Distribution, Correlation, Source Apportionment, Bioaccessibility and Health Risk Assessments of Selected Metals in Water, Sediments, Soil and Fish from Mangla Lake, Pakistan

By

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2017

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A dissertation submitted in partial fulfillment of the
requirements for the degree of

Doctor of Philosophy

In

Analytical/Inorganic Chemistry

Submitted By
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under the supervision of
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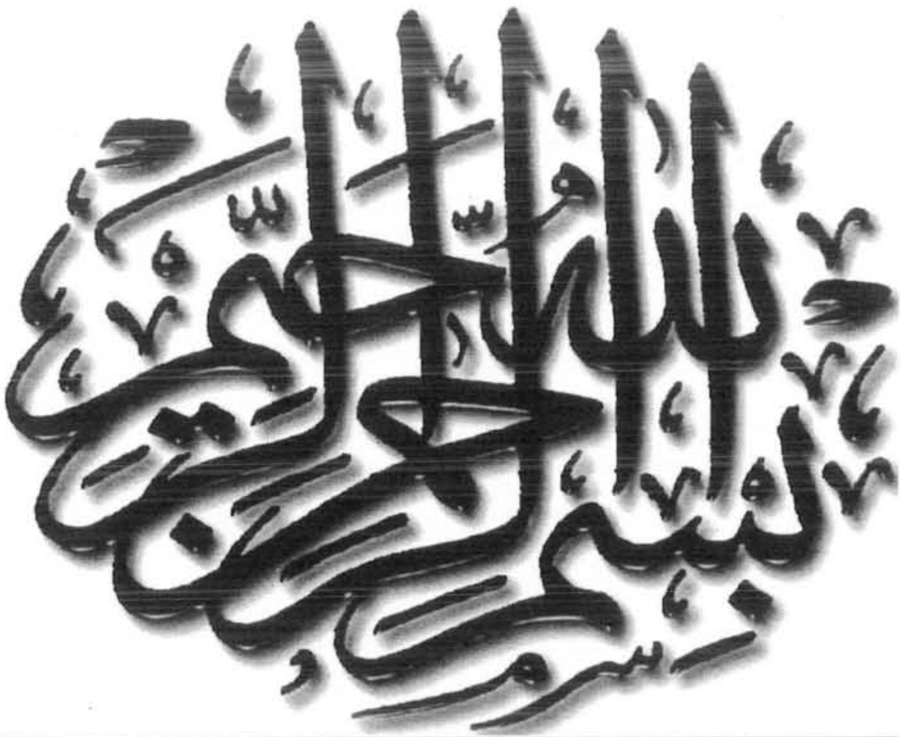
Department of Chemistry, Quaid-i-Azam University
Islamabad 45320, Pakistan (2017)



IN THE NAME OF ALLAH,
THE MOST BENEFICENT,
THE MOST MERCIFUL

List of Publications

Following research articles have been published/submitted for publication from the present work:

1. **Saleem M**, Iqbal J, Shah MH, 2013. Study of seasonal variations and risk assessment of selected metals in sediments from Mangla Lake, Pakistan. Journal of Geochemical Exploration, 125, 144–152.
2. **Saleem M**, Iqbal J, Shah MH, 2014. Non-carcinogenic and carcinogenic health risk assessment of selected metals in soil around a natural water reservoir, Pakistan. Ecotoxicology and Environmental Safety, 108, 42-51.
3. **Saleem M**, Iqbal J, Shah MH, 2014. Dissolved concentrations, sources, and risk evaluation of selected metals in surface water from Mangla Lake, Pakistan. Scientific World Journal, 2014, Article ID 948396, 12 pages.
4. **Saleem M**, Iqbal J, Shah MH, 2015. Geochemical speciation, anthropogenic contamination, risk assessment and source identification of selected metals in freshwater sediments—a case study from Mangla Lake, Pakistan. Environmental Nanotechnology, Monitoring and Management, 4, 27-36.
5. **Saleem M**, Iqbal J, Akhter G, Shah MH, 2015. Spatial/Temporal characterization and risk assessment of trace metals in Mangla Reservoir, Pakistan. Journal of Chemistry, 2015, Article ID 928019, 11 pages.
6. **Saleem M**, Iqbal J, Shah MH, 2016. Spatio-Temporal variability and pollution assessment of selected metals in freshwater sediments, Pakistan. CLEAN - Soil, Air, Water, 44, 402–410.
7. **Saleem M**, Iqbal J, Shah MH, 2016. Assessment of water quality for drinking/irrigation purpose from Mangla dam, Pakistan. Geochemistry: Exploration, Environment, Analysis, 16, 137-145.
8. **Saleem M**, Iqbal J, Akhter G, Shah MH. Fractionation, bioavailability, contamination and environmental risk of heavy metals in the sediments from a freshwater reservoir, Pakistan. (Submitted).
9. **Saleem M**, Iqbal J, Shah MH. Seasonal variability, risk assessment and source identification of selected metals in Mangla Reservoir, Pakistan. (Submitted).
10. **Saleem M**, Iqbal J, Shah MH. Health risk assessment of selected metal levels in economically important fish species from the Mangla Lake. (Submitted).

FOREIGN EXAMINERS

This dissertation entitled *"Distribution, Correlation, Source Apportionment, Bioaccessibility and Health Risk Assessments of Selected Metals in Water, Sediments, Soil and Fish from Mangla Lake, Pakistan"* by *Mr. Muhammad Saleem*, Department of Chemistry, Quaid-i-Azam University, Islamabad, Pakistan, has been evaluated by following panel of foreign examiners and adjudged suitable for the award of Ph.D. degree in Analytical/Inorganic Chemistry.

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ACKNOWLEDGEMENTS

All praises and thanks are to Allah, the Almighty, on whom ultimately we depend for sustenance and guidance. May Allah's peace and blessing be upon our beloved Prophet Muhammad (PBUH) who is a mercy unto us from Allah, who character and nobility none has seen before or after Him (PBUH).

I am grateful to *Prof Dr. Muhammad Siddiq*, Chairman, Department of Chemistry, Quaid-i-Azam University, Islamabad, for providing the facilities during my research work. My sincere appreciation goes to my supervisor, *Dr. Syed Munir Hussain Shah*, Associate Professor, Department of Chemistry, Quaid-i-Azam University, Islamabad, whose guidance, support and encouragement facilitated the completion of this research work. I am very thankful to the *Dr. Javed Iqbal*, NESCOM, Islamabad, whose guidance, support and encouragement helped me in the completion of this research work. I am also thankful to the *Dr. Zongbo Shi*, School of Geography, Earth and Environmental Sciences, University of Birmingham, United Kingdom who guided and supported me during my foreign visit. I am thankful to the Higher Education Commission, Islamabad, for providing me fruitful funding to complete this research work. I am grateful to the Education Department, Azad Jammu and Kashmir, for granting me the study leave.

I am thankful to the management of Mangla dam, Mirpur, Azad Jammu & Kashmir for facilitating me in samples collection. I owe my deepest gratitude to my brothers (Muhammad Ameen, Arslan Afzal, Usman Afzal, Rizwan Afzal and Ahtsham ul Haq) and friends (Tariq Mehmood, Muhammad Ishfaq, Abdul Wahab and Safder Shafiq) for their valuable cooperation during the study period. I wish to thank all the army persons at the army boat club to provide the boat facilities during sampling campaign. I would like to express my deepest appreciation to my lab fellows & friends (Hafiz Muhammad Abdul Qayyum, G. Mujtaba Hashmi and Asim Ilyas) and all departmental staffs for their help and support during this research work. I owe my gratitude to the love and prayers of my mother, sisters and brothers. I owe my deepest gratitude to Principal, Prof. Khalid Javed (Late) and Madam Farzana Rasool (Deputy Director) for their sincere cooperation. I would like to show my deepest gratitude to my father, who is no longer with me but his love, prayers, care, courage and words will always be accompanying me. Lastly, I offer my regards and blessings to all of those who supported me in any aspect during the completion of this research work.

Muhammad Saleem
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Dedicated to

My Mother

&

Family

The most strengthening part of my life,
Whom sincere devotion stood aside me
in my whole life

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List of Abbreviations

ATSDR	Agency for Toxic Substances and Disease Registry
BCR	European Community Bureau of Reference
CA	Cluster Analysis
C_{deg}	Degree of Contamination
CEC	Commission for Environmental Cooperation
CF	Contamination Factor
EC	European Commission
DO	Dissolved Oxygen
EC	Electrical Conductivity
EDI	Estimated Daily Intake
EF	Enrichment Factor
Ei	Potential Ecological Risk Factor
EPA	Environmental Protection Agency
EWI	Estimated Weekly Intake
FAAS	Flame Atomic Absorption Spectrometer
FAO	Food and Agricultural Organization
GCF	Global Contamination Factor
HEI	Heavy Metal Evaluation Index
HI	Hazard Index
HQ	Hazard Quotient
ICF	Individual Contamination Factor
ICPMS	Inductively Coupled Plasma Mass Spectrometer
I_{geo}	Geoaccumulation Index
IOM	Institute of Medicine
IWQ	Irrigation Water Quality
KR	Kelly's Ratio
Kurt	Kurtosis
LEL	Lowest Effect Level
MAC	Maximum Admissible Concentrations
MAR	Magnesium Adsorption ratio
Mg/Ca	Magnesium Calcium ratio
MAFF	Ministry of Agriculture, Fisheries and Food
MC	Moisture Contents
Min	Minimum
Max	Maximum
MOE	Margin of Exposure
NRC	National Research Council
Pak-EPA	Pakistan Environmental Protection Agency
PCA	Principal Component Analysis
PCs	Principle Components
PEL	Probable Effects Level
PI	Permeability Index
PLI	Pollution Load Index
PS	Percent Sodium
PTDI	Permissible Tolerable Daily Intake
PTWI	Provisional Permissible Tolerable Weekly Intake
RAC	Risk Assessment Code
RI	Potential Ecological Risk Index
RSBC	Residual Sodium Bicarbonate
SAR	Sodium Adsorption Ratio
SD	Standard Deviation
SE	Standard Error
SEL	Severe Effect Level
Skew	Skewness
SQGs	Sediment Quality Guidelines
TA	Total Alkalinity
TDS	Total Dissolved Solids
TCR	Target Cancer Risk
TEL	Threshold Effects Level
TH	Total Hardness
TU	Toxic Units
USEPA	United States Environmental Protection Agency
WHO	World Health Organization

Abstract

Freshwater resources are under severe threat by anthropogenic pollution all around the world. There is a dire need for proper environmental monitoring and assessment for future planning and management of these assets. The present investigation was carried out in order to evaluate the distribution, correlation, source identification, bioaccessibility, health/ecological risk assessment, seasonal and spatial variations of selected metals (As, Ca, Cd, Co, Cr, Cu, Hg, Fe, K, Li, Mg, Mn, Na, Ni, Pb, Se, Sr and Zn) in the water, surface sediments, soil and selected fish species from/around Mangla Lake, Pakistan. The samples were collected during summer, winter, pre-monsoon, monsoon and post-monsoon seasons. In addition, various physicochemical parameters, such as, pH, Temperature (T), Dissolved oxygen (*DO*), Total alkalinity (*TA*), Electrical Conductivity (*EC*), Total Dissolved Solids (*TDS*), Total Hardness (*TH*), Bicarbonate ion (HCO_3^-), Residual Sodium Bicarbonate (*RSBC*), Sodium Adsorption Ratio (*SAR*), Percent Sodium (*PS*), Kelly's Ratio (*KR*), Magnesium Calcium Ratio (*Mg/Ca*), Magnesium Adsorption Ratio (*MAR*), Permeability Index (*PI*) in the water and/or sediments/soil were also estimated. Water samples were also analysed for selected anions (fluoride, chloride, nitrate and sulphate), while soil/sediments were assessed for their particle size distribution and texture. In case of soil/sediments, chemical fractionation of selected metals was carried out by sequential extraction, employing modified Community Bureau of Reference (*m*BCR) procedure. Bioavailability of the metals was assessed by using calcium nitrate extraction. Measurement of the metal levels in water, sediments, soil and fish samples was accomplished by flame atomic absorption spectrophotometer and inductively coupled plasma mass spectrometer under optimum analytical conditions. Correlation analysis was used to identify the mutual viable relationships among the metals and multivariate analysis including principal component analysis (PCA) and cluster analysis (CA) were used to categorize the pollution sources. Pollution indices, including enrichment factor (*EF*), geo-accumulation index (I_{geo}), contamination factor (*Cf*), degree of contamination (C_{deg}), potential ecological risk factor (E_i), potential ecological risk index (*RI*), potential acute toxicity (*TU*), individual contamination factor (*ICF*), global contamination factor (*GCF*), risk assessment code (*RAC*) and heavy metal pollution index (*HEI*) were calculated to appraise the ecological risks associated with the pollutants in freshwater reservoir. Water quality of the freshwater reservoir for drinking and irrigation purposes was also assessed. Health risk assessment including exposure assessment, margin of exposure, hazard quotients, estimated daily/weekly intakes, non-carcinogenic and carcinogenic risk assessment (via ingestion and dermal exposure) was calculated to evaluate the adverse health effects on the exposed population.

The pH, EC, TDS and Cl^- levels in the water samples were within acceptable limits, while DO contents were comparatively lower, manifesting reducing conditions in the reservoir. Among the metals, dominant contributions were found for Ca, K, Mg and Na, while As, Li, Se, and Mn showed relatively lower contributions in the water samples. Most of the metals in water samples exhibited random distribution. Strong metal-to-metal correlations were noted among various metal pairs in water samples which indicated their communal variations/contributions. Mean levels of As, Cd, Co, Cr, Ni and Pb were higher than the national/international water quality guidelines, thus emerging as potential pollutants in the reservoir. PCA and CA evidenced largely anthropogenic contributions for As, Cd, Co, Cr, Ni and Pb in the water reservoir, which was found to be heavily polluted by As, Cd, Co, Ni, Cr and Pb. Water samples were observed to be unsuitable for irrigation with respect to bicarbonate and RSBC levels in all seasons, however, on the basis of *SAR*,

KR, PS, MAR and *Mg/Ca*, water was suitable and safe for irrigation. Similarly, *IWQ* index exhibited high to medium suitability of water for irrigation purpose. Heavy metal pollution index (*HEI*) and degree of contamination (C_d) suggested medium degree of pollution in the water. HQ_{ing} and *HI* values for As, Cd, Co, Cr, Ni and Pb were higher than safe limit (unity) indicating non-carcinogenic risks to the local population.

The sediments and soil samples revealed comparatively higher concentrations for Ca, Mg, Fe, Na, Mn and K, while lowest concentrations were noted for Hg, Se, Cd and Li. Electrical conductivity (*EC*) and *TDS* showed large variations in the sediments/soil samples. Generally, selected metal concentrations in the sediment and soil samples exhibited random distribution as evidenced by higher skewness, SD and SE values. Strong and significant correlations were noted among various metals in the soil and sediment samples thus manifesting their common variations/origin. Concentrations of most of the metals in sediments/soil were significantly higher at sampling sites located near highly urbanized/semi-urban areas. PCA and CA showed anthropogenic contributions of As, Cd, Cr, Co, Hg, Ni, Pb and Se in the sediment and soil samples. Particle size analysis exhibited sandy loam texture of the soil/sediments. Enrichment factor, geoaccumulation index and contamination factor showed that among selected metals, As, Cd, Co, Hg, Pb and Se were highly enriched and accumulated in the sediments and soil samples. Potential acute toxicity indicated by toxic units (*TUs*) of the metals revealed that among the selected metals, As, Cd, and Hg showed relatively higher potential toxicity in the sediment/soil samples. Potential ecological risk index indicated very high risk in the sediment/soil samples. Pollution load index, degree of contamination and potential ecological risk index indicated more contamination during pre-monsoon than other seasons. Sediment quality guidelines (*SQGs*) indicated that As, Cd, Hg, Ni and Pb are likely to result in frequently occurring harmful effects on sediment-dwelling biota. Health risk assessment of the metals via ingestion/dermal route in sediments/soil showed little/no risk. Sediment and soil samples were found to be heavily/significantly polluted by As, Cd, Cr, Co, Hg, Ni, Pb and Se. Overall, As, Cd, Co, Cr, Hg, Ni, Pb and Se were primarily contributed by anthropogenic intrusions such as, agricultural activities, industrial activities, fuel combustion, atmospheric deposition and recreational activities and Ca, Cu, Fe, Li, K, Mg, Mn, Na, Sr and Zn were mainly contributed by natural inputs in the reservoir.

Concentrations of selected metals were also measured in the muscles, gills and scales of fish species (*Cyprinus carpio, Catla catla, Hypophthalmichthys molitrix, Wallago attu* and *Sperata sarwari*) collected from the water reservoir. Generally, fish species exhibited higher concentrations of Ca, Fe, K, Mg, Na and Zn, while lowest concentrations were observed for As, Cd, Hg and Li. Highest concentrations of most of the metals were found in the gills, followed by scales and muscles. Most of the metal levels in the fish samples exhibited symmetric and normal distribution, except Ca, K, Na and Zn which showed predominantly non-Gaussian distribution. PCA and CA evidenced anthropogenic contributions of As, Cd, Co, Cr, Hg, Ni and Pb in the fish muscles. *EWI* and *EDI* values of As, Cd, Cr, Hg, Ni and Pb were noted to be higher than the recommended *PTWI* and *PTDI* values, respectively. Higher *MOE* values for As, Cd, Cr, Hg, Ni, Pb and Se in the muscles specified higher dose exposure, which may result in chronic non-carcinogenic effects to the consumers. HQ_{ing} revealed that contaminated fish consumption may cause non-carcinogenic risks associated with the elevated levels of As, Cd, Cr, Hg, Ni, Pb, Se and Zn. Target cancer risk (*TCR*) demonstrated that the consumption of fish from Mangla Lake on continuous basis can result in exposure of elevated contents of As, Cd, Cr, Ni and Pb with a significant probability of lifetime carcinogenic risk to the consumers.

Chapter 1

INTRODUCTION

1.1 Freshwater Reservoirs: General Aspects

Freshwater is vital component of humans' activities, such as, drinking, cooking, washing, farm/garden irrigation, livestock production, transportation, industrial materials, recreation/sports, hydroelectric power generation, construction, fishery and agriculture (Simmons, 1999). Consequently, it is priceless; life is impossible without it and it has no replacement. It is also delicate as anthropogenic intrusions can immensely influence the quality and quantity of the available freshwater. Presently, as never before, there is threat for scarcity of good quality freshwater reservoirs around the globe (Awake, 2001). Worldwide, approximately 3.1% of deaths (1.7 million) and 3.7% of disability-adjusted-life-years (54.2 million) are related to unsafe water, poor sanitation and unhygienic conditions (Abate *et al.*, 2015; WHO, 2005). Human interactions with the environment to accomplish his basic needs contaminate the water reservoirs thus making water unhealthy and the situation may worsen further by increasing population growth (Oyegun, 1983).

Provision of safe water is indispensable to human health, protection of aquatic & terrestrial life, sustainable development and biodiversity (Iqbal *et al.*, 2012a; Jindal *et al.*, 2014; WHO, 2011). The ground and surface water reservoirs are most imperative for living organisms. Surface water quality is affected by seasons, precipitation, human activities, catchments and geographical location (Ouyang *et al.*, 2006; Scheili *et al.*, 2015). Continuously escalating population and uncontrolled urbanization/industrialization resulted in deterioration of water quality, which may affect human interests directly and it is a serious threat to crops yield and soil properties (Ho *et al.*, 2003; Saleem *et al.*, 2014a; Simsek and Gunduz, 2007). Overall, freshwater is about 3% of the total water on earth surface but only 0.01% of the water is of suitable quality and available for human use (Graham and Farmer, 2007). Unfortunately, even this small fraction of freshwater is under stress and threat (Azizullah *et al.*, 2011). In many cities, surface water from the reservoirs is used as drinking water (Mudiam *et al.*, 2012). Generally, advanced municipalities are capable of ensuring safe drinking water by applying treatment technologies; however, the situation is dismal in developing countries (NCCPH, 2011; Scheili *et al.*, 2015).

Freshwater reservoirs are usually built in areas of water scarcity in order to make sure the consistent and manageable water supply during the demanding periods and to prevent the downstream areas from being flooded during rainfall or snow melt periods (Cowie *et al.*, 2002). Reservoirs can be developed for single or multiple purposes, such as, to supply water for cities, to provide irrigation water, to lift water levels, to make navigation possible and to generate the electricity. Their size and depth are dependent upon their uses, volume of flow, topography, height and geological characteristics. Normally, they are recharged with water coming from rainfall, runoffs, groundwater seepage and pumping from ground & surface water sources. They are managed to offer water for drinking, domestic, industrial, recreation, irrigation, shipping, fishery, landscape and energy production purposes (Upadhyay, 2012). Nowadays intensifying crises of water have made the reservoirs very crucial to preserve the available water in large quantities for supporting aquatic and terrestrial lives. Generally, 25% of the water flowing to oceans has been impounded in the reservoirs (UNEP, 1991). River regulation, flood control, aesthetic/recreational uses, navigation, canalization, and waste disposal further enhance their importance, although the reservoirs are losing their capacity due to continuous sedimentation.

Nonetheless, there are some limitations of the reservoirs including water loss via rapid evaporation, deprivation of water habitat for fish, risk of downstream flooding, deprivation of nutrient rich silt for downstream cropland, displacement of people, destruction of cropland or forests, downstream erosion and loss of property (McLaughlin *et al.*, 2006; Shakir *et al.*, 2014). Moreover, water seepage from the reservoirs may affect the surrounding soil and fluctuations in the temperature and relative humidity of surrounding environment may also influence the immediate terrestrial habitats (Shakir *et al.*, 2014). The reservoirs can have ancillary benefits due to their ability to trap sediment, the efficiency of which depends on the length of time that water stays in the reservoir. Clay particles are not effectively trapped by reservoirs because of their small size and long settling time. The sediment trapping function may appear to mitigate poor land use practices and can cause downstream bed coarsening, a relative shift of the sediment particle size distribution from finer to larger materials. Further, accumulating sediment decreases water storage capacity, limiting the functional life of the reservoir or requiring investment in dredging and sediment removal. Contaminants associated with accumulated sediment can further increase the cost of removal and disposal (Cowie *et al.*, 2002).

and undesirable chemical reactions (WHO, 2011). Discharge of acid mine, organic substances and industrial wastes may decrease the pH of water, whereas carbonates, hydroxides and carbonic acids may increase the pH of the water. Generally, it ranges from 4 to 9 in freshwaters, while relatively lower value (< 5.6) is observed in rain water. Natural water bodies are alkaline in natures due to carbonate-bicarbonate system; however they might become acidic with passage of time due to acidic materials contributed by dry deposition (acidic material on dust, smoke, or other aerosols) and wet precipitation or industrial effluents. Water pH may affect the species configuration of aquatic ecosystem, the availability of nutrients and comparative noxiousness of trace elements. Furthermore, various industries, such as, bleaching, brewing, photography, electroplating, ore dressing and photo engraving may also be influenced by pH of supply water (Wellby *et al.*, 2010).

1.2.3 Electrical Conductivity (EC)

It is the ability of water to conduct an electrical current. It provides a good indication of the changes in the water composition, especially in its mineral levels. It is particularly sensitive to variations of dissolved solids, but provides no indication of the relative quantities of the various components. Organic compounds such as, oil, phenol, alcohol, and sugar do not conduct electrical current very well and therefore, have a low EC (O'Neill *et al.*, 1994). It is also affected by temperature; warmer water show relatively higher conductivity, therefore, EC measurements are reported as conductivity at 25°C (Boman *et al.*, 2002). Generally, it varies from 50 to 150 μS/cm in surface water whereas the ground and arid waters exhibit relatively higher EC (~1000 μS/cm). It is usually elevated when groundwater infiltration contribute substantial segment of stream-flow while it is minimum when water is diluted by snow melting. Its value can increase to 10,000 μS/cm due to discharge of untreated industrial wastes; however, the values less than 250 μS/cm are acceptable for drinking water (WHO, 2011).

1.2.4 Total Dissolved Solids (TDS)

It is a measure of amount of dissolved substances which may alter the physical and chemical characteristics of water (O'Neill *et al.*, 1994). Generally, dissolved materials in water are contributed by high surface runoffs and overland flows. In addition, agricultural runoffs, aerosol fallout, untreated municipal and industrial wastes also elevate its load in water. The guidelines for TDS are related to taste and palatability rather than harmful effects on human and aquatic organisms. Commonly, TDS levels of less than 600 mg/L are considered to be safe, whereas the levels higher than 1000 mg/L may affect the palatability (WHO, 2011). Laxative effects are observed in human and livestock when TDS levels exceed 2000 mg/L. Excessively higher levels make water unsuitable for drinking use and industries. Elevated concentration of TDS may reduce light penetration, and lower the photosynthetic activity of phytoplankton, algae and macrophytes, which may result in decreased fish population (Aecos, 2015).

