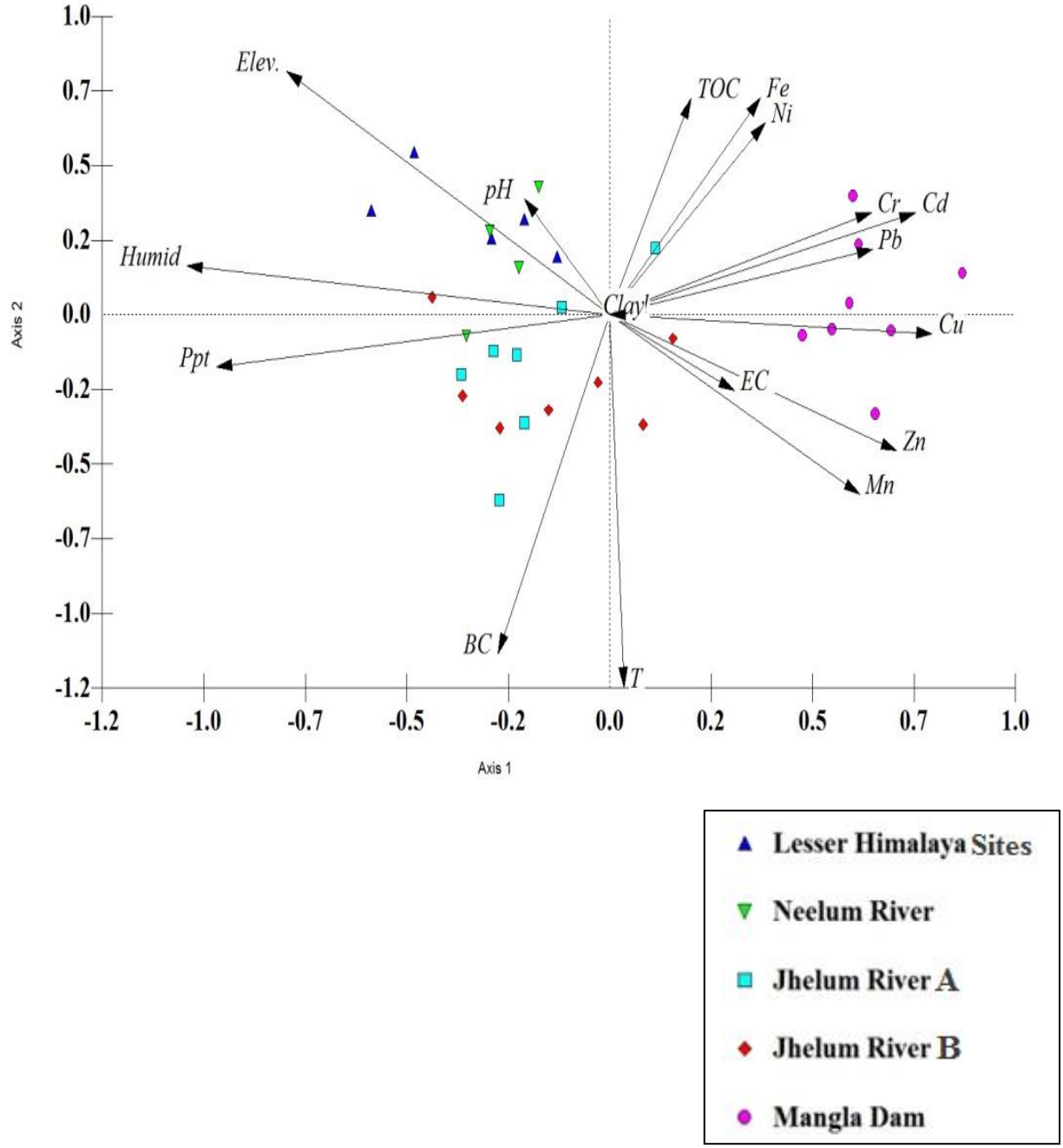

Figure 3.2 (b) Biplot for grouping of data in sediments

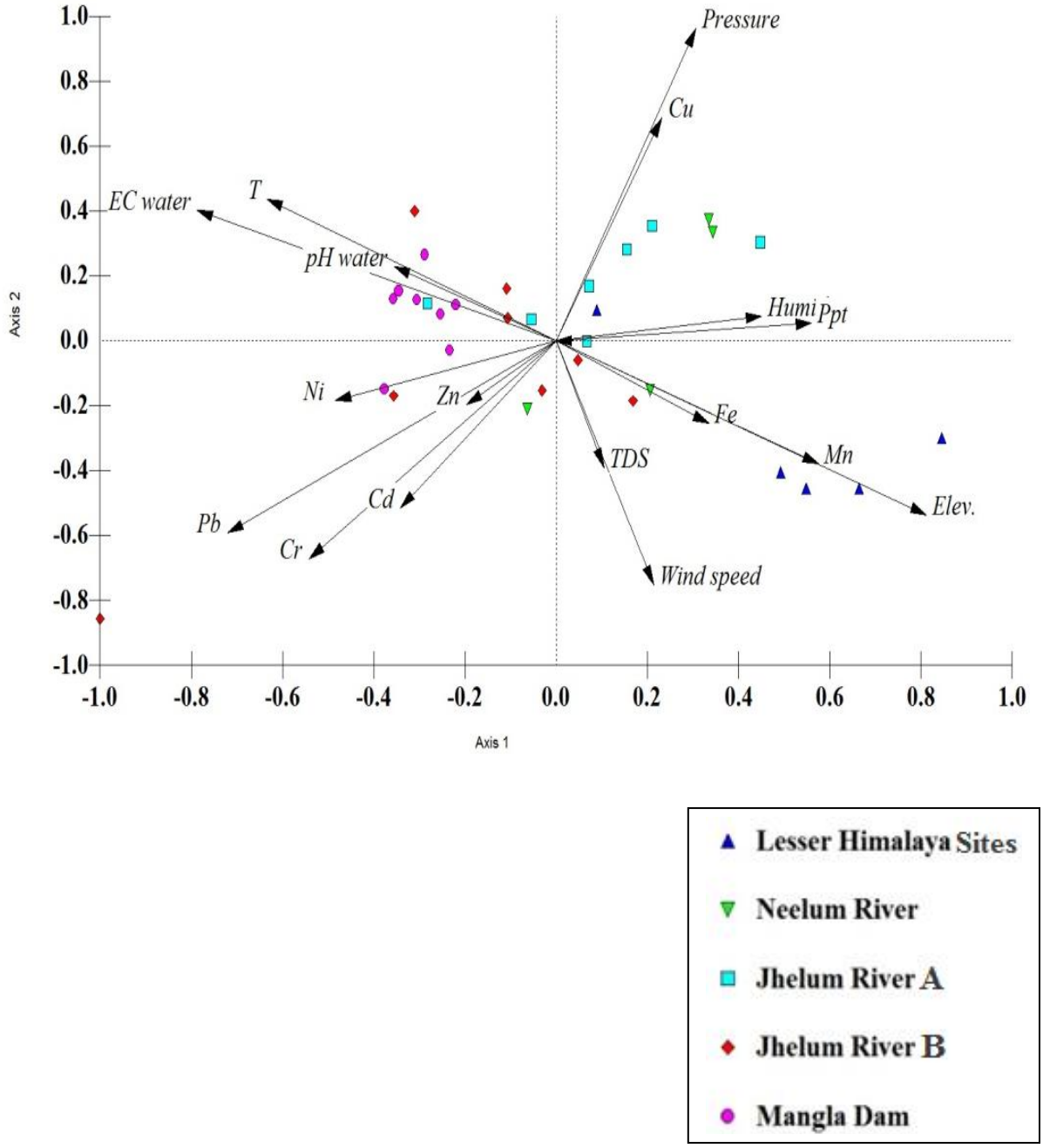

Figure 3.2 (c) Biplot for grouping of data in water

Table 3.2 (a) Contribution factor loadings for source apportionment of metals in soil

Variable	F1	F2	F3
Pb	0.000	**0.500**	-0.156
Zn	**-0.649**	-0.199	0.183
Cu	0.191	-0.070	**0.715**
Mn	**-0.599**	**0.530**	-0.052
Cr	**-0.769**	-0.025	-0.080
Fe	**0.693**	-0.275	-0.102
Cd	-0.104	**0.512**	-0.026
Ni	**0.553**	0.162	**0.554**
Elevation	**0.729**	0.052	**0.483**
EC Soil	-0.057	-0.092	**-0.520**
TOC	**0.842**	-0.329	0.084
BC	0.103	**0.614**	0.155
Precipitation	0.059	0.176	**0.491**
Eigen Value	3.2	1.7	1.5
Variability%	19.882	11.268	12.340
Cumulative%	19.882	31.150	43.489
Contribution%	67.69	2.87	29

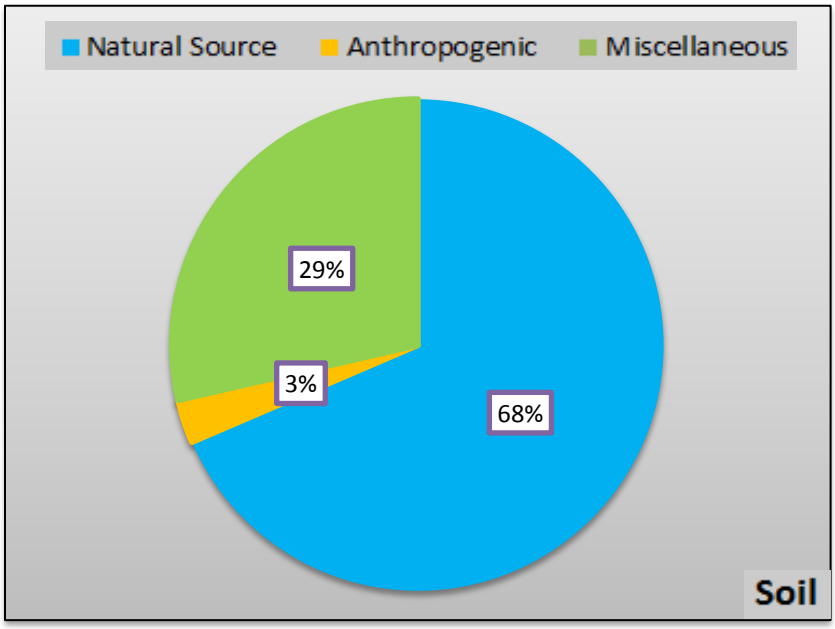

Figure 3.3 (a) Percentage source contribution chart for soil

Table 3.2 (b) Contribution factor loadings for source apportionments of metal in sediments

Variables	F1	F2	F3
Mn	0.188	0.040	**0.844**
Cr	-0.047	**0.754**	0.048
Cd	**0.705**	0.091	0.304
Ni	0.063	0.315	**0.534**
Pb	0.444	**0.523**	-0.237
Fe	-0.064	0.219	**0.651**
Zn	**0.743**	-0.220	-0.019
Cu	0.392	0.245	-0.398
Elevation	**0.779**	0.016	0.266
BC	0.137	**0.658**	-0.081
TOC	0.028	**0.728**	0.127
Precipitation	**0.633**	0.189	0.371
Eigen value	3.4	2.5	1.6
Variability %	20.926	16.260	13.800
Cumulative %	20.926	37.185	50.985
Contribution%	73.15	9.43	17.97

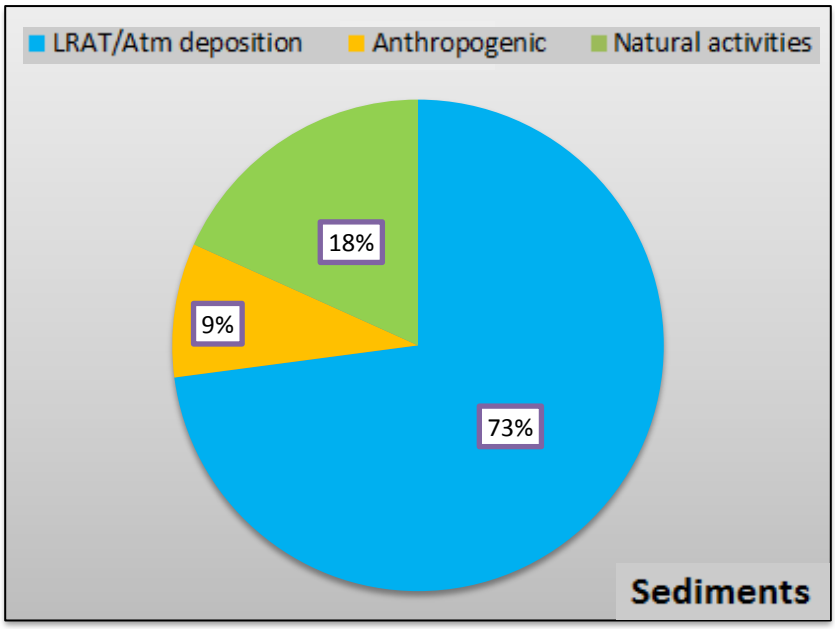

Figure 3.3 (b) Percentage source contribution chart for sediments

Table 3.2 (c) Contribution factor loadings for source apportionments of metal in water

Variables	F1	F2	F3
Elevation	**0.551**	-0.471	0.377
Pb	-0.119	**0.825**	-0.023
Zn	-0.125	0.358	**0.653**
Cu	0.026	**-0.538**	-0.322
Mn	**0.751**	-0.212	0.017
Cr	-0.061	**0.561**	0.263
Fe	**0.662**	-0.029	-0.151
Cd	0.148	**0.609**	0.292
Ni	-0.187	**0.661**	-0.108
EC water	-0.466	0.009	**-0.556**
pH water	**-0.582**	0.324	0.058
TDS	-0.100	0.055	**0.877**
Precipitation	0.211	-0.312	**0.699**
Eigen value	3.1	2.03	1.3
Variability %	19.785	21.637	12.755
Cumulative %	19.785	41.422	54.177
Contribution%	40	37	23

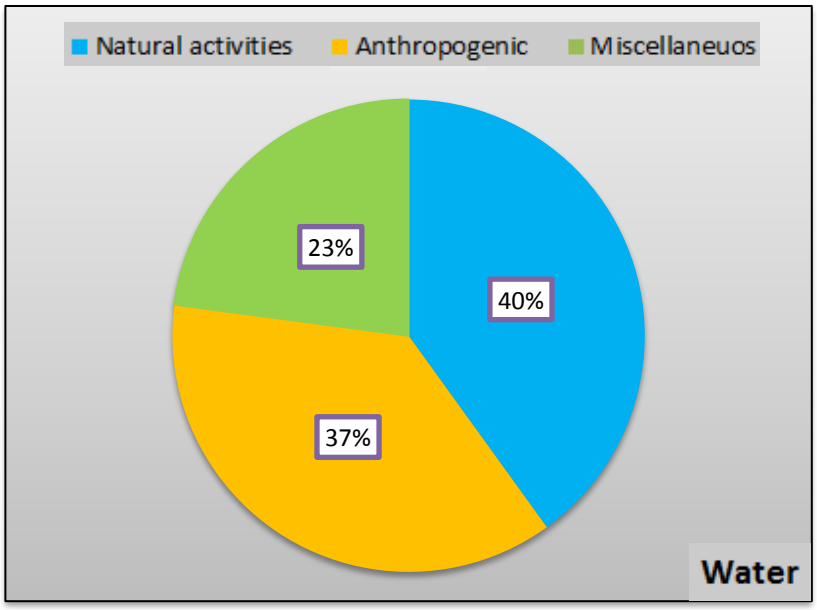

Figure 3.3 (c) Percentage source contribution chart for water

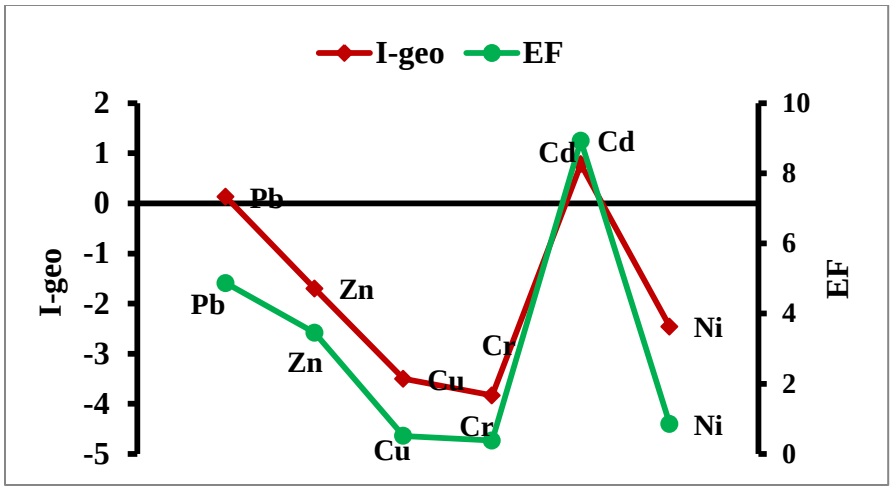

Figure 3.4(a) I-geo and EF for metals in soil

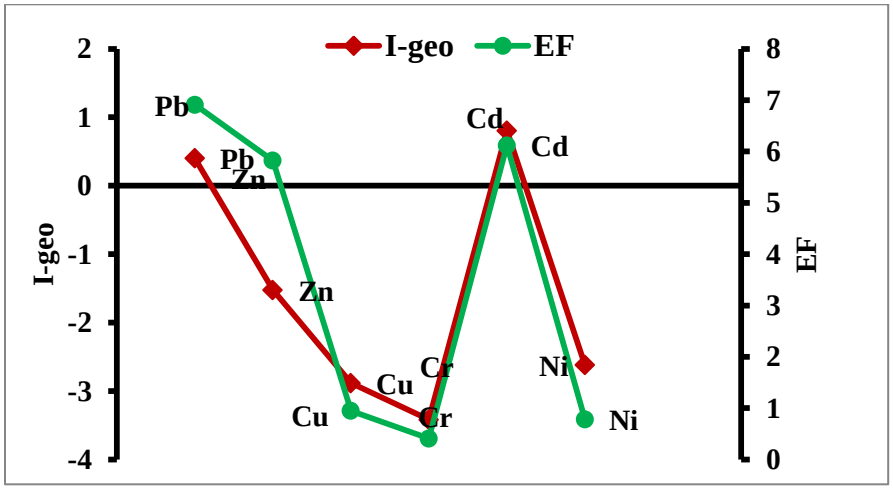

Figure 3.4 (b) I-geo and EF for metals in sediments

Table 3.3 (a) EF values of heavy metals in soil of study zones

	Pb	Zn	Cu	Mn	Cr	Fe	Cd	Ni
Zone 1	0.3	-1.6	-3.1	-6.6	-4.64	-1.9	0.9	-3.18
Zone 2	-0.2	-1.7	-3.4	-7.6	-4.32	-2.05	0.8	-2.39
Zone 3	0.05	-2	-4.3	-7.4	-3.64	-1.88	1	-2.18
Zone 4	0.2	-1.8	-4	-6.7	-3.87	-1.9	0.2	-2.32
Zone 5	0.3	-1.4	-2.7	-7.2	-2.7	-2	1	-2.23
LHR	0.13	-1.7	-3.5	-7.1	-3.834	-1.946	0.78	-2.46