1.2.5 Dissolved Oxygen (DO)

Dissolved oxygen in water is essential for fish and other aquatic organisms. Its levels should not be less than 5 mg/L for healthy aquatic biota (Radojevic and Bashkin, 1999). Generally, DO levels are less than 10 mg/L in surface water while its maximum solubility in freshwater ranges from ~15 mg/L at 0°C to 8 mg/L at 25°C at sea level. Elevated levels of DO are acceptable for drinking as it improve the palatability whereas its deficiency/absence is desirable for some industrial applications to avoid corrosiveness of water (Caduto, 1990). DO along with water velocity and temperature influence the life cycles and inter-relationships of aquatic biota, such as, invertebrates, amphibians, fishes and birds. Its levels may be lowered by elevating the temperature, especially during summer; the affect may become more prominent in lower river systems and standing waters where the aeration is limited. Additionally, its levels may decrease by decomposition of organic wastes and oxidation of inorganic substances (O'Neill *et al.*, 1994; Whitehead *et al.*, 2009).

1.2.6 Alkalinity

Alkalinity is the measure of water capacity to neutralize acids, especially the salts of weak acids (Agdag and Sponza, 2005). As pH indicates power of an acid or base, alkalinity specifies the strength of water to react with acid and buffer its pH. Generally, it is contributed by carbonate, bicarbonate and hydroxide together with, borates, phosphates, silicates and other basic compounds (Ramachandra and Solanki, 2007). Water with low buffering capacity or low alkalinity (< 24 mg/L as $CaCO_3$) can be prone to variations in pH, especially from atmospheric acidic deposition. It is vital for fish and aquatic life as it resists against pH change, thus makes water less susceptible to the acid rain. Alkalinity also helps the stability of water and controls its corrosion to supply pipe and appliances; otherwise it may result in contamination of drinking water and pose adverse effects on taste and appearance of water (WHO, 2011).

1.2.7 Hardness

Hardness is mainly attributed to calcium and magnesium; designated by formation of soap scum and results in the use of more soap for cleaning. The taste threshold for calcium ion is 100-300 mg/L, depending upon other anions and taste threshold for magnesium is probably less than that of calcium. Occasionally, consumers may tolerate its concentration more than 500 mg/L. Depending on pH and alkalinity, water hardness greater than 200 mg/L may results in scaling in treatment work, supply pipes and work tanks. Calcium carbonate scaling may be a consequence by heating the hard water. Contrary, soft water having hardness below 100 mg/L exhibits lesser buffering capacity and may cause more corrosiveness to water pipes (WHO, 2011).

1.2.8 Chloride (Cl^-)

Chloride can originate from natural inputs, sewage/industrial effluents, urban runoffs, de-icing salt and saline intrusions. Human generally ingest it from food in greater amount than water (WHO, 2011). During snow/icy periods, roads salting may increase its levels in groundwater (Chapman, 1996). It may cause corrosion of metals in supply systems, depending upon alkalinity of the water. This may result in increase of metal levels in the supply water. Its concentration slightly greater than 250 mg/L may give rise noticeable taste while further higher levels may give salty taste (WHO, 2011). Plants are also affected by its higher concentrations and some harmful effects may be observed even at levels as low as 70-250 mg/L (Radojevic and Bashkin, 1999).

1.2.9 Nitrate (NO_3^-)

Nitrate, an important plant nutrient is naturally occurring in the environment and it is found in all plants in different concentrations. Nitrate can enter into the surface water and groundwater by agricultural activity, wastewater disposal and oxidation of nitrogenous waste products (Singh *et al.*, 2008; WHO, 2011). Surface water nitrate levels can change quickly due to agriculture runoffs, uptake by phytoplankton and denitrification by bacteria. In general, the most important source of human exposure to nitrate is through vegetables and meat in the diet. Sometimes drinking-water can also make a significant contribution to nitrate intake. The guideline value for nitrate in drinking water is 50 mg/L while the excessive levels show detrimental effects (WHO, 2011). High concentrations of nitrates can cause methanemoglobinaemia, gastric cancer, goitre, birth malformations and hypertension (Majumdar and Gupta, 2000; Singh *et al.*, 2008).

1.2.10 Fluoride (F^-)

Fluoride is an important component for growth of bones, teeth and dental enamel (Bell and Ludwig, 1970; Singh *et al.*, 2008). It is believed to be beneficial in drinking water below 0.7 mg/L but considered dangerous beyond the safe limit of 1.5 mg/L (Pak-EPA, 2008; WHO, 2011). Its levels may increase in groundwater with lowering of calcium concentration and increasing bicarbonate alkalinity (Bulusu and Pathak, 1980). Its disproportionate consumption may cause fluorosis. It is originated from weathering of fluoride containing rocks, resulting in making of minerals, such as, muscovite, biotite, fluorite, fluoroapatite, topaz, cryolite, phosphorite, theorapatite, etc. (Singh and Maheshwari, 2001; Singh *et al.*, 2008). It is mainly ingested through drinking water (70-80% of daily intake), however, it may also be taken via food, drugs, cosmetics, etc. (Meenakshi *et al.*, 2004).

1.2.11 Sulphate (SO_4^{-2})

Sulphates are the constituents of natural water, soil and rock in the form of Glauber's salt, Epsom salt, pyrite and Gypsum (Berner and Berner, 1987). In aquatic ecosystems, it is originated from rocks weathering, fossil fuel burning, volcanism and cycling salts. Its elevated levels may result in dehydration, diarrhoea, respiratory problems and catharsis in humans. Sulphate may also affect corrosion of metals in the water distribution system, particularly in waters having low alkalinity (Morris & Levy, 1983; WHO, 2011). It may result in bitter or medicinal or unpleasant taste to drinking water if its levels are higher than 250 mg/L which is the safe limit (Lenntech, 2015; WHO, 2011). It is commonly used in fertilizers, chemicals, dyes, glass, paper, soaps, textiles, fungicides, insecticides, astringents, emetics, mining, wood pulp, metal/plating industries, sewage treatment and leather processing (Greenwood & Earnshaw, 1984). Aluminium sulphate is used in drinking water treatment for the sedimentation and copper sulphate is added to control the algal growth in water supplies (McGuire *et al.*, 1984).

1.3 Water Pollution and Trace Metals

Water contamination by trace and toxic metals has become a serious problem worldwide due to numerous sources, such as, roadside runoffs, atmospheric deposition, rocks weathering, fertilizers, vehicular emissions, industrial emissions, mineral processing, electroplating, untreated urban and agricultural wastes (Bengraine and Marhaba, 2003;

Iqbal *et al.*, 2012a,b; Srebotnjak *et al.*, 2012; WHO, 2008). Dispersal of the metals in aquatic ecosystem has emerged as an important area of investigation in environmental studies. On discharge into the water bodies, metals may get either dissolve to form ions or complexes, or suspended as particulate matter or settled down on the bottom sediments (Tuna *et al.*, 2007). Though some of the metals (e.g., Fe, Cu, Zn, etc.) are vital to living organisms, but even they are lethal at elevated levels (Kavcar *et al.*, 2009; Yu *et al.*, 2010). Contamination of metals may cause serious health hazards via food chain magnification and damage the water quality and biodiversity (He *et al.*, 2001; Li *et al.*, 2008a). Intake of water containing toxic metals may pose severe health effects including various types of cancers (Costa and Klein, 2006; Liang *et al.*, 2011). Accumulation of trace metals in freshwater reservoirs can cause antagonistic effects, consequently, investigations related to the quantification and risk evaluation of toxic metals are being carried out on global scale (Ali *et al.*, 2013; Krishna *et al.*, 2009; Oyebog *et al.*, 2012; Pertsemli and Voutsa, 2007; Varol, 2013; Wu *et al.*, 2009). Commonly, toxic metals exhibit low concentrations in ambient environment and their major contributing sources are the natural rocks and soil weathering (Karbassi *et al.*, 2008). Surface water may be contaminated by various geological and anthropic sources which impair its use for drinking, industrial, agricultural and recreation purposes (Saleem *et al.*, 2015a,b; Varol and Sen, 2012; Zhang *et al.*, 2009).

1.4 Health Effects of Selected Metals

Metals exist in nature and exhibit the tendency of accumulation into different living organisms in which they play vital roles in various biological and physiological processes. Some metals are essential at lower concentrations, but may become toxic at higher levels and their long time exposure may cause detrimental effects to humans. Major health effects of selected metals are described in the following sections.

1.4.1 Arsenic (As)

Arsenic is a well known carcinogen which exists in earth crust, water and air (ATSDR, 2007). Drinking water is an important source of As; however, other significant sources are contaminated food, air, mining, industrial runs offs, ceramics production, occupational environment, wood combustion/preservative, coal burning, insecticides, pesticides, glass manufacturing, waste incineration, etc (ATSDR, 2007; Chung *et al.*, 2014, Garelick et al., 2008). It may cause tracheae bronchitis, pharyngitis, nasal congestions, black-foot disease, foetal/teratogenic diseases, gastro-intestinal problems, anaemia, anuria, convulsions, coma, localized edema and decrease in white/red blood cells production (Gumpu *et al.*, 2015, Kazi *et al.*, 2009; Liu *et al.*, 2003; Xia and Liu, 2004). In addition, it may affect the central nervous system & peripheral nervous system, disrupt the heart rhythm, melanosis, hyperkeratosis and cancer (Abernathy *et al.*, 2003; Caussy, 2006; Gumpu *et al.*, 2015, Hughes *et al.*, 2011; Kazi *et al.*, 2009; Liu *et al.*, 2003; Patel *et al.*, 2012; Valko *et al.*, 2005; Xia and Liu, 2004).

1.4.2 Calcium (Ca)

Calcium is an integral part of bones, teeth, soft tissues and a variety of metabolic activities in human. It is essential for membrane activity, nerve impulse transmission, hormone discharge, stabilization of blood pH, proteins transmission along secretory route, functioning of myocardial system, heart and muscles contractility, intracellular information transmission, blood coagulability and carbohydrates/fats metabolism (Dolman and Tepikin, 2006; Zemel *et al.*, 2004). Its deficiency may cause osteoporosis, obesity, depression, elevated blood cholesterol, hypertension and cancer (Butler *et al.*, 2010; Kozisek, 2003). Nonetheless, long time exposure of calcium in excess may cause hypercalcemia and related side effects, such as, hypercalciuria, urinary tract calculi, calcification in soft tissues & in arterial walls, and suppression of bone remodelling (Heaney *et al.*, 1982; Yiu *et al.*, 2015). Its major dietary sources are plants, milk/milk products, green leafy vegetables, fruit, nuts and beans (Bacher *et al.*, 2010; Brown, 2009).

1.4.3 Cadmium (Cd)

Cadmium is considered as a carcinogenic element (Wang *et al.*, 2012). It is relatively mobile in the environment and it is contributed by both anthropogenic (such as, fertilizers, paints, plastics, ceramics, glass manufacture, batteries, metal coatings, cigarette etc.) and natural sources (Demlie and Wohnlich, 2006; Gowd and Govil, 2007; Saleem et al., 2013; Sayadi and Sayyed, 2011). It may cause diarrhoea, weight loss, fatigue, reproductive problems, osteomalacia, hypertension, anaemia, tumours and hepatic dysfunction, renal tubular dysfunction, skeletal damage and lung cancer (Al-Busaidi *et al.*, 2011; Ercal *et al.*, 2001; Gumpu *et al.*, 2015; Ikem *et al.*, 2002; Rahman *et al.*, 2012). It may also minimize human semen efficiency and may cause inhibition of many enzymes functions and a variety of disorders, such as, DNA damage and weakening of reproductive function, etc. (Barrento *et al.*, 2008; Walker *et al.*, 2001). Generally, it is ingested through diet in relatively larger concentrations from plant than meat, apart from eggs, milk/milk products and fish muscles (Ilyasova and Schwartz, 2005; Jarup and Akesson, 2009).

1.4.4 Cobalt (Co)

Cobalt is recognized as central bonding element of vitamin B12, which is needed for metabolism of folates/fatty acids and co-factoring of methylmalonyl-CoA mutase and methionine synthase enzymes in human (Arnich et al., 2012). It is helpful for ischemia and tissue hypoxia by increasing oxygen-carrying capacity of the blood. It may accumulate in liver, kidney, pancreas, heart, skeleton and skeletal muscles (Simonsen *et al.*, 2012). Environment is contaminated by Co from diverse sources including both natural as well as anthropogenic such as, rock weathering, industrial emission, coal-fired power plants, incinerators, vehicular exhaust, industrial mining, cobalt alloys/chemicals, radioactive waste dumping and nuclear power plant operations (ATSDR, 2004; Jayakumar and Jaleel, 2009; Matsumoto *et al.*, 2003; Mocini *et al.*, 2007; Singh *et al.*, 2010). In addition, cobalt (II) compounds are categorized as 'possibly carcinogenic to humans' (group 2B) (IARC, 1991). It may influence the processes of haematopoiesis—stimulation of erythropoietin production and haemoglobin synthesis (Angelova *et al.*, 2014; Yamada, 2013). Elevated exposure to Co may result in asthma, thyroid alterations, allergic contact, dermatitis testicular deterioration, vasodilation and oxidative damage to DNA, proteins and lipids (Arnich *et al.*, 2012; Petit *et al.*, 2005; Sauni *et al.*, 2010).

1.4.5 Chromium (Cr)

It occurs in different oxidation states ranging from 0 to VI; however, Cr (III) and Cr (VI) are considered as stable states in the environment (Horcsik *et al.*, 2006). Cr (III) is present naturally in various vegetables, fruits, meats, yeasts and grains, but its natural concentrations in various foods may be different depending upon food preparation and storage conditions (Ramachandra *et al.*, 2015). It may be contributed in the environment from anthropogenic sources such as, tanneries, pharmaceuticals, pigments, metal works, along with natural inputs (Kumar *et al.*, 2008). Cr (VI) has been recognized as a human carcinogen (Li *et al.*, 2008b). Commonly, Cr is considered as a vital element for carbohydrate and fat metabolism in human (Cefalu and Hu, 2004), nonetheless, its disproportionate amounts (especially Cr-VI) may cause perforation of septum, DNA damage, carcinogenicity, interference with normal enzymatic activity, embryotoxicity, dermatitis, and digestive, excretory, respiratory and reproductive disorders (Dayan and

Paine, 2001; Dey and Roy, 2009; Gumpu *et al.*, 2015).

1.4.6 Copper (Cu)

Copper is an essential part of several enzymes and required for synthesis of haemoglobin, biological electron transport and development of connective tissues (Barrento *et al.*, 2008; Madsen and Gitlin, 2007; Rahman *et al.*, 2012). Its deficiency may cause hair loss, anaemia, aneurysms and arthritis (Mukherjee, 2011). Its toxicity may result in irritation to mouth, nose, and eyes; severe mucosal irritation, widespread capillary damage, central nervous problems, depression, cystic fibrosis, stomach-aches, diarrhoea, alopecia, autism, diabetes, haemorrhaging and kidney disorders (Gumpu *et al.*, 2015; Sengil *et al.*, 2009). Its disproportionate concentrations may result in liver and kidney damage, and even death. Its chronic poisoning may cause Wilson's disease, brain damage, and copper deposition in the cornea (Burke, 2013; Gumpu *et al.*, 2015; Mukherjee, 2011; Sengil *et al.*, 2009). Anthropogenic sources of Cu included nonferrous metal production and mining, wood production, iron and steel production, waste incineration, industrial applications, coal combustion, oil and gasoline combustion, agricultural activities and phosphate fertilizers (ATSDR, 2004; Willis and Bishop, 2016).

1.4.7 Iron (Fe)

Iron exists in large amounts in earth crust and it is vital for normal physiological processes. It is an integral component of haemoglobin, myoglobin, ferritin, hemosiderin and different enzymes; it also play vital role in DNA synthesis and brain functioning (Edelstein and Sharlin, 2009; Erdogrul and Erbilir, 2007). The excessive concentration of Fe is stored in liver. It is also present in larger amount in bone marrow which is responsible for haemoglobin production (Nadadur *et al.*, 2008). It has been estimated that about 4 g of Fe is present in human body; of which nearly 70% exists in red blood cells (Saljoughian, 2007). Its deficiency may lead to anaemia, while excess may cause variety of adverse health effects, such as, cancer, diabetes, liver & heart diseases, neuro-degenerative disorders and siderosis (Adebiyi *et al.*, 2008; Atolaiye *et al.*, 2009; Rasmussen *et al.*, 2001; Sayre *et al.*, 2000).

1.4.8 Mercury (Hg)

Mercury is a non-essential and carcinogenic metal for human. Natural mercury sources include volcanic eruptions, forest fires, cannabar (ore) and fossil fuels while anthropogenic sources are industrial effluents, coal combustion, landfills, dental preparations, laboratory use, municipal/medical waste combustion, gold mining, non-ferrous metals production, cement production, boilers, fossil fuels, etc. (Galimberti *et al.*, 2016; Mozaffarian & Rimm, 2006; Pacyna *et al.*, 2010). Nutritional intake (especially food/fish), dental amalgam and its vapours discharged from amalgam fillings are major routes of exposures to human (Jarup, 2003; WHO, 1990). In aquatic ecosystems, it may affect the reproductive system of fish (Crump and Trudeau, 2009). It has been reported as a likely neurotoxin compared to other elements. It has the strongest tendency of biomagnification among the metals through food chain and it may reduce neurologic development; influence digestive system, immune system, lungs, kidneys, coronary heart, skin and eyes, acrodynia and increase salivation, hypotonia and hypertension (Barringer *et al.*, 2012; Gumpu *et al.*, 2015; Kobal *et al.*, 2004; Luiz *et al.*, 2008; Salonen *et al.*, 1995).

1.4.9 Potassium (K)

Potassium is a vital element; essential to both cellular and electrical functions. It is one of the most important electrolytes in the human body. It is found in varying amounts in almost all foods. Vegetables, especially green leafy varieties, are generally richest sources of K (Larsson *et al.*, 2011; Macdonald, 2007). It is an essential nutrient for plant development and growth; it maximizes crop repelling ability to diseases & starch production and control root growth as well as opening/closing of stomata in plant cells (Blatt, 2004). It plays a significant role in glucose metabolism and nerve functions; controls the damage to heart/arteries and may reduce cardiovascular risk (Larsson *et al.*, 2011). Its higher amounts may result in lowering of blood pressure, stroke risk, urinary calcium excretion, kidney stone risk, osteoporosis, renal vascular, glomerular and tubular damage (He and MacGrego, 2008 & 2001). Its deficiency may result in depression, muscle weakness, heart rhythm disorder and confusion (Weiner and Wingo, 1997). The exposure of K through dust or mists may irritate eyes, nose, throat, lungs with sneezing, coughing and sore throat. Its direct exposure to skin and eyes may result in burning leading to permanent damage (Permyakov, 2009).

1.4.10 Lithium (Li)

Recently, Li has been liked with some important biological processes in human body although previous studies reported its non-essential character (Aral and Vecchio-Sadus, 2008; Leonard *et al.*, 1995). Its deficiency has been linked with high rates of suicides, homicides and drug cases (Marshall, 2015). It can participate in some biological processes, such as, functioning of enzymes, hormones and vitamins (Oruch *et al.*, 2014; Schrauzer, 2002). Its long term exposure may be beneficial for bipolar disorder, guarding from depression/mania and for minimizing risk of suicide and short term mortality (Cipriani *et al.*, 2005; Kapusta *et al.*, 2011; Schrauzer, 2002). It is also related to urinary problems, gastrointestinal disturbances, oedema, tremor, hypothyroidism, hyperparathyroidism and weight gain (Kjolholt *et al.*, 2003; McKnight *et al.*, 2012). In addition to natural contribution from earth crust, Li is also derived from variety anthropogenic activities such as, pharmaceuticals and electronic devices, manufacturing wastes (from aluminium, glass and ceramic production), lithium-ion battery and fertilizers. Combined effect of these sources are responsible to increase the Li levels in the environment (Aral and Vecchio-Sadus, 2008; Porter and Bernot, 2010).

1.4.11 Magnesium (Mg)

Magnesium is an essential nutritional element; human body has about 25 g of Mg, of which 60% is found in bones and 40% in muscles/tissues (Arnaud, 2008; James, 2010). Generally, the daily requirements of Mg are between 250 to 350 mg and it is antagonistic to Ca; both often participate in same types of biological processes (Anastassopoulou and Theophanides, 2002). It is responsible for maintaining muscle, membrane and nerve functions; controls blood sugar levels, energy metabolism, protein synthesis, blood pressure, heart rhythm, healthy immune system, bones strength, muscles contraction and DNA replication (Chillemi and Chillemi, 2007, Chubanov *et al.*, 2005). It also helps to avoid various disorders, such as, hypertension, cardiovascular disease and diabetes (Barbagallo *et al.*, 2007). Its deficiency may result in loss of appetite, nausea, fatigue, weakness and hypocalcaemia (Morley and Thomas, 2007). The excessive intake of Mg may cause muscle weakness, injury, lethargy, and confusion (Chillemi and Chillemi, 2007).

1.4.12 Manganese (Mn)

It is an indispensable element for human lives (Emsley, 2003); it acts as a cofactor of various enzymes in human body (Erdogrul and Erbilir, 2007; Sures *et al.*, 1999). It is commonly contributed by pesticides, fuel additive, domestic/municipal waste, industrial emissions, fossil fuel combustion, iron and steel plants, power plants, erosion of manganese-containing soil, and volcanic eruptions, etc. Its deficiency may result in obesity, skin diseases, lowering of cholesterol levels, glucose intolerance, skeleton disorders, birth defects, osteoporosis, reproductive disorder, epilepsy and neurological symptoms (Keen *et al.*, 2000). Its excess may result in severe disordering of nervous system and brain (Crossgrove and Zheng, 2004; USEPA, 2004a; Barbeau, 1984; Mohan and Sreelakshmi, 2008). It is mostly ingested through spinach, grains, rice, soya beans, eggs, nuts, olive oil, green beans, tea and herbs.

1.4.13 Sodium (Na)

Sodium is an essential nutrient and about 300 mg/day is required for good human health (Hemat, 2009). It has tendency to control extra cellular fluids, acid-base balance, and membrane potential in addition to sustain stability of physical fluids system, nerve and muscle working (Doyle and Glass, 2010). Its deficiency may result in dehydration, convulsion, muscle paralysis, decreased growth and general numbness, while its direct contact may cause irritation to skin, eyes, nose/throat, coughing, itching, tingling, thermal and caustic burns (Appel *et al.*, 2001; Sittig, 1991). The elevated exposure may result in suffocation, coughing and chemical bronchitis whereas the excessive intake may cause hypertension, stroke, osteoporosis and renal stones (Adrogue and Madias, 2008; Permyakov, 2009). Its higher concentrations may cause salty taste to water and make it unsuitable for drinking and irrigation uses and may also exert osmotic stress on the aquatic biota (Raza *et al.*, 2007).

1.4.14 Nickel (Ni)

Nickel is a ubiquitous element in nature and needed mostly for normal growth and reproduction in living organisms. It occurs at lower concentrations in the environment and the elevated levels may result in carcinogenic effects (WHO, 2011). Elevated levels of Ni might be due to industrial activities (nickel plating, ceramics colouring, batteries, catalysts, nickel alloys production, metallurgical, chemical and food processing industries), fossil fuel combustion, waste incineration, and sewage sludge (ATSDR, 2005; Cempel and Nikel, 2006; Iyaka, 2011). It is an established haemato-toxic, immune-toxic, neuro-toxic, geno-toxic, reproductive toxic, pulmonary toxic, nephron-toxic, hepato-toxic and carcinogenic agent (Cempel and Nikel, 2006; Das *et al.*, 2008; Sharma 2013; Zirwas and Molenda, 2009). It may lead to lung inflammation, contact dermatitis, DNA/proteins damage, cardiovascular diseases, kidney and respiratory problems in human (Azizullah *et al.*, 2011; Das *et al.*, 2008; Kazi *et al.*, 2009; McGregor *et al.*, 2000; Tian *et al.*, 2012;

Zirwas and Molenda, 2009). It is commonly found in water, air and various foods, such as, cereals, offal, poultry, fish, eggs, green vegetables, nuts, fresh fruits, oils, fats roasted, salted cashews, custard, lentils, mixed nuts, dried peas, haricot beans, coffee bean, cocoa, tea leaves, chocolate, fruit and vegetable juices, wine, cocktails and soya beans (Cempel and Nikel, 2006; Osma *et al.*, 2013; Ysart *et al.*, 1999).