Table 3.3 (b) EF values of heavy metals in sediments of study zones

	Pb	Zn	Cu	Mn	Cr	Fe	Cd	Ni
Zone 1	0.3	-1.6	-3.1	-6.6	-4.64	-1.9	0.9	-3.18
Zone 2	-0.2	-1.7	-3.4	-7.6	-4.32	-2.05	0.8	-2.39
Zone 3	0.05	-2	-4.3	-7.4	-3.64	-1.88	1	-2.18
Zone 4	0.2	-1.8	-4	-6.7	-3.87	-1.9	0.2	-2.32
Zone 5	0.3	-1.4	-2.7	-7.2	-2.7	-2	1	-2.23
LHR	0.13	-1.7	-3.5	-7.1	-3.834	-1.946	0.78	-2.46

Table 3.4 (a) I-geo values and classification of heavy metals in soil of study zones

I-geo

	Z1	Z2	Z3	Z4	Z5
Pb	0.3	-0.2	0.05	0.2	0.3
Zn	-1.6	-1.7	-2	-1.8	-1.4
Cu	-3.1	-3.4	-4.3	-4	-2.7
Mn	-6.6	-7.6	-7.4	-6.7	-7.2
Cr	-4.64	-4.32	-3.64	-3.87	-2.7
Fe	-1.9	-2.05	-1.88	-1.9	-2
Cd	0.9	0.8	1	0.2	1
Ni	-3.18	-2.39	-2.18	-2.32	-2.23

Classification

	Z1	Z2	Z3	Z4	Z5
Pb	2	1	2	2	2
Zn	1	1	1	1	1
Cu	1	1	1	1	1
Mn	1	1	1	1	1
Cr	1	1	1	1	1
Fe	1	1	1	1	1
Cd	2	2	2	2	2
Ni	1	1	1	1	1

Table 3.4 (b) I-geo values and classification of heavy metals in sediments of study zones

I-geo

	Z1	Z2	Z3	Z4	Z5
Pb	0.17	0.5	0.26	0.4	0.67
Zn	-2.3	-1.9	-1.32	-1.1	-1
Cu	-2.5	-4.6	-3.32	-2.3	-1.7
Mn	-6.5	-6.4	-5.8	-5.8	-5.7
Cr	-3.32	-3.18	-3.57	-3.83	-3.19
Fe	-2.3	-1.7	-2.1	-2.18	-2.4
Cd	0.92	1	0.5	0.6	1
Ni	-2.6	-2.4	-2.7	-2.9	-2.5

Classification

	Z1	Z2	Z3	Z4	Z5
Pb	2	2	2	2	2
Zn	1	1	1	1	1
Cu	1	1	1	1	1
Mn	1	1	1	1	1
Cr	1	1	1	1	1
Fe	1	1	1	1	1
Cd	2	2	2	2	2
Ni	1	1	1	1	1

Table 3.5 MPI values of metals in each zone and water quality status

	Z1	Z2	Z3	Z5	Z5	Quality
Mn	0.026	0.026	0.013	0.026	0.033	Very pure
Zn	0.017	0.012	0.016	0.02	0.072	Very pure
Cu	0.034	0.02	0.019	0.034	0.04	Very pure
Cr	0.04	0.04	0.08	0.08	0.11	Very pure
Fe	0.01	0.013	0.016	0.017	0.02	Very pure
Cd	0.4	0.5	0.4	0.5	0.6	Pure
Ni	0.046	0.06	0.073	0.106	0.12	Very pure

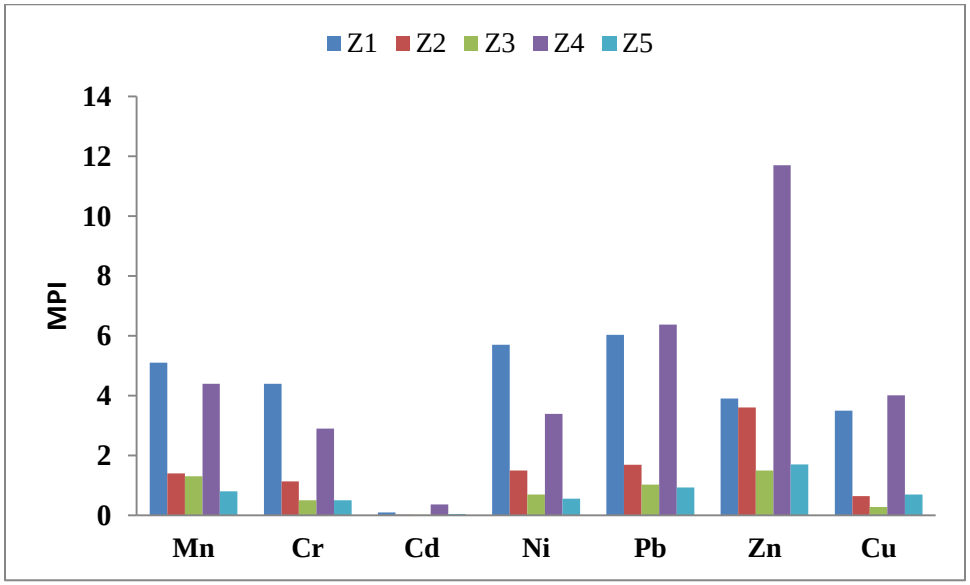

Figure 3.5 MPI values for metals in surface water

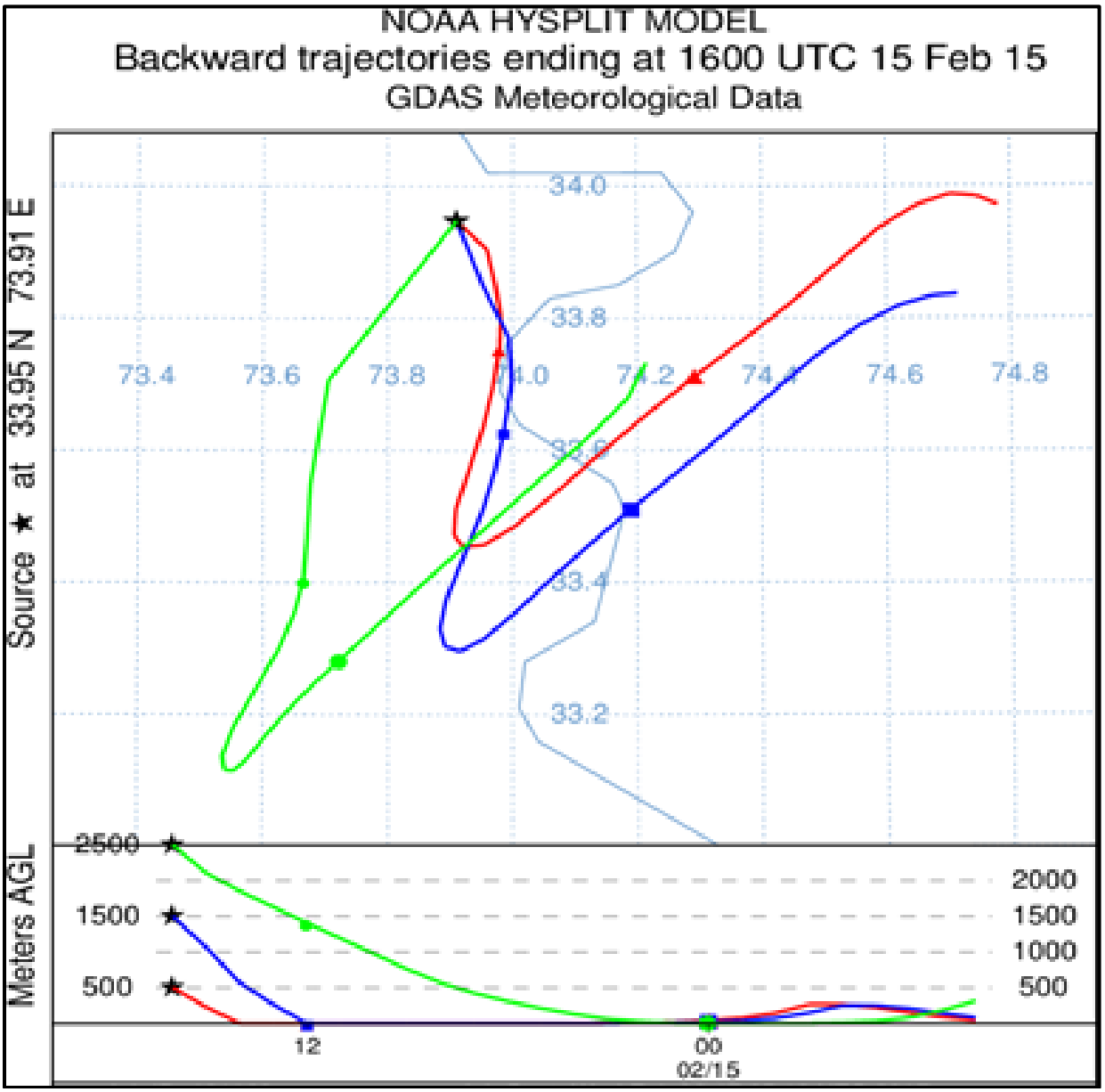

Figure 3.6 (a) HYSPLIT Model output displays local sources of contamination

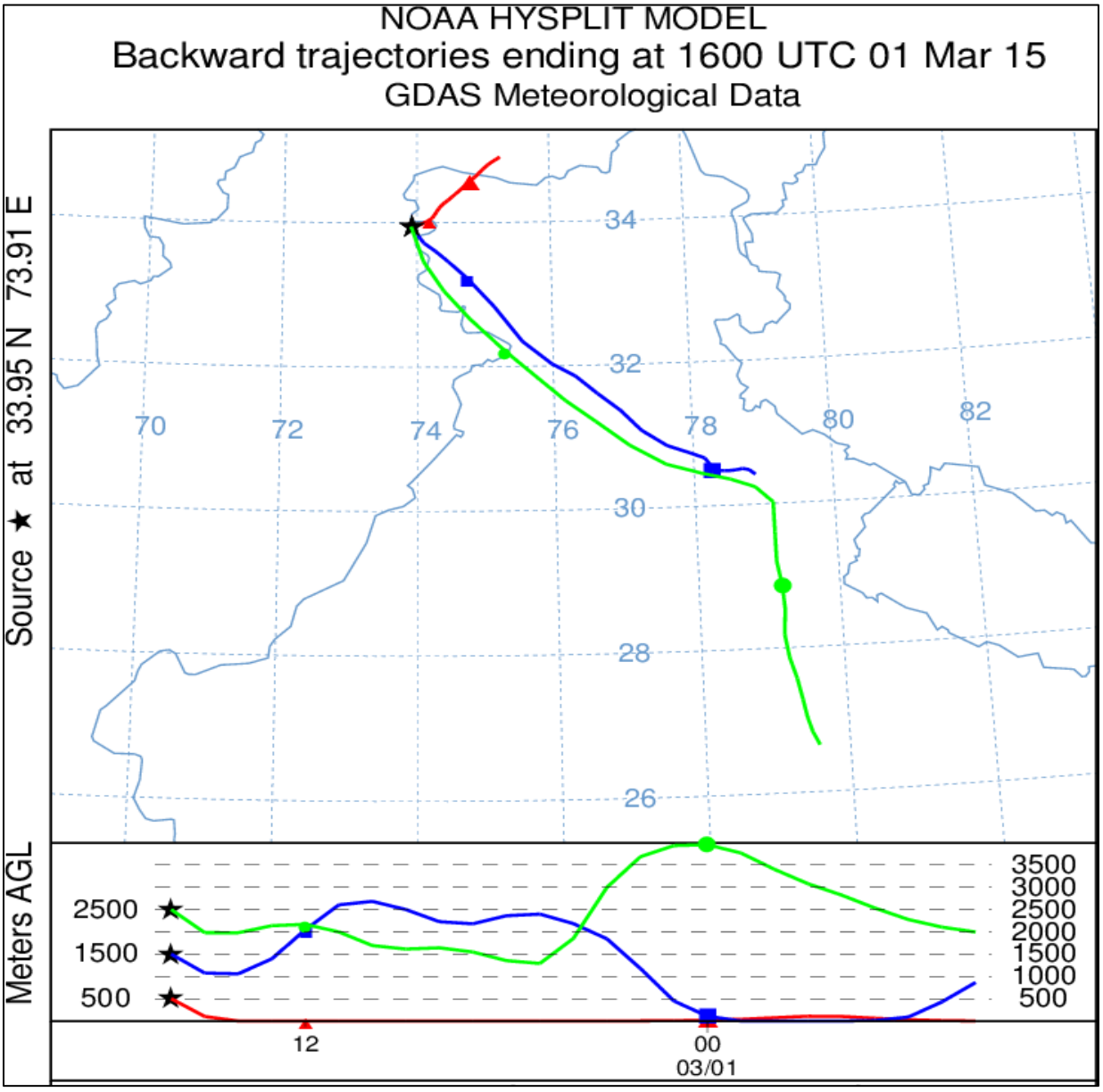

Figure 3.6 (b) HYSPLIT Model output displays transboundary sources of contamination

Table 3.6 Burial Fluxes of BC and TOC ($g.cm^{-2}yr^{-1}$)

	Zone 1	Zone 2	Zone 3	Zone 4	Zone 5
d (g/cm^3)	2.72	2.64	2.61	2.57	2.51
ω (cm/yr)	0.44	0.44	0.44	0.44	0.44
TOC(mg/g)	12.32	24.7	2.3	8.6	15.2
BC(mg/g)	1.12	7.7	5.1	10.2	14.7
F_{burial} TOC	136.2	275.7	25.7	100.9	174.1
F_{burial} BC	14.9	89	167.1	117	55