1.4.15 Lead (Pb)

Lead is a persistent and non-essential metal with no known biological function in human; however, it may show carcinogenic effects on aquatic biota and human (Adeyeye *et al.*, 1996; Raviraja *et al.*, 2008). Elevated concentrations of Pb in environment may be attributed to fertilizer, paint industries, smelting, vehicular exhaust, corrosion of lead pipes, municipal/industrial wastes, etc. (Gowd and Govil, 2007; Sayadi and Sayye, 2011). Pb is commonly used in batteries, ammunition, solder, piping, pigments, insecticides and alloys (Sayadi and Sayye, 2011). It may cause disturbance in haemoglobin biosynthesis, in addition to high blood pressure, nephrotoxicity, kidney/liver damage, subtle abortions and neurotoxicity (Castro-Gonzalez and Mendez-Armenta, 2008; Garcia-Leston *et al.*, 2010; Jarup, 2003; Kazi *et al.*, 2009; Rahman *et al.*, 2012). It is also involved in disruption of cardiovascular, digestive, hematopoietic, reproductive and immunological systems and may exhibit damage to skeleton, brain and DNA (Azizullah *et al.*, 2011; Kazi *et al.*, 2009; Venkatesh, 2004). It is also linked with various cancers, decline semen fertility, behavioural disruptions of children, such as, aggression, impulsive behaviour and hyperactivity, developmental delay, low birth weight and serious damage to the nervous system and the brains of foetus (Bellinger, 2005; Garcia-Leston *et al.*, 2010; Jarup, 2003; Venkatesh, 2004; Watt *et al.*, 2000).

1.4.16 Selenium (Se)

Selenium is a well-known antioxidant/anti-inflammatory agent and an important constituent of various selenoproteins that avoid damage from free radicals and reactive oxygen species (Pieczynska and Grajeta, 2015; Strange *et al.*, 2010). Consequently, it guards against different cancers including lung, bladder, colorectal, liver, oesophageal, gastric-cardia, thyroid and prostate cancers (Rayman, 2012). It also defends from cardiovascular diseases, impede platelet accumulation, minimize inflammation, stop thyroid cells exposure from hydrogen peroxide and avoid irremediable brain impairment and type 2 diabetes (Amaral *et al.*, 2010; Brinkman *et al.*, 2006; Burk and Hill, 2009;

Etminan *et al.*, 2005; Schomburg and Kohrle, 2008). In addition, it helps in functioning of brain, immunity, fertility, reproduction, oxidative stress, thyroid function and autoimmune thyroid disease (Akbaraly *et al.*, 2005; Bleys *et al.*, 2008; Carlson *et al.*, 2010). It plays very significant role in modulation of growth and development and in oxidative stress defence (FAO/WHO, 2002). It is most commonly found in meats, seafood, cereals, grains, agricultural crops, milk/milk products, fruits and vegetables (Rayman, 2012). Beside the natural sources, it is mostly contributed by industrial wastes (electronics industry; glass industry; plastics industry, paints, enamels, pharmaceuticals; antidandruff shampoos), coal combustion, municipal wastes, agricultural activities, poultry and livestock wastes, etc. (ATSDR, 2003; US EPA, 2015).

1.4.17 Strontium (Sr)

Strontium is a persistent element in nature and found in rocks, soil, dust, coal, oil, plants and animals. It is mainly present in drinking water and various foods, such as, fish, vegetables, livestock, grain, leafy vegetables and dairy products (ATSDR, 2004; Nielsen, 2004). It is naturally occurring element found in rocks, soil, dust, coal, and oil. Strontium compounds are used in making ceramics and glass products, pyrotechnics, paint pigments, fluorescent lights, and medicines (ATSDR, 2004). Generally, it has not been found to be toxic in the environment through some exposure routes; however excess intake may result in adverse health effects such as bone growth problems in children, hypocalcaemia, phosphorus deficiency, anaemia and cancer (ATSDR, 2004; Chen *et al.*, 2012; Nielsen, 2004). Excess of Sr in the human body is generally considered as a risk factor towards the progression and development of cardiovascular disease as it plays a critical role in arterial stiffness that may be explained by its potential role in the enhancement of oxidative stress (Wu *et al.*, 2012).

1.4.18 Zinc (Zn)

Zinc is an essential metal for living organisms. It is an integral constituent of different enzymes and beneficial for synthesis and dehydration of carbohydrates, lipids, proteins and nucleic acids (FAO/WHO, 2002; Jeejeebhoy, 2009). It is also involved in gene processing, cell replication, tissues growth, sexual development and protection from some metal's toxicity (Early *et al.*, 1992; FAO/WHO, 2002; Skowerski *et al.*, 1997a,b). It is known as an antioxidant agent and benefits in stabilization of cell membrane (Maret and Sandstead, 2006). Its deficiency may lead to birth defect, sexual immaturity, damage to immune and enzymes systems, tastelessness, skin changes, poor appetite, respiratory disorders, metal fume fever, slow wound healing, mental lethargy, prostate cancer risks, neurosensory disorders, macular degeneration and cell-mediated immune disorders (Chasapis *et al.,* 2012; Eze *et al.,* 2014; Gumpu *et al.,* 2015; Nriagu, 2007; Prasad, 2008, 1995; Smalinskien *et al.,* 2005). Its excess may lead to nausea, vomiting, dizziness, fevers, diarrhoea, stomach cramps, skin irritations, nephritis, anuria, anaemia, damage to pancreas and arteriosclerosis (Eze *et al.*, 2014; Khan *et al.,* 2013; Nriagu, 2007). Generally, it is found in red meat, poultry, beans, nuts, seafood, whole grains, fortified breakfast cereals and dairy products (Antonetti, 2013). Anthropogenic sources of Zn are mining, metal productions, brass works, coal/fuel combustion, waste incineration, iron and steel production, cement production, wood preservatives, discharges of smelter slags and waste, urban wastes, agricultural run-offs, etc. (Councell *et al.,* 2004; Callender and Rice, 2000).

1.5 Significance and Contamination of Sediments

Sediment is organic and/or inorganic solid material that is derived from the rock's weathering and is carried by suspended in or dropped by air, water or ice and eventually forms layers on the bed of an aquatic reservoir as gravel sand, silt or mud (Mustapha and Lawal, 2014). They are generally complex entities, comprising of inorganic materials and organic matter. Additionally, they are physicochemically stable and environmentally may reveal average status of an aquatic ecosystem (Masoud *et al.*, 2007; Varol, 2011). Sediments are very sensitive ecological indicators for short and long term geogenic and anthropogenic contamination (Balogh *et al.*, 1999; Cheng *et al.*, 2015; Kazemi *et al.*, 2012). They exhibit the ability to accumulate the trace levels of toxic elements from overlying water column. However, deposition of trace elements is subjected to the nature of adsorbed pollutants, sediment texture, mineralogical configuration, adsorption and desorption processes, reduction/oxidation state, physical transport and the predominant physicochemical circumstances (ElNemr *et al.*, 2007; Tam and Wong, 2000). Consequently, they are well-known as an eventual sink and carriers for different pollutants added in the water reservoir; they may release soluble and particulate-bound pollutants because of leaching, uptake by the benthic flora, sediments re-suspension, desorption, redox reactions and solubility to overlying water column. As a result, they may exert adverse effects on the aquatic reservoirs via bioaccumulation and bio-magnification and can be lethal to the benthic biota (Adams *et al.*, 1992; Cheng *et al.*, 2015; Christophoridis and Fytianos, 2006; Wright and Mason, 1999).

Among different pollutants, trace metals are the most persistent and hazardous ones in the water reservoirs (Arnason and Fletcher, 2003; Yoshimura *et al.*, 2005). Some of the trace metals may result in hazardous consequences because of their toxicity, persistent and tendency of bioaccumulation (Diagomanolin *et al.*, 2004). However, their toxicity is subjected to the metals' concentrations and the existing physicochemical conditions of the reservoir (Stauber and Florence, 1987). Toxic metals' contamination of bottom sediments can substantially influence the water quality, thereby affecting the food chain and eventually risking the human health (An and Kampbell, 2003; Rodrigues *et al.*, 2010). The possible sources of deposition/adsorption of metals on sediments may be fuel combustion, processing of ores, industrialization, urbanization, agricultural activities, soil erosion, biological activities, smelting, metallurgical processes and road runoffs (Bandl, 1995; Dassenakis *et al.*, 2003; Deepulal *et al.*, 2012; Von Gunten *et al.*, 1997).

1.6 Significance and Contamination of Soil

Soil is primarily derived from rocks weathering and it is the combination of various organisms, minerals, water, gases, inorganic and organic materials (Manahan, 1999). Entire food production and living things are dependent on soil and it is also responsible for trace metals intake to plants in the form of micro-nutrients and pollutants (Kabata-Pendias, 2004). Typically, major components of soil are calcium, magnesium, nitrogen, carbon, phosphorus and potassium, whereas, boron, chloride, copper, iron, manganese, molybdenum, etc. are the minor constituents (Zheng *et al.*, 2007). Soil has the highest prominence in environmental investigations as it is responsible for numerous kinds of interactions among minerals, air, water and living things (Lal and Shukla, 2004; Zhai *et al.*, 2003). It is relatively less affected by external influences compared with water and air, and has the ability to fix different materials including toxic metals (Luo *et al.*, 2007). It is commonly reputed as incessant sink of toxic/trace metals, such as, Cd, Cr, Hg, Pb, Cu, Zn, Ni, and As. It can retain the trace metals for long periods and subsequently can damage the microbiota, flora and fauna after conversion from solid to ionic form (Chen *et al.*, 2016; Nriagu, 1990). Additionally, soil metals' may damage the human health through food web and contaminate surface and groundwater by leaching and runoffs (Luo *et al.*, 2010).

Human health can also be affected by metal contents of soil via direct ingestion or inhalation or dermal contact routes (Huang *et al.*, 2007). In recent times, soil pollution by trace metals has been recognized as a serious concern because mostly they are toxic, persistent and have the ability of bio-accumulation and bio-magnification (Giller and McGrath, 1988; Liu and Diamond, 2005; Nriagu, 1990; Teng *et al.*, 2014). Some of the metals, such as, Cd, Cr, As, Hg, Pb, Cu, Zn and Ni have been identified as priority pollutants by United States Environmental Protection Agency. Frequently, trace metals are accumulated at relatively higher proportion in smaller size soil particles which are easily dispersed in atmosphere by wind erosion (Lin *et al.*, 1998; Ljung *et al.*, 2006; Meza-Montenegro *et al.*, 2012). Generally, the trace metals in soil are contributed by several anthropic and natural sources, such as, vehicular emissions (exhaust, brake lining & tire wear particles), industrial emissions, domestic wastes, atmospheric deposition, mining, waste disposal, sewage, pesticides, fertilizers, soil erosion and rock weathering (Fernandez *et al.*, 2002; Franco-Uria *et al.*, 2009; Manzoor *et al.*, 2006; Schuhmacher *et al.*, 1997; Tam *et al.*, 1987).

1.7 Bioavailability of Metals

Bioavailability has got major significance in environmental and human health risk investigations (NRC, 2003). The existence of toxic or essential metals in environment may not be the source of future adversity; however, intake of the metals into human body and their accumulation may be the cause of imminent adverse effects (An and Kampbell, 2003; Rodrigues *et al.*, 2010). Generally, bioavailability is related to the hazardous materials in soil/sediments available to receptors and/or the ability of receptors to receive hazardous chemicals which are involved in the metabolism of receptor organisms (Adriano *et al.*, 2004; Campbell, 1995; Dissanayake, 2011; NRC, 2003). Metal bioavailability plays an important role in risk assessment for metal contaminated soil/sediment in highly industrialized/urbanized areas. The harmful effects are subjected to various factors including target organisms, contaminant nature & source, contact period, redox potential of substrate, transfer rate to organisms, accumulation of toxicants in organisms and the consequent effects (Harmsen, 2007; Hund-Rinke and Kordel, 2003; Kabata-Pendias, 1993). These can be measured by involving the organisms, however, chemical extractions at similar conditions close to real ones, can be enormously good techniques for the estimation of metals bio-availability from sediments/soil. Among various methodologies, extractions by using weak electrolyte solutions are frequently used for assessing the metals bio-availability, assuming that the extracted metals would be mobile and easily available to the receptors (Conder and Lanno, 2000; Luo *et al.*, 2012).

Bioavailability refers to the availability of the chemicals to living organisms which integrate chemical, physiological and toxicological features of the environment. The total amount of any metal in the soil is not available because they are adsorbed or bound by organic and inorganic constituents in the soil such as, organic matter, Fe and Al oxides and clay minerals (Fayiga and Saha, 2016). Thus, total metal level consists of fractions of different solubility and availability. The pseudototal/total metal levels are useful indicators of contamination and ecological risk assessment. However, it is well-recognized that the metals' toxicity, bioavailability and mobility cannot be assessed by total contents, whereas the bioavailable concentration of a metal is directly related to its toxicity and mobility to the receptors Bioavailability of metals can be determined by measuring the fraction of free metals present in the soil solution or by determining uptake by plants, soil biota or absorption into blood stream of humans (An and Kampbell, 2003; Fayiga and Saha, 2016; McLaughlin *et al.*, 2000; Rodriguez *et al.*, 2009; Zhao *et al.*, 2011).

1.8 Fractionation of Metals

Evaluation of total concentration of a metal indicates its accumulation in the receptors, but the hazards of bioavailability, toxicity and re-mobilization of the metal to the receptors cannot be gauged by total contents (Su and Wong, 2003; Zhao *et al.*, 2011). Chemical fractionation/speciation of trace metals might provide valuable information about their bioavailability, toxicity, reactivity, mobility and chemical nature (Ahlf *et al.*, 2009; Arnason and Fletcher, 2003; Hooda, 2010; Sundaray *et al.*, 2011). Recently, the fractionation has been frequently used to distinguish metals' associations with various geochemical phases and sources of the metals in soil/sediments (Davutluoglu *et al.*, 2011; Passos *et al.*, 2010). Among various extraction methods to evaluate the geochemical associations of the metals, modified-BCR (European Community of Bureau of Reference) sequential extraction method is very common for fractionation/speciation of the metals in soils/sediments (Davutluoglu *et al.*, 2010; Rauret *et al.*, 2001; Tessier *et al.*, 1979; Ure *et al.*, 1993). This method is mainly consisted of three steps; exchangeable/acid soluble, reducible and oxidiseable fractions. For fractionation, various reagents, such as, inert electrolytes, weak acids, reducing/oxidizing agents and strong mineral acids in an order of increasing their extraction strengths are used (Passos *et al.*, 2010). The exchangeable fractions (weakly bound to fine particles) are readily available for plants/organisms (Black *et al.*, 2011). The metal concentrations in different fractions are mainly subjected to the physicochemical characteristics of soil/sediments (Selim and Sparks, 2001; Zhao *et al.*, 2011). In agricultural soil, large proportions of the metals remained in residual fractions; however, in contaminated soil, the major proportions of metals resided in non-residual fractions (Brazauskiene *et al.*, 2008; Hu *et al.*, 2006; Zhao *et al.*, 2011).

1.9 Significance and Contamination of Fish Species

Ecological biomonitoring is related to the measurement of toxicants in the environment in order to gauge ecological pathways and probable impairment to benthic biota (Zauke *et al.*, 1998). A biomarker or biomonitor can be practiced to establish the environmental and time-based changes in the bioavailability of pollutants by quantifying the accumulated levels in particular tissues (Rainbow, 1995). Different organisms living in the aquatic ecosystems can be employed as biomarkers, such as, fish, benthic invertebrates, crustaceans, molluscs, annelids, zooplankton, phytoplankton, aquatic macrophytes, periphyton, microorganisms, algae and other organisms (Rashed, 2001a). However, in order to assess the trace metal pollution in water bodies, fish are believed as most appropriate biomarkers as they are at high trophic level and considered essential diet for human (Abdel–Baki *et al.*, 2011; Monroy *et al.*, 2014). They are also economical, balanced and vital element of human nutrition to support good health. They are considered as an excellent source of proteins, fats, energy, calcium, zinc, iron, vitamins and polyunsaturated fatty acids (Copat *et al.*, 2012; Sthanadar *et al.*, 2015). These constituents are beneficial for reducing cholesterol levels, as well as lowering the risk of coronary heart disease and customary neurodevelopment (Olmedo *et al.*, 2013; Swanson *et al.*, 2012).

Fish have the ability to accumulate large quantities of some essential and toxic metals in their tissues and organs from water, nutrition and sediments; however intake of the environmental pollutants in various tissues of fish is subjected to way of contact (Alam *et al.*, 2002; Rashed, 2001b; Yilmaz *et al.*, 2010). They can enrich water soluble contaminants through biological membranes and ionic exchange processes (Rahman *et al.*, 2014a; Yohannes *et al.*, 2013). Therefore, fish contamination by metals is an emerging global concern as they are not only hazard to fish, but also a serious health hazard to the consumers (Benzer *et al.*, 2013; Tiwari and Dwivedi, 2014). Although some metals are essentially required for physiological roles in fish, however, toxic metals may cause harmful effects in fish. These metals may cause distortions in structural/biological roles of biomolecules and bioaccumulated via food web to hazardous levels, resulting in adverse health risks to the consumers (Foran *et al.*, 2005; Mathews and Fisher, 2009; Tiwari and Dwivedi, 2014; Tuzen, 2003a). For instance, Hg may cause damage to reproductive system of fish, while Pb and Cd contaminated fish consumption can lower human semen quality, DNA damaging and result in weakening of reproductive function in human (Crump and Trudeau, 2009; Telisman *et al.*, 2000). Consequently, biomonitoring of trace metals is imperative to evaluate the ecosystem health and fish are frequently applied for gauging of the ecological and health effects of anthropogenic contaminants (Benzer *et al.*, 2013; Dural *et al.*, 2007; Tekin-Ozan and Kir, 2008).

1.10 Aims and Objectives of the Present Study

Considering the environmental significance of the metal pollutants in aquatic ecosystems, the present investigation is designed to evaluate the environmental risk of Mangla Lake by measuring the metal contents in water, sediment, and fish in the reservoir and soil quality around the reservoir along with health risk associated with the metal levels for human. Therefore, the present study is based on following major objectives:

- To develop the baseline data on present status of physicochemical parameters and selected metal levels in water, sediments, soil and fish from Mangla reservoir.
- To determine the water quality from the freshwater reservoir for drinking and irrigation purposes.
- To evaluate the spatial and temporal variability of selected metal levels in water, sediments and soil.
- To assess the distribution of selected metals in different geochemical fractions of the sediments and soil.
- To find out the mutual correlations among selected metals in water, sediments, soil and fish from the reservoir.
- To identify the major pollution sources in the reservoir by multivariate statistical methods.
- To estimate the relative contributions of bioavailable/mobile metal contents in the sediments and soil.
- To find out the ecological risks associated with the metal levels by computing enrichment factor, geoaccumulation index, contamination factor, degree of contamination, potential ecological risk factor, potential ecological risk index,

potential acute toxicity, individual contamination factor, global contamination factor, risk assessment code and heavy metal evaluation index.

- To analyse the human health risks including exposure assessment, margin of exposure, hazard quotients, estimated daily/weekly intakes and non-carcinogenic as well as carcinogenic risk assessments.
- To assess the risks associated with the pollutants by comparing metal levels with the sediment quality guidelines.
- To compare the present metal levels with the reported levels around the world and the safe limits recommended by world health authorities.
- To suggest the remedial measures and policies aimed at controlling the pollutants in freshwater reservoir.

Chapter 2

EXPERIMENTAL METHODOLOGY

2.1 Study Area

Mangla Lake located in Mirpur district of Azad Jammu and Kashmir, Pakistan (longitude: 73.65 (73° 39' 0 E); latitude: 33.15 (33° 8' 60 N)) is the 12th largest lake in the world (Ali *et al.,* 2011). The lake is almost 100 km south-east of the capital city, Islamabad, Pakistan and it was constructed during 1961-1967 by damming Jhelum River (Figure 1). Other major rivers that contribute to the water storage are Neelum, Kunhar, Kansi and Poonch. It has six reservoir pockets; Jhelum, Kanshi, Poonch, Main, Khud, and Jari. It is comprised of 4 embankment lakes, 2 spillways, 5 power-cum-irrigation tunnels, a 1000 MW power station and upper Jhelum canal. The main lake is 3140 m long and 138 m high (above core trench) with a reservoir of 253 km^2. Since its construction, the water storage capacity of Mangla Lake has been reduced from 7,254.74 to 5,764.31 million cubic meters due to the sedimentation (Butt *et al.*, 2011; Haq and Abbas, 2007).

The lake has already contributed significantly towards agriculture growth, job opportunities and improvement of living standard. Many thousands acres of land are irrigated using this water. Availability of additional water and hydropower production further enhances the positive impacts. The population around the lake is about 0.5 million. The lake was designed primarily to increase the amount of water that could be used for irrigation from the flow of the Jhelum River and its tributaries, while its secondary function was to generate electrical power at the artificial head of the reservoir. The lake supplies water for irrigation purpose to support more than 3 million people through food production. In addition, the lake water is being used by the surrounding inhabitants for drinking and domestic uses (Ali *et al.*, 2011; Saleem *et al.*, 2014a). The climate around the lake is sub-tropical with hot/rainy summer and cold/dry winter. Average rainfall is about 1300 mm per year and temperature varies from 45°C in summer to -2°C in winter (AJK at Glance, 2013; Pakistan Bureau of Statistics, 2010).

The lake water is used for irrigation, drinking, domestic, industrial and hydropower production purposes, therefore, any type of contamination in and/or around the lake would severely affect the water quality. Recently, rapid urbanization and anthropogenic intrusions were observed around the lake. Additionally, excursions, boating, sailing, water skating and diving activities are being carried out in the lake, which is also well known for commercial fishing. The untreated municipal wastes, industrial effluents, atmospheric deposition, runoffs from poultry farms & agricultural fields and contaminants discharged during the recreational activities are the major pollutants sources in the lake. The pollutants may enter into the food web resulting in adverse health effects to the consumers (Butt *et al.*, 2011; Saleem *et al.*, 2013; Water Quality Monitoring in AJK, 2004).