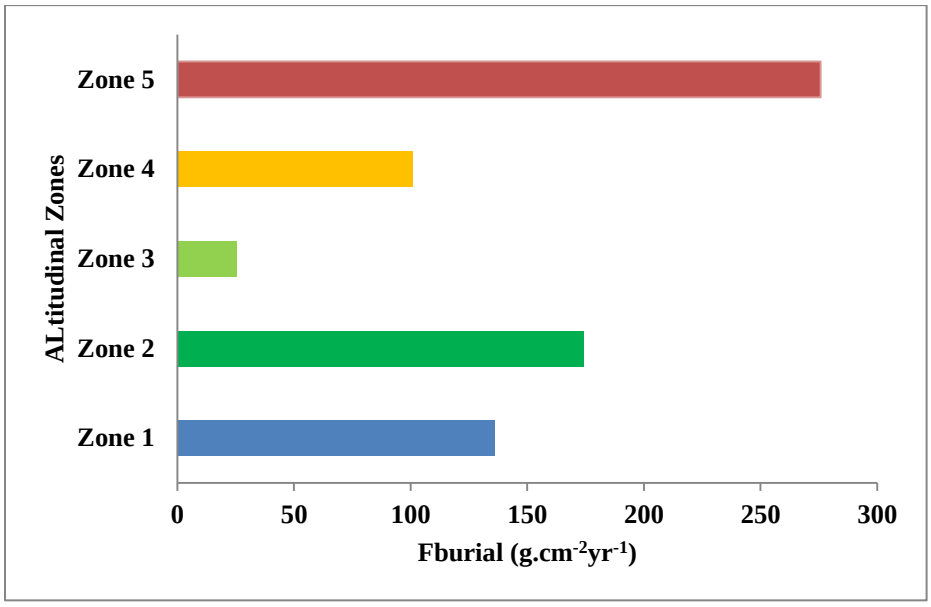

Figure 3.7 (a) TOC burial fluxes

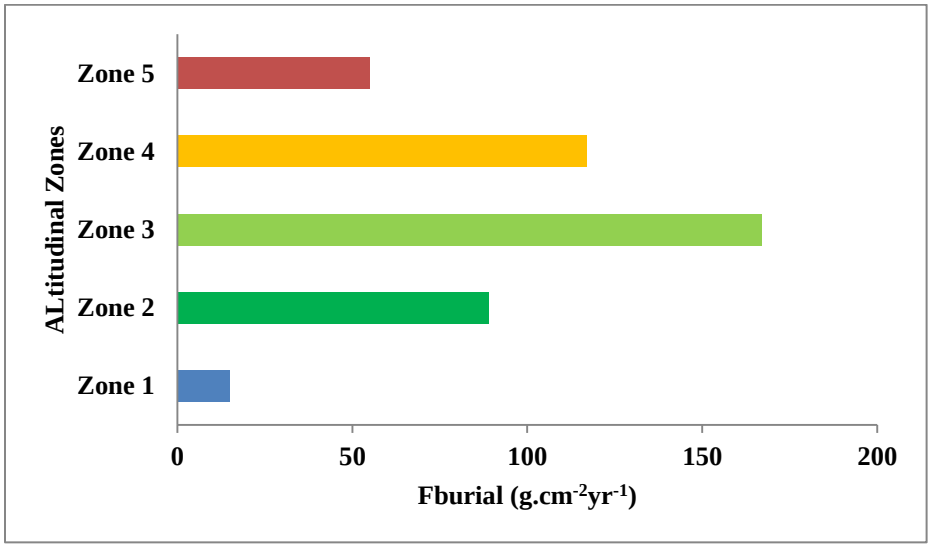

Figure 3.7 (b) BC burial fluxes

Table 3.7 Annual deposition flux of heavy metals (t/yr) in sediments of the study area

	Z1 (n=5)	Z2 (n=4)	Z3 (n=7)	Z4 (n=8)	Z5 (n=8)
Height (masl)	1301-2374	951-1300	751-950	376-750	300-375
(S) Km^2	135	32	27	140	21
Mn	5.1	1.4	1.3	4.4	0.8
Cr	4.4	1.13	0.5	2.9	0.5
Cd	0.1	0.02	0.02	0.36	0.04
Ni	5.7	1.5	0.7	3.39	0.56
Pb	6.03	1.69	1.03	6.38	0.93
Zn	3.9	3.6	1.5	11.7	1.7
Cu	3.5	0.64	0.28	4.01	0.7

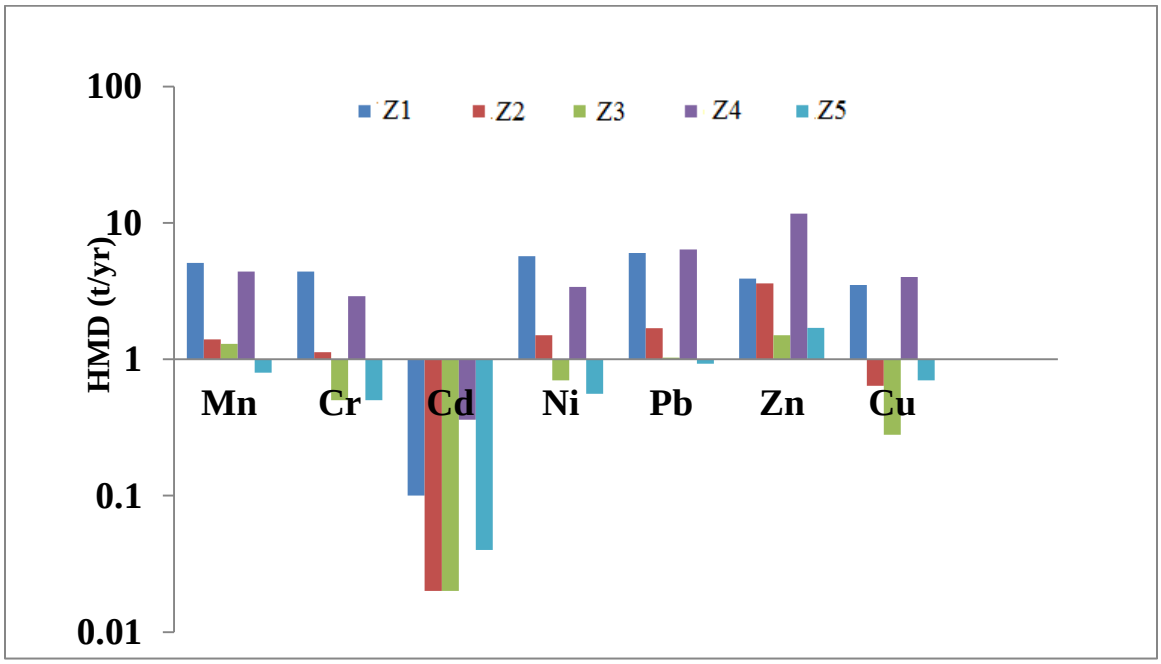

Figure 3.8 Heavy metal depositional flux

Table 3.8 Mass Inventory for heavy metals (Metric tonnes) in sediments of entire LHR

Metal	MI
Mn	1.1×10^4
Cr	6.5×10^3
Cd	4.4×10^2
Ni	8.7×10^3
Pb	1×10^4
Zn	2×10^4
Cu	9.7×10^3

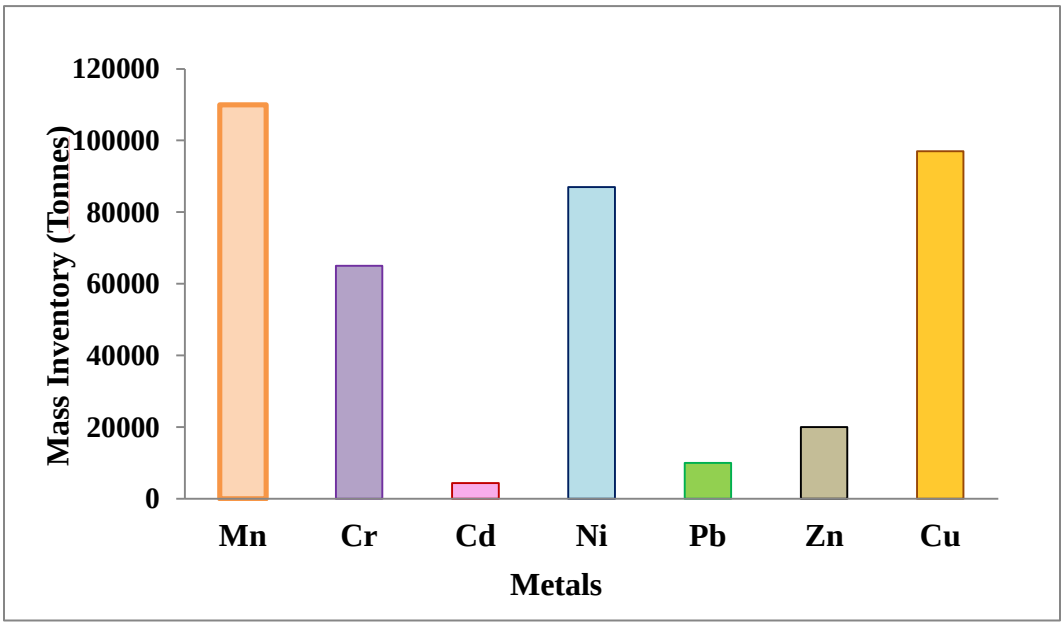

Figure 3.9 Sedimentary Mass Inventory of metals in LHR

A. Ilyas and T. Sarwar, "Study of trace elements in drinking water in the vicinity of Palosi drain, Peshawar," *Pakistan Journal of Biological Sciences*, vol. 6, pp. 86–91, 2003

A. M. Yousafzal, A. R. Khan, and A. R. Shakoori, "Heavy metal pollution in River Kabul affecting the inhabitant fish population," *Pakistan Journal of Zoology*, vol. 40, no. 5, pp. 331– 339, 2008.

Abbasi, A. M., Khan, M. A., Ahmad, M., Qureshi, R., Arshad, M., Jahan, S., & Sultana, S. (2010). Ethnobotanical study of wound healing herbs among the tribal communities in Northern Himalaya Ranges District Abbottabad, Pakistan. Pak J Bot, 6, 3747-3753.

Abdel-Ghani, N. T., & Elchaghaby, G. A. (2007). Influence of operating conditions on the removal of Cu, Zn, Cd and Pb ions from wastewater by adsorption. *International Journal of Environmental Science & Technology*, *4*(4), 451-456.

Abdullah, E. J. (2013). Quality assessment for Shatt Al-Arab river using heavy metal pollution index and metal index. *J Environ Earth Sci*, *3*(5), 114-20.

Accardi-Dey, A., & Gschwend, P. M. (2002). Assessing the combined roles of natural organic matter and black carbon as sorbents in sediments. *Environmental Science & Technology*, *36*(1), 21-29.

Acosta, J. A., Faz, A., Martínez-Martínez, S., Zornoza, R., Carmona, D. M., & Kabas, S. (2011). Multivariate statistical and GIS-based approach to evaluate heavy metals behavior in mine sites for future reclamation. *Journal of Geochemical Exploration*, *109*(1), 8-17.

Adam, G., & Duncan, H. (2001). Development of a sensitive and rapid method for the measurement of total microbial activity using fluorescein diacetate (FDA) in a range of soils. Soil Biology and Biochemistry, 33(7), 943-951.

Akcay, H., Oguz, A., & Karapire, C. (2003). Study of heavy metal pollution and speciation in Buyak Menderes and Gediz river sediments. *Water Research*, *37*(4), 813-822.

Akcay, H., Oguz, A., & Karapire, C. (2003). Study of heavy metal pollution and speciation in Buyak Menderes and Gediz river sediments. *Water Research*, *37*(4), 813-822.

Akram, M., Iqbal, A., Husaini, S. N., & Malik, F. (2011). Determination of Boron Contents in Water Samples Collected from the Neelum valley, Azad Kashmir, Pakistan. *Biological trace element research*, *139*(3), 287-295.

Al-Hejuje, M. M., Hussain, N. A., & Al-Saad, H. T. (2015). Total Petroleum Hydrocarbons (TPHs) n-alkanes and Polynuclear Aromatic Hydrocarbons (PAHs) in water of Shatt AlArab River–part 1. *Global Journal of Biology Agriculture and Health Sciences N*, *4*, 88-94.

Ali, U., Malik, R. N., Syed, J. H., Mehmood, C. T., Sánchez-García, L., Khalid, A., & Chaudhry, M. J. I. (2015). Mass burden and estimated flux of heavy metals in Pakistan coast: sedimentary pollution and eco-toxicological concerns. *Environmental Science and Pollution Research*, *22*(6), 4316-4326.

Ali, U., Syed, J. H., Malik, R. N., Katsoyiannis, A., Li, J., Zhang, G., & Jones, K. C. (2014). Organochlorine pesticides (OCPs) in South Asian region: a review. *Science of the Total Environment*, *476*, 705-717.

Ali, U., Syed, J.H., Junwen, L., Sánchez-García, L., Malik, R.N ., Chaudhry, M.J.I., Arshad, M., Li, J.,Zhang, G., Jones, K.C., (2014a). Assessing the relationship and influence of black carbon on distribution status of organochlorines in the coastal sediments from Pakistan. Environmental Pollution 190, 82-90.

Alleman, L. Y., Lamaison, L., Perdrix, E., Robache, A., & Galloo, J. C. (2010). PM 10 metal concentrations and source identification using positive matrix factorization and wind sectoring in a French industrial zone. Atmospheric Research, 96(4), 612-625.

Alloway, B. J. (2013). Sources of heavy metals and metalloids in soils. In *Heavy metals in soils* (pp. 11-50). Springer Netherlands.

Amadi, A. N. (2011). Assessing the Effects of Aladimma dumpsite on soil and groundwater using water quality index and factor analysis. Australian Journal of Basic and Applied Sciences, 5(11), 763-770.

Anh, P.T., C. Kroeze, S.R. Bush, A.P.J. Mol, 2010. Water pollution by intensive brackish shrimp farming in south-east Vietnam: Causes and options for control. *Agricultural Water Management, 97*(6): 872-882.

Arkoosh, M.R., D. Boylen, J. Dietrich, B.F. Anulacion, GinaYlitalo, C.F. Bravo, *et al*., 2010. Disease susceptibility of salmon exposed to polybrominated diphenyl ethers (PBDEs). *Aquatic Toxicology, 98*(1): 51-59.

Bai, J., Cui, B., Chen, B., Zhang, K., Deng, W., Gao, H., & Xiao, R. (2011). Spatial distribution and ecological risk assessment of heavy metals in surface sediments from a typical plateau lake wetland, China. *Ecological Modelling*, *222*(2), 301-306.

Balistrieri, L. S., Seal, R. R., Piatak, N. M., & Paul, B. (2007). Assessing the concentration, speciation, and toxicity of dissolved metals during mixing of acid-mine drainage and ambient river water downstream of the Elizabeth Copper Mine, Vermont, USA. *Applied Geochemistry*, *22*(5), 930-952.

Barbante, C., Turetta, C., Gambaro, A., Capodaglio, G., & Scarponi, G. (1998). Sources and origins of aerosols reaching Antarctica as revealed by lead concentration profiles in shallow snow. *Annals of Glaciology*, *27*(1), 674-678.

Barrie, L. A., & Schemenauer, R. S. (1989). Wet deposition of heavy metals. In *Control and Fate of Atmospheric Trace Metals* (pp. 203-231). Springer Netherlands.

Bastami, K. D., Bagheri, H., Kheirabadi, V., Zaferani, G. G., Teymori, M. B., Hamzehpoor, A., ... & Ganji, S. (2014). Distribution and ecological risk assessment of heavy metals in surface sediments along southeast coast of the Caspian Sea. *Marine pollution bulletin*, *81*(1), 262-267.

Baudoin, E., Benizri, E., & Guckert, A. (2003). Impact of artificial root exudates on the bacterial community structure in bulk soil and maize rhizosphere. *Soil Biology and Biochemistry*, *35*(9), 1183-1192.

Begin, Z. B., & Schumm, S. A. (1979). Instability of alluvial valley floors: a method for its assessment. *Transactions of the American Society of Agricultural Engineers*, *22*(2).

Bessou, C., Ferchaud, F., Gabrielle, B., & Mary, B. (2011). Biofuels, greenhouse gases and climate change. In *Sustainable Agriculture Volume 2* (pp. 365-468). Springer Netherlands.

Bettinelli, M., Beone, G. M., Spezia, S., & Baffi, C. (2000). Determination of heavy metals in soils and sediments by microwave-assisted digestion and inductively coupled plasma optical emission spectrometry analysis. *Analytica Chimica Acta*, *424*(2), 289-296.

Beyer, L. (2000). Properties, formation, and geo-ecological significance of organic soils in the coastal region of East Antarctica (Wilkes Land). *Catena*, *39*(2), 79-93.

Bing, H., Wu, Y., Zhou, J., Li, R., & Wang, J. (2016). Historical trends of anthropogenic metals in Eastern Tibetan Plateau as reconstructed from alpine lake sediments over the last century. *Chemosphere*, *148*, 211-219.

BioMed Research International NWFP and Sindh provinces with respect to trace elements," *International Journal of Agriculture and Biology*, vol. 7, pp. 214– 217, 2005

Bogdal, C., Bucheli, T. D., Agarwal, T., Anselmetti, F. S., Blum, F., Hungerbühler, K., ... & Sobek, A. (2011). Contrasting temporal trends and relationships of total organic carbon, black carbon, and polycyclic aromatic hydrocarbons in rural low-altitude and remote high-altitude lakes. *Journal of environmental monitoring*, *13*(5), 1316-1326.

Bolan, N. S., & Thiagarajan, S. (2001). Retention and plant availability of chromium in soils as affected by lime and organic matter amendments. *Soil Research*, *39*(5), 1091-1103.

Bouloubassi, I., Roussiez, V., Azzoug, M., & Lorre, A. (2012). Sources, dispersal pathways and mass budget of sedimentary polycyclic aromatic hydrocarbons (PAH) in the NW Mediterranean margin, Gulf of Lions. *Marine chemistry*, *142*, 18-28.

Bu, J., Sun, Z., Zhou, A., Xu, Y., Ma, Rui., Wei, W and Liu, M. (2016). Heavy metals n surface sol in upper reaches of the Heihe River, Northeatern Tibetan Plateau, China. *Int. J. Environ. Res. Public Health*. *13*(3), 247.

Caeiro, S., Costa, M. H., Ramos, T. B., Fernandes, F., Silveira, N., Coimbra, A., ... & Painho, M. (2005). Assessing heavy metal contamination in Sado Estuary sediment: an index analysis approach. *Ecological indicators*, *5*(2), 151-169

Caruso, B. S., Mirtskhulava, M., Wireman, M., Schroeder, W., Kornilovich, B., & Griffin, S. (2012). Effects of manganese mining on water quality in the Caucasus Mountains, Republic of Georgia. *Mine Water and the Environment*, *31*(1), 16-28.