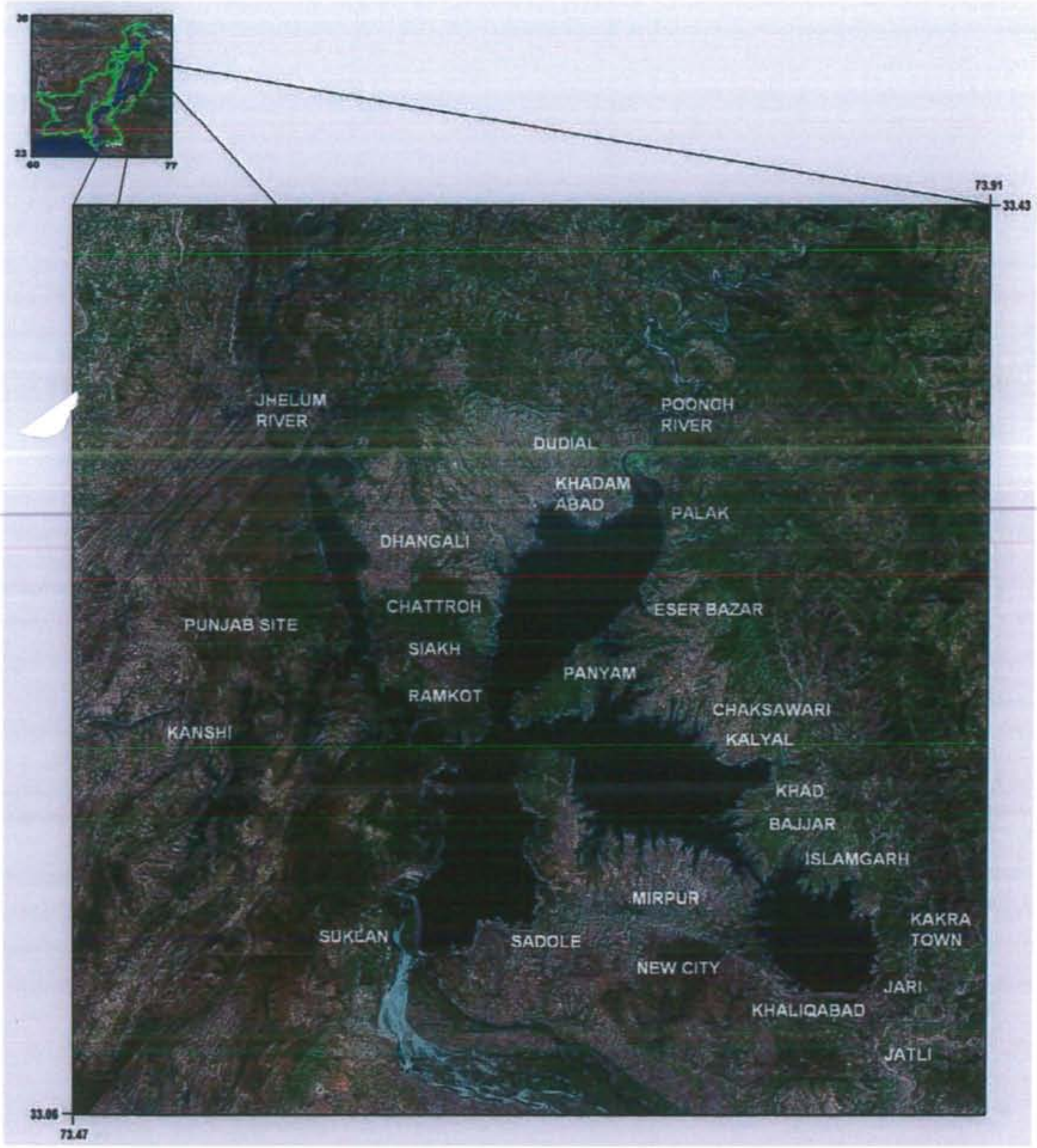

Figure 1. Location map of the study area

2.2 Sample Collection and Storage

Composite surface water samples were collected in triplicate from different parts of the lake in polyethylene bottles (1.5 L) by direct method as per standard methodology (APHA, 1995, USEPA, 2003a). Each composite sample was comprised of 3-5 sub-samples of equal volume collected from an area of 10-50 m^2. The samples were placed in airtight ice-cooled plastic containers and immediately transported to the laboratory, where they were stored in a refrigerator before further analyses. During sample collection, fresh sampling bottles were used at each sampling point. The sampling was carried out in summer (2011), winter (2011), pre-monsoon (2012), monsoon (2012) and post-monsoon (2012).

Composite surface sediments (1-15 cm, top layer) were collected in triplicate from different parts of the lake in pre-cleaned zip-locked polythene bags using a snapper (Φ 5 cm) after carefully removing the debris. Each sample (~1 kg) was a composite of well mixed 3-15 sub-samples collected over an area of 20-100 m^2. The overlying water was decanted and the sediment samples were kept in ice-cold containers. Composite sampling is generally preferred for the assessment of inorganic contaminants in the sediments/soil with the potential advantages of improved coverage of the area without increasing sample number, more information about average contaminant concentration, ability to detect hot spots, more representative estimates of mean concentrations, accurate exposure point concentrations and reduced sampling cost (Carson, 2001; Correll, 2001; USEPA, 1991). Although composite sampling methodology may result in partial loss of spatial variability but considering the size of Mangla Lake it was considered more appropriate to cover the maximum part of the lake in order to assess the overall pollution stress. The sediment samples were air dried, followed by oven dried, grounded, homogenized and sealed in clean polythene bags and then stored in a refrigerator until further processing (Sakai *et al.*, 1986; USEPA, 1994b, 2001 and 2003b). The samples were collected in summer (2011) & winter (2011) and pre-monsoon, monsoon & post-monsoon (2012).

Similarly, composite surface soil samples (0-15 cm, top layer) were collected in different seasons (summer (2011), winter (2011); and pre-monsoon, monsoon & post-monsoon, 2012), using a plastic scoop and trowel. Prior to sampling, all the soil samples were cleaned manually for any foreign matter, such as, leaves, twigs, etc. All the samples were collected in triplicate in pre-cleaned zip-locked polythene bags. Every soil sample (~1 kg) was a composite of 5-10 sub-samples collected over an area of 10-20 m^2. The soil samples were oven dried, grounded, homogenized, sieved through a 2 mm plastic sieve to remove stones, gravels, coarse particles and then stored in zip-locked polythene bags before further analyses (Cai *et al.*, 2015; Huo *et al.*, 2010; Saleem *et al.*, 2014b; USEPA, 2000).

Five fish species, local (English and *Latin* in bracket) namely Gulfam (Common Carp, *Cyprinus carpio),* Thaila (Indian Carp, *Catla catla),* Silver (Silver carp, *Hypophthalmichthys molitrix),* Mulli (Wallago catfish, *Wallago attu)* and Singhari (Indus catfish, *Sperata sarwari)* were included in the present study. The fish samples were collected by seining method in 2011 and 2012 following the reported procedure (USEPA, 2003c). The method is very efficient to trap the fish with net, lower end was weighed down by lead weights/a lead line and floats were attached to the upper end of the net. In order to avoid escaping of the fish, the lead line was allowed to touch the bottom and float line were kept above the water surface. Poles were equal to the height of the net and held at 45° angle away from the direction of movement during dragging the net. After collection, the fish samples were placed in pre-cleaned ice-cooled plastic bags and immediately transported to laboratory for further processing (USEPA, 2003c).

2.3 Sample Processing

Water samples were filtered through fine filters (0.45 μm, pore size) to remove the suspensions and other floating materials. The filter surface was rinsed with a small portion of the samples which was discarded and the remaining portions of the filtrate were stored. Each water sample was divided into two portions; one portion was used as such for the measurement of physicochemical parameters and the other portion was employed for the analyses of selected metals after acidification with concentrated HNO_3 maintaining $pH < 2$. The samples were stored in a refrigerator in pre-cleaned polythene bottles till analyses (Adam *et al.*, 2001; Radojevic and Bashkin, 1999; USEPA, 1994a, 2003a; Varol, 2013).

The preservation of soil and sediment samples is not commonly recommended, therefore, these samples were oven dried, grounded, thoroughly mixed, sieved through 2 mm mesh, placed in pre-cleaned polythene bags and kept in a refrigerator until further analyses (Cai *et al.*, 2015; Iqbal and Shah, 2011; Lu *et al.*, 2012; Nemati *et al.*, 2011; Radojevic and Bashkin, 1999; USEPA, 2000 and 2003b).

The fish samples were carefully washed with doubly distilled water and stored in a refrigerator to avoid their deterioration until further processing. Total lengths (mm), body weights (g) and condition factors (K) were accurately measured before dissecting the fish samples into muscles, gills and scales (Iqbal and Shah, 2014a; Tekin-Ozan and Kir, 2008).

2.4 Preparation of Water Sample

Water samples were acidified and their pH was maintained less than 2 by nitric acid for the measurement of total dissolved metal contents. The samples were only filtered whenever they were not clear and/or having insoluble materials to avoid clogging of the instrument nebulizer (USEPA, 1992). Nonetheless, some physicochemical parameters were recorded on-site while others were measured in laboratory without adding any preservative/chemical to the sample.

2.5 Preparation of Sediments/Soil Sample

2.5.1 Single Extraction Procedure

Evaluation of bioavailability of selected metals in soil/sediments is imperative to determine their potential mobility to living biota. Among single extraction methods, weak acids/electrolytes extraction procedures are very common to estimate the bioavailability of metals in soil/sediments. In the present study, single-step extraction was carried out using $Ca(NO_3)_2$ solution. About 50 mL of 0.1 M $Ca(NO_3)_2$ solution was added to 5.0 g of soil/sediment sample in a pre-cleaned glass vessel which was shaken on an auto-shaker at 240 vibrations per minutes for 16 hours. A reagent blank was also processed with the same amount of $Ca(NO_3)_2$ solution without the sample. Triplicate extractions were performed for every sample. The extracts were segregated from the solid residue through filtration using fine filters (0.45 μm, pore size) (An and Kampbell, 2003; Radojevic and Bashkin, 1999; Rodrigues *et al.*, 2010).

2.5.2 Sequential Extraction (*m*BCR) Procedure

Fractionation of the metals can provide useful information related to their chemical nature, potential mobility and bioavailability (Yang *et al.*, 2009). Numerous sequential extraction methods and their modified version have been reported in literature (Borovec *et al.*, 1993; Campanella *et al.*, 1995; Gomez-Ariza *et al.*, 2000; Kersten and Forstner, 1986; Tessier *et al.*, 1979). However, a much faster and simpler modified multi-step sequential extraction method suggested by European Community Bureau of Reference (*m*BCR) has been adopted in the present study. The *m*BCR sequential extraction procedure is composed of four fractions, namely, the acid extractable (exchangeable and bound to metal carbonates), reducible (bound to Fe and Mn oxides), oxidiseable (bound to sulphides and organic matter) and residual (immobile) fractions of the metals. The method provided information related to the mobility and bioavailability of metals and their health risks to the aquatic organisms (Nemati *et al.*, 2011; Nguyen *et al.*, 2009; Passos *et al.*, 2010). The complete sequence of extraction procedure is described below:

i) Exchangeable and Weak Acid Soluble Fraction (F1, Stage-I)

An aliquot of 40 mL of 0.11 M acetic acid was added to 1.0 g of soil/sediment sample (oven dried) in pre-cleaned vessel. The mixture was agitated at ambient conditions on an auto-shaker at 320 vibrations per minute for 16 hours. The extracts were separated from the solid residue by centrifugation at 3000 rpm for 20 minutes. The supernatant obtained by decantation was kept in pre-cleaned polythene bottles for further analyses. The solid phase was washed with 20 mL of de-ionized water on an auto-shaker for 20 minutes, centrifuged at 3000 rpm for 20 minutes and the supernatant were discarded.

ii) Reducible Fraction (F2, Stage-II)

In the solid residue of stage-I, an aliquot of 40 mL of a 0.5 M hydroxylammonium chloride solution (pH = 1.5) was added and the mixture was shaken on an auto-shaker at 320 vibrations per minute at ambient conditions for 16 hours. The extracts were separated in the same manner as in stage-I.

iii) Oxidiseable Fraction (F3, Stage-III)

An aliquot of 10 mL of 8.8 M H_2O_2 solution (pH = 2–3) was added into a glass vessel containing solid residue from stage-II. The mixture was left at room temperature for 1 hour with occasional shaking. Afterward, it was heated to 85 ± 2°C for 1 hour in a water bath until the volume was reduced to 2-3 mL, to which 10 mL of 8.8 M H_2O_2 solution was again added and the mixture was heated near to dryness. After cooling, 50 mL of 1.0 M ammonium acetate solution (pH = 2) was added and shaken on an auto-shaker at 320 vibrations per minute for 16 hours. Finally, the extracts were isolated from the residue by centrifugation, as mentioned above. The extracts in each extraction stage were evaporated near to dryness and then diluted up to 50 mL with 1.0 M HNO_3.

iv) Residual Fraction (F4, Stage-IV)

The final residue in a glass vessel was digested with 10 mL of freshly prepared aqua-regia solution (1:3 conc. HNO_3:HCl, v/v), which was added drop by drop to reduce fuming and foaming. The vessel was left overnight for slow dissolution of the residue and then refluxed for 2 hours. After cooling, the digests were separated through fine filters and washed with 0.5 M HNO_3 solution and final volume was adjusted with 0.5 M HNO_3. Reagents blanks were also prepared with each batch of extraction having same quantity of the reagents without soil/sediment samples.

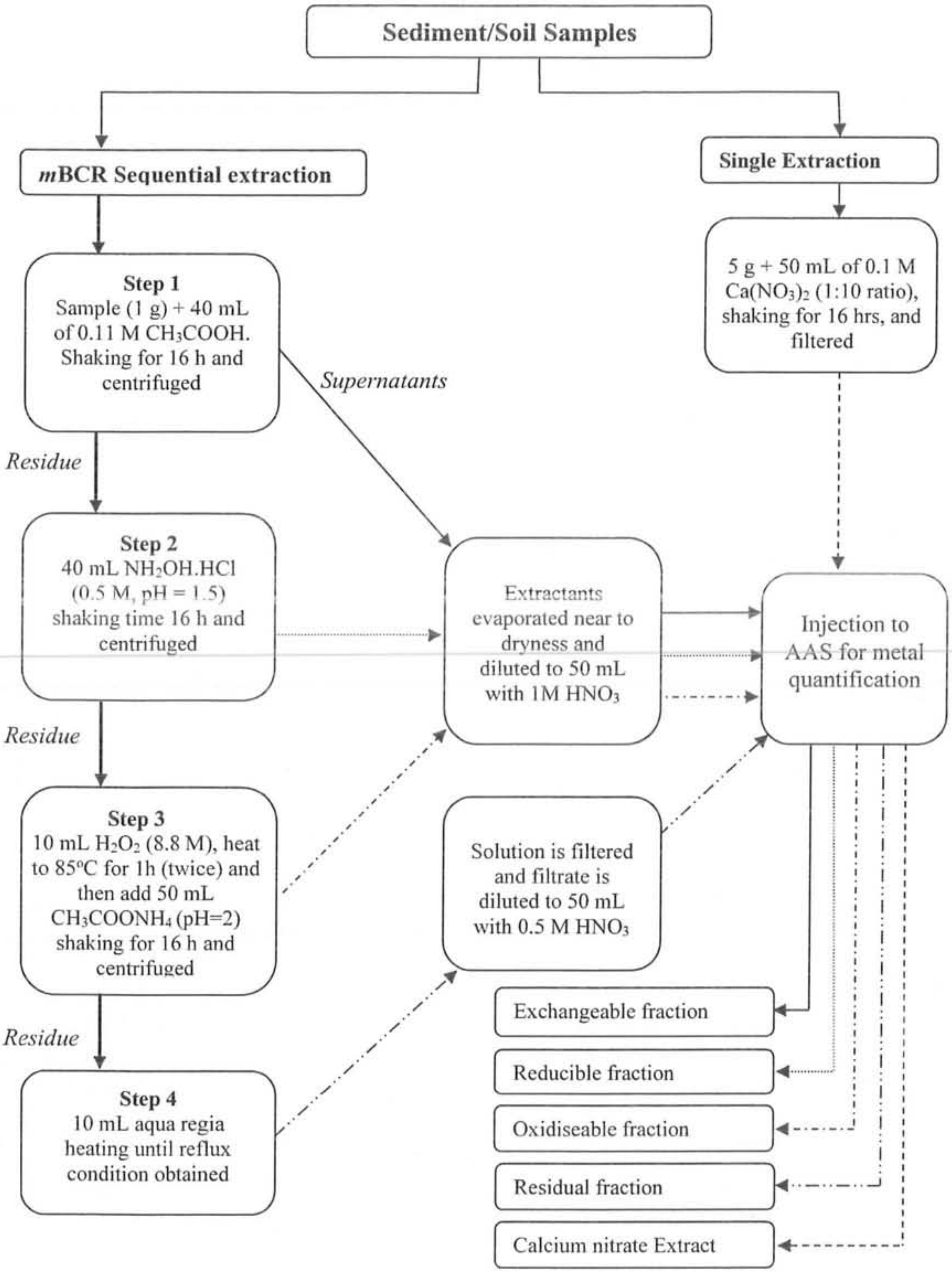

Figure 2. Flow diagram of the modified BCR sequential and single extraction procedure

Though residual fraction extraction was not the part of the original sequential procedure, it was carried out for quality purpose to compare the sum of all steps including residual fraction with the results obtained from a separate aqua-regia digestion for measuring the pseudo-total metal concentrations

2.5.3 Pseudo-total Metal Concentrations (Acid-Extract)

For the assessment of pseudo-total metal concentrations, the soil/sediment samples were initially air dried then oven dried, crushed, grounded and mixed to obtain homogenous samples. About 1-2 g of the sample was digested with a freshly prepared mixture of concentrated HNO_3 (9.0 ± 0.1 mL) and HCl (3.0 ± 0.1 mL) in a digestion vessel of a laboratory microwave unit (USEPA, 2007). The digestion vessel containing sample and acids mixture was tightened and placed in the microwave system as per the manufacturer's recommended directions. The vessel was heated to 175 ± 5°C in almost 5.50 ± 0.25 minutes and maintained at 175 ± 5°C for 10 minutes. The heating process was repeated for four times to completely digest the soil/sediment sample. The vessel was allowed to cool for 5 minutes between each cycle. Finally, the vessel was cooled and its seal was checked manually. The digested sample was wasted if its weight loss exceeded 1% of actual weight of the sample and acid mixture. Before uncapping, the vessel was put into a fume hood to avoid a rush of vapours. The digests were filtered through fine (0.45 µm pore) filter paper and final volume up to 50 mL was adjusted with 0.5 M HNO_3 solution (USEPA, 2007).

2.6 Preparation of Fish Sample

The defrosted fish specimens were bisected for muscles, gills and scales using pre-cleaned scissor and plastic spatula. The fish tissues were dried at 102°C for 12 hours, grounded and well mixed to get homogenized samples. Each fish tissue (1.000 ± 0.001 g) was digested with a freshly prepared mixture of concentrated HNO_3 (4 mL) and de-ionized water (4 mL) using a laboratory microwave oven system. The digestion vessel was heated for 5 minutes at 300 W and 80°C, followed by 5 minutes at 600 W and 100°C, 5 minutes at 900 W and 130°C, and 10 minutes at 1200 W power and 170°C temperature, respectively. The vessel was allowed to cool for 5 five minutes between each step (Jones and Laslett, 1994). Finally, the vessel was cooled and its seal was checked manually. The digested sample was wasted if its weight loss exceeded 1% of actual weight of tissue and acid-water mixture. Before uncapping, the vessel was put into a fume hood to avoid a rush of vapours. The digests were filtered through fine (0.45 µm pore) filter paper and final volume up to 50 mL was adjusted with 0.5 M HNO_3 solution (Jones and Laslett, 1994).

2.7 Measurement of Physicochemical Parameters

2.7.1 Hydrogen Ion Concentration (pH) and Temperature (T)

Hydrogen ion concentration (pH) and temperature (T) of the water samples were measured on the sampling sites immediately after their collection using a multimeter (Mi 180, Martini Instrument) and thermometer, respectively. However, the pH and temperature of soil/sediment samples were measured by shaking the water extract thoroughly and then allowed to stand for 2-5 minutes before recording the reading. Water extracts of the soil/sediments were obtained by agitating an aliquot of sediment/soil in de-ionized water (1:2 ratio) for 15 minutes on an auto-shaker. The slurry was allowed to settle and then pH and temperature were measured in the supernatant. The multimeter electrode and probe were immersed in water/water-extracts without touching with walls of the vessels and keeping 2 cm above the bottom of the vessel and then measurement was recorded. Prior to use, the multimeter was calibrated with buffer solutions of pH 4, 7 and 10. The electrode and probe were washed thoroughly with de-ionized water between every two consecutive readings (Bartoli *et al.*, 2012; Radojevic and Bashkin, 1999; USEPA, 2004a).

2.7.2 Electrical Conductivity (EC) and Total Dissolved Solids (TDS)

A multimeter (Mi 180, Martini Instrument) was used to measure both EC and TDS in water and water-extracts of the soil/sediments. Both these parameters were measured *in-situ* immediately after the collection for water samples, whereas in case of soil/sediments, these parameters were measured in water-extracts as described above for pH and T (Bartoli *et al.*, 2012; Radojevic and Bashkin 1999). Calibration of the multimeter was done with standard KCl solution (0.01 M & 0.1 M) every time prior to use. All the precautions as discussed in earlier section were taken while recording the measurements.

2.7.3 Dissolved Oxygen (DO)

Oxygen is dissolved in water because of the diffusion from the air, aeration of water and as a product in photosynthesis process. It was measured instantly after the sample collection using a digital DO meter (Mi 190, Martini Instrument) following the manufacture's instructions and procedure. The reading was noted in water samples after 2 minutes rest of shaking and ensuring all the precautions as described in earlier sections. The electrode of DO meter was washed with de-ionized water each time between consecutive readings (Radojevic and Bashkin, 1999; Tinker and Krajcik, 2001).

2.7.4 Alkalinity

Alkalinity is very important parameter for water as it buffers its pH changes and provides suitable medium for fish species and aquatic life. It was estimated by following the standard methodology (APHA, 2006), in which known volume of water or water-extract sample is titrated against H_2SO_4 or HCl. In case, pH of the samples is higher than 8.3, the titration is generally completed in two steps; firstly it is carried out using phenolphthalein indicator to a pH of 8.3 (phenolphthalein alkalinity, PA), and secondly it is performed using methyl orange indicator to a pH of 4.5 (total alkalinity, TA). However, if pH of the samples is less than 8.3, then only total alkalinity is determined. In the present study, pH of the samples was noted to be less than 8.3, so total alkalinity (TA) was measured only. The solution of H_2SO_4 was standardized against primary standard Na_2CO_3 (dried at 110°C for 2 hours) using methyl orange as an indicator. Afterward, alkalinity was determined by titrating 20 mL of the sample (water/water-extract) against standard solution of H_2SO_4 using methyl orange indicator. Subsequently, the volume of titrant was noted to calculate the alkalinity (Radojevic and Bashkin, 1999). It was calculated in the water samples as below:

$$\text{Alkalinity (mg CaCO}_3\text{/L)} = 1000 \times V_t \times M/V_s \qquad [1]$$

where, V_t = Volume of the titrant used (mL)

V_s = Volume of the sample taken (mL)

M = Mass (mg) of $CaCO_3$ equivalent to 1 mL of titrant

In case of water-extracts of soil/sediments samples, TA was computed as below:

$$\text{Alkalinity (mg CaCO}_3\text{/g)} = A \times V/M \qquad [2]$$

where, A = Alkalinity in water-extract of soil/sediments (mg $CaCO_3$/L)

V = Volume of the water-extract (L)

M = Weight of the soil/sediment sample (g)

The concentration of bicarbonate ions in water samples was also calculated using following relationship (Radojevic and Bashkin, 1999):

$$\text{Bicarbonate ion (mg/L)} = \text{TA} \times 1.22 \qquad [3]$$

2.7.5 Chloride Estimation

There are many reported methods, such as, argentometric method, mercuric nitrate method, potentiometric method and ferricyanide method for the determination of chloride ion concentration (APHA, 2006). Among them, argentometric method (commonly known as Mohr's method) was selected for this purpose in the present study. In this method, a standard solution of $AgNO_3$ was titrated against a known volume of water sample using potassium chromate as an indicator (Radojevic and Bashkin, 1999; USEPA, 1994c). The solution of $AgNO_3$ (0.0141 M) was standardized against primary standard sodium chloride (0.0141 M) using potassium chromate as an indicator. An aliquot of 20 mL of water sample was taken into the conical flask and its pH was adjusted to the phenolphthalein end point (pH = 8.3) using NaOH solution (if necessary) and titrated against 0.0141 M $AgNO_3$ until orange-red colour was observed. Subsequently, chloride ion concentration was calculated using following relationship (Radojevic and Bashkin, 1999):

$$\text{Chloride (mg/L)} = 35453 \times M \times (V_t/V_s) \qquad [4]$$

where, M = Molarity of silver nitrate (titrant)

V_t = Volume of titrant used (mL)

V_s = Volume of the sample taken (mL)

The pH of the sample was adjusted to 8.3 as chromate ion is changed to dichromate ion at lower pH while silver is precipitated as hydroxide at higher pH.

2.7.6 Organic Matter

Loss on ignition method was used to determine the organic matter in the samples gravimetrically. This method demonstrates a rough estimation of organic matter present in the samples (Radojevic and Bashkin, 1999). Organic matter (OM) begins to ignite at about 200°C and is completely depleted at about 550°C. Organic matter content (%) was estimated by measuring the loss of weight of 1 g of dry soil (105°C) on ignition at 550°C for 4 to 5 h in a pre-cleaned crucible (Diaz-de-Alba *et al.*, 2011). It was calculated by the weight difference before and after igniting the sample (Radojevic and Bashkin, 1999).

2.7.7 Anions Determination by Ion Chromatography

Ion chromatography is widely used for the determination of anions commonly present in the environmental matrices. Various anions (chloride, bromide, fluoride, nitrate, nitrite, sulphate, sulphite, phosphate, etc.) are analysed rapidly by ion chromatography. In the present investigation, the concentrations of fluoride, chloride, sulphate and nitrate were measured by ion chromatography following standard protocols (EPA Method 300). In this method 2-3 mL of sample was introduced into an ion chromatograph. The separation and measurement of anions was done by a system comprised of a guard column, analytical column, suppressor device, and conductivity detector. An ion chromatograph (Dionex ICS2000) was employed for the measurement of these anions. During the analyses, following appropriate columns were used:

- Ion Pac AS11HC analytical column (2 x 250 mm) Product No. 052691
- Ion Pac AG11HC guard column (2 x 50 mm) Product No. 052963

De-ionized water (18 MΩ·) was used as the eluent and calibration standards were used with a concentration less than 100 mg/L and the samples were diluted if required. Calibration standards ranging 0.01-100 mg/L were prepared afresh on the day of analysis from stock standard solution (1000 mg/L) which were prepared from analytical grade reagents.