Cenci, R. M., & Martin, J. M. (2004). Concentration and fate of trace metals in Mekong River Delta. *Science of the total Environment*, *332*(1), 167-182.

Cenci, R. M., & Martin, J. M. (2004). Concentration and fate of trace metals in Mekong River Delta. Science of the total Environment, 332(1), 167-182.

Censi, P. A. O. L. O., Spoto, S. E., Saiano, F. I. L. I. P. P. O., Sprovieri, M., Mazzola, S., Nardone, G., ... & Ottonello, D. (2006). Heavy metals in coastal water systems. A case study from the northwestern Gulf of Thailand. *Chemosphere*, *64*(7), 1167-1176.

Champion, S. H., Seth, S. K., & Khattak, G. M. (1965). Forest types of Pakistan. *Forest types of Pakistan.*

Chang, H. (2008). Spatial analysis of water quality trends in the Han River basin, South Korea. *Water research*, *42*(13), 3285-3304.

Chapra, S. C., Canale, R. P., & Amy, G. L. (1997). Empirical models for disinfection by-products in lakes and reservoirs. *Journal of Environmental Engineering*, *123*(7), 714-715.

Charman, P. E., & Murphy, B. W. (Eds.). (2007). *Soils, their properties and management*. Melbourne Vic: Oxford University Press.

Chen, C. W., Kao, C. M., Chen, C. F., & Dong, C. D. (2007). Distribution and accumulation of heavy metals in the sediments of Kaohsiung Harbor, Taiwan. *Chemosphere*, *66*(8), 1431-1440.

Cheng, H., & Hu, Y. (2010). Lead (Pb) isotopic fingerprinting and its applications in lead pollution studies in China: a review. *Environmental Pollution*, *158*(5), 1134-1146.

Chhawchharia, R., & Puliyel, J. M. (2014). Commentary–Controversies surrounding mercury in vaccines: autism denial as impediment to universal immunisation.

Christoforidis, A., & Stamatis, N. (2009). Heavy metal contamination in street dust and roadside soil along the major national road in Kavala's region, Greece. Geoderma, 151(3), 257-263.

Christoforidis, A., & Stamatis, N. (2009). Heavy metal contamination in street dust and roadside soil along the major national road in Kavala's region, Greece. Geoderma, 151(3), 257-263.

Chuan, M. C., Shu, G. Y., & Liu, J. C. (1996). Solubility of heavy metals in a contaminated soil: effects of redox potential and pH. *Water, Air, & Soil Pollution*, *90*(3), 543-556.

Cong, Z., Kang, S., Zhang, Y., & Li, X. (2010). Atmospheric wet deposition of trace elements to central Tibetan Plateau. *Applied Geochemistry*, *25*(9), 1415-1421.

Cornelissen, G., Gustafsson, Ö., Bucheli, T. D., Jonker, M. T., Koelmans, A. A., & van Noort, P. C. (2005). Extensive sorption of organic compounds to black carbon, coal, and kerogen in sediments and soils: mechanisms and consequences for distribution, bioaccumulation, and biodegradation. *Environmental Science & Technology*, *39*(18), 6881-6895.

Czuba, J. A., Magirl, C. S., Czuba, C. R., Grossman, E. E., Curran, C. A., Gendaszek, A. S., & Dinicola, R. S. (2011). *Sediment load from major rivers into Puget Sound and its adjacent waters*. US Department of the Interior, US Geological Survey.

Daly, G. L., & Wania, F. (2005). Organic contaminants in mountains. *Environmental science & technology*, *39*(2), 385-398.

Divrikli, U., Horzum, N., Soylak, M., & Elci, L. (2006). Trace heavy metal contents of some spices and herbal plants from western Anatolia, Turkey. International journal of food science & technology, 41(6), 712-716.

Dollar, E. S. J., James, C. S., Rogers, K. H., & Thoms, M. C. (2007). A framework for interdisciplinary understanding of rivers as ecosystems. *Geomorphology*, *89*(1), 147-162.

Dou, Y., Li, J., Zhao, J., Hu, B., & Yang, S. (2013). Distribution, enrichment and source of heavy metals in surface sediments of the eastern Beibu Bay, South China Sea. Marine pollution bulletin, 67(1), 137-145.

Draxler, R. R., & Rolph, G. D. (2003). HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) model access via NOAA ARL READY website (http://www. arl. noaa. gov/ready/hysplit4. html). NOAA Air Resources Laboratory, Silver Spring.

Dubé, J. S., & Galvez-Cloutier, R. (2005). Applications of data on the mobility of heavy metals in contaminated soil to the definition of site-specific remediation criteria. *Journal of Environmental Engineering and Science*, *4*(5), 399-411.

E. Pertsemli and D. Voutsa, "Distribution of heavy metals in Lakes Doirani and Kerkini, Northern Greece," Journal of Hazardous Materials, vol. 148, no. 3, pp. 529–537, 2007.

Elghobashy, H. A., Zaghloul, K. H., & Metwally, M. A. (2001). Effect of some water pollutants on the Nile tilapia Oreochromis niloticus collected from the River Nile and some Egyptian Lakes. *Egyptian Journal of Aquatic Biology and Fisheries*, *5*(4), 251-279.

Elik, A. (2003). Heavy metal accumulation in street dust samples in Sivas. *Communications in Soil Science and Plant Analysis*, *34*(1-2), 145-156.

Eqani, S. A. M. A. S., Malik, R. N., Cincinelli, A., Zhang, G., Mohammad, A., Qadir, A., ... & Katsoyiannis, A. (2013). Uptake of organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs) by river water fish: the case of River Chenab. *Science of the Total Environment*, *450*, 83-91.

Falconer, R. A., & Lin, B. (2003). Hydro-environmental modelling of riverine basins using dynamic rate and partitioning coefficients. *International Journal of River Basin Management*, *1*(1), 81-89.

Farkas, A., Erratico, C., & Viganò, L. (2007). Assessment of the environmental significance of heavy metal pollution in surficial sediments of the River Po. Chemosphere, 68(4), 761-768.

Fernández-Olmo, I., Puente, M., & Irabien, A. (2015). A comparative study between the fluxes of trace elements in bulk atmospheric deposition at industrial, urban, traffic, and rural sites. *Environmental Science and Pollution Research*, *22*(17), 13427-13441.

Flora, S. J. (2011). Arsenic-induced oxidative stress and its reversibility. *Free Radical Biology and Medicine*, *51*(2), 257-281.

Fu, Y., Freymueller, J. T., & Jensen, T. (2012). Seasonal hydrological loading in southern Alaska observed by GPS and GRACE. *Geophysical Research Letters*, *39*(15).

G. Forghani, F. Moore, S. Lee, and A. Qishlaqi, "Geochemistry and speciation of metals in sedimentsof themaharlusaline lake,shiraz, sw iran," Environmental Earth Sciences, vol. 59, no. 1, pp.173–184, 2009.

G.M.Mastoi, S. G. S. Shah, and M. Y. Khuhawar, "Assessment of water quality of Manchar Lake in Sindh (Pakistan)," *EnvironmentalMonitoring and Assessment*, vol. 141, no. 1-3, pp. 287–296, 2008.

Gatari, M. J., & Boman, J. (2003). Black carbon and total carbon measurements at urban and rural sites in Kenya, East Africa. *Atmospheric Environment*, *37*(8), 1149-1154.

Gavrilescu, M. (2009). Behaviour of persistent pollutants and risks associated with their presence in the environment–integrated studies. *Environmental Engineering and Management Journal*, *8*(6), 1517-1531.

Gélinas, Y., Prentice, K. M., Baldock, J. A., & Hedges, J. I. (2001). An improved thermal oxidation method for the quantification of soot/graphitic black carbon in sediments and soils. *Environmental science & technology*, *35*(17), 3519-3525.

Gerdol, R., & Bragazza, L. (2006). Effects of altitude on element accumulation in alpine moss. Chemosphere, 64(5), 810-816.

Ghrefat, H. A., Yusuf, N., Jamarh, A., & Nazzal, J. (2012). Fractionation and risk assessment of heavy metals in soil samples collected along Zerqa River, Jordan. *Environmental Earth Sciences*, *66*(1), 199-208.

Giger, W. (2009). The Rhine red, the fish dead—the 1986 Schweizerhalle disaster, a retrospect and long-term impact assessment. *Environmental Science and Pollution Research*, *16*(1), 98-111.

Gustafsson, O., Bucheli, T. D., Kukulska, Z., Andersson, M., Largeau, C., Rouzaud, J. N., ... & Eglinton, T. I. (2001). Evaluation of a protocol for the quantification of black carbon. *Global Biogeochemical Cycles*, *15*, 881-890.

Guzzella, L., Poma, G., De Paolis, A., Roscioli, C., & Viviano, G. (2011). Organic persistent toxic substances in soils, waters and sediments along an altitudinal gradient at Mt. Sagarmatha, Himalayas, Nepal. *Environmental pollution*, *159*(10), 2552-2564.

H. Bem, M. Gallorini, E. Rizzio, and M. Krzemi´nska, "Comparative studies on the concentrations of some elements in the urban air particulate matter in Lodz City of Poland and in Milan, Italy," Environment International, vol. 29, no. 4, pp. 423– 428, 2003.

Habersack, H. M. (2000). The river-scaling concept (RSC): a basis for ecological assessments. *Hydrobiologia*, *422*, 49-60.

Hailin, W., ZHUANG, Y., Ying, W., Yele, S. U. N., Hui, Y., ZHUANG, G., & Zhengping, H. A. O. (2008). Long-term monitoring and source apportionment of PM 2.5/PM 10 in Beijing, China. *Journal of Environmental Sciences*, *20*(11), 1323-1327.

Hamed, M. A. (1998). Distribution of trace metals in the River Nile Ecosystem Damietta branch between Mansoura city and Damiette province. Journal-Egyptian German Society Of Zoology, 27, 399-416.

Hammes, K., Smernik, R. J., Skjemstad, J. O., & Schmidt, M. W. (2008). Characterisation and evaluation of reference materials for black carbon analysis using elemental composition, colour, BET surface area and 13 C NMR spectroscopy. *Applied Geochemistry*, *23*(8), 2113-2122.

Harner, T., Bartkow, M., Holoubek, I., Klanova, J., Wania, F., Gioia, R., ... & Jones, K. C. (2006). Passive air sampling for persistent organic pollutants: Introductory remarks to the special issue. *Environmental Pollution*, *144*(2), 361-364.

He, S., Kapp, P., DeCelles, P. G., Gehrels, G. E., & Heizler, M. (2007). Cretaceous–Tertiary geology of the Gangdese Arc in the Linzhou area, southern Tibet. *Tectonophysics*, *433*(1), 15-37.

He, Z. L., Yang, X. E., & Stoffella, P. J. (2005). Trace elements in agroecosystems and impacts on the environment. *Journal of Trace elements in Medicine and Biology*, *19*(2), 125-140.

Heredia, O. S., & Cirelli, A. F. (2009). Trace elements distribution in soil, pore water and groundwater in Buenos Aires, Argentina. *Geoderma*, *149*(3), 409-414.

Hernandez, L., Probst, A., Probst, J. L., & Ulrich, E. (2003). Heavy metal distribution in some French forest soils: evidence for atmospheric contamination. Science of the Total Environment, 312(1), 195-219.

Hickin, E. J. (1995). Hydraulic geometry and channel scour, Fraser River, British Columbia, Canada. *Wiley: Chichester*, 155-167.

Hjortenkrans, D., Bergbäck, B., & Häggerud, A. (2006). New metal emission patterns in road traffic environments. Environmental Monitoring and Assessment, 117(1), 85-98.

Hsieh, Y. P., & Bugna, G. C. (2008). Analysis of black carbon in sediments and soils using multi-element scanning thermal analysis (MESTA). *Organic Geochemistry*, *39*(11), 1562-1571.

Hu, L., Shi, X., Bai, Y., Fang, Y., Chen, Y., Qiao, S., Liu, S., Yang, G., Kornkanitnan, N., Khokiattiwong, S., (2016). Distribution, input pathway and mass inventory of black carbon in sediments of the Gulf of Thailand, SE Asia. Estuarine, Coastal and Shelf Science 170, 10-19.

Huang, X., Sillanpää, M., Duo, B. U., & Gjessing, E. T. (2008). Water quality in the Tibetan Plateau: metal contents of four selected rivers. *Environmental Pollution*, *156*(2), 270-277.

Huaxing, B. I., Bin, L. I. U., Jie, W. U., Lei, Y. U. N., Zhihan, C. H. E. N., & Zhewei, C. U. I. (2009). Effects of precipitation and landuse on runoff during the past 50 years in a typical watershed in Loess Plateau, China. *International Journal of Sediment Research*, *24*(3), 352-364.

Hussain, F., & Ilahi, I. (1991). Ecology and Vegetation of Lesser Himalayas Pakistan. *Department of Botany, University of Peshawar*, *187*.

Ikenaka, Y., Nakayama, S. M., Muzandu, K., Choongo, K., Teraoka, H., Mizuno, N., & Ishizuka, M. (2010). Heavy metal contamination of soil and sediment in Zambia. African Journal of Environmental Science and Technology, 4(11), 729-739.

Iqbal, J., & Shah, M. H. (2014). Occurrence, risk assessment, and source apportionment of heavy metals in surface sediments from Khanpur Lake, Pakistan. *Journal of Analytical Science and Technology*, *5*(1), 28.

Islam, M. S., Shuping, H. A. N., AHMED, M. K., & Masunaga, S. (2014). Assessment of trace metal contamination in water and sediment of some rivers in Bangladesh. *Journal of Water and Environment Technology*, *12*(2), 109-121.

J. Iqbal and M. H. Shah, "Health risk assessment of metals in surface water from Freshwater Source Lakes, Pakistan," *Human and Ecological isk Assessment*, vol. 19, no. 6, pp. 1530–1543, 2013.

J. Iqbal, M. H. Shah, and G. Akhter, "Characterization, source apportionment and health risk assessment of trace metals in freshwater Rawal Lake, Pakistan," *Journal of Geochemical Exploration*,

Jacobson, M. C., Hansson, H. C., Noone, K. J., & Charlson, R. J. (2000). Organic atmospheric aerosols: Review and state of the science. *Reviews of Geophysics*, *38*(2), 267-294.

Jacobson, R. B., Blevins, D. W., & Bitner, C. J. (2009). Sediment regime constraints on river restoration—An example from the Lower Missouri River. *Geological Society of America Special Papers*, *451*, 1-22.

Jeffers, J. N. (1988). Statistical and mathematical approaches to issues of scales in ecology. Scope, 35.

Jurado, E., Dachs, J., Duarte, C. M., & Simo, R. (2008). Atmospheric deposition of organic and black carbon to the global oceans. *Atmospheric Environment*, *42*(34), 7931-7939.

Kaiser, H. F. (1960). Directional statistical decisions. *Psychological Review*, *67*(3), 160.

Kaizer, A. N., & Osakwe, S. A. (2007). Water chemistry in the Upper and Middle Ethiope River, Southwest Nigeria. *Nigerian Journal of Science and Environment*, *6*, 146-157.

Kalbus, E., Oswald, S., Wang, W., Kolditz, O., Engelhardt, I., Al-Saud, M. I., & Rausch, R. (2011). Large-scale modeling of the groundwater resources on the Arabian platform. *Int. J. Water Res. Arid Environ*, *1*(1), 38-47.

Kamala-Kannan, S., Batvari, B. P. D., Lee, K. J., Kannan, N., Krishnamoorthy, R., Shanthi, K., & Jayaprakash, M. (2008). Assessment of heavy metals (Cd, Cr and Pb) in water, sediment and seaweed (Ulva lactuca) in the Pulicat Lake, South East India. *Chemosphere*, *71*(7), 1233-1240.

Kang, S., Xu, Y., You, Q., Flügel, W. A., Pepin, N., & Yao, T. (2010). Review of climate and cryospheric change in the Tibetan Plateau. *Environmental Research Letters*, *5*(1), 015101.

Kaspari, S. D., Schwikowski, M., Gysel, M., Flanner, M. G., Kang, S., Hou, S., & Mayewski, P. A. (2011). Recent increase in black carbon concentrations from a Mt. Everest ice core spanning 1860–2000 AD. *Geophysical Research Letters*, *38*(4).

Kazi, T. G., Arain, M. B., Jamali, M. K., Jalbani, N., Afridi, H. I., Sarfraz, R. A., & Shah, A. Q. (2009). Assessment of water quality of polluted lake using multivariate statistical techniques: A case study. Ecotoxicology and Environmental Safety, 72(2), 301-309.

Kent, M. p. Coker (1992). Vegetation description and analysis: a practical approach. John and Sons.

Khattak, G. A., Owen, L. A., Kamp, U., & Harp, E. L. (2010). Evolution of earthquake-triggered landslides in the Kashmir Himalaya, northern Pakistan. *Geomorphology*, *115*(1), 102-108.

Kotti, M. E., Vlessidis, A. G., Thanasoulias, N. C., & Evmiridis, N. P. (2005). Assessment of river water quality in Northwestern Greece. *Water Resources Management*, *19*(1), 77-94.

Kotti, M. E., Vlessidis, A. G., Thanasoulias, N. C., & Evmiridis, N. P. (2005). Assessment of river water quality in Northwestern Greece. *Water Resources Management*, *19*(1), 77-94.