2.7.8 Particle Size Measurement of Sediment/Soil

Particle size distribution is the quantitative measure of the size of solid fraction, while soil/sediment texture states to qualitative measure of particle size that is based on gradation of the material (Lal and Shukla, 2004). The structure of soil/sediment is directly associated to its mineral composition and particle size distribution which is measured as one of the important physical features of soil/sediment (Eshel *et al.*, 2004; Glinski *et al.*, 2002). Soil/Sediment texture may affect their mechanical and physical properties and the movement of water contents (Eshel *et al.*, 2004). Particle size analyses of soil/sediments comprised of two-steps; fractionation and dispersion. Fractionation states to the physical separation of the particles into different size ranges, whereas dispersion includes separation of the particles through removal of cementing material to break secondary particles into primary particles. Particle size was analysed and calculated by two methods, hydrometer and sieve method (Lal and Shukla, 2004). The distribution of particle sizes larger than 75 μm (retained on sieve No. 200) was determined by sieving, while the distribution of particle sizes smaller than 75 μm was determined by a sedimentation process, using a hydrometer (Ashwortha *et al.*, 2001). In the present study, particle size of the soil/sediments was determined by the ASTM 422 method (1998). In this method, 50 g of the sample was soaked in 125 mL of sodium hexametaphosphate solution (dispersing agent) which was prepared by dissolving 40 g of sodium hexametaphosphate in 1000 mL of distilled water. The mixture was stirred and left for 16 h and then transferred to a 1000 mL cylinder and filled with distilled water up to mark and thoroughly mixed by turning the cylinder upside down and back upright for one minute. Cylinder was put down and time was recorded. Hydrometer readings were recorded after elapsed time of 2, 5, 8, 15, 30, 60 minutes and 24 hour. The reading was noted by seeing the top of meniscus made by the suspension and the hydrometer stem and the equivalent particle diameter (D) was calculated by following equation:

$$D = K\sqrt{\frac{L}{t}} \qquad [5]$$

where, K is the constant depending on the specific gravity of the soil/sediments particles and the temperature of the suspension; L is the effective depth for hydrometer in cm; and t is the time in minutes. The value of K remains constant for a series of readings constituting a test, while values of t and L may vary.

The percentage of each fraction was calculated by following relationship:

$$P = [(100000/W)G/(G - G_1)](R - G_1) \qquad [6]$$

where, P is the percentage of particles in suspension as measured by hydrometer; W is oven-dried mass of the test sample; G is the specific gravity of particles; G_1 is the specific gravity of suspension liquid; R is the hydrometer reading with applied composite correction.

In the sieve method, 20 g of the sample was dried in an electric oven at 105°C and homogenized by adding the sample on a clean polyethylene sheet, mixed, coned and quartered by hand. Then each sample was placed on the sieves which were placed on mechanical shaker consisting of different mesh No. 10 (1.68 mm), 25 (0.707 mm), 35 (0.420 mm), 48 (0.297 mm), 65 (0.210 mm), 100 (0.149 mm), 120 (0.125 mm), 140 (0.106 mm), 170 (0.088 mm) and 200 (0.075 mm). Particles were separated on the sieves having different opening size. After shaking on mechanical shaker for 10 min, weight of each fraction was calculated with digital balance up to three decimals. The sieves were thoroughly cleaned before the analysis of next sample. Percentage (P) of different size particles present on the sieve was calculated by following relationship;

$$P = \frac{Mass.retained.on.each.sieve}{Initial.mass} \times 100 \qquad [7]$$

2.8 Quantification of Selected Metals

The most important aspect of the present study was the measurement of selected essential, trace and toxic metals in various environmental samples. A number of different instrumental methods for the determination of the metals have been reported in literature. In the present investigation, selected metals including As, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Li, Mg, Mn, Na, Ni, Pb, Se, Sr and Zn were quantified in the water, soil, sediments and fish samples by flame atomic absorption spectrometry (FAAS) and inductively coupled plasma mass spectrometry (ICP-MS).

2.8.1 Flame Atomic Absorption Spectrometry (FAAS)

Flame atomic absorption spectrometry (FAAS) is one of the most commonly used technique in analytical laboratories for elemental analyses as it has a number of advantages, such as, high selectivity, speed, fairly low operational cost and sensitivity up to ppm/ppb level (Durana *et al.*, 2009; Ivanova *et al.*, 2004; Patnaik, 2010). This technique is similar to other high resolution spectroscopic techniques, but it differs in radiation source's nature and the use of heat energy to generate the absorbing species (Lagalante, 2004). Generally, hollow cathode lamp (HCL) of a specific wavelength is used as a radiation source for a particular element, whereas flame is mostly used as thermal energy source for vaporizing the analyte and breaking the chemical bonds within the molecules to produce free atoms in atomizer. The samples were analyzed for selected metals under optimum analytical conditions using a Shimadzu Atomic Absorption Spectrophotometer (Model; AA-670, Japan) equipped with automatic background compensation. Various analytical parameters, such as, absorption wavelength, HC Lamp current, slit width, flame type and fuel/oxidant flow rates were optimized for the analysis of each metal independently. These optimum analytical conditions for the analysis of selected metals are given in Appendix-A. Quantification of the metals in various samples was done by calibration line method. Standard stock solution (1000 mg/L) of each metal was used to prepare the fresh working standards of appropriate ranges just before the analysis. Doubly distilled water was used throughout the study for the preparation of the samples and standards. At least five standards were prepared and run covering the absorption range of the samples and to construct a calibration line of absorbance versus concentration. New calibration line was drawn every time before running the samples on AAS system. The reproducibility was checked frequently by making measurements with the standard solutions. The blanks were routinely used to estimate the metal levels in the reagents. Three sub-samples of each sample were treated and run separately onto the spectrophotometer to pool the mean concentrations. If the signal of the sample fell outside the range of standards, dilution was performed. Standard reference materials i.e. SRM 1643d (Trace Elements in Water), SRM 2711 (Montana Soil: Moderately elevated trace element concentrations), SRM 2709 (San Joaquin Soil: Baseline trace element concentrations), SRM 1946 (Lake Superior Fish Tissue) and BCR 701 (Lake sediment: extractable trace elements in sediment using a sequential extraction procedure) and reagents blanks, with each batch of samples were used to ensure the reliability of the quality of metal analysis. The SRMs showed good accuracy of analyses (92-108%, $n = 3$).

2.8.2 Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)

Inductively coupled plasma mass spectrometry (ICP-MS) is a relatively modern technique used for elemental analysis in industrial, biological, environmental, pharmaceutical and forensic sciences. It has numerous advantages mostly associated with low detection limit, high sensitivity, multicomponent, versatile & rapid analysis and a wide linear calibration dynamic range (Bolshakov *et al.*, 2006; Winefordner *et al.*, 2004). In this technique, the elements are atomized and excited in plasma and then pass to a mass spectrometer, where the ions are accelerated by high voltage, pass through a series of ion optics, an electrostatic analyser and finally through a magnet. The ions are separated by changing the magnetic strength according to charge to mass ratio, travel through a fine slit into detector which records a very small atomic mass range at a given time. By changing the magnet and electrostatic analyzer settings, the complete atomic mass range may be scanned within a relatively short period of time. This is an excellent technique for rapid multielement analyses (WHO, 2011). In the present study, samples were analysed on an Agilent ICP-MS (7500ce) operated in the helium collision mode for Cr, Ni, As and Se (to eliminate interference from polyatomic species) and in standard mode for Cd, Hg and Pb. The RF power was 1500 W and the isotopes measured were ^{52}Cr, ^{60}Ni, ^{75}As, ^{82}Se, ^{114}Cd, ^{201}Hg and ^{208}Pb employing ^{72}Ge, ^{115}In, ^{193}Ir and ^{209}Bi as internal standards. Quantification of the metals in various samples was done by calibration line method maintaining the optimum analytical conditions (Appendix B). The calibration standards in the range of 0.1 to 50 μg/L of the metals were prepared from VWR (UK) stock solutions (1000 mg/L) and the reliability of the finished data was ensured through the analyses of the standard reference materials.

2.9 Glassware, Apparatus and Reagents

High purity chemical reagents (AR grade, certified purity >99.9%) procured from E-Merck, Germany or BDH, UK were used throughout the present study. Working standards of the metals were prepared from stock solutions (1000 mg/L) of each metal by successive dilution with doubly distilled or de-ionized (≤ 18 MΩ/cm) water, which were also used for the dilution of the samples whenever required. The glassware used in this study was decontaminated/cleaned by washing with tap water & detergent solution (5%, w/v), soaking overnight in HNO_3 (20%, v/v) bath, and followed by repeated rinsing with doubly distilled water. The glassware was also rinsed with acetone if adherent organic impurities were suspected. Finally, the glassware was dried in an electric oven maintained at 80-90°C for about eight hours prior to use. The sampling and storage apparatus was cleaned by leaching with a dilute nitric acid solution (10%, v/v) for about 24 hours, then rinsed with de-ionized water and dried in a clean environment (Diaz-de-Alba *et al.*, 2011; USEPA, 2007).

2.10 Quality Assurance and Quality Control

Quality assurance (QA) and quality control (QC) are essential components of the investigations involving analyses of trace metals. The reliability of the metal data can only be validated by evaluating assay performance against defined/accepted standards. Quality control comprises of those steps and actions that monitor the effectiveness of quality assurance procedures with respect to defined objectives. Thus, QA/QC refers to a controlled process which confirms a specified degree of confidence in the collected data. Various steps were applied during sample collection, sample processing and the analyses to ensure the quality control/assurance. Keeping health/safety aspects, a site survey was carried before sampling campaigns. A sampling plan was made before the start of every campaign and the hazards were identified for suitable precautions to confirm the safety. Safety precautions related to boat activities were strictly followed during sampling. The field data were very cautiously noted during the sample collection. Cross contamination of the samples was avoided by using fresh pair of polythene gloves, new sampling containers and polythene bottles/bags each time. The sampling equipment were decontaminated prior to reuse with detergent, rinsing with distilled water, acetone and finally washed with plenty of deionized water. Finally they were air dried and kept wrapped until use. Fish samples were carefully examined for comparable weights before transport and storage.

The nets used for trapping the fish species were examined regularly and repaired when required. During water sampling, the sample bottles were kept below the water surface to avoid the debris. The sample bottles were rinsed with surface water before sampling. The *in-situ* measurements were made on separate samples in the field. The collected samples were stored in ice-cooled containers to avoid deterioration/loss. Freshly prepared chemical reagents were used throughout the study. High purity chemical reagents were used through the sample processing. Recommended procedures of the microwave equipment/vessels were followed. Concentrated acids were slowly added to the samples to avoid exposure to highly reactive fumes on heating. Reagent blanks were prepared to measure the purity of reagents, contamination of sampling bottles, containers, glassware, filter papers, and digestion vessels. Standard reference materials (SRM 1643d, SRM 1946, SRM 2709, SRM 2711, BCR, 701) were processed and analysed to ensure the reliability of the method and protocol throughout the present study (Appendices C & D). Chemical processing and digestion of the samples was carried out in a fume hood to avoid exposure to toxic vapours. Standard/appropriate methodologies and equipment were used throughout the study.

2.11 Statistical Analysis

The metal data were subjected to both univariate and multivariate statistical analyses. The statistical software MS-EXCEL and STATISTICA were used for this purpose. Univariate analysis of the data included basic statistical parameters, such as, minimum, maximum, mean, medium, standard deviation (SD), standard error (SE), skewness & kurtosis and correlation analysis, which was computed to assess the degree of mutual associations between different variables (Gong *et al.*, 2010). Multivariate statistical analysis including principal component analysis (PCA) and cluster analysis (CA) were employed to explore the apportionment and plausible sources of the metals by STATISTICA software (StatSoft, 1999). PCA simplifies the measured analytical data to latent factors which explain most of the variance in the analyzed data (Li and Zhang, 2010). It is mostly employed along with correlation analysis to identify potential sources of the metals (Mico *et al.*, 2006; Shtangeeva *et al.*, 2009; Wang *et al.*, 2012, Wang *et al.*, 2015). CA classifies a set of observations into two or more mutually exclusive unknown groups based on a combination of internal variables (Lu *et al.*, 2010). The results were shown in a dendrogram where steps in the hierarchical clustering solution and values of the distances between clusters were represented. In order to explore the interrelationship of collected data, the CA is usually coupled with PCA to check the final results and to group individual parameters and variables (Li *et al.*, 2013a; Wang *et al.*, 2014b).

2.12 Water Quality Indices

2.12.1 Irrigation Water Quality (IWQ) Index

The IWQ index is a cohesive method comprising of five irrigation water quality parameters which can influence the soil quality and crop yield. In this index, five groups are sequentially added to get a single index value which is used to evaluate the suitability of water for irrigation (Iqbal *et al.*, 2012a; Saleem *et al.*, 2015b; Simsek and Gunduz, 2007). These groups included the water quality parameters based on guidelines given by Ayers and Westcot (1994). The IWQ index is considered to be a suitable tool for agricultural management plans and is crucial for evaluating the overall water quality. In this index, EC represents the salinity hazard; EC and SAR represent the infiltration and permeability hazard; chloride and SAR represent the specific ion toxicity; linear combination of trace metals represent the metal toxicity; and linear combination of bicarbonate and pH represent miscellaneous effects to sensitive crops (Ayers and Westcot, 1994). In this method, each parameter is assigned a weighing coefficient from 1 to 5 and rating factors from 1 to 3 (Appendices E & F). The suggested IWQ index was computed as follow:

$$IWQ - Index = \sum_{i=1}^{5} G_i \qquad [8]$$

where '*i*' is an incremental index and '*G*' shows contribution of each parameter of five hazard classes used to evaluate the quality of an irrigation water reservoir. The first class is the salinity hazard represented by EC value of water and computed as:

$$G_1 = w_1 r_1 \qquad [9]$$

where '*w*' is the weight value of this hazard group and '*r*' is the rating value of the parameter. The second class is the infiltration and permeability hazard represented by EC-SAR and computed as:

$$G_2 = w_2 r_2 \qquad [10]$$

where '*w*' is the weight value of this hazard group and '*r*' is the rating value of the parameter. The third group is the specific ion toxicity represented by SAR and chloride ion in the water and computed as a weighted average of the both ions:

$$G_3 = \frac{W_3}{2}\sum_{j=1}^{2} r_j \qquad [11]$$

where '*j*' is an incremental index, '*w*' is the weight value of this group and '*r*' is the rating value of each parameter. The fourth group is the trace metal toxicity represented by the metals and computed as a weighted average of all the metals available for chemical analysis:

$$G_4 = \frac{W_4}{N}\sum_{k=1}^{N} r_k \qquad [12]$$

where '*k*' is an incremental index, '*w*' is the weight value of this group, '*N*' is the total number of trace metals available for chemical analysis and '*r*' is the rating value of each parameter. The fifth class is the miscellaneous effects to sensitive crops represented by bicarbonate ion and the pH of the water, and computed as a weighted average:

$$G_5 = \frac{W_5}{2}\sum_{m=1}^{2} r_m \qquad [13]$$

where '*m*' is an incremental index, '*w*' is the weight value of this group and '*r*' is the rating value of each parameter. The classification IWQ index is given in Appendix G.

2.12.2 Degree of Contamination (C_d)

The water quality may be evaluated by calculating contamination index (C_d) which is computed independently for each water sample. It is sum of contamination factors exceeding the upper permissible limits set by recognized authority. Thus, it summarises the collective effects of various water quality variables which are considered dangerous (Backman *et al.*, 1997; Bhuiyan *et al.*, 2010 & 2015; Iqbal *et al.*, 2013a; Prasanna *et al.*, 2012). It was computed by using the following relationship:

$$C_d = \sum_{i=1}^{n} C_{fi} \qquad [14]$$

$$C_{fi} = \frac{C_{Ai}}{C_{Ni}} - 1 \qquad [15]$$

where, 'C_{fi}', 'C_{Ai}', and 'C_{Ni}' are the contamination factor, analytical value and upper permissible concentration of the i^{th} component, respectively. *N* is the 'normative value' and C_{Ni} is the maximum admissible concentration (MAC).

2.12.3 Heavy Metal Evaluation Index (*HEI*)

The *HEI* evaluates water quality as a whole regarding to heavy metal levels (Bhuiyan *et al.*, 2015; Edet and Offiong, 2002; Iqbal *et al.*, 2013b) and computed as:

$$HEI = \sum_{i=1}^{n} \frac{H_C}{H_{MAC}} \qquad [16]$$

where, 'H_c' and 'H_{MAC}' are the measured and maximum admissible concentrations (MAC) of the *i*th parameter, respectively.

2.12.4 Sodium Adsorption Ratio (*SAR*)

It is a key parameter for defining the water suitability for irrigation use because Na levels can reduce the soil permeability & texture and may pose alkali/sodium hazard to the crops (Simsek and Gunduz, 2007; Sundaray *et al.*, 2009; Todd, 1980). Higher Na contents can change the soil pH, replace adsorbed Ca and Mg, affect physical condition/structure of soil, result in formation of crusts, water-logging, reduced soil aeration, reduced infiltration rate and soil permeability (Ayers and Westcot, 1994; El-Sayed and Salem, 2015). It was computed using the following relationship (Bashir *et al.*, 2015; Goyal *et al.*, 2010):

$$SAR = \frac{Na}{\sqrt{(Ca + Mg)/2}} \qquad [17]$$

where, all the ionic concentrations are expressed in 'meq/L'.

2.12.5 Percent Sodium (*PS*)

It is an important parameter for irrigation water classification as sodium interacts with soil, reduces its permeability and supports little or no plant growth. It was computed using the following equation (Goyal *et al.*, 2010; Sharma *et al.*, 2015):

$$PS = \left(\frac{Na + K}{Ca + Mg + Na + K}\right) \times 100 \qquad [18]$$

where, all the ionic concentrations are expressed in 'meq/L'.

2.12.6 Residual Sodium Bicarbonate (*RSBC*)

The presence of carbonate ions ($HCO_3^- + CO_3^{2-}$) can affect the water quality by precipitating the Ca and Mg ions and thereby increasing the Na levels (Michael, 1978). Residual Sodium Bicarbonate (*RSBC*) can be computed using the expression (Gupta 1983; Rahman *et al.*, 2014b):

$$RSBC = HCO_3^- - Ca \qquad [19]$$

where, all the ionic concentrations are expressed in 'meq/L'.

2.12.7 Permeability Index (*PI*)

Reduction in infiltration rate of soil causes hindrance in moisture supply to crops. This permeability issue is responsible for two water quality factors, namely salinity of water and its Na content relative to Ca and Mg. The permeability index (*PI*) was calculated as below (Bashir *et al.*, 2015; Doneen, 1964; Sharma *et al.*, 2015):

$$PI = \left(\frac{Na + \sqrt{HCO_3^-}}{Ca + Mg + Na} \right) \times 100 \qquad [20]$$

where, the concentration unit of all ions is 'meq/L'

2.12.8 Kelly Ratio (*KR*)

Another important parameter, 'Kelly Ratio' is measured as a ratio of Na to Ca & Mg and used to categorize the water suitability for irrigation use (Bashir *et al.*, 2015; Kelly, 1963; Paliwal, 1967). It was computed using the following equation (Kelly, 1963):

$$KR = \frac{Na}{Ca + Mg} \qquad [21]$$

where, all ionic contents are taken in 'meq/L'.

2.12.9 Magnesium Adsorption Ratio (*MAR*)

Commonly, Ca and Mg are found in a state of equilibrium in water. Higher contents of Mg severely affect the crops yield. Magnesium adsorption ratio (*MAR*) was computed as below (Bashir *et al.*, 2015; Raghunath, 1987; Rahman *et al.*, 2014b):

$$MAR = \frac{Mg \times 100}{Ca + Mg} \qquad [22]$$

where, all ionic contents are taken in 'meq/L'.

2.12.10 Total Hardness (*TH*)

Hardness, a property of water, prevents formation of lather with soap and enhances the boiling point of water. Various ions are responsible for water hardness, such as, calcium, magnesium, strontium, iron, carbonate, bicarbonate, chloride, and sulphate. Ferric iron and aluminium ions may also cause hardness (Simsek and Gunduz, 2007;

Sundaray *et al.*, 2009). Total hardness (*TH*) was computed as follow (Raghunath, 1987):

$$TH = (Ca + Mg) \times 50 \qquad [23]$$

where, concentrations unit for calcium and magnesium is 'meq/L'.

The classifications of these water parameters were given in Appendices G & H.

2.13 Sediment/Soil Quality Indices

2.13.1 Enrichment Factor (*EF*)

Enrichment factors are calculated to find out whether the metals present in the examined sediment/soil samples are in higher concentrations than their levels in earth's crust. Therefore, *EF* shows anthropogenic intrusions of the pollutants (Diop *et al.*, 2015; Duan *et al.*, 2010; Martin *et al.*, 2012; Sakan *et al.*, 2009). It is a very effective tool to assess the extent of metals contamination in the studied environment (Adamo *et al.*, 2005; Selvaraj *et al.*, 2004). *EF* can be calculated by following relationship:

$$EF = \frac{[X/M_{ref}]_{sample}}{[X/M_{ref}]_{crust}} \qquad [24]$$

where, $[X/M_{ref}]_{sample}$ and $[X/M_{ref}]_{crust}$ refer to the ratio of mean concentrations (mg/kg, dry weight) of the target metal in the examined sediment/soil and continental crust, respectively. The earth crust reference value for As (1.8 mg/kg), Ca (41500 mg/kg), Cd (0.15 mg/kg), Co (25 mg/kg), Cr (102 mg/kg), Cu (60 mg/kg), Fe (56300 mg/kg), Hg (0.085 mg/kg), K (20900 mg/kg), Li (20 mg/kg), Mg (23300 mg/kg), Mn (950 mg/kg), Na (23600 mg/kg), Ni (84 mg/kg), Pb (14 mg/kg), Se (0.05 mg/kg), Sr (370 mg/kg) and Zn (70 mg/kg) were used to calculate the EF (Lide, 2005). Various elements (Al, Fe, K, Li, Sc, Ga, Zr and Ti) can be used as normalizing/reference element (Daskalakis and Connor, 1995; Hassan *et al.*, 2013; Zhang *et al.*, 2007). In the present study, Fe was used as normalization element because it is associated with fine solid surfaces; it is a major sorbent phase for trace metals; its geochemistry is similar to that of many trace metals; and it is a quasiconservative tracer of the natural metal-bearing phases in the soil/sediments (Bhuiyan *et al.*, 2010; Hassan *et al.*, 2013; Wang *et al.*, 2014a).

2.13.2 Geoaccumulation Index (I_{geo})

Geoaccumulation index is used to assess the metal contamination by matching the present levels with the pre-industrial levels of the metals in sediments/soil (Diop *et al.*, 2015; Duan *et al.*, 2010; Muller, 1969; Wang *et al.*, 2014a; Yu *et al.*, 2008; Zhao *et al.*, 2012). It was computed using following equation:

$$I_{geo} = \log_2\left(\frac{C_n}{1.5B_n}\right) \qquad [25]$$

where, 'C_n' is the average concentration of metal in the studied sediment/soil and 'B_n' is the concentration of metal in the pre-industrial levels taken from literature as earth crust level (Lide, 2005). The factor 1.5 is used to minimize the probable variations in pre-industrial levels due to lithogenic effects.

2.13.3 Contamination Factor (C_f) and Degree of Contamination (C_{deg})

The potential contamination of sediments/soil can be evaluated by using contamination factor and degree of contamination (Abrahim and Parker, 2008; Hakanson, 1980; Maanan *et al.*, 2015). The 'C_f' is the ratio between metal concentrations in the examined sediments/soil and in pre-industrial soil. It was calculated as follow:

$$C_f = {}^{C_n}\!/_{C_b} \qquad [26]$$

where, 'C_n' and 'C_b' refer to the mean concentrations of a metal in the sediments/soil and earth crust, respectively.

Degree of contamination (C_{deg}), a cumulative index, is computed as numeric sum of individual 'C_f' of each sample (Hakanson, 1980). It showed an overall degree of contamination in the sediments/soil sample using following equation:

$$C_{\deg} = \sum_{i=1}^{i=n} C_f^i \qquad [27]$$

where, 'C_f' is the single metal index; and sum of contamination factors of all estimated metals represents the degree of contamination 'C_{deg}'.

2.13.4 Potential Ecological Risk Factor (E_i) and Potential Ecological Risk Index (RI)

The *RI* was adapted to find out extent of heavy metals pollution in sediments and soil. It can be computed, based on toxicity of the metals and sensitivity of organism, using following relationships (Hakanson, 1980):

$$RI = E_i \qquad [28]$$

$$E_i = T_i f_i \qquad [29]$$

$$f_i = {C_i}/{C_b} \quad [30]$$

where, 'RI' is potential ecological risk index; 'E_i' is potential ecological risk factor; 'T_i' is toxicity factor; 'f_i' is contamination factor; 'C_i' is metal concentration in the studied soil/sediment; and 'C_b' is the background metal levels. The sequence of heavy metals toxicity is Hg > Cd > As > Pb = Cu > Cr > Zn having toxic factors values as 40, 30, 10, 5, 5, 2 and 1, respectively (Hakanson, 1980; Jiang *et al.*, 2014; Protano *et al.*, 2014).

2.13.5 Pollution Load Index (*PLI*)

It is a simple and comparative index to determine the degree of metals pollution (Tomlinson *et al.*, 1980; Varol, 2011). It is computed as the n^{th} root of n CF_n multiplied together using the following equation:

$$PLI = (CF1 \times CF2 \times CF3 \times \cdots\cdots \times CFn)^{1/n} \quad [31]$$

where CF refer to contamination factor; The PLI value >1 shows a polluted condition, while PLI <1 indicates no significant pollution (Tomlinson *et al.*, 1980; Varol, 2011).

2.13.6 Individual Contamination Factor (*ICF*) & Global Contamination Factor (*GCF*)

Estimation of contamination factor shows the extent of risk of a metal to the environment with respect to its retention time (Ikem *et al.*, 2003). The *ICF* can be estimated by dividing the sum of the non-residual fractions (Exchangeable (F1) + Reducible (F2) + Oxidiseable fraction (F3)) of a metal by its residual fraction (F4) while *GCF* was calculated by summing *ICF* of all the metals for each site (Ikem *et al.*, 2003; Nemati *et al.*, 2011; Saleem *et al.*, 2015c; Zhao *et al.*, 2012). The classifications of *ICF* and *GCF* were interpreted as suggested by Zhao *et al.*, (2012).

2.13.7 Risk Assessment Code (*RAC*)

Association of the metals with different geochemical phases determines their bio-availability and associated adverse health risks in the aquatic ecosystems. Risk assessment code (*RAC*) is computed as a percent contribution by dividing concentration of the metals in first geochemical fraction by sum of remaining three fractions. The metals bound to first fraction are softly bound to the solid phase and may cause adverse health risk to organisms (Choque *et al.*, 2013; Nemati *et al.*, 2011; Passos *et al.*, 2010; Perin *et al.*, 1985).

The classifications of above sediment/soil quality indices were given in Appendices H & I.

2.13.8 Ecotoxicological Studies and Sediment Quality Guidelines (*SQGs*)

Sediment quality guidelines (*SQGs*) are widely used to find out ecotoxicological sensibility of the pollutants and contaminants of concern in freshwater ecosystems (MacDonald *et al.*, 1996 & 2000). Using USEPA sediments guidelines, sediments can be classified into three categories; non-polluted, moderately polluted and heavily polluted (Giesy and Hoke, 1990). These guidelines are used to assess the degree of contaminated sediment which might have adverse impacts, such as, mortality, growth or reproduction of living organisms and are designed to help in the understanding of sediment quality (Almasoud *et al.*, 2015; Li *et al.*, 2013b; MacDonald *et al.*, 2000; Varol, 2011). The *SQGs* reveal sediment contamination by comparing the sediment concentration with the corresponding quality guidelines (MacDonald *et al.*, 2000; Swartz, 1999). Different sets of *SQGs* are used to envisage the sediment quality condition; these include threshold effect level (*TEL*) & probable effect level (*PEL*); lowest effect level (*LEL*) & severe effect level (*SEL*); effect range low (*ERL*) & effect range median (*ERM*); and threshold effect concentration (*TEC*) & probable effect concentration (*PEC*) (Maanan *et al.*, 2015; MacDonald *et al.*, 2000; Persaud *et al.*, 1993). To assess the adverse biological effects of each contaminant, the measured levels are compared with the corresponding *SQGs* values: *TEL* and *LEL* represent the concentrations below which adverse effects upon the sediment dwelling biota would be rarely observed, while the *PEL* and *SEL* represent the concentrations above which adverse effects are likely to occur (Almasoud *et al.*, 2015; Long *et al.*, 1995; MacDonald *et al.*, 1996 & 2000). Moreover, toxic units (*TUs*) are also applied to normalize the toxicity of various toxic metals. It is defined as the ratio of measured concentration to *PEL* value (Pedersen *et al.*, 1998). Potential acute toxicity of the pollutants can be calculated as the numeric sum of all toxic units (*TUs*).

2.14 Human Health Risk Assessment

2.14.1 Water

Health risk assessment is a multi-stage method comprising of data collection and evaluation, exposure assessment, toxicity assessment and risk characterisation (De Miguel *et al.*, 2007; USDOE, 2011; USEPA, 1989 & 2004). Human health risk assessment is widely used for aquatic ecosystems (Filipsson *et al.*, 2009; Iqbal and Shah, 2012; Liu *et* *al.*, 2011; USEPA, 1989). Exposure of human to the metals may occur through three main ways; direct digestion, inhalation and dermal absorption through skin. However, ingestion and dermal intake are common routes of exposure of the metals in water (Iqbal and Shah, 2012; USEPA, 2004; Wu *et al.*, 2010). Mathematical expression for risk assessment can be obtained from USEPA Risk Assessment Guidance for Superfund (RAGS) methodology (Iqbal and Shah, 2012; Saleem *et al.*, 2014a; USEPA, 1989):

$$D_{ing} = \frac{C_{water} \times IR \times EF \times ED}{BW \times AT} \qquad [32]$$

$$D_{derm} = \frac{C_{water} \times SA \times K_p \times ET \times EF \times ED \times CF}{BW \times AT} \qquad [33]$$

where, D_{ing} - exposure dose through ingestion of water (μg/kg-day); D_{derm} - exposure dose through dermal absorption (μg/kg-day); C_{water} - concentration of the metals in water samples (μg/L); IR - ingestion rate (L/day); EF - exposure frequency (days/year); ED - exposure duration (years); BW - average body weight (kg); AT - averaging time (days); SA - exposed skin area (cm^2); ET - exposure time (hours/day); CF - unit conversion factor (L/cm^3); and K_p - dermal permeability coefficient (cm/h) (USEPA, 1989 & 2004). These parameters are explained in Appendix J.

Non-carcinogenic risk hazard quotient (HQ) can be computed as a ratio of calculated exposure from each exposure pathway to the reference dose as described in USEPA (1989):

$$HQ_{ing/derm} = \frac{D_{ing/derm}}{RfD_{ing/derm}} \qquad [34]$$

where, $HQ_{ing/derm}$ - hazard quotient via ingestion or dermal contact (unitless); $D_{ing/derm}$ - exposure dose through ingestion or dermal contact of water (μg/kg-day); and $RfD_{ing/derm}$ – reference dose for oral ingestion or dermal absorption (μg/kg-day). The RfD_{ing} and RfD_{derm} values can be obtained from literature (Li and Zhang, 2010; Liang *et al.*, 2011; USEPA, 1989; Wu *et al.*, 2010).

The HQ is estimated for systematic toxicity of a single metal within a single route of exposure. To determine overall non-carcinogenic risk posed by all the metals, hazard index (HI) is computed using the following expression (USEPA, 1989):

$$HI = \sum_{i=1}^{n} HQ_{ing/derm} \qquad [35]$$

where, $HI_{ing/derm}$ - hazard index via ingestion intake or dermal contact (unitless). When HQ and HI exceed unity, there may be a concern for potential non-carcinogenic human health risks caused by the exposure to metal levels in water (USEPA, 2004).

2.14.2 Soil/Sediments

In case of soil/sediments, human exposure to the metals can occur through three main pathways; (i) direct oral ingestion of substrate particles; (ii) inhalation of suspended particulates through mouth/nose; (iii) dermal absorption of the metals in particles adhered to exposed skin. Amongst these routes, oral intake and dermal contact are most significant exposure routes which can calculated as (USEPA, 1989 & 2004):

$$Exp_{ing} = \frac{C_{soil/sed} \times IR \times CF \times EF \times ED}{BW \times AT} \qquad [36]$$

$$Exp_{derm} = \frac{C_{soil/sed} \times CF \times SA \times AF \times ABS \times EF \times ED}{BW \times AT} \qquad [37]$$

where, Exp_{ing} - ingestion exposure (mg/kg-day); Exp_{derm} - dermal uptake (mg/kg-day); $C_{soil/sed}$ - mean concentration of the metals in soil or sediments (mg/kg); EF - exposure frequency (days/year); IR - ingestion rate (mg/day); BW - body weight (kg); AF - adherence factor for soil/sediments to the skin (mg/cm^2); ED - exposure duration (years); ABS - dermal absorption from soil/sediments (unitless); CF - unit conversion factor (kg/mg); AT - average time (years); and SA - surface area (cm^2/day). These parameters are explained in Appendix K.

Non-carcinogenic risk in terms of hazard quotient (HQ) can be computed following standard USEPA (2004) methodology as:

$$HQ_{ing/derm} = \frac{Exp_{ing/derm}}{RfD_o} \qquad [38]$$

where, $HQ_{ing/derm}$ - hazard quotient through ingestion or dermal route (unitless); RfD_o - oral reference dose (mg/kg-day). Generally, the hazard quotient values below unity are considered safe/non-hazardous.

2.14.3 Fish

Health risk assessment associated with fish consumption was also evaluated in the present study. The mathematical expression for risk characterization through oral ingestion was obtained from USEPA (1989) Risk Assessment Guidance for Superfund (RAGS):

$$Exp_{ing} = \frac{C_{fish} \times IR \times FI \times EF \times ED}{BW \times AT} \qquad [39]$$

where, Exp_{ing} - ingestion exposure (mg/kg/day); C_{fish} - mean concentration of the metals in fish muscle (mg/kg); *IR* - ingestion rate (mg/day); *FI* - fraction of fish ingested (unitless); *EF* - exposure frequency (meals/year); *ED* - exposure duration (years); *BW* - body weight (kg); and *AT* - average time (days). These parameters are explained in Appendix L.

Non-carcinogenic hazard quotient (*HQ*) and carcinogenic risk (*CR*) were also computed following USEPA standard methodology (USEPA, 1989):

$$HQ_{ing} = \frac{Exp_{ing}}{RfD_o} \qquad [40]$$

$$CR_{ing} = Exp_{ing} \times SF_o \qquad [41]$$

where, HQ_{ing} - hazard quotient (unitless); CR_{ing} - cancer risk through ingestion route (unitless); RfD_o - oral reference dose (mg/kg-day); & SF_o - oral slope factor (kg-day/mg).

Species-specific risk from the consumption of fish muscles was also calculated in terms of margin of exposure (*MOE*) using the following relationship (Costa and Hartz, 2009; Watanabe *et al.*, 2003):

$$MOE = (MCC \times IRF) / (BW \times RfD) \qquad [42]$$

where, *MCC* - species-specific maximum concentration (µg/g, wet weight) of the metals in fish muscles; *IRF* - ingestion rate (0.250 kg/day); *BW* - body weight (70 kg); and *RfD* - reference dose for the specific metal (µg/g/day). These values were taken from the literature (FAO/WHO, 2004; Shah *et al.*, 2009; USEPA, 2011).

Daily and weekly intakes of the metals were also assessed in order to evaluate the extent of risk to the consumers. Average daily consumption of fish in Pakistan is about 0.250 kg/day/person (1.75 kg/week/person) (Iqbal and Shah, 2014a; Shah *et al.*, 2009). The *EWI* and *EDI* of the metals for an adult person were calculated using the following expressions (Iqbal and Shah, 2014a; Turkmen *et al.*, 2009):

$$EWI = C_{max} \times IR_{fish} \qquad [43]$$

$$EDI = EWI / 7 \qquad [44]$$

where, C_{max} - maximum level of the metals (µg/g); and *IR* - fish consumption rate.

Chapter 3

RESULTS AND DISCUSSION

3.1 Layout of Data

The data pertaining to various physicochemical parameters (T, pH, EC, TDS, DO, Cl^-, NO_3^-, SO_4^{2-}, F^- and TA) and/or selected metals (As, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Li, Mg, Mn, Na, Ni, Pb, Se, Sr and Zn) in the water, soil, sediments and fish samples during different seasons were statistically evaluated for their comparative distribution, mutual correlations, multivariate source apportionment and health/ecological risk assessment. The entire data related to these aspects were presented in 140 Tables and 86 Figures, which were divided into the four sections: **Section-I** revealed the distribution, correlation and spatial/temporal variations of selected metals and physicochemical parameters in water samples during different seasons. Additionally, health and ecological risk assessment associated with the metal levels; source apportionment by multivariate principal component analysis (PCA) and cluster analysis (CA); drinking/irrigation water quality indices; and comparison of the present metal levels with the reported levels around the world as well as national/international water quality guidelines were also carried out.

Sediments and soil samples collected in different seasons were evaluated for the distribution, mutual associations and spatiotemporal variations of selected metals and physicochemical parameters in **Section-II & III**, respectively. These samples were also characterized for bioavailable concentrations (calcium nitrate extract), total extractable contents (acid extract) and geochemical fractionation (*m*BCR sequential extraction) of the metals. Additionally, sediments/soil texture; source identification; health/ecological risk assessment; and comparison of the metal levels with national/international reported levels were also executed. **Section-IV** presented the comparative distribution, correlations and source apportionment of selected metals in muscles, gills and scales of different fish species. Health implications associated with the metal intake through fish consumption were also evaluated. Moreover, the measured metal levels were compared with the permissible levels along with the reported levels from other parts of the world. Salient findings of the present study and recommendations towards rectification of the pollution scenario were given at the end. These aspects are now comprehensively described in the forthcoming sections in chronological order.

Section-I: WATER

3.2 Sampling Progress

Surface water samples were collected from Mangla Lake in 2011 (summer & winter) and 2012 (pre-monsoon, monsoon and post-monsoon). In each season, composite water samples were collected in order to cover the maximum area of the lake and to assess the overall pollution status of the reservoir. Each water sample was composed of 3 to 5 equal volume sub-samples from an area of 10–50 m^2. In 2011, one hundred fifty water samples were randomly collected during summer (n = 150) and winter (n = 150) each. However, in 2012, a total of 450 water samples were collected during pre-monsoon, monsoon and post-monsoon (n = 150 in each season) from five major sites of the lake as shown in the location map (Figure 3).

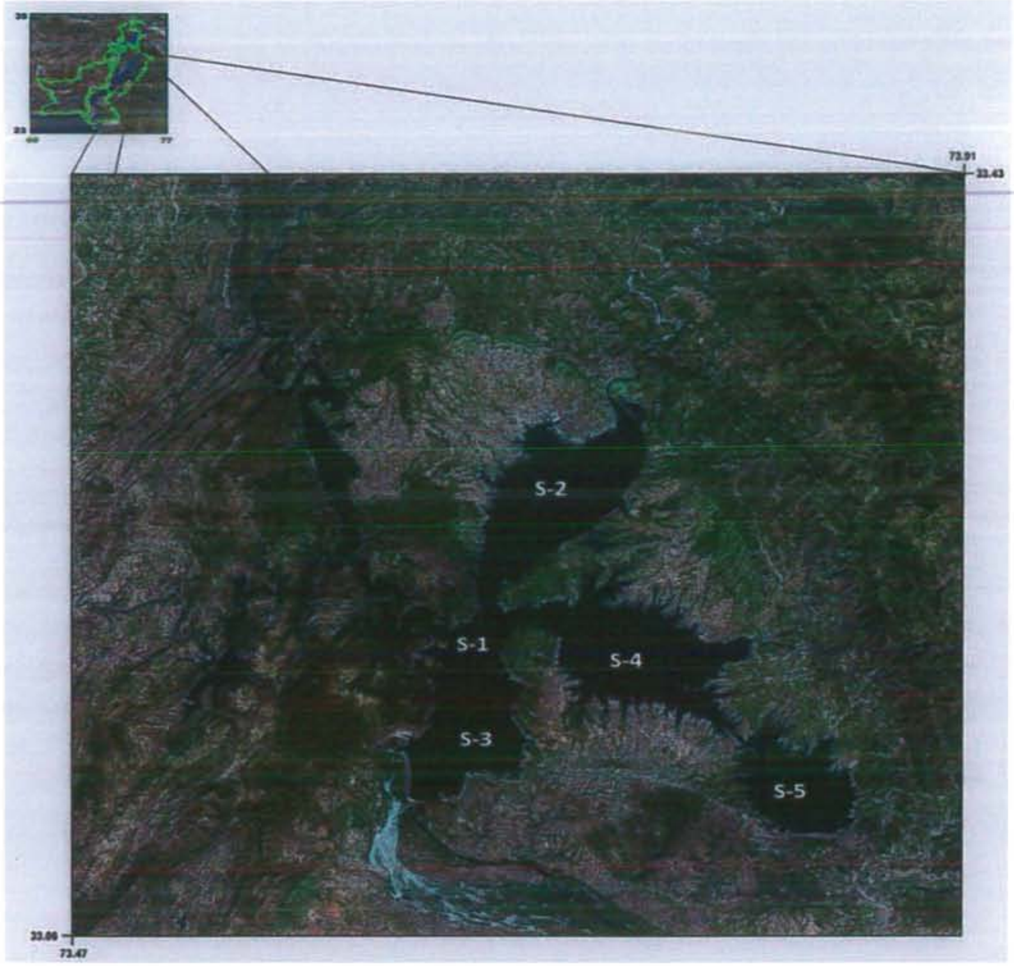

Figure 3. Location map indicating the water sampling sites from Mangla Lake

3.3 Distribution of Physicochemical Parameters in Water Samples

Statistical summary related to the distribution of physicochemical parameters in surface water during summer is given in Table 1. Temperature showed very narrow range and on the average basis, it was observed at 37.9°C with almost similar median values. Similarly, pH ranged from 7.62 to 8.23 with a mean value of 8.02, thus showing slightly basic character for the water samples. The standard deviation (SD) and standard error (SE) values of pH remained very small, thus manifesting regular/systematic equilibrium in hydrogen ion concentrations in the lake water. The mean levels of electrical conductivity (EC) and total dissolved solids (TDS) of water were 139.9 μS/cm and 69.97 mg/L, respectively; and both the variables showed random distribution as shown by relatively higher values of SD, SE, skewness and kurtosis. Total alkalinity (TA) and chloride (Cl^-) contents were found to be comparatively higher with significant dispersion in the water samples. Average level of dissolved oxygen (DO) was measured as 4.313 mg/L and relatively normal distribution for observed for DO as shown by narrow range and relatively small SD and SE values, along with lower skewness value. Among rest of the parameters, NO_3^-, SO_4^{2-} and F^- levels in the water samples varied as 0.674–21.16 mg/L, 5.626-40.02 mg/L and 0.089–0.158 mg/L with mean values of 8.929 mg/L, 21.24 mg/L and 0.113 mg/L, respectively. Considerably asymmetric distribution was shown by EC, TDS and SO_4^{2-} as exhibited by comparatively large skewness and kurtosis values.

Basic statistical data for the distribution of physicochemical parameters in surface water during winter are also shown in Table 1. During winter, the temperature of the water samples ranged from 10.0 to 12.6°C with a mean value of 10.7°C. The pH ranged from a minimum value of 7.42 to a maximum value of 8.32 while the mean value was found at 7.84 with matching median value. Consequently, pH exhibited slightly alkaline nature of the water samples. The mean EC and TDS levels during winter were 250.4 μS/cm and 125.2 mg/L, respectively, which were markedly higher compared with the summer levels. Such variations may be associated with the reduced inflow of water during winter and dilution effects during the summer when water flow was recorded at maximum. Generally, it was observed that water capacity of the reservoir was diminished to less than half during the winter. On the whole, EC and TDS showed random distribution in the water samples exhibited by relatively higher SD, SE, skewness and kurtosis values. Among rest of the parameters, TA, Cl^-, DO, NO_3^-, SO_4^{2-} and F^- levels in the water samples ranged from 30.00-195.0 mg/L as $CaCO_3$, 4.999-15.00 mg/L, 3.570-4.940 mg/L, 1.989-13.90 mg/L, 11.43-30.30 mg/L and 0.058-0.296 mg/L, with the mean values of 93.86 mg $CaCO_3$/L, 8.819 mg/L, 4.317 mg/L, 5.791 mg/L, 17.37 mg/L and 0.128 mg/L, respectively. Very narrow distribution was observed by DO and F^- contents in the water as shown by relatively small SD/SE values, whereas, TA, SO_4^{2-}, NO_3^- and Cl^- showed large differences during winter season.

Table 1. Statistical distribution of physicochemical parameters in the water samples during summer and winter

		Min	Max	Mean	Median	SD	SE	Skew	Kurt
Summer (*n* = 150)	T (°C)	37.4	38.2	37.9	37.9	0.124	0.021	-1.088	7.172
	pH	7.62	8.23	8.02	8.08	0.158	0.027	-1.174	0.384
	EC (μS/cm)	130.6	158.7	139.9	138.9	5.608	0.948	1.179	2.359
	TDS (mg/L)	65.30	79.60	69.97	69.20	2.843	0.480	1.233	2.553
	DO (mg/L)	3.580	4.900	4.313	4.580	0.384	0.065	-0.923	-0.434
	Cl^- (mg/L)	9.927	14.89	11.34	9.927	1.733	0.293	0.831	-0.464
	NO_3^- (mg/L)	0.674	21.16	8.929	7.398	6.193	1.385	0.619	-0.810
	SO_4^{2-} (mg/L)	5.626	40.02	21.24	19.50	7.946	1.777	1.217	2.106
	F^- (mg/L)	0.089	0.158	0.113	0.103	0.021	0.005	0.986	-0.247
	TA (mg/L as $CaCO_3$)	58.00	290.0	143.8	130.5	53.15	8.983	0.806	0.248
Winter (*n* = 150)	T (°C)	10.0	12.6	10.7	10.7	0.41	0.070	2.950	14.97
	pH	7.42	8.32	7.84	7.84	0.33	0.060	-0.040	-1.700
	EC (μS/cm)	180.3	477.0	250.4	214.2	69.05	11.67	1.963	4.119
	TDS (mg/L)	90.50	238.0	125.2	107.2	34.39	5.814	1.950	4.049
	DO (mg/L)	3.570	4.940	4.317	4.490	0.419	0.071	-0.293	-1.529
	Cl^- (mg/L)	4.999	15.00	8.819	8.748	2.810	0.475	0.764	0.073
	NO_3^- (mg/L)	1.989	13.90	5.791	4.267	3.719	0.832	1.086	-0.102
	SO_4^{2-} (mg/L)	11.43	30.30	17.37	18.17	4.211	0.942	1.233	3.693
	F^- (mg/L)	0.058	0.296	0.128	0.100	0.075	0.017	1.636	1.493
	TA (mg/L as $CaCO_3$)	30.00	195.0	93.86	75.00	41.69	7.048	0.825	-0.111

Basic statistical parameters associated with the distribution of physicochemical parameters in water samples during pre-monsoon season are shown in Table 2. Mean value of temperature was observed at 31.6°C with matching median value. The pH values varied from 7.35 to 8.27 with a mean value of 7.92. Very narrow and symmetrical variation was noted in pH as evidenced by small SD, SE, skewness and kurtosis values.

The ranges of EC and TDS were 140.6-460.0 μS/cm and 70.30-229.0 mg/L, respectively. Mean values of TA, Cl^-, DO, NO_3^-, SO_4^{2-} and F^- were 332.1 mg/L as $CaCO_3$, 19.06 mg/L, 4.340 mg/L, 20.23 mg/L, 12.64 mg/L and 0.237 mg/L, respectively. Considerably, higher SD and SE values for EC, TDS, Cl^-, NO_3^-, SO_4^{2-} and TA indicated their higher differences and random fluctuations in the water samples, whereas relatively lower SD and SE values for DO and F^- showed their consistent and unvarying contributions during pre-monsoon. Moreover, comparatively higher skewness and kurtosis values for EC, TDS, SO_4^{2-} and F^- indicated their predominant asymmetric distribution while DO exhibited almost symmetrical distribution in the water samples.