Kyllönen, K., Karlsson, V., & Ruoho-Airola, T. (2009). Trace element deposition and trends during a ten year period in Finland. *Science of the total environment*, *407*(7), 2260-2269.

Lambert, J. M., & Dale, M. B. (1964). The use of statistics in phytosociology. Advances in ecological research, 2, 59-99.

Langland, M., & Cronin, T. (2003). *A summary report of sediment processes in Chesapeake Bay and watershed* (No. 2003-4123).

Lee, C. M., Lin, T. Y., Lin, C. C., Kohbodi, G. A., Bhatt, A., Lee, R., & Jay, J. A. (2006). Persistence of fecal indicator bacteria in Santa Monica Bay beach sediments. *Water Research*, *40*(14), 2593-2602.

Lee, K., Do Hur, S., Hou, S., Hong, S., Qin, X., Ren, J., ... & Boutron, C. F. (2008). Atmospheric pollution for trace elements in the remote high-altitude atmosphere in central Asia as recorded in snow from Mt. Qomolangma (Everest) of the Himalayas. *Science of the total environment*, *404*(1), 171-181.

Lenntech, K. (2004). Water treatment and air purification. *Published by Rotter Dam Seweg, Netherlands*.

Li, J. R., Sculley, J., & Zhou, H. C. (2012). Metal–organic frameworks for separations. *Chem. Rev*, *112*(2), 869-932.

Li, Q., Wu, Z., Chu, B., Zhang, N., Cai, S., & Fang, J. (2007). Heavy metals in coastal wetland sediments of the Pearl River Estuary, China. *Environmental Pollution*, *149*(2), 158-164.

Li, S., Xu, Z., Cheng, X., & Zhang, Q. (2008). Dissolved trace elements and heavy metals in the Danjiangkou Reservoir, China. Environmental Geology, 55(5), 977-983.

Li, Z., Ma, Z., van der Kuijp, T. J., Yuan, Z., & Huang, L. (2014). A review of soil heavy metal pollution from mines in China: pollution and health risk assessment. *Science of the Total Environment*, *468*, 843-853.

Liaghati, T., Cox, M. E., & Preda, M. (2005). Distribution of Fe in waters and bottom sediments of a small estuarine catchment, Pumicestone Region, southeast Queensland, Australia. Science of the total environment, 336(1), 243-254.

Liu, S., Xia, X., Zhai, Y., Wang, R., Liu, T., Zhang, S. (2011). Black carbon (BC) in urban and surrounding rural soils of Beijing, China: spatial distribution and relationship with polycyclic aromatic hydrocarbons (PAHs). Chemosphere 82, 223-228.

Loewen, M. D., Sharma, S., Tomy, G., Wang, F., Bullock, P., & Wania, F. (2005). Persistent organic pollutants and mercury in the Himalaya. *Aquatic Ecosystem Health & Management*, *8*(3), 223-233.

Loewen, M. D., Sharma, S., Tomy, G., Wang, F., Bullock, P., & Wania, F. (2005). Persistent organic pollutants and mercury in the Himalaya. *Aquatic Ecosystem Health & Management*, *8*(3), 223-233.

Lokeshwari, H., & Chandrappa, G. T. (2006). Heavy Metals Content in Water, Water Hyacinth and Sediments of Lalbagh Tank, Bangalore(India). Journal of environmental science & engineering, 48(3), 183-188.

Luo, Z., Wang, E., & Sun, O. J. (2010). Can no-tillage stimulate carbon sequestration in agricultural soils? A meta-analysis of paired experiments. *Agriculture, Ecosystems & Environment*, *139*(1), 224-231.

M. H. S. Wattoo, F. H. Wattoo, S. A. Tirmizi, T. G. Kazi, M. I. Bhanger, and J. I. Qbal, "Pollution of phulali canal water in the city premises of Hyderabad: Metal monitoring," *Journal of the Chemical Society of Pakistan*, vol. 28, no. 2, pp. 136–143, 2006.

M. J. Butt, R. Mahmood, and A.Waqas, "Sediments deposition due to soil erosion in the watershed region of Mangla Dam," Environmental Monitoring and Assessment, vol. 181, no. 1–4, pp. 419–429, 2011.

M.Varol, "Dissolved heavymetal concentrations of the Kralkızı,dicle and batman dam reservoirs in the tigris river basin, turkey," Chemosphere, vol. 93, no. 6, pp. 954–962, 2013.

Madoni, P., & Romeo, M. G. (2006). Acute toxicity of heavy metals towards freshwater ciliated protists. *Environmental Pollution*, *141*(1), 1-7.

Malik, N., Biswas, A. K., Qureshi, T. A., Borana, K., & Virha, R. (2010). Bioaccumulation of heavy metals in fish tissues of a freshwater lake of Bhopal. *Environmental Monitoring and Assessment*, *160*(1), 267-276.

Massas, I., Ehaliotis, C., Gerontidis, S., & Sarris, E. (2009). Elevated heavy metal concentrations in top soils of an Aegean island town (Greece): total and available forms, origin and distribution. *Environmental Monitoring and Assessment*, *151*(1), 105-116.

Mastoi, G. M., Shah, S. G. S., & Khuhawar, M. Y. (2008). Assessment of water quality of Manchar Lake in Sindh (Pakistan). Environmental monitoring and assessment, 141(1-3), 287-296.

McLean, J. E., & Bledsoe, B. E. (1996). Behavior of metals in soils. *EPA Environmental Assessment Sourcebook*, *19*.

Meyers, P. A. (1994). Preservation of elemental and isotopic source identification of sedimentary organic matter. *Chemical Geology*, *114*(3-4), 289-302.

Meynell, Peter-John and Nazia Zakir. (2014). EIA Guidelines for Large-Scale Hydropower In Pakistan. Islamabad: IUCN Pakistan. 136 pp.

Miao, C., Ni, J., & Borthwick, A. G. (2010). Recent changes of water discharge and sediment load in the Yellow River basin, China. *Progress in Physical Geography*, *34*(4), 541-561.

Middelburg, J. J., Nieuwenhuize, J., & van Breugel, P. (1999). Black carbon in marine sediments. *Marine Chemistry*, *65*(3), 245-252.

Middelburg, J.J., Soetaert, K., Herman, P.M., (1997). Empirical relationships for use in global diagenetic models. Deep Sea Research Part I: Oceanographic Research Papers 44, 327-344.

Midrar-Ul-Haq, R. A. Khattak, H. K. Puno, M. S. Saif, and K. S. Memon, "Surface and ground water contamination in

Mohammed, A. S., Kapri, A., & Goel, R. (2011). Heavy metal pollution: source, impact, and remedies. In *Biomanagement of metal-contaminated soils* (pp. 1-28). Springer Netherlands.

Morillo, J., Usero, J., & Gracia, I. (2004). Heavy metal distribution in marine sediments from the southwest coast of Spain. *Chemosphere*, *55*(3), 431-442.

Morisawa, M., & LaFlure, E. (1979). Hydraulic geometry, stream equilibrium and urbanization. *Adjustments of the fluvial system*, *10*, 333-350.

Mostert, M. M., Ayoko, G. A., & Kokot, S. (2010). Application of chemometrics to analysis of soil pollutants. *TrAC Trends in Analytical Chemistry*, *29*(5), 430-445.

Munthe, J., Wängberg, I., Pirrone, N., Iverfeldt, Å., Ferrara, R., Ebinghaus, R., ... & Lindberg, S. E. (2001). Intercomparison of methods for sampling and analysis of atmospheric mercury species. *Atmospheric Environment*, *35*(17), 3007-3017.

Muri, G., Cermelj, B., Faganeli, J., & Brancelj, A. (2002). Black carbon in Slovenian alpine lacustrine sediments. *Chemosphere*, *46*(8), 1225-1234.

Murillo, J. H., Roman, S. R., Marín, J. F. R., & Cardenas, B. (2013). Source apportionment of PM2. 5 in the metropolitan area of Costa Rica using receptor models. *Atmospheric and Climate Sciences*, *3*(04), 562.

N. Raza, S. B. Niazi, M. Sajid, F. Iqbal, and M. Ali, "Studies on relationship between season and inorganic elements of Kallar Kahar Lake (Chakwal), Pakistan," *Journal of Research (Science), Bahauddin Zakariya University*, vol. 18, pp. 61–68, 2007.

Nagajyoti, P. C., Lee, K. D., & Sreekanth, T. V. M. (2010). Heavy metals, occurrence and toxicity for plants: a review. *Environmental Chemistry Letters*, *8*(3), 199-216.

Nawaz, M. F., & Shafique, M. M. (2003). Data integration for flood risk analysis by using GIS/RS as tools.

Nazeer, S., Hashmi, M. Z., & Malik, R. N. (2014). Heavy metals distribution, risk assessment and water quality characterization by water quality index of the River Soan, Pakistan. *Ecological indicators*, *43*, 262-270.

Nguyen, H. L., Leermakers, M., Osán, J., Török, S., & Baeyens, W. (2005). Heavy metals in Lake Balaton: water column, suspended matter, sediment and biota. Science of the Total Environment, 340(1), 213-230.

Nguyen, T. H., Brown, R. A., & Ball, W. P. (2004). An evaluation of thermal resistance as a measure of black carbon content in diesel soot, wood char, and sediment. *Organic Geochemistry*, *35*(3), 217-234.

Nicholson, F. A., Smith, S. R., Alloway, B. J., Carlton-Smith, C., & Chambers, B. J. (2003). An inventory of heavy metals inputs to agricultural soils in England and Wales. *Science of the total environment*, *311*(1), 205-219.

Nogawa, K. (1981). Itai-itai disease and follow-up studies. *JOHN WILEY & SONS, INC., 605 THIRD AVE., NEW YORK, NY 10158.*, 1-37.

Nouri, J., Lorestani, B., Yousefi, N., Khorasani, N., Hasani, A. H., Seif, F., & Cheraghi, M. (2011). Phytoremediation potential of native plants grown in the vicinity of Ahangaran lead–zinc mine (Hamedan, Iran). *Environmental Earth Sciences*, *62*(3), 639-644.

Nriagu, J. O. (1996). A history of global metal pollution. *Science*, *272*(5259), 223.

NSDWQ. (2008). *National Standards for Drinking Water Quality*. Pakistan Environmental Protection Agency, Ministry of Environment, Islamabad: Government of Pakistan

Ochieng, E. Z., Lalah, J. O., & Wandiga, S. O. (2008). Water quality and trace metal distribution in a Pristine Lake in the Lake Basin in Kenya. Bulletin of environmental contamination and toxicology, 80(4), 362-368.

Oecd, O. E. C. D. (1994). Guidelines for the Testing of Chemicals. *Organization for Economic*.

Olivares-Rieumont, S., De la Rosa, D., Lima, L., Graham, D. W., Katia, D., Borroto, J., ... & Sánchez, J. (2005). Assessment of heavy metal levels in Almendares River sediments—Havana City, Cuba. *Water Research*, *39*(16), 3945-3953.

Osman, A. G., & Kloas, W. (2010). Water quality and heavy metal monitoring in water, sediments, and tissues of the African catfish Clarias gariepinus (Burchell, 1822) from the river Nile, Egypt. *Journal of Environmental Protection*, *1*(04), 389.

Ouhadi, V. R., & Goodarzi, A. R. (2007). Factors impacting the electro conductivity variations of clayey soils. *Iranian Journal of Science and Technology*, *31*(B2), 109.

Ozkan, E. Y., & Buyukisik, B. (2012). Geochemical and statistical approach for assessing heavy metal accumulation in the southern Black Sea sediments. *Ekoloji*, *21*(83), 11-24.

Pacyna, E. G., Pacyna, J. M., Fudala, J., Strzelecka-Jastrzab, E., Hlawiczka, S., Panasiuk, D., ... & Friedrich, R. (2007). Current and future emissions of selected heavy metals to the atmosphere from anthropogenic sources in Europe. *Atmospheric Environment*, *41*(38), 8557-8566.

Pagotto, C., Remy, N., Legret, M., & Le Cloirec, P. (2001). Heavy metal pollution of road dust and roadside soil near a major rural highway. *Environmental Technology*, *22*(3), 307-319.

Pak, E. P. A. (2006). Environmental survey of industrial estate (I-9 & I-10) Islamabad. *PAK EPA, Islamabad*.

Pakistan Water and Power Development Authority. (2016). Neelum Jhelum Hydropower Project's first unit to be commissioned in June 2017 Lahore – January 21, 2016.

Patel, M. M., Hoepner, L., Garfinkel, R., Chillrud, S., Reyes, A., Quinn, J. W., ... & Miller, R. L. (2009). Ambient metals, elemental carbon, and wheeze and cough in New York City children through 24 months of age. American journal of respiratory and critical care medicine, 180(11), 1107-1113.

Pekey, H. (2006). The distribution and sources of heavy metals in Izmit Bay surface sediments affected by a polluted stream. *Marine Pollution Bulletin*, *52*(10), 1197-1208.

Perona, E., Bonilla, I., & Mateo, P. (1999). Spatial and temporal changes in water quality in a Spanish river. *Science of the Total Environment*, *241*(1), 75-90.

Petersen, G., Munthe, J., Pleijel, K., Bloxam, R., & Kumar, A. V. (1998). A comprehensive Eulerian modeling framework for airborne mercury species: Development and testing of the tropospheric chemistry module (TCM). *Atmospheric Environment*, *32*(5), 829-843.

Phan, K., Sthiannopkao, S., Heng, S., Phan, S., Huoy, L., Wong, M. H., & Kim, K. W. (2013). Arsenic contamination in the food chain and its risk assessment of populations residing in the Mekong River basin of Cambodia. *Journal of hazardous materials*, *262*, 1064-1071.

Planchon, F. A., Boutron, C. F., Barbante, C., Cozzi, G., Gaspari, V., Wolff, E. W., ... & Cescon, P. (2002). Changes in heavy metals in Antarctic snow from Coats Land since the mid-19th to the late-20th century. *Earth and Planetary Science Letters*, *200*(1), 207-222.

Poot, A., Quik, J. T., Veld, H., & Koelmans, A. A. (2009). Quantification methods of Black Carbon: Comparison of Rock-Eval analysis with traditional methods. *Journal of Chromatography A*, *1216*(3), 613-622.

Portier, K. M. (2001). Statistical issues in assessing anthropogenic background for arsenic. *Environmental Forensics*, *2*(2), 155-160.

Pueyo, M., Sastre, J., Hernandez, E., Vidal, M., Lopez-Sanchez, J. F., & Rauret, G. (2003). Prediction of trace element mobility in contaminated soils by sequential extraction. *Journal of Environmental Quality*, *32*(6), 2054-2066.

Qiu, J. (2008). China: the third pole. *Nature News*, *454*(7203), 393-396.

Raymond, A., Okieimen, E., & Okieimen, F. E. (2011). Heavy metal in contaminated soils. *International Scholarly Research Network ISRN Ecology*.

Redman, A. D., Macalady, D. L., & Ahmann, D. (2002). Natural organic matter affects arsenic speciation and sorption onto hematite. *Environmental Science & Technology*, *36*(13), 2889-2896.

Rehman, I. H., Ahmed, T., Praveen, P. S., Kar, A., & Ramanathan, V. (2011). Black carbon emissions from biomass and fossil fuels in rural India. *Atmospheric Chemistry and Physics*, *11*(14), 7289-7299.

Reiners, W. A., Marks, R. H., & Vitousek, P. M. (1975). Heavy metals in subalpine and alpine soils of New Hampshire. *Oikos*, 264-275.

Reporter, S., 2008. A special report on India: Creaking, groaning: Infrastructure is India's biggest handicap". . The Economist .December 11, 2008.

Saeed, S. M., & Shaker, I. M. (2008, October). Assessment of heavy metals pollution in water and sediments and their effect on Oreochromis niloticus in the northern delta lakes, Egypt. In 8th International Symposium on Tilapia in Aquaculture (Vol. 2008, pp. 475-490).

Saeedi, M., Hosseinzadeh, M., Jamshidi, A., & Pajooheshfar, S. P. (2009). Assessment of heavy metals contamination and leaching characteristics in highway side soils, Iran. *Environmental monitoring and assessment*, *151*(1), 231-241.

Sakan, S., Đorđević, D., Dević, G., Relić, D., Anđelković, I., & Đuričić, J. (2011). A study of trace element contamination in river sediments in Serbia using microwave-assisted aqua regia digestion and multivariate statistical analysis. Microchemical Journal, 99(2), 492-502.

Saleem, M., Aftab, J., Hasaney, S. I., Kahkishan, S., Haider, S. W., & Muzaffar, M. (2014). Toxicity levels, Ecological risk assessment of Heavy metals and distribution in the

surface sediment of Hub River, Hub River estuary and Gadani coast, Baluchistan, Pakistan.

Saleem, M., Iqbal, J., Shah, M.H., (2013). Study of seasonal variations and risk assessment of selected metals in sediments from Mangla Lake, Pakistan. Journal of Geochemical Exploration 125, 144-152.

Salma, S. Rehman, and M. A. Shah. "Water Resources and Conservation Strategy of Pakistan." Pakistan Journal of Meteorology 9, no. 17 (2012).

Salonen, V. P., & Korkka-Niemi, K. (2007). Influence of parent sediments on the concentration of heavy metals in urban and suburban soils in Turku, Finland. *Applied Geochemistry*, *22*(5), 906-918.