Statistical distribution of physicochemical parameters in the water samples during monsoon season is presented in Table 2. The range and mean values of temperature and pH were recorded as 20.0-28.1°C & 24.3°C, and 6.89-7.81 & 7.37, respectively. Both pH and temperature showed almost symmetrical distribution as revealed by rather lower values of skewness and kurtosis. Similarly, EC and TDS showed variations ranging from 172.2 to 771.0 μS/cm and 79.30 to 385.0 mg/L with mean values of 278.9 μS/cm and 139.2 mg/L, respectively. Average DO contents were noted at 6.117 mg/L with a minimum of 5.440 mg/L and maximum of 6.530 mg/L. Among rest of the parameters, mean values of Cl^-, NO_3^-, SO_4^{2-}, F^- and TA were found at 17.51 mg/L, 18.07 mg/L, 15.90 mg/L, 0.116 mg/L and 259.0 mg/L as $CaCO_3$, correspondingly. Some of the parameters (EC, TDS, NO_3^- and TA) exhibited relatively large differences and asymmetrical distribution as indicated by considerably higher SD, SE, skewness and kurtosis values. However, DO and F^- showed symmetric distribution during the monsoon season.

Statistical summary related to the distribution of physicochemical parameters in surface water during post-monsoon season is given in Table 2. In this season, temperature ranged from 13.3 to 14.2°C (mean 13.8°C), pH varied from 6.21 to 6.83 (mean 6.43), EC fluctuated from 119.6 to 270.5 μS/cm (mean 158.7 μS/cm), TDS ranged from 60.10 to 139.3 mg/L (mean 79.35 mg/L) and DO varied from 5.74 to 7.39 mg/L (mean 6.54 mg/L). Among the anions, Cl^- levels were found at a minimum of 14.09 mg/L and a maximum of 47.15 mg/L with the mean levels of 25.31 mg/L, while F^- ranged from 0.187 to 0.627 mg/L with average contribution of 0.320 mg/L. Mean level of NO_3^- was found at 12.02 mg/L whereas, SO_4^{2-} showed mean concentration of 20.15 mg/L. Similarly, TA varied from 90.34 to 283.9 mg/L as $CaCO_3$ with mean level of 140.9 mg/L as $CaCO_3$ in the water samples during post-monsoon season. Some of the parameters including EC, TDS, Cl^-, NO_3^-, SO_4^{2-} and TA showed predominantly random distribution, while T, pH, DO and F^-

displayed relatively symmetric distribution as indicated by their SD and SE values.

Table 2. Statistical distribution of physicochemical parameters in the water samples during pre-monsoon, monsoon and post-monsoon

		Min	Max	Mean	Median	SD	SE	Skew	Kurt
Pre-monsoon (*n* = 150)	T (°C)	31.0	32.5	31.6	31.5	0.396	0.056	0.450	-0.659
	pH	7.35	8.27	7.92	8.06	0.271	0.038	-0.593	-1.115
	EC (µS/cm)	140.6	460.0	183.8	163.8	62.41	8.827	2.231	7.332
	TDS (mg/L)	70.30	229.0	91.95	82.35	31.19	4.410	2.209	7.152
	DO (mg/L)	3.570	4.940	4.340	4.560	0.427	0.060	-0.385	-1.440
	Cl^- (mg/L)	9.007	37.23	19.06	17.37	5.963	0.843	0.845	0.971
	NO_3^- (mg/L)	6.731	40.56	20.23	17.79	10.93	2.444	0.616	-0.873
	SO_4^{2-} (mg/L)	10.65	23.40	12.64	11.99	2.768	0.619	3.464	13.15
	F^- (mg/L)	0.108	0.535	0.237	0.224	0.113	0.025	1.248	1.567
	TA (mg/L as $CaCO_3$)	275.3	492.7	332.1	304.3	56.27	11.25	1.093	0.988
Monsoon (*n* = 150)	T (°C)	20.0	28.1	24.3	24.4	3.680	0.520	-0.005	-2.076
	pH	6.89	7.81	7.37	7.40	0.231	0.033	-0.328	-0.838
	EC (µS/cm)	172.2	771.0	278.9	261.8	111.1	15.71	2.780	9.378
	TDS (mg/L)	79.30	385.0	139.2	130.9	55.79	7.890	2.736	9.190
	DO (mg/L)	5.440	6.530	6.117	6.135	0.240	0.034	-0.435	0.197
	Cl^- (mg/L)	11.03	28.79	17.51	16.88	3.720	0.526	0.586	0.291
	NO_3^- (mg/L)	2.214	116.1	18.07	10.64	25.63	5.732	3.272	12.12
	SO_4^{2-} (mg/L)	11.77	27.42	15.90	15.64	3.161	0.707	2.584	9.669
	F^- (mg/L)	0.059	0.248	0.116	0.103	0.052	0.012	1.347	1.253
	TA (mg/L as $CaCO_3$)	200.0	425.9	259.0	230.1	58.46	11.69	1.093	0.988
Post-monsoon (*n* = 150)	T (°C)	13.3	14.2	13.8	13.8	0.192	0.027	-0.024	0.257
	pH	6.21	6.83	6.43	6.38	0.132	0.019	1.664	2.577
	EC (µS/cm)	119.6	270.5	158.7	153.7	27.63	3.907	1.796	4.528
	TDS (mg/L)	60.10	139.3	79.35	76.95	13.94	1.972	2.023	6.030
	DO (mg/L)	5.740	7.390	6.540	6.470	0.276	0.039	0.796	2.796
	Cl^- (mg/L)	14.09	47.15	25.31	24.82	6.362	0.900	0.980	1.902
	NO_3^- (mg/L)	2.773	24.14	12.02	13.26	6.010	1.344	0.025	-0.623
	SO_4^{2-} (mg/L)	15.45	29.43	20.15	19.65	3.326	0.744	1.518	2.671
	F^- (mg/L)	0.187	0.627	0.320	0.262	0.135	0.030	1.391	0.639
	TA (mg/L as $CaCO_3$)	90.34	283.9	140.9	116.1	50.08	10.02	1.093	0.988

On the whole, no drastic change in temperature was observed in any season, although there were significant seasonal variations during pre-monsoon, monsoon and post-monsoon seasons. The lake water was slightly alkaline in nature during pre-monsoon and monsoon seasons, while slightly acidic in post-monsoon season. On the average basis, EC and TDS levels were relatively higher during monsoon season, followed by post-monsoon and pre-monsoon seasons, which might be due to their larger inputs through runoffs from the surrounding areas during wet season. Generally, EC and TDS contents were associated with human activities in the catchments areas. The DO contents were comparatively lower during the pre-monsoon season compared with monsoon and post-monsoon seasons, thus suggesting more stress on the aquatic ecosystem during former period. This variability might be partially due to warmer period during pre-monsoon, in addition to flow regime, seasonal effects and anthropogenic impacts. Untreated discharge of municipal effluents, solid wastes from nearby towns/cities and wastes released from poultry farms in the catchments areas might be contributing to lower DO contents during the dry season. Relatively higher concentrations of Cl^-, SO_4^{2-} and F^- were observed during post-monsoon season, while NO_3^- and TA were moderately higher during pre-monsoon season.

3.4 Distribution of Selected Metals in Water Samples

Basic statistical parameters for distribution of selected metals in the water samples during summer season are shown in Table 3. On the average basis, highest levels were noted for Ca (43.37 mg/L), followed by Mg (3.390 mg/L), Na (2.410 mg/L) and K (1.344 mg/L), while the lowest levels were found for Mn (0.014 mg/L), As (0.011), Li (0.008 mg/L) and Se (0.0013 mg/L). Rest of the metals revealed concentration levels between 0.0014 to 1.344 mg/L. Overall, mean metal levels in the water samples during summer showed following decreasing order: Ca > Mg > Na > K > Pb > Co > Sr > Fe > Ni > Cr > Cd > Zn > Cu > Mn >As > Li > Se. Among the selected metals, As, Fe, K, Mg, Mn, Li, Se and Zn exhibited almost comparable mean and median levels. Generally, most of the metals revealed relatively normal distribution pattern as revealed by considerably lower SD and SE values, while Ca, Pb, Na and Mg showed somewhat random distribution pattern as shown by comparatively higher SD and SE values. The skewness and kurtosis values were noted to be higher for As, Ca, Pb, Li, Mn, Ni and Cd thus evidencing their asymmetry distribution in the water samples. In addition, Hg was also analysed during the present study but its concentration in the water samples during all seasons was less than the limit of detection (0.10 µg/L). The quartile distribution of metal concentrations in the water samples was also evaluated in the present study and the results are shown as box-whisker plot in Figure 4. Most of the metals showed broader differences and asymmetry in their distribution, however, As, Na, K and Mg showed very narrow distribution with overlapping of lower and upper quartiles. Nevertheless, Li and Mn exhibited relatively symmetrical and uniform distribution in the water samples during summer season.

Table 3. Statistical distribution of selected metal levels (mg/L) in the water samples during summer ($n = 150$)

	Min	Max	Mean	Median	SD	SE	Skew	Kurt
As	0.000	0.040	0.011	0.011	0.006	0.001	2.649	12.69
Ca	14.01	47.55	43.37	44.35	5.454	0.922	-4.812	26.26
Cd	0.002	0.103	0.033	0.027	0.025	0.004	1.103	1.076
Co	0.014	0.501	0.254	0.242	0.124	0.021	0.116	-0.395
Cr	0.001	0.214	0.077	0.071	0.054	0.009	0.653	-0.029
Cu	0.001	0.049	0.018	0.014	0.014	0.002	0.708	-0.545
Fe	0.020	0.328	0.148	0.154	0.071	0.012	0.245	-0.262
K	1.192	1.553	1.344	1.359	0.081	0.014	0.325	-0.141
Li	0.001	0.026	0.008	0.008	0.006	0.001	1.047	1.325
Mg	3.032	3.701	3.390	3.356	0.178	0.030	0.069	-0.928
Mn	0.001	0.053	0.014	0.010	0.013	0.002	1.359	1.573
Na	2.109	2.799	2.410	2.363	0.209	0.035	0.414	-1.072
Ni	0.005	0.415	0.129	0.110	0.087	0.015	1.295	2.567
Pb	0.024	1.501	0.381	0.237	0.324	0.055	1.541	3.000
Se	0.0001	0.0026	0.0013	0.0013	0.0007	0.00013	-0.221	-1.109
Sr	0.065	0.291	0.192	0.205	0.065	0.011	-0.432	-0.823
Zn	0.002	0.069	0.032	0.031	0.021	0.004	0.099	-1.330

Basic statistical distribution parameters for selected metals in the water samples during winter are given in Table 4. In this case, ranges (lower-highest, mg/L) and average levels (in bracket, mg/L) were found in the water samples as As 0.002-0.015 (0.007), Ca 41.38-169.1 (79.26), Cd 0.001-0.083 (0.027), Co 0.011-0.411 (0.160), Cr 0.009-0.194 (0.075), Cu 0.001-0.056 (0.022), Fe 0.001-0.381 (0.134), K 0.608-2.032 (1.315), Li 0.001-0.017 (0.009), Mg 3.794-8.444 (4.857), Mn 0.002-0.059 (0.018), Na 3.444-34.55 (6.758), Ni 0.009-0.293 (0.107), Pb 0.001-2.208 (0.339), Se 0.0008-0.003 (0.008), Sr 0.113-0.391 (0.219) and Zn 0.001-0.076 (0.031). The average metal concentrations in the water during winter revealed following order: Ca > Na > Mg > K > Pb > Sr > Co > Fe > Ni > Cr > Zn > Cd > Cu > Mn > Li > As > Se. Some of the metals including As, Fe, Li, Ni, Sr and Zn showed nearly comparable mean and median levels thus indicating relatively Gaussian distribution during winter. The quartile distribution of metal concentrations in the water samples during winter is illustrated in Figure 5, which demonstrated relatively broader dispersion for most of the metals. Some of the metals (As, Ca and Sr) exhibited moderately symmetrical distribution, however, Mg and Na showed very narrow distribution with overlapping of outer quartiles. Nonetheless, highest dispersion and asymmetry was observed in the distribution of Pb, Fe, Cd and Zn levels in the water samples during winter.

Table 4. Statistical distribution of selected metal levels (mg/L) in the water samples during winter ($n = 150$)

	Min	Max	Mean	Median	SD	SE	Skew	Kurt
As	0.002	0.015	0.007	0.006	0.003	0.001	0.317	-0.527
Ca	41.38	169.1	79.26	71.37	24.49	4.139	2.367	7.160
Cd	0.001	0.083	0.027	0.018	0.026	0.004	0.813	-0.612
Co	0.011	0.411	0.160	0.133	0.116	0.020	0.920	-0.084
Cr	0.009	0.194	0.075	0.070	0.045	0.008	0.932	0.381
Cu	0.001	0.056	0.022	0.017	0.018	0.003	0.672	-0.916
Fe	0.001	0.381	0.134	0.135	0.086	0.015	0.534	0.351
K	0.608	2.032	1.315	1.207	0.307	0.052	0.746	0.762
Li	0.001	0.017	0.009	0.009	0.004	0.001	0.015	-0.063
Mg	3.794	8.444	4.857	4.054	1.276	0.216	1.046	-0.082
Mn	0.002	0.059	0.018	0.013	0.015	0.003	1.407	1.466
Na	3.444	34.55	6.758	4.223	6.469	1.093	3.519	12.69
Ni	0.009	0.293	0.107	0.104	0.068	0.011	0.359	0.142
Pb	0.001	2.208	0.339	0.210	0.414	0.070	3.045	11.86
Se	0.00008	0.003	0.0008	0.0005	0.0008	0.0001	1.509	1.855
Sr	0.113	0.391	0.219	0.224	0.061	0.010	0.406	0.501
Zn	0.001	0.076	0.031	0.030	0.018	0.003	0.650	0.324

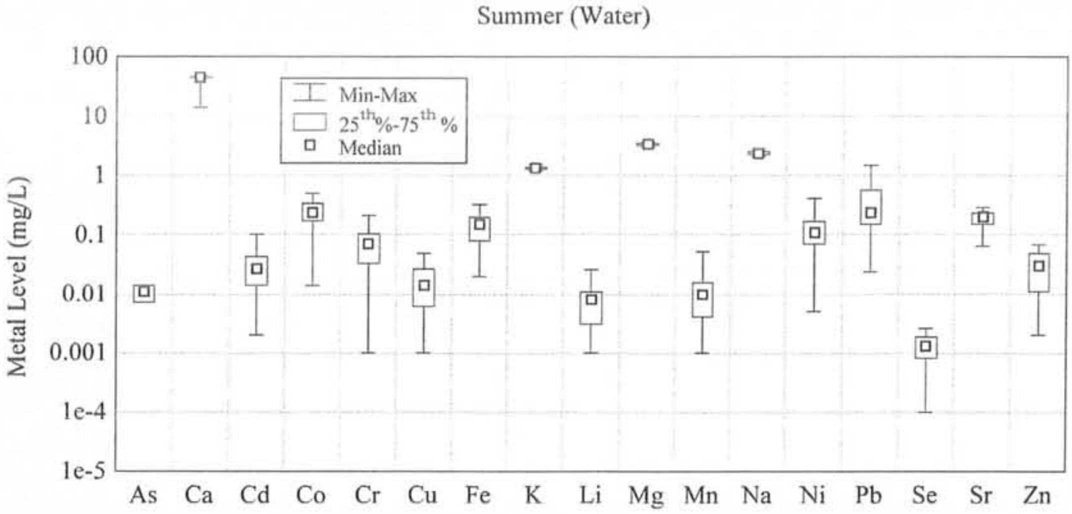

Figure 4. Quartile distribution of selected metal levels (mg/L) in the water samples during summer

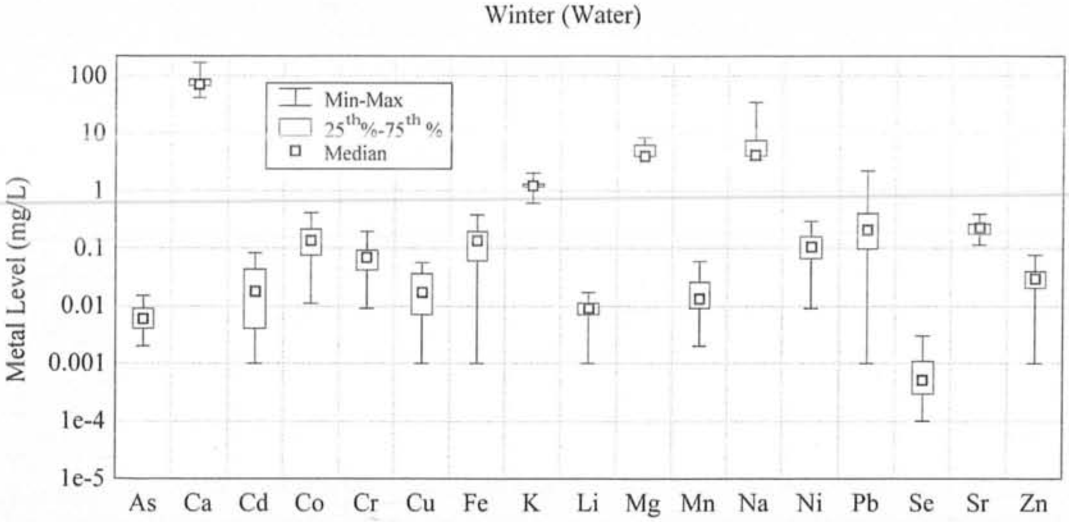

Figure 5. Quartile distribution of selected metal levels (mg/L) in the water samples during winter

Seasonal variations in the metals levels indicated that average concentrations of As, Cd, Co, Fe, Ni, Pb and Se were relatively higher during summer than winter, while measured levels of Ca, Cu, Li, Mg, Na, Mn and Sr were considerably higher during winter season. Nevertheless, almost comparable contributions of Cr, K and Zn levels in the water reservoir were noted during both seasons as shown in Figure 6. Comparatively higher concentrations of As, Cd, Co, Cr, Fe, K, Ni, Pb, Se and Zn during summer were mostly associated with higher precipitation, snow melting and excessive anthropogenic activities in the catchment areas during summer while elevated metal levels during winter might be attributed to reduced inflow and shortage of water supply, which resulted in the build-up and enrichment of the metal levels in the lake. Present study revealed significantly elevated concentrations of Pb and Co which were noted to be higher than Fe and Zn. Likewise, Cr, Ni and Cd also exhibited relatively larger contributions which may result in serious health concerns to the consumers.

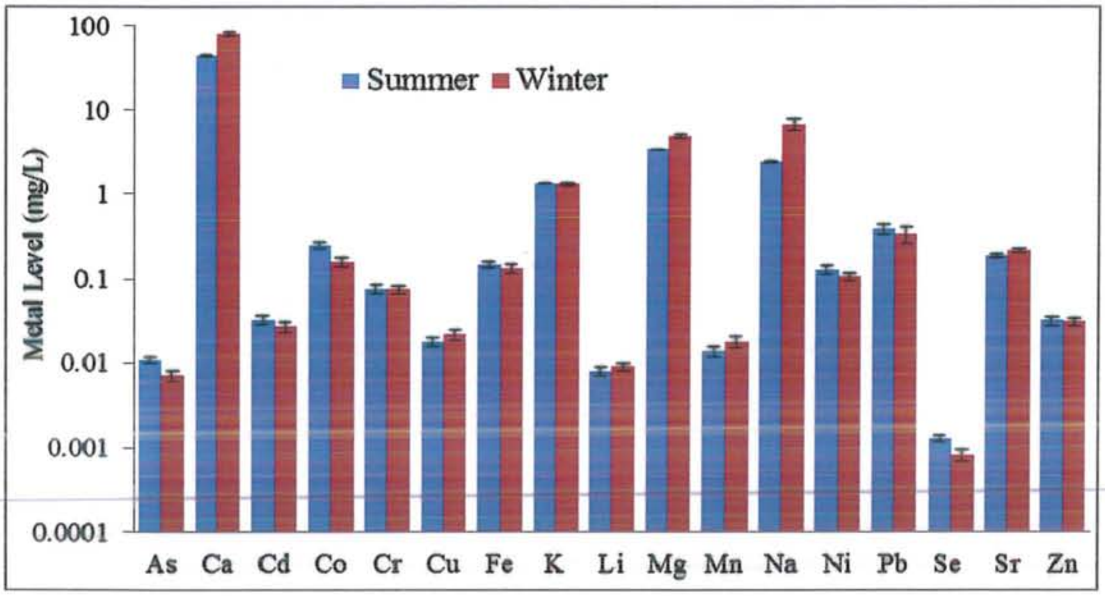

Figure 6. Comparison of average metal levels (mg/L, ±SE) in the water samples during summer and winter

Statistical distribution of selected metals in the water samples during pre-monsoon (Table 5) showed the highest contribution of Ca (26.13 mg/L), followed by considerable average levels of Na (4.905 mg/L), Mg (4.832 mg/L), K (1.880 mg/L), Pb (0.339 mg/L) and Ni (0.331 mg/L), while mean levels of Cu (0.020 mg/L), As (0.019 mg/L), Mn (0.013 mg/L) and Se (0.002 mg/L) exhibited rather lower contributions. Overall, the metals exhibited the following decreasing order based on average concentration in the water samples during pre-monsoon: Ca > Na > Mg > K > Pb > Ni > Co > Sr > Fe > Cr > Cd > Zn > Cu > As > Mn > Li > Se. Most of the metals showed fairly normal distribution pattern in their concentrations as shown by relatively lower SD and SE values, however, Ca, Mg and Na indicated relatively random distribution and Cr, K, Li, Mg, Mn, Na and Pb showed somewhat asymmetrical distribution.