Samecka-Cymerman, A., & Kempers, A. J. (2004). Toxic metals in aquatic plants surviving in surface water polluted by copper mining industry. Ecotoxicology and Environmental Safety, 59(1), 64-69.

Sawaske, S. R., & Freyberg, D. L. (2010, December). A Comparison of Past Dam Removals in Highly Sediment Impacted Systems. In *AGU Fall Meeting Abstracts*.

Schiff, K. C., & Weisberg, S. B. (1999). Iron as a reference element for determining trace metal enrichment in southern California coastal shelf sediments. *Marine Environmental Research*, *48*(2), 161-176.

Schmidt, M. W., & Noack, A. G. (2000). Black carbon in soils and sediments: analysis, distribution, implications, and current challenges. *Global biogeochemical cycles*, *14*(3), 777-793.

Schumm, S. A. (1985). Patterns of alluvial rivers. *Annual Review of Earth and Planetary Sciences*, *13*(1), 5-27.

Sdiri, A., Higashi, T., Chaabouni, R., & Jamoussi, F. (2012). Competitive removal of heavy metals from aqueous solutions by montmorillonitic and calcareous clays. Water, Air, & Soil Pollution, 223(3), 1191-1204.

Seshadri, B., Bolan, N. S., & Naidu, R. (2015). Rhizosphere-induced heavy metal (loid) transformation in relation to bioavailability and remediation. *Journal of soil science and plant nutrition*, *15*(2), 524-548.

Shanbehzadeh, S., Vahid Dastjerdi, M., Hassanzadeh, A., & Kiyanizadeh, T. (2014). Heavy metals in water and sediment: a case study of Tembi River. *Journal of environmental and public health*, *2014*.

Sharma, S. K., & Subramanian, V. (2010). Source and distribution of trace metals and nutrients in Narmada and Tapti river basins, India. *Environmental Earth Sciences*, *61*(7), 1337-1352.

Sheng, Y., L. C. Smith, G. M. MacDonald, K. V. Kremenetski, K. E. Frey, A. A. Velichko, M. Lee, D. W. Beilman, and P. Dubinin (2004), A highresolution GIS-based inventory of the west Siberian peat carbon pool, Global Biogeochem. Cycles, 18, GB3004

Sheykhi, V., Moore, F., & Kavousi-Fard, A. (2015). Combining self-organizing maps with WQI and PCA for assessing surface water quality–a case study, Kor River, southwest Iran. International Journal of River Basin Management, 13(1), 41-49.

Shi, G., Chen, Z., Xu, S., Zhang, J., Wang, L., Bi, C., & Teng, J. (2008). Potentially toxic metal contamination of urban soils and roadside dust in Shanghai, China. *Environmental Pollution*, *156*(2), 251-260.

Shikazono, N., Tatewaki, K., Mohiuddin, K. M., Nakano, T., & Zakir, H. M. (2012). Sources, spatial variation, and speciation of heavy metals in sediments of the Tamagawa River in Central Japan. *Environmental Geochemistry and Health*, *34*(1), 13-26.

Shomar, B. H., Müller, G., & Yahya, A. (2005). Geochemical features of topsoils in the Gaza Strip: natural occurrence and anthropogenic inputs. Environmental Research, 98(3), 372-382.

Shotyk, W., Weiss, D., Kramers, J. D., Frei, R., Cheburkin, A. K., Gloor, M., & Reese, S. (2001). Geochemistry of the peat bog at Etang de la Gruère, Jura Mountains, Switzerland, and its record of atmospheric Pb and lithogenic trace metals (Sc, Ti, Y, Zr, and REE) since 12,370 14 C yr BP. *Geochimica et Cosmochimica Acta*, *65*(14), 2337-2360.

Shrestha, S., & Kazama, F. (2007). Assessment of surface water quality using multivariate statistical techniques: A case study of the Fuji river basin, Japan. *Environmental Modelling & Software*, *22*(4), 464-475.

Siddique, A., Mumtaz, M., Zaigham, N. A., Mallick, K. A., Saied, S., Zahir, E., & Khwaja, H. A. (2009). Heavy metal toxicity levels in the coastal sediments of the Arabian Sea along the urban Karachi (Pakistan) region. *Marine pollution bulletin*, *58*(9), 1406-1414.

Singh, A., Sharma, R. K., Agrawal, M., & Marshall, F. M. (2010). Risk assessment of heavy metal toxicity through contaminated vegetables from waste water irrigated area of Varanasi, India. *Tropical Ecology*, *51*(2), 375-387.

Singh, K. P., Malik, A., Sinha, S., Singh, V. K., & Murthy, R. C. (2005). Estimation of source of heavy metal contamination in sediments of Gomti River (India) using principal component analysis. *Water, Air, & Soil Pollution*, *166*(1), 321-341.

Singh, M. (2001). Heavy metal pollution in freshly deposited sediments of the Yamuna River (the Ganges River tributary): a case study from Delhi and Agra urban centres, India. *Environmental Geology*, *40*(6), 664-671.

Smith, D. R., Owens, P. R., Leytem, A. B., & Warnemuende, E. A. (2007). Nutrient losses from manure and fertilizer applications as impacted by time to first runoff event. *Environmental Pollution*, *147*(1), 131-137.

Snoeyink, V. L., & Jenkins, D. (1980). *Water chemistry*. Wiley.

Sofowote, U. M., McCarry, B. E., & Marvin, C. H. (2008). Source apportionment of PAH in Hamilton Harbour suspended sediments: comparison of two factor analysis methods. Environmental Science & Technology, 42(16), 6007-6014.

Song, Y., Ji, J., Yang, Z., Yuan, X., Mao, C., Frost, R. L., & Ayoko, G. A. (2011). Geochemical behavior assessment and apportionment of heavy metal contaminants in the bottom sediments of lower reach of Changjiang River. *Catena*, *85*(1), 73-81.

Standard, A. S. T. M. (2010). Standard practice for classification of soils for engineering purposes (Unified Soil Classification System). In *Annual Book of ASTM Standards*. ASTM, International West Conshohocken, PA.

Steinnes, E., & Friedland, A. J. (2006). Metal contamination of natural surface soils from long-range atmospheric transport: existing and missing knowledge. Environmental Reviews, 14(3), 169-186.

Streets, D. G., Bond, T. C., Carmichael, G. R., Fernandes, S. D., Fu, Q., He, D., ... & Woo, J. H. (2003). An inventory of gaseous and primary aerosol emissions in Asia in the year 2000. *Journal of Geophysical Research: Atmospheres*, *108*(D21).

Su, L., Shi, X., Guo, G., Zhao, A., & Zhao, Y. (2013). Stabilization of sewage sludge in the presence of nanoscale zero-valent iron (nZVI): abatement of odor and improvement of biogas production. *Journal of Material Cycles and Waste Management*, *15*(4), 461-468.

Szymanowska, A., Samecka-Cymerman, A., & Kempers, A. J. (1999). Heavy metals in three lakes in West Poland. Ecotoxicology and Environmental Safety, 43(1), 21-29.

Tang, W., Shan, B., Zhang, H., Zhang, W., Zhao, Y., Ding, Y., ... & Zhu, X. (2014). Heavy metal contamination in the surface sediments of representative limnetic ecosystems in eastern China. *Scientific reports*, *4*.

Taylor, S. R. (1964). Trace element abundances and the chondritic earth model. Geochimica et cosmochimica acta, 28(12), 1989-1998.

Tchobanoglous, G., & Schroeder, E. D. (1987). Water Quality: Characteristics..

Turekian, K. K., & Wedepohl, K. H. (1961). Distribution of the elements in some major units of the earth's crust. Geological Society of America Bulletin, 72(2), 175-192.

Tüzen, M. (2003). Determination of heavy metals in soil, mushroom and plant samples by atomic absorption spectrometry. *Microchemical Journal*, *74*(3), 289-297.

Ulbrich, K., Marsula, R., Jeltsch, F., Hofmann, H., & Wissel, C. (1997). Modelling the ecological impact of contaminated river sediments on wetlands. Ecological modelling, 94(2-3), 221-230.

UNEP World Conservation Monitoring Centre, & Census of Marine Life on Seamounts (Programme). Data Analysis Working Group. (2006). *Seamounts, deep-sea corals and fisheries: vulnerability of deep-sea corals to fishing on seamounts beyond areas of national jurisdiction* (No. 183). UNEP/Earthprint.

Valdiya, K. S. (2001). *Himalaya: emergence and evolution*. Universities Press.

Varol, M. (2013). Dissolved heavy metal concentrations of the Kralkızı, Dicle and Batman dam reservoirs in the Tigris River basin, Turkey. Chemosphere, 93(6), 954-962.

Waheed, S., Malik, R. N., & Jahan, S. (2013). Health risk from As contaminated fish consumption by population living around River Chenab, Pakistan. *Environmental toxicology and pharmacology*, *36*(2), 579-587.

Wang, H., Bi, N., Saito, Y., Wang, Y., Sun, X., Zhang, J., & Yang, Z. (2010). Recent changes in sediment delivery by the Huanghe (Yellow River) to the sea: causes and environmental implications in its estuary. *Journal of Hydrology*, *391*(3), 302-313.

Wang, S. X., Wang, Z. H., Cheng, X. T., Li, J., Sang, Z. P., Zhang, X. D., & Wang, Z. Q. (2007). Arsenic and fluoride exposure in drinking water: children's IQ and growth in Shanyin county, Shanxi province, China. *Environmental health perspectives*, 643-647.

Wang, S., Fu, B., Piao, S., Lü, Y., Ciais, P., Feng, X., & Wang, Y. (2015). Reduced sediment transport in the Yellow River due to anthropogenic changes. *Nature Geoscience*.

Wania, F., (2003). Assessing the potential for persistent organic chemicals for long-range transport and accumulation in polar regions. Environmental Science and Technology37 (7), 1344–1351.

Wanklyn JA & Chapman ET 1868, Water Analysis: Practical Treatise on the Examination of Potable Water, Trübner & Co., London

Wetzel, R. G. (2001). *Limnology: lake and river ecosystems*. Gulf Professional Publishing.

Wierzbicka, A., Lillieblad, L., Pagels, J., Strand, M., Gudmundsson, A., Gharibi, A., ... & Bohgard, M. (2005). Particle emissions from district heating units operating on three commonly used biofuels. *Atmospheric Environment*, *39*(1), 139-150.

Wilcox, A. C., O'Connor, J. E., & Major, J. J. (2014). Rapid reservoir erosion, hyperconcentrated flow, and downstream deposition triggered by breaching of 38 m tall Condit Dam, White Salmon River, Washington. *Journal of Geophysical Research: Earth Surface*, *119*(6), 1376-1394.

Wireman, M. (2012, May). The Occurrence of Nitrate in Groundwater and the Connection to Nutrient Loading to Surface Water. In *2012 NGWA Ground Water Summit: Innovate and Integrate*. Ngwa.

World Health Organization guidelines for drinking water quality.(2006). Cryptosporidium." *WHO, New York* 138

World Health Organization. (2006). *Air quality guidelines: global update 2005: particulate matter, ozone, nitrogen dioxide, and sulfur dioxide*. World Health Organization.

Wu, J., & Loucks, O. L. (1995). From balance of nature to hierarchical patch dynamics: a paradigm shift in ecology. *The Quarterly review of biology*, *70*(4), 439-466.

Xu, J., Grumbine, R. E., Shrestha, A., Eriksson, M., Yang, X., Wang, Y. U. N., & Wilkes, A. (2009). The melting Himalayas: cascading effects of climate change on water, biodiversity, and livelihoods. *Conservation Biology*, *23*(3), 520-530.

Yang, L. X., Wang, D. C., Cheng, S. H., Wang, Z., Zhou, Y., Zhou, X. H., & Wang, W. X. (2007). Influence of meteorological conditions and particulate matter on visual range impairment in Jinan, China. *Science of the Total Environment*, *383*(1), 164-173.

Yang, Y., Fang, J., Tang, Y., Ji, C., Zheng, C., He, J., & Zhu, B. (2008). Storage, patterns and controls of soil organic carbon in the Tibetan grasslands. *Global Change Biology*, *14*(7), 1592-1599.

Yang, Z. S., Wang, H. J., Saito, Y., Milliman, J. D., Xu, K., Qiao, S., & Shi, G. (2006). Dam impacts on the Changjiang (Yangtze) River sediment discharge to the sea: The past 55 years and after the Three Gorges Dam. Water Resources Research, 42(4).

Yuan, H. Z., Shen, J., Liu, E. F., Wang, J. J., & Meng, X. H. (2011). Assessment of nutrients and heavy metals enrichment in surface sediments from Taihu Lake, a eutrophic shallow lake in China. *Environmental geochemistry and health*, *33*(1), 67-81.

Z. Ullah, H. Khan, A. Waseem, Q. Mahmood, and U. Farooq, "Water quality assessment of the River Kabul at Peshawar, Pakistan: industrial and urban wastewater impacts," *Journal of Water Chemistry and Technology*, vol. 35, pp. 170–176, 2013.

Zdorikov, N. N., Karpov, O. V., Maksimov, I. I., Seiku, E. E., & Sobol', V. V. (1998). State primary standard for the pH scale. *Measurement techniques*, *41*(6), 499-503.

Zhai, H., Cui, B., Hu, B., & Zhang, K. (2010). Prediction of river ecological integrity after cascade hydropower dam construction on the mainstream of rivers in Longitudinal Range-Gorge Region (LRGR), China. *Ecological Engineering*, *36*(4), 361-372.

Zhang, F., Yan, X., Zeng, C., Zhang, M., Shrestha, S., Devkota, L. P., & Yao, T. (2012). Influence of traffic activity on heavy metal concentrations of roadside farmland soil in mountainous areas. International journal of environmental research and public health, 9(5), 1715-1731.

Zhang, L., Ye, X., Feng, H., Jing, Y., Ouyang, T., Yu, X., ... & Chen, W. (2007). Heavy metal contamination in western Xiamen Bay sediments and its vicinity, China. *Marine pollution bulletin*, *54*(7), 974-982.

Zhang, X. Y., Lin, F. F., Wong, M. T., Feng, X. L., & Wang, K. (2009). Identification of soil heavy metal sources from anthropogenic activities and pollution assessment of Fuyang County, China. Environmental Monitoring and Assessment, 154(1), 439-449.

Zheng, N., Liu, J., Wang, Q., & Liang, Z. (2010). Health risk assessment of heavy metal exposure to street dust in the zinc smelting district, Northeast of China. *Science of the Total Environment*, *408*(4), 726-733

Zhiyuan, W., Dengfeng, W., Huiping, Z., & Zhiping, Q. I. (2011). Assessment of soil heavy metal pollution with principal component analysis and geoaccumulation index. Procedia Environmental Sciences, 10, 1946-1952.

Appendix1

International reported studies for heavy metal pollution in surface water

Location	Matrices	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Zn	References
Danjiangkou Reservoir, China	Water	0.00117	0.00629	0.01332	0.01	0.005	0.00173	0.01059	0.002	(Li et al., 2008)
Kainji Dam, Nigeria	Water	NR	0.0022	0.0013	0.013	0.009	0.0009	0.0012	0.009	(Oyewale and Musa, 2006)
Lake Gilow, Poland	Water	0.0058	0.0009	0.048	0.006	0.39	0.076	0.0005	0.167	(Cymerman and Kempers, 2004)
Kanyaboli Lake, Kenya	Water	0.0044	0.02154	0.02395	NR	0.28427	0.01638	0.02065	0.032	(Ochieng et al., 2008)
Manchar Lake, Pakistan	Water	0.0053	0.00764	0.0189	2.96	0.0726	0.035	0.0824	0.73	(Kazi et al. 2009)
Kralkızı Dam Reservoir, Turkey	Water	0.0036	0.02206	0.00283	0.05863	NR	0.01575	0.00256	0.00502	(Varol, 2013)
Dicle Dam Reservoir, Turkey	Water	0.003	0.01858	0.00212	0.06207	NR	0.01586	0.00184	0.004	(Varol, 2013)
Batman Dam Reservoir, Turkey	Water	0.0044	0.0165	NR	0.05766	NR	0.01596	0.00156	0.004	(Varol, 2013)
Northern Delta Lakes, Egypt	Water	0.019	NR	0.186	0.804	0.244	NR	0.064	0.177	(Saeed and Shakir, 2008)
Lake Manzala, Egypt	Water	NR	NR	0.19	3.2	NR	NR	0.11	1.37	(Elghobashy et al., 2001)
Beijing/China	Soil	0.15	35.6	23.7	NR	NR	27.8	28.6	65.6	(Zheng et al., 2008)
Khathmando Nepal	Soil	0.36	NR	19.99	NR	NR	NR	22.57	76.3	(Zhang et al., 2012)
Shanghai/China	Soil	0.52	107.9	59.25	NR	NR	31.14	70.69	301.43	(Guitao Shi et al., 2008)
Yanqi, Xinjiang/ China	Soil	0.19	51.27	18.56	NR	491.65	21.56	29.25	61.29	(Mamat et al., 2014)
Yuanyang county, China	Soil	2.47	62.27	NR	NR	NR	NR	43.19	NR	(Zhang et al., 2012)
Mount Gonga, TP, China	Soil	NR	NR	NR	44mg/g	843	NR	NR	NR	(Bing et al., 2014)
Tehran–Karaj Highway, Iran	Soil	3.9	47.98	NR	NR	899.89	90.32	669.3	614.312	(Saeedi et al., 2009)
Heihe River TP, China	Soil	2.93	57.29	56.38	NR	818.84	70.22	37.335	178.68	(Bu et al., 2016)
Gediz River, Turkey	Sediments	NR	170–220	108–152	NR	NR	101–129	105–140	NR	(Akcay et al., 2003)
Almemdares River, Cuba	Sediments	2.5	138	158	NR	NR	NR	93	262	(Rieumount et al., 2005)
River Ganges, India	Sediments	0.14–1.4	1.8–6.4	0.98–4.4	NR	NR	NR	4.3–8.4	NR	(Gupta et al., 2009)
Aswan, River Nile, Egypt	Sediments	0.4	8.8	0.03	397.053	210.36	NR	3.1	101.1	(Osman and Kloas., 2010)
Beni Suef, River Nile, Egypt	Sediments	0.6	10.3	0.027	536.5	221.72	NR	11.5	126.6	(Osman and Kloas., 2010)
South east Coastal Rivers	Sediments	0.925	142	54.7	NR	NR	60.5	61.9	192	(Tang et al., 2014)
Tembi River, Iran	Sediments	24	42	49	230	302	129	151	32	(Shanbehzade et al., 2014)
Korotoa, Bangladesh	Sediments	1.2	109	76	NR	NR	95	58	NR	(Islam et al., 2015)

Appendix 1.1

Reported studies from Pakistan for heavy metal pollution in surface water

Surface water	Matrix	Zn	Cu	Fe	Mn	Cd	Cr	Ni	Pb	References
Kabul River	Water	0.07	NR	1.1	NR	0.03	NR	0.2	0.52	(Ullah et al., 2013)
Palosi Drain	Water	0.12	NR	1.12	0.12	0.004	NR	0.18	0.34	(Ilyas and sarwar, 2003)
Malir River	Water	0.16	0.31	0.78	0.33	0.04	0.1	0.59	0.19	(Haq et al., 2005)
Phulali Kanal	Water	0.17	0.063	1.45	0.59	0.004	0.0082	0.005	0.026	(Wattoo et al., 2006)
Manchar Lake	Water	0.016	0.009	0.012	NR	0.001	NR	0.004	0.009	(Mastoi et al., 2008)
Kalar Kahar, Lake	Water	2.84	1.2	5.46	NR	0.05	NR	0.25	0.3	(Razaet al. 2007)
Warsak Dam	Water	0.08	0.042	NR	NR		0.05	0.012	0.009	(Yousafzai et al., 2008)
Jhelum River	Water	0.02	1.22	2	0.07	0.4	0.23	2.67	0.4	(Khan et al., 2010)
Soan River	Water	0.09	0.24	0.4	0.16	0.1	0.11	0.42	1.1	(Nazeer et al., 2014)
Khanpur lake	Water	15 (µg/L)	9 (µg/L)	51 (µg/L)	11 (µg/L)	20 (µg/L)	46 (µg/L)	NR	221 (µg/L)	(Iqbal and Shah, 2013)
Rawal Lake	Water	22 (µg/L)	17 (µg/L)	76 (µg/L)	13 (µg/L)	25 (µg/L)	97 (µg/L)	NR	126 (µg/L)	(Iqbal and Shah, 2013)
HingolRiver, Balochistan	Water	1.6	0.02	0.53	0.4	NR	0.0025	1.5	1.4	(Khan et al., 2014)
Mangla Lake	Water	0.0117	0.0137	0.109	0.0189	0.0183	0.103	0.124	0.129	(Saleem et al. 2015)
Mangla lake	Water	0.03	0.02	0.13	0.02	0.03	0.07	0.11	0.34	(Saleem et al. 2014)
River Ravi	Sediment	NR	64.09 (µg/g)	NR	NR	2.16 (µg/g)	53.93 (µg/g)	NR	NR	(Rauf et al., 2009)
Mahmiid, Booti	Sediment	NR	26.6 (µg/g)	NR	NR	2.09 (µg/g)	29.9 (µg/g)	NR	NR	(Rauf et al., 2009)
Hudiara Drain,	Soil	24.9	9.41	51.44	27.3	0.61	0.002	1.07	3.75	(Kashif et al., 2009)
River Chenab	Water	NR	NR	NR	NR	NR	20.72 (µg/g)	NR	NR	(Azmat, 2016)
River Chenab	Sediment	NR	NR	NR	NR	NR	76.39 (µg/g)	NR	NR	(Azmat, 2016)
Baloki head works	Water	0.48	0.37	2.06	NR	NR	0.136	0.075	NR	(Tabinda et al., 2013)

Appendix 1.2

Table: Properties of metals (Lenntech, 2004) and (ASTDR, 2008)

Metal	Chemical Properties	Anthropogenic source	Health Impact	Crustal values
Cadmium	Atomic no. 48 Atomic Mass 112.41g/mol Density 8.65g/cm^3 at 20 °C	Used in manufacturing of alloys, pigments and batteries. Cigarette smoke and Tobacco	Damage pulmonary functions, gastrointestinal irritant, carcinogen and cause chronic osteoporosis	0.41mg/kg
Chromium	Atomic no. 24 Atomic Mass 7.19 g/mol Density 7.19 g/cm^3 at 20 °C	Used in tanning of leather, chrome pigment production, wood preservation and stainless steel welding	Carcinogen, nose irritant, cardiovascular diseases, renal and hepatic damages, nose and stomach ulcers	60mg/kg
Lead	Atomic no. 82 Atomic Mass 207 g/mol Density 11 g/cm^3 at 20 °C	Fossil fuel burning, Used in production of lead acid batteries, metallic products, X-ray shielding instruments, ceramics and paints	Damages the central nervous system, respiratory tract problem and harmful for reproduction system. Chronic exposure induces carcinogenicity and renal diseases	27mg/kg
Manganese	Atomic no. 25 Atomic Mass 54.9g/mol Density 7.44 g/cm^3 at 20 °C	Industrial waste, microbial action on manganese minerals at low Eh, tire wear	Headaches, lung diseases, Parkinson's disease and insomnia, skeletal disorders	448mg/kg
Copper	Atomic no. 29 Atomic Mass 63.5 g/mol Density 8.92 g/cm^3	Metal plating, industrial and domestic wastes, plumbing, tire abrasion, guns	Hepatic and renal damages, nose irritation loss of intelligence metal fever.	38.9mg/kg
Zinc	Atomic no. 30 Atomic Mass 65.38 g/mol Density 7.13 g/cm^3 at 20 °C	Industrial wastes, metal plating, plumbing, galvanizing steel, alloys	Damage pancreas, cause metal fever due to oversensitivity of workers, disturbs protein metabolism	70mg/kg
Nickel	Atomic no. 28 Atomic Mass 58.69 g/mol Density 8.90 g/cm^3 at 20 °C	Alloys, chemical manufacturing, nickel-steels (particularly stainless steel), corrosion of cars	Heart diseases, asthma, bronchitis, birth defects, lung embolism	29mg/kg
Iron	Atomic no. 26 Atomic Mass 55.8 g/mol Density 7.87 g/cm^3 at 20 °C	Corroded metal, industrial wastes, low Eh water in contact with iron minerals, brake pads	Conjunctivitis and siderosis, increases risk of lung cancer	3.5%

Appendix 2.1

Table: Sampling sites according to sampling strategy with climatic data

Sampling Zone	Sampling Site	Code	Latitude Decimal degree	Longitude Decimal degree	Precipitation mm/yr	Temperature ^{o}C	Humidity %
Neelum River	Taobat	N1	34.7266	74.71228	1166	2	60.6
	Kel	N2	34.82228	74.36408	1230	3	63.5
	Karen	N3	34.67721	73.96028	1486	9.8	61.9
	Athmuqam	N4	34.58414	73.90377	1657	14	60.2
	Nausadda	N5	34.40756	73.7139	1902	19.7	60.8
	Pattika	N6	34.45264	73.54899	1940	14.5	58.4
	Ghori	N7	34.44056	73.49722	1767	18	58.0
Jhelum River	Chinari	J1	34.15817	73.82743	1719	15.6	57.4
	Hattian Bala	J2	34.17137	73.74392	1717	16.4	57.9
	Garhi Dupatta	J3	34.22635	73.61579	1733	22.3	58.1
	Thota	J4	34.25639	73.58284	1733	24	59.3
	Langarpura	J5	34.3062	73.54293	1792	25	58.9
	Domail	J6	34.3546	73.46786	1641	22	57.8
	Dolai	J7	34.24388	73.4773	1577	17	58.3
	Kalas	J8	34.20689	73.49872	1655	14	59.0
	Shahdara	J9	34.15696	73.49479	1530	17.9	58.3
	Kohala	J10	34.09674	73.49828	1355	26	53.1
	Johlailal Birote	J11	34.01981	73.50505	1665	14.5	56.8
	Tain Dhalkot	J12	33.91512	73.5764	1590	12.3	54.3
	Mang	J13	33.74954	73.59884	1518	11	52.9
	Pona	J14	33.69417	73.59314	1460	16.5	52.5
	Nawan	J15	33.53589	73.63817	1219	21	49.2
	Banndi	J16	33.49478	73.60297	861	22	48.6
	Balathi	J17	33.32612	73.5999	679	20	45.0
Mangla Dam	Salmotha	D1	33.30109	73.66401	663	18.6	45.9
	Khadamabad	D2	33.34054	73.75435	617	19	45.7
	Roopyaal	D3	33.24916	73.74369	652	15.4	45.6
	Kakra Town	D4	33.12467	73.87866	629	10.5	46.4
	Mirpur Bypass	D5	33.16283	73.76475	640	12	45.1
	Kharuk	D6	33.1984	73.70861	644	18	46.3
	Mangla road	D7	33.14007	73.67535	565	14	44.3
	Pali	D8	33.18672	73.63924	586	9.5	44.7

Appendix 2.2

Table. Contamination indices

a. Enrichment factor (Saleem et al., 2013)

EF	Class	Status
0 to <1	1	No enrichment
1 to 3	2	Minor enrichment
3 to 5	3	Moderate enrichment
5 to 10	4	Moderate to severe enrichment
10 to 25	5	Severe enrichment
25 to 50	6	Very severe enrichment
>50	7	Extremely severe enrichment

b. Geo accumulation Index (Muller, 1981)

I geo (grading)	Class	Quality of soil/sediment
Igeo>0	1	Not contaminated
0>Igeo>1	2	No to moderate level contaminated
1>Igeo>2	3	Moderately contaminated
2>Igeo>3	4	Moderate to strongly contaminated
3>Igeo>4	5	Strongly contaminated
4>Igeo>5	6	Strong to very strongly contaminated
5>Igeo	7	Very strongly contaminated

c. Metal Pollution Index (Caerio et al., 2005)

MPI	Classification	Quality of Water
<0.3	1	Very pure
0.3-1.0	2	Pure
1.0-2.0	3	Slightly affected
2.0-4.0	4	Moderately affected
4.0-6.0	5	Strongly affected
>6.0	6	Seriously affected

Appendix 3.1

Table: Heavy metals concentration (mg/kg)

a) Soil

	Pb	Zn	Cu	Mn	Cr	Fe (%)	Cd	Ni
Zone 1								
Taobat	17	25.915	16	21	15	2.1352	1.59	32
Kel	20	87.53	15	17	7.65	2.4592	0.01	35.27
Karen	25	18.665	23	25.75	9.65	1.2221	0.08	14.5
Athmuqam	40	32.45	21	27	4.87	2.2579	2.5	37.5
Tain Dhalkot	24.9	28.678	2.05	14.8	13.04	2.58	1.25	26.79
Zone 2								
Chinari	27.5	10.55	18	28.9	5	2.77	1.23	15.65
Birote	6.62	28.46	3	13.33	13	2.19	2.2	41.02
Kalas	15	5.575	5.68	27.75	11	2.114	1	12.55
Nausadda	27	15.68	10.09	18	8	1.192	3.5	21
Zone 3								
Hattian Bala	30	28.915	6.2	15	5.97	2.5463	1.07	32
Shahdara	17.5	49.305	5	18	10	2.024	1.03	31.4
Mang	21.56	20	12	5	10.09	2.2196	3.4	25.934
Garhi Dupatta	19.5	22.79	2.3	17.19	12	2.12	0.02	11.5
Domail	31	40.5	1.67	14	15.32	2.7086	1.5	34.05
Dolai	12.5	51.375	13	11	12	2.6877	2	21
Thota	15	77.44	10	12	19	2.122	1.05	20.28
Zone 4								
Pattika	35	60.19	7.43	11.5	6	2.2055	0.25	18
Pona	27	12	0.05	10	12	2.2845	2	37.75
Langarpura	23	17.25	15	25.29	19.75	2.167	0.05	18.07
Ghori	18.5	39.38	19.55	20.64	2.11	1.8952	3.08	10.96
Nawan	22.45	74	1.4	11	17.8	2.29	1.15	13.6
Kohala	20.5	25	12	23	14.5	2.598	1.05	30.64
Banndi	30	31.77	7	4.67	15	2.15	1.3	23.4
Balathi	12.5	78.96	16	1.32	20	1.9758	0.05	29.87
Zone 5								
Salmotha	28	27.33	4.2	8	17.15	2.199	1	13.67
Kakra Town	25	10.84	6	17	26	2.6425	1.35	36
Roopyaal	25.61	21.5	10	1.05	25.79	2.77	0.05	21.9
Khadamabad	18.95	33.2	15	0.8	19	1.85	1.57	15
Mirpur Bypass	27.5	18.19	8	4.49	21	2.076	2.5	39.86
Kharuk	30	25.845	3	23	27.63	2.1325	1.52	14.98
Pali	15	23.56	25	14	27	1.8446	2.5	27.45
Mangla road	24	17.65	9	8.75	18.95	1.7805	1.27	21

b) Sediments

	Pb	Zn	Cu	Mn	Cr	Fe (%)	Cd	Ni
Zone 1								
Taobat	3.7	25	5	15	21	3.1305	0.1	21
Kel	15	19	3	21	3	1.6007	0.56	17
Karen	36	33	45	30	15	1.2253	0.05	5
Athmuqam	29	10	17	27	10	1.0504	2	35
Tain								
Dhalkot	32.87	55.83	14	13	20	2.105	1	16
Zone 2								
Chinari	18	26	9.5	18	14	1.5835	1	18
Birote	43	13	15	17	2	3.979	0.8	30
Kalas	27.66	47	2	25	10	1.2687	1.1	21
Nausadda	25	21	1	12.55	27	3.5106	0.05	26.51
Zone 3								
Hattian Bala	31	65	2.8	21	12	2.2431	0.1	15
Shahdara	44	87	2.31	8	13	1.0767	1.01	22.76
Mang	28	69	40	15	4	4.7957	3	27.57
Gari Dupatta	27	18	1.78	19.28	10	1.1005	1	14
Domail	14.64	85	38	25	2	1.2201	0.4	8
Dolai	19	49	3.8	20.96	20	2.0115	0.09	15
Thota	21	12	21	47	18	1.366	0.3	30
Zone 4								
Pattika	5	15	7	18	14	3.3025	0.05	12
Pona	25	77	16	25	7	1.0662	0.5	20
Langarpura	30	25	18	40	13	1.163	0.1	18.45
Ghori	10	23.5	9.1	16	10	2.016	0.06	20.5
Nawan	33	73	18	10	9	4.1625	1.5	12
Kohala	12	68	64	34	10	1	1.2	1
Banndi	21	45	2.1	35	11	1.4433	0.08	15
Balathi	31	64	2.3	19	20	1.0172	1	11
Zone 5								
Salmotha	44	66	19	22	21	3.0405	2.5	21
Kakra Town	40	72	56	57	20	2.0008	0.4	17
Roopyaal	31	55	63	42	26	4.184	1.8	24
Khadamabad	37	84	28	71	17	2.1006	2	31
Mirpur								
Bypass	45	87	55	30	24.83	2.0985	0.8	19.8
Kharuk	34	63	35	27	22	4.0078	3.5	29
Pali	27	70	60	25	25	2.1369	1.27	34
Mangla road	35	62.96	52	48	27.57	3.0056	3.1	27

b) Water

	Zn	Pb	Cu	Mn	Cr	Fe	Cd	Ni
Zone 1								
Taobat	0.1	0.08	0.027	0.02	0.01	0.09	0.05	0.041
Kel	0.21	0.045	0.02	0.1	0.08	0.087	0.008	0.05
Karen	0.17	0.097	0.015	0.039	0.07	0.08	0.01	0.19
Athmuqam	1.11	0.14	0.09	0.05	0.038	0.05	0.06	0.047
Tain Dhalkot	0.09	0.075	0.019	0.033	0.0113	0.071	0.09	0.061
Zone 2								
Chinari	0.133	0.069	0.03	0.052	0.0171	0.093	0.04	0.013
Birote	0.0289	0.03	0.015	0.05	0.09	0.084	0.003	0.152
Kalas	0.18	0.088	0.011	0.02	0.08	0.094	0.11	0.188
Nausadda	0.237	0.058	0.03	0.055	0.01	0.17	0.07	0.013
Zone 3								
Hattian Bala	0.09	0.064	0.0133	0.01	0.0135	0.091	0.017	0.061
Shahdara	0.2	0.08	0.018	0.03	0.048	0.19	0.04	0.2
Mang	0.09	0.07	0.0198	0.04	0.091	0.062	0.089	0.14
Garhi								
Dupatta	1.3	0.12	0.029	0.06	0.09	0.14	0.009	0.015
Domail	0.194	0.081	0.015	0.018	0.0151	0.092	0.01	0.27
Dolai	0.21	0.093	0.019	0.021	0.18	0.2	0.02	0.043
Thota	0.17	0.052	0.022	12	0.13	0.177	0.12	0.058
Zone 4								
Pattika	1.1	0.065	0.011	0.037	0.027	0.1	0.01	0.351
Pona	0.068	0.13	0.0188	0.07	0.11	0.195	0.063	0.069
Langarpura	0.09	0.08	0.022	0.09	0.048	0.087	0.01	0.051
Ghori	0.087	0.25	0.018	0.05	0.15	0.2	0.054	0.38
Nawan	0.127	0.074	0.026	0.053	0.0576	0.13	0.003	0.26
Kohala	0.019	0.37	0.15	0.032	0.0162	0.275	0.004	0.024
Banndi	1.27	0.079	0.012	0.03	0.19	0.06	0.02	0.098
Balathi	0.02	0.07	0.019	0.027	0.092	0.152	0.13	0.1
Zone 5								
Salmotha	1.7	0.12	0.0191	0.033	0.18	0.261	0.06	0.358
Kakra Town	0.06	0.65	0.02	0.093	0.19	0.247	0.008	0.161
Roopyaal	0.02	0.02	0.18	0.05	0.062	0.078	0.097	0.22
Khadamabad	0.035	0.07	0.06	0.01	0.016	0.28	0.005	0.13
Mirpur								
Bypass	0.8	0.8	0.0191	0.08	0.095	0.052	0.08	0.068
Kharuk	0.44	0.06	0.019	0.029	0.2	0.31	0.11	0.31
Pali	0.07	1.07	0.019	0.033	0.075	0.198	0.05	0.157
Mangla road	1	0.14	0.0179	0.078	0.094	0.09	0.025	0.061

Appendix 3.2

Table a. Chinese Screening Values in mg/kg (GB15618-1995Standards) by (Wang and Shan, 2013).

Metals	Screening Value
Zn	100
Ni	40
Cu	35
Cr	90
Cd	0.2
Pb	35

Table b. Canadian Freshwater Sediment Quality Guidelines (SQGs) in mg/kg (CCME, 2001)

Metals	SQGs
Zn	123
Ni	60
Cu	35.7
Cr	37.3
Cd	0.9
Pb	35

Table c. Comparison of measured metals values in water with national and international freshwater quality standards

Metals	Values	WHO (2008)	Pak EPA (2009)	NEQS (2010)
Cd	0.0685	0.003	0.001	0.1
Cr	0.043	0.05	0.05	1
Cu	0.032	2	2	1
Fe	0.142	…	…	8
Mn	0.08	0.1	…	1.5
Ni	0.13	0.07	0.02	1
Pb	0.3	0.01	0.05	…
Zn	0.16	3	5	5

Appendix 3.3

Table: Spatial distribution of heavy metals along altitudinal zones

a) Soil

Metal	Zones	Sig.
Pb	Z1-Z3	0.03
Cu	Z4-Z5	0.04
Cd	Z3-Z5	0.04
Ni	Z1-Z3	0.03
	Z5-Z1	0.05

b) Sediments

Metal	Zones	Sig.
Pb	Z3-Z5	0.04
	Z5-Z1	0.03
Zn	Z1-Z5	0.05
	Z1-Z3	0.05
Cu	Z1-Z2	0.04
	Z5-Z4	0.01
Mn	Z1-Z5	0.01
	Z3-Z5	0.01
	Z4-Z5	0.01
Cr	Z3-Z5	0.03
	Z4-Z5	0.01
Cd	Z1-Z5	0.05
	Z2-Z5	0.03
	Z3-Z5	0.05
	Z4-Z5	0.01
Ni	Z2-Z4	0.04
	Z4-Z5	0.01

c) Water

Metal	Zone	Sig.
Pb	Z3-Z5	0.01
Zn	Z1-Z5	0.03

Appendix 3.4

Table. Pearson's correlation analysis

a) Soil

	Pb	Zn	Cu	Mn	Cr	Fe	Cd	Ni	BC	TOC	Ele	pH	EC	Ppt	T	Hm
Pb	**1**															
Zn	**0.61**	**1**														
Cu	-0.32	0.13	**1**													
Mn	0.34	-0.20	0.09	**1**												
Cr	-0.01	0.30	0.17	**0.46**	**1**											
Fe	-0.03	0.20	**0.41**	-0.07	0.2	**1**										
Cd	**0.42**	**0.53**	-0.05	0.018	0.23	0.12	**1**									
Ni	-0.13	0.04	-0.01	-0.034	**0.4**	0.32	0.3	**1**								
BC	**0.60**	-0.05	-0.14	**0.477**	-0.10	0.25	-0.2	.01	**1**							
TOC	-0.01	0.21	0.08	-0.138	-0.05	0.06	0.03	**0.48**	0.18	**1**						
Ele	-0.06	-0.02	0.02	0.291	**-0.6**	-0.2	**0.72**	**-0.5**	**0.5**	0.17	**1**					
pH	-0.16	**0.59**	-0.09	-0.253	-0.08	0.16	-0.2	-0.01	0.18	0.23	-0.11	**1**				
EC	-0.02	0.10	-0.11	0.17	-.05	0.13	-0.1	0.086	0.07	.015	-0.04	0.16	**1**			
Ppt	**0.51**	**-0.4**	-0.22	0.21	**-0.7**	-0.04	-0.1	-0.15	0.3	0.19	**0.4**	0.3	0.1	**1**		
T	0.16	-0.2	-0.30	-0.02	.060	0.09	-0.1	0.093	0.28	-0.2	**-0.5**	0.34	0.01	.19	**1**	
Hm	-0.06	-0.19	-0.09	0.34	**-0.7**	-0.1	-0.1	-0.29	0.2	0.22	**0.7**	0.1	0.12	**0.8**	-.1	**1**

b) Sediments

	Pb	Zn	Cu	Mn	Cr	Fe	Cd	Ni	TOC	BC	Ele	EC	pH	Ppt	T	Hm
Pb	**1**															
Zn	**0.68**	**1**														
Cu	0.32	**0.40**	**1**													
Mn	0.25	0.26	**.498**	**1**												
Cr	0.06	0.13	.298	**0.47**	**1**											
Fe	0.04	0.07	.125	-.18	.253	**1**										
Cd	**0.43**	**0.36**	.348	.150	.166	**.401**	**1**									
Ni	0.28	-0.1	-.06	.107	.268	.334	**.439**	**1**								
TOC	**0.72**	-.09	**0.5**	.061	.233	-.02	.073	**.64**	**1**							
BC	**-0.51**	0.13	-.18	.119	-.29	-.22	**-.42**	-.02	**-0.5**	**1**						
Ele	**-0.40**	**-0.5**	-.17	**-.39**	-.23	-.11	-.320	-.07	-.03	-.14	**1**					
EC	0.12	0.09	.042	**.38**	.046	.103	.051	.335	.204	-.21	-.28	**1**				
pH	-.089	-0.1	-.19	-.21	-.16	.030	-.247	**-.5**	-.16	-.19	.292	-.07	**1**			
Ppt	**-.409**	**-0.5**	**-.52**	**-.47**	**.71**	-.17	**.648**	-.13	-.06	.33	**.454**	**-.64**	.27	**1**		
T	.176	0.08	-.19	.160	-.15	-.23	-.009	-.16	-.18	**.58**	**-.57**	.046	-.03	.19	**1**	
Hm	**-.49**	**-0.7**	**-.54**	**-.4**	**-.48**	-.25	**-.52**	-.13	-.05	.17	**.765**	**-.64**	.32	**.86**	.11	**1**

c) Water

	Elev	Pb	Zn	Cu	Mn	Cr	Fe	Cd	Ni	EC	pH	TDS	Pre	T
Elev	**1**													
Pb	**-0.41**	**1**												
Zn	0.06	0.16	**1**											
Cu	0.02	**-0.4**	0.06	**1**										
Mn	**0.49**	-0.18	0.28	0.15	**1**									
Cr	-0.17	**0.58**	0.15	-0.25	-0.13	**1**								
Fe	0.27	-0.13	0.22	-0.04	**0.40**	0.17	**1**							
Cd	-0.11	0.29	0.25	**-0.49**	-0.11	0.07	0.01	**1**						
Ni	-0.29	**0.39**	0.01	-0.29	-0.19	0.15	0.13	**0.42**	**1**					
EC	-0.28	0.11	0.21	0.003	**-0.41**	-0.18	-0.23	-0.15	0.13	**1**				
pH	**0.575**	0.284	**0.59**	-0.04	-0.332	0.104	-0.20	0.027	0.38	0.03	**1**			
TDS	0.176	0.045	0.01	-0.18	-0.076	0.192	-0.13	0.268	0.03	0.31	0.05	**1**		
Ppt	**0.642**	0.18	**0.46**	**0.54**	-0.026	0.183	-0.19	0.247	0.01	0.31	-0.8	0.053	**1**	
T	-0.572	-3.15	0.25	-0.01	-0.28	0.16	-0.15	-0.17	0.24	0.48	0.108	0.188	0.1	**1**

Appendix 3.5

Table: Factor loadings elucidated by Principle Component Analysis

a) Soil

	Axis 1	Axis 2	Axis 3	Axis 4	Axis 5	Axis 6	Axis 7
Pb	-0.017	-0.088	-0.013	-0.378	-0.427	-0.189	0.363
Zn	-0.008	-0.242	-0.09	0.433	0.282	-0.391	0.058
Cu	-0.117	0.346	0.221	0.235	0.032	-0.245	0.27
Mn	-0.361	0.078	0.101	-0.099	-0.173	0.207	0.287
Cr	0.391	0.071	0.02	-0.045	0.182	0.143	0.217
Fe	0.007	-0.316	-0.192	-0.286	0.304	0.085	0.304
Cd	-0.012	0.166	0.223	-0.355	-0.083	-0.26	-0.56
Ni	-0.028	0.026	-0.193	-0.398	0.461	-0.271	-0.114
BC	-0.293	-0.223	0.107	-0.042	0.318	0.144	-0.028
TOC	-0.184	0.021	-0.171	-0.264	0.059	0.45	0.021
Elevation	-0.399	0.177	-0.113	0.031	0.183	-0.153	0.103
pH Soil	0.12	-0.455	-0.045	0.03	0.079	0.043	-0.154
EC Soil	-0.058	-0.214	-0.357	0.101	-0.267	-0.22	0.218
temperature	-0.42	0.307	0.134	-0.199	0.194	-0.102	-0.102
Humidity	-0.47	-0.069	-0.012	0.115	-0.003	-0.021	-0.068
Sand	-0.019	0.119	0.464	0.041	0.283	0.235	0.184
Silt	0.015	0.205	-0.321	0.344	0.035	0.345	-0.17
Clay	0.019	0.215	-0.457	0.022	-0.099	0.171	-0.157
Precipitation	-0.239	0.056	0.044	-0.128	0.038	-0.241	-0.241
Eigenvalues	4.028	2.487	2.031	1.688	1.537	1.421	1.152
Percentage	21.201	13.089	10.69	8.885	8.087	7.48	6.063
Cumulative %	21.201	34.29	44.98	53.864	61.952	69.431	75.494

b) Sediments

	Axis 1	Axis 2	Axis 3	Axis 4	Axis 5	Axis 6
Elevation	-0.322	0.296	0.179	-0.03	0.132	-0.271
Pb	0.254	0.141	-0.358	0.096	0.077	0.186
Zn	0.282	-0.139	-0.355	-0.06	0.216	-0.286
Cu	0.323	-0.039	0.235	0.057	0.223	-0.098
Mn	0.248	-0.218	0.243	0.414	0.147	-0.002
Cr	0.26	0.124	0.199	-0.051	0.017	0.143
Fe	0.145	0.296	-0.034	-0.086	-0.457	-0.276
Cd	0.302	0.149	-0.093	-0.023	-0.318	-0.045
Ni	0.143	0.303	0.057	0.401	-0.434	0.178
BC	-0.106	-0.444	-0.002	0.143	-0.349	-0.043
TOC	0.08	0.265	0.275	0.019	0.226	0.614
Precipitation	-0.067	-0.008	0.117	-0.156	0.168	-0.392
temperature	-0.474	-0.233	0.097	-0.119	0.383	0.019
Humidity	-0.42	0.05	0.137	0.119	-0.005	0.011
moisture	-0.235	0.319	-0.516	0.013	0.026	0.111
EC	0.137	-0.174	0.413	-0.286	-0.377	0.04
pH	-0.085	0.148	-0.354	-0.484	-0.082	0.339
Eigenvalues	4.028	2.487	2.031	1.688	1.537	1.421
Percentage	21.201	13.089	10.69	8.885	8.087	7.48
Cumulative%	21.201	34.29	44.98	53.864	61.952	69.431

c) Water

	Axis 1	Axis 2	Axis 3	Axis 4	Axis 5	Axis 6
Pb	-0.353	-0.29	-0.067	0.049	-0.182	0.116
Zn	-0.096	-0.096	0.476	-0.074	0.177	-0.346
Cu	0.113	0.336	0.122	-0.209	-0.258	-0.558
Mn	0.281	-0.186	0.125	0.203	-0.262	-0.262
Cr	-0.265	-0.329	0.072	-0.278	-0.275	0.136
Fe	0.164	-0.125	0.388	0.401	-0.161	0.166
Cd	-0.168	-0.253	-0.004	0.33	0.501	-0.271
Ni	-0.237	-0.09	-0.2	0.335	0.268	-0.001
EC water	-0.386	0.196	-0.065	0.093	-0.227	-0.079
pH water	-0.174	0.112	0.362	0.136	-0.033	0.013
Elevation	0.397	-0.263	0.014	-0.085	0.065	0.014
temperature	0.214	0.225	-0.183	0.033	0.275	-0.31
Wind speed	-0.369	-0.003	-0.349	0.248	-0.111	0.105
Pressure	0.15	0.472	-0.122	0.256	0.219	0.034
Humidity	0.037	-0.379	-0.18	0.022	0.179	0.22
TDS	0.051	-0.192	-0.263	0.388	-0.455	-0.098
Precipitation	0.026	0.359	0.096	0.029	0.479	0.274
Eigenvalues	4.217	2.442	1.99	1.503	1.279	1.077
Percentage	24.806	14.364	11.707	8.841	7.523	6.335
Cumulative%	24.806	39.171	50.877	59.718	67.241	73.576

Appendix 3.6

Table: Sedimentary BC and TOC profile along sampling zones

	BC	TOC	BC/TOC	Source	TOC_{burial} ($g/m^2/yr$)	BC_{burial} ($g/m^2/yr$)
Zone 1						
Taobat	2.2	5.2	0.42	Biomass	52.03	22.01
Kel	1.6	0.8	2	Traffic	8.8	17.6
Karen	0.4	26.9	0.01	Biomass	311.64	4.63
Athmuqam	1.1	25.9	0.04	Biomass	316.72	13.45
Tain Dhalkot	0.3	2.8	0.1	Biomass	173.1	3.001
Zone 2						
Chinari	29.2	20.8	1.4	Traffic	169.49	55.03
Birote	0.8	32.6	0.02	Biomass	22.012	214.87
Kalas	0.5	28.2	0.01	Biomass	254.36	357.095
Nausadda	0.3	17.3	0.02	Biomass	8.109	150.61
Zone 3						
Hattian Bala	13	0.7	18.5	Traffic	22.012	124.3
Shahdara	0.3	0.6	0.5	Traffic	4.63	268.78
Mang	12	0.3	40	Traffic	158.98	289.83
Gari Dupatta	9.6	1.7	5.64	Traffic	9.06	389.7
Domail	30.1	0.7	43	Traffic	123	159.3
Dolai	15.2	11.7	1.29	Traffic	310	5.5
Thota	23.2	0.4	58	Traffic	6	3
Zone 4						
Pattika	5	15.4	0.32	Biomass	314	2.4
Pona	25.1	1.5	16.7	Traffic	378	9.26
Langarpura	23.7	13	1.82	Traffic	34.2	3.66
Ghori	20.5	2.1	9.76	Traffic	3.475	139.02
Nawan	3.3	1.8	1.83	Traffic	15	251
Kohala	0.2	25	0.008	Biomass	18	34.59
Banndi	1.2	0.8	1.5	Traffic	9.5	14.27
Balathi	2.7	9.1	0.29	Traffic	105	31.2
Zone 5						
Salmotha	12.8	1.8	7.1	Traffic	20.31	144
Kakra Town	0.9	9.5	0.09	Biomass	86.47	242
Roopyaal	8.9	3.6	2.47	Traffic	45.28	111
Khadamabad	15.4	5.5	2.8	Traffic	92.94	8.8
Mir Bypass	1.4	11.9	0.11	Biomass	135.02	5.6
Kharuk	0.5	12.7	0.03	Biomass	133.12	14.6
Pali	0.5	50.7	0.009	Biomass	291.67	5.5
Mangla road	0.5	26.5	0.01	Biomass	558	5.5