Table 5. Statistical distribution of selected metal levels (mg/L) in the water samples during pre-monsoon (n = 150)

	Min	Max	Mean	Median	SD	SE	Skew	Kurt
As	0.004	0.030	0.019	0.016	0.007	0.001	0.207	-1.033
Ca	17.39	33.91	26.13	26.01	4.310	0.610	-0.206	-0.719
Cd	0.001	0.103	0.036	0.031	0.027	0.004	0.663	-0.420
Co	0.016	0.501	0.235	0.231	0.126	0.018	0.198	-0.850
Cr	0.003	0.312	0.075	0.053	0.070	0.010	1.545	2.428
Cu	0.001	0.056	0.020	0.016	0.016	0.002	0.884	-0.292
Fe	0.001	0.381	0.128	0.127	0.082	0.012	0.643	0.273
K	1.378	2.978	1.880	1.838	0.270	0.038	1.776	5.327
Li	0.001	0.028	0.008	0.006	0.006	0.001	1.249	1.196
Mg	3.481	9.145	4.832	4.637	1.269	0.180	1.460	2.256
Mn	0.001	0.059	0.013	0.010	0.013	0.002	2.107	5.271
Na	2.416	18.93	4.905	4.084	2.948	0.417	3.612	14.56
Ni	0.011	0.682	0.313	0.322	0.189	0.027	0.328	-0.710
Pb	0.001	1.501	0.339	0.241	0.315	0.045	1.585	2.893
Se	0.00063	0.00397	0.00191	0.00178	0.00099	0.00014	0.371	-1.237
Sr	0.110	0.360	0.200	0.200	0.056	0.008	0.512	0.426
Zn	0.001	0.076	0.031	0.031	0.021	0.003	0.312	-0.910

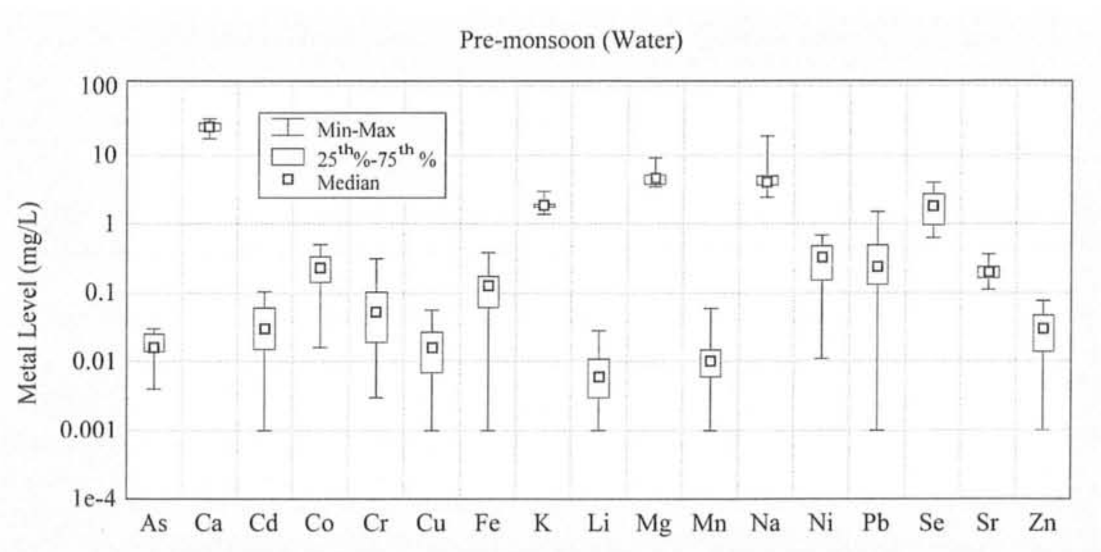

Figure 7. Quartile distribution of selected metal levels (mg/L) in the water samples during pre-monsoon

Table 6. Statistical distribution of selected metal levels (mg/L) in the water samples during monsoon (*n* = 150)

	Min	Max	Mean	Median	SD	SE	Skew	Kurt
As	0.009	0.025	0.013	0.012	0.004	0.001	2.085	4.175
Ca	15.03	29.47	22.45	22.85	3.889	0.550	-0.215	-0.936
Cd	0.010	0.053	0.031	0.031	0.010	0.001	0.018	-0.364
Co	0.003	0.547	0.157	0.116	0.139	0.020	1.471	1.594
Cr	0.001	0.214	0.067	0.054	0.048	0.007	0.936	0.265
Cu	0.001	0.055	0.014	0.011	0.013	0.002	1.675	2.672
Fe	0.001	0.278	0.089	0.067	0.069	0.010	1.000	0.255
K	1.112	2.123	1.511	1.451	0.228	0.032	0.844	0.390
Li	0.002	0.021	0.010	0.008	0.005	0.001	0.628	-0.237
Mg	2.921	6.524	4.536	4.002	1.006	0.142	1.070	-0.424
Mn	0.001	0.024	0.008	0.008	0.006	0.001	1.047	0.685
Na	2.066	7.953	4.767	4.104	1.544	0.218	1.080	-0.074
Ni	0.005	0.415	0.126	0.127	0.083	0.012	0.963	2.089
Pb	0.021	0.465	0.226	0.228	0.116	0.016	0.091	-0.743
Se	0.000017	0.00303	0.0012	0.0011	0.00067	0.00009	0.451	0.784
Sr	0.096	0.332	0.187	0.190	0.052	0.007	0.541	1.000
Zn	0.001	0.072	0.008	0.005	0.011	0.002	4.427	24.48

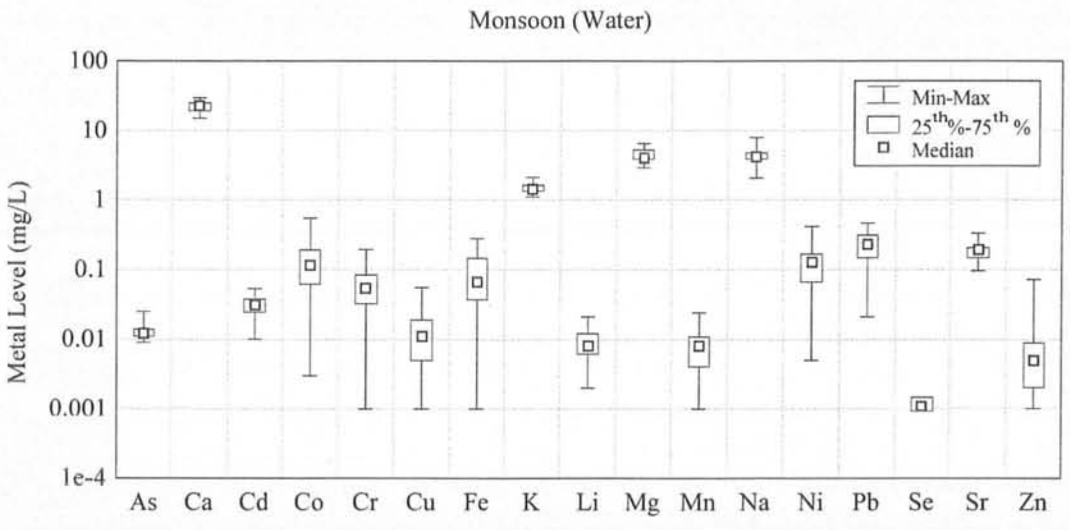

Figure 8. Quartile distribution of selected metal levels (mg/L) in the water samples during monsoon

Table 7. Statistical distribution of selected metal levels (mg/L) in the water samples during post-monsoon ($n = 150$)

	Min	Max	Mean	Median	SD	SE	Skew	Kurt
As	0.006	0.017	0.010	0.009	0.002	0.000	1.128	0.902
Ca	7.309	45.11	20.27	19.93	4.547	0.643	2.770	19.38
Cd	0.002	0.040	0.018	0.017	0.011	0.001	0.312	-0.814
Co	0.010	0.254	0.103	0.099	0.062	0.009	0.396	-0.710
Cr	0.001	0.063	0.021	0.017	0.017	0.002	0.846	0.055
Cu	0.001	0.030	0.014	0.013	0.008	0.001	0.314	-0.772
Fe	0.002	0.454	0.109	0.079	0.097	0.014	1.415	2.383
K	1.187	3.057	1.635	1.552	0.392	0.055	1.720	3.313
Li	0.001	0.022	0.011	0.011	0.006	0.001	0.117	-0.705
Mg	2.929	17.81	4.772	4.255	2.535	0.358	3.422	14.88
Mn	0.002	0.043	0.019	0.018	0.009	0.001	0.587	0.486
Na	1.658	43.85	8.583	3.852	9.998	1.414	2.236	5.246
Ni	0.036	0.405	0.124	0.116	0.068	0.010	1.875	5.380
Pb	0.001	0.267	0.129	0.124	0.070	0.010	0.013	-0.796
Se	0.000097	0.0044	0.00115	0.00080	0.00114	0.00016	1.677	2.180
Sr	0.024	0.257	0.155	0.166	0.046	0.007	-0.576	0.427
Zn	0.001	0.031	0.012	0.011	0.007	0.001	0.955	0.971

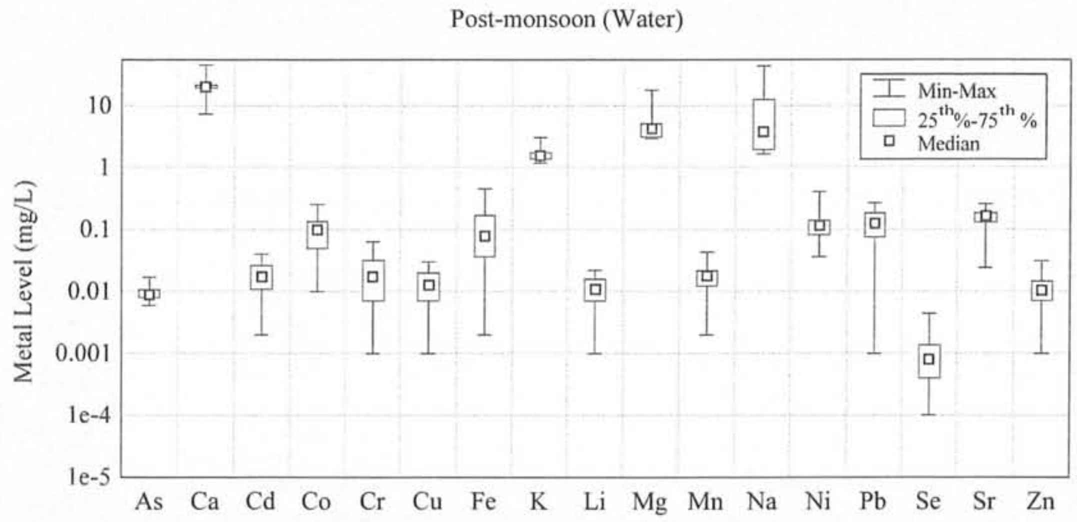

Figure 9. Quartile distribution of selected metal levels (mg/L) in the water samples during post-monsoon

The quartile distribution of selected metal concentrations in the water samples during pre-monsoon season is shown in Figure 7 as box-whisker plot. Most of the metals revealed broad and asymmetric distribution, nonetheless, Se, K and Sr showed relatively symmetrical distribution while Sr, K and Ca displayed very narrow distribution. Among the metals, highest spreading was demonstrated by Pb, followed by Fe, Cd, Ni, Cr and Zn during this season.

Table 6 shows the basic statistical distribution parameters for selected metal levels in the water samples during monsoon season. Mostly the metals displayed large variation in their minimum and maximum levels. Average concentrations of As, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, Pb, Se, Sr and Zn in the water samples during monsoon season were measured at 0.013, 22.45, 0.031, 0.157, 0.067, 0.014, 0.089, 1.511, 0.010, 4.536, 0.008, 4.767, 0.126, 0.226, 0.0012, 0.187 and 0.008 mg/L, respectively. Among the metals, As, Ca, Cd, Li and Mn showed almost equivalent mean and median levels, indicating more or less normal distribution in the water samples. Overall, mean concentrations of the metals revealed following decreasing order: Ca > Na > Mg > K > Pb > Sr > Co> Ni > Fe > Cr > Cd > Cu > As > Li >Mn > Zn > Se. Some of the metals (Ca, Mg and Na) exhibited predominantly non-Gaussian distribution, as indicated by their larger SD and SE values. Fairly symmetric distribution was found for Ca, Cd, Pb and Li as shown by lower skewness and kurtosis values. Box-Whisker plot showing the quartile distribution of metals in the water during monsoon is given in Figure 8. As shown in the figure, Co, Cr, Fe, Ni, Pb and Zn displayed large disparities in their quartile levels, while As, Ca, K, Mg, Na and Sr exhibited relatively narrow distribution in the water samples. Selenium showed very narrow distribution as evidenced by overlapping of the lower and upper quartiles.

Basic statistical distribution parameters for the metals in water samples during post-monsoon season are shown in Table 7. Most of the metals exhibited significant variations in their extremum levels. Highest mean level in the water was noted for Ca (20.27 mg/L), followed by, Na (8.583 mg/L), Mg (4.772 mg/L), K (1.635 mg/L), Sr (0.155 mg/L), Pb (0.129) and Ni (0.124), while, average concentrations of Zn (0.012 mg/L), Li (0.011 mg/L), As (0.010 mg/L) and Se (0.001 mg/L) demonstrated the least contributions. Overall, the metals showed following decreasing order based on average concentrations in the water samples: Ca > Na > Mg > K > Sr > Pb > Ni > Fe > Co > Cr > Mn > Cd > Cu > Zn > Li > As > Se. Some of the metals including As, Cd, Cu, Li, Mn and Zn exhibited almost comparable mean and median levels, showing more or less normal distribution in the water samples. Nevertheless, Ca, Mg, Na and K showed non-Gaussian distribution pattern in their concentration as shown by comparatively higher SD and SE values. Lower values of skewness and Kurtosis for Li and Pb indicated their symmetrical distribution; however, relatively higher skewness and kurtosis values for As, Ca, Fe, K, Mg, Na, Ni, Se and Zn indicated their asymmetrical distribution in the water samples. The quartile distribution of metal concentrations in the water samples during post-monsoon is shown in Figure 9. Among the selected metals, As and K showed relatively narrow distribution, whereas highest dispersion was shown by Pb, followed by, Fe and Cr. Most of the metals showed broad distribution in the water samples during post-monsoon season.

Comparative evaluation of the metal data revealed that average levels of As, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Ni, Pb, Se, Sr and Zn were found to be significantly higher (ANOVA: Single Factor; F ratio is larger than the F critical value) during pre-monsoon season, while elevated concentrations of Li, Na, and Mn were noted during post-monsoon as shown in Figure 10. Sum of concentrations of all the metals (As, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Ni, Pb, Se, Sr and Zn) in the Lake water displayed the average levels of 2.304 mg/L, 2.012 mg/L and 2.117 mg/L during pre-monsoon, monsoon and post-monsoon seasons, respectively. Consequently, most of the metal concentrations were higher during pre-monsoon season compared with the other seasons, which indicated different seasonal inputs to the water reservoir due to hydrological regime and seasonal anthropogenic intrusions. Elevated concentrations of most of the metals during pre-monsoon season might be attributed to the intense anthropogenic activities (agriculture, domestic, & industrial activities) in the catchments area during this period. High precipitation and large water inputs from the tributaries and rivers were the most plausible causes for the lowest total concentrations during monsoon and post-monsoon seasons. High precipitation during monsoon season mixed large volumes of uncontaminated runoffs water with contaminated water to reduce the total metal concentrations in the water reservoir. About 80% of annual precipitation was observed during monsoon season in the study area, resulting in dilution of the pollutants and lowering of the metal concentrations during monsoon and post-monsoon seasons. Some of the metals, such as, Li, Na and Mn showed higher contributions during varying hydrological seasonality, which were resulted from their mixed sources (natural contributions as well as anthropogenic intrusions). Sometimes the variations in metal concentrations might also be influenced by changes in lithological inputs, hydrological effects, geological features, cultural influences and type of vegetation cover.

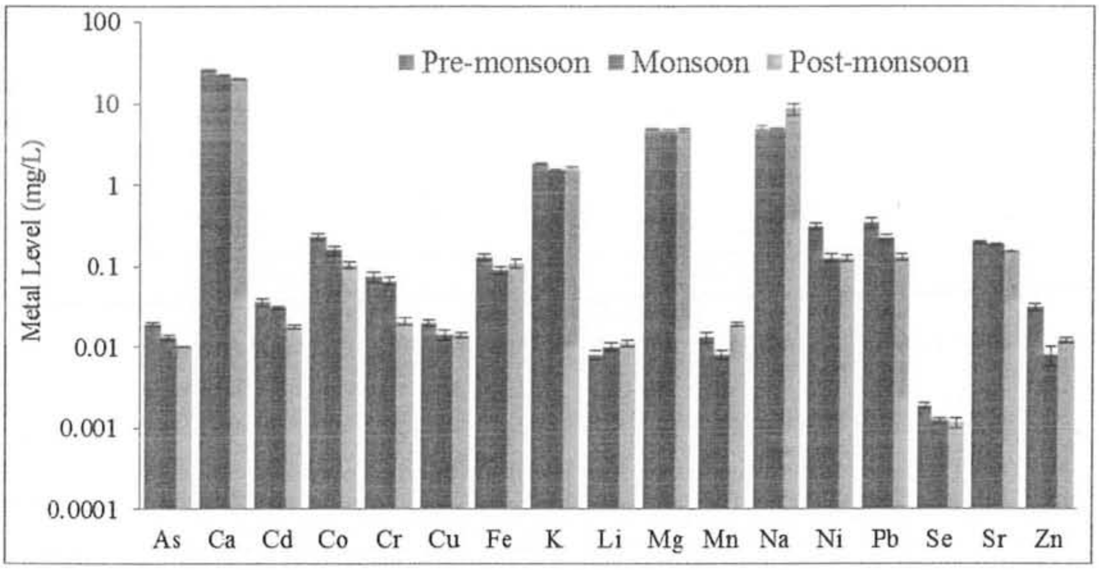

Figure 10. Comparison of average metal levels (mg/L, ±SE) in the water samples during pre-monsoon, monsoon and post-monsoon

3.5 Comparisons of Present Metal Levels with International and National Guideline Values and Worldwide Reported Levels

Average concentrations of selected metals in the water samples collected during summer and winter seasons were compared with water quality guidelines set by national and international authorities which are given in Appendix M. In the present study, mean levels of Cd, Co and Pb during summer and winter were found to be higher than the maximum permissible levels recommended by WHO (2011), USEPA (2012), and Pak-EPA (2008) (Table 8). During the summer, 90% samples for Cd, 94% samples for Co and 95% samples for Pb exceeded the water quality guidelines, whereas 89% samples for Cd & Co, and 94% samples for Pb exceeded the water guidelines during winter. Similarly, Cr levels in 63% samples and Ni contents in 75% samples were higher than the WHO and Pak-EPA guidelines during summer, while Cr (69% samples) and Ni (71% samples) levels were also higher than the water guidelines (Pak-EPA, 2008; WHO, 2011) during winter. Mean concentration of As in 69% samples was higher than the WHO and USEPA guidelines during summer whereas, during winter, 15% samples for As exceeded the water quality guidelines (USEPA 2012; WHO, 2011). Nevertheless, rest of the metals and water quality parameters were well within the recommended limits set by national and international authorities (Pak-EPA 2008; USEPA, 2012; WHO, 2011). Overall, As, Cd, Co, Cr, Ni, and Pb emerged as the major pollutants in Mangla Lake during both seasons.

Table 8. Comparison of mean metal levels (mg/L) and water quality parameters of the water samples during summer and winter with national/international guidelines

	Summer			Winter			WHO	USEPA	Pak-EPA
	Min	Max	Mean	Min	Max	Mean	(2011)	(2012)	(2008)
As	0.000	0.04	0.011	0.002	0.015	0.007	0.01	0.01	0.05
Ca	14.01	47.55	43.37	41.38	169.1	79.26	100	-	200
Cd	0.002	0.103	0.033	0.001	0.083	0.027	0.003	0.005	0.01
Co	0.014	0.501	0.254	0.011	0.411	0.16	0.04	-	-
Cr	0.001	0.214	0.077	0.009	0.194	0.075	0.05	0.1	0.05
Cu	0.001	0.049	0.018	0.001	0.056	0.022	2	1.3	2
Fe	0.02	0.328	0.148	0.001	0.381	0.134	0.3	0.3	-
K	1.192	1.553	1.344	0.608	2.032	1.315	12	-	-
Li	0.001	0.026	0.008	0.001	0.017	0.009	-	-	-
Mg	3.032	3.701	3.39	3.794	8.444	4.857	50	-	-
Mn	0.001	0.053	0.014	0.002	0.059	0.018	0.1	0.05	0.5
Na	2.109	2.799	2.41	3.444	34.55	6.758	200	-	-
Ni	0.005	0.415	0.129	0.009	0.293	0.107	0.07	0.7	0.02
Pb	0.024	1.501	0.381	0.001	2.208	0.339	0.01	0.015	0.05
Se	0.0001	0.0026	0.0013	0.00008	0.003	0.0008	0.04	0.05	0.01
Sr	0.065	0.291	0.192	0.113	0.391	0.219	-	-	-
Zn	0.002	0.069	0.032	0.001	0.076	0.031	3	5	5
pH	7.62	8.23	8.02	7.42	8.32	7.8	6.5-8.5	6.5-8.5	6.5-8.5
EC	130.6	158.7	139.9	180.3	477.0	250.4	1500	-	-
TDS	65.30	79.60	69.97	90.50	238.0	125.2	1200	500	1000
Cl^-	9.927	14.89	11.34	4.999	15.00	8.819	250	250	250
NO_3^-	0.674	21.16	8.929	1.989	13.90	5.791	50	10	50
SO_4^{2-}	5.626	40.02	21.24	11.43	30.30	17.37	-	250	-
F^-	0.089	0.158	0.113	0.058	0.296	0.128	1.5	4	1.5
TA	58.00	290.0	143.8	30.00	195.0	93.9	200	-	-

EC (μS/cm), TDS (mg/L), Cl^- (mg/L), NO_3^- (mg/L), SO_4^{2-} (mg/L), F^- (mg/L), TA (mg/L as $CaCO_3$)

Average concentrations of selected metal levels in the water samples measured in the present study during summer and winter were also compared with the results of other reported studies as shown in Table 9. Present mean levels of As were higher than Wetland of Wadi Gaza (summer) and Nakambe watershed Burkina Faso (Ouedraogo and Amyot, 2013; Shomar *et al.*, 2005); but lower than Great Salt Lake and Manchar Lake during both seasons (Adam *et al.*, 2015; Arain *et al.*, 2008). Present mean levels of Ca were higher than those reported by Anshumali and Ramanathan (2007), Iqbal *et al.*, (2013) & Ouedraogo and Amyot (2013), however, lower than the reported levels for Manchar Lake, wetland of Wadi Gaza, Wielkie and Boszkowo Lakes (Arain *et al.*, 2008; Shomar *et al.*, 2005; Szymanowska *et al.*, 1999). Average concentrations of K, Mg, Na, Li and Sr in the present study were lower than most of the reported levels in the Table. Among the metals, Cd, Co, Cr, Cu, Ni and Pb levels were found to be higher than the reported levels for Manchar Lake, Watland of Wadi Gaza, Sapanca Lake, Bellandur Lake, Lalbagh Tank and Rawal Lake during both seasons (Arain *et al.*, 2008; Duman *et al.*, 2007; Iqbal *et al.*, 2013a; Lokeshwari and Chandrapa, 2006a & 2006b; Mastoi *et al.*, 2008; Shomar *et al.*, 2005). Mean concentrations of Fe in the present study were considerably higher than the results reported for Manchar Lake, Wetland of Wadi Gaza (winter) and Rawal Lake (Iqbal *et al.*, 2013a; Mastoi *et al.*, 2008; Shomar *et al.*, 2005), but lower than those reported by Arain *et al.*, (2008), Lokeshwari and Chandrapa (2006a & 2006b), Majagi *et al.*, (2008) and Szymanowska *et al.*, (1999). Similarly, average levels of Se were higher than those reported by Ouedraogo and Amyot (2013) but lower than those reported by Adam *et al.*, (2015). However, average concentrations of Mn in the present study were noticeably lower than those reported by Arain *et al.*, (2008), Duman *et al.*, (2007), Majagi *et al.*, (2008), Shomar *et al.*, (2005) and Szymanowska *et al.*, (1999). Mean concentrations of Zn were higher than the reported levels by Iqbal *et al.*, (2013) and Mastoi *et al.*, (2008) but lower than those reported by Arain *et al.*, (2008), Duman *et al.*, (2007), Lokeshwari and Chandrapa (2006a & 2006b), Majagi *et al.*, (2008) and Shomar *et al.*, (2005) (Table 9).

Average metal concentrations in the water samples during pre-monsoon, monsoon and post-monsoon seasons were compared with national and international water quality guidelines for drinking water as shown in Table 10. Mean concentrations of As in the present study during the three seasons were higher than WHO and USEPA guidelines while those of Cd and Pb were higher than the water quality guidelines set by WHO, USEPA and Pak-EPA in all seasons (Pak-EPA, 2008; USEPA, 2012; WHO, 2011). Present mean levels of As were higher than WHO & USEPA guidelines in 90%, 74% and 34% samples during pre-monsoon, monsoon and post-monsoon, respectively,

Table 9. Comparison of mean metal levels (mg/L) in the water samples during summer and winter with the worldwide reported levels

Water body	As	Ca	Cd	Co	Cr	Cu	Fe	K	Li	Mg	Mn	Na	Ni	Pb	Se	Sr	Zn	Reference
Mangla Lake, Pakistan (S)	0.011	43.37	0.033	0.254	0.077	0.018	0.148	1.344	0.008	3.390	0.014	2.41	0.129	0.381	0.0013	0.19	0.032	Present study
Mangla Lake, Pakistan (W)	0.007	79.26	0.027	0.16	0.075	0.022	0.134	1.315	0.009	4.857	0.018	6.758	0.107	0.339	0.0008	0.22	0.031	Present study
Manchar Lake, Pakistan	-	70.7	0.001	0.004		0.009	0.012	17.6	-	56.2		521.5	0.004	0.009	-	-	0.016	Mastoi *et al*. 2008
Great Salt Lake, USA	0.112	-	-	-	-	0.004	-	-	-	-	-	-	-	-	0.006	-	-	Adam *et al*. 2015
Wielkie Lake, Poland	-	82	7.81	13.4	5.69	5.46	110	6.9	-	15.9	4.09	-	10.7	76.5	-	-	-	Szymanowska *et al*. 1999
Boszkowo Lake, Poland	-	108	11.14	24.7	7.25	5.63	180	7.2	-	15.1	2.86	-	11.2	61.2	-	-	-	Szymanowska *et al*. 1999
Domimickie Lake, Poland	-	51	8.47	14.3	5.87	3.93	140	2.9	-	16.3	3.23	-	9	63.4	-	-	-	Szymanowska *et al*. 1999
Lake Beysehir, Turkey	-	-	0.11	-	0.086	-	-	-	-	-	-	-	-	0.028	-	-	-	Altindag & Yigit, 2005
Watland of Wadi Gaza (S)	0.002	136.0	0.006	0.043	0.065	0.004	0.382		-	89.00	0.423	678.0		0.012	-	-	0.082	Shomar *et al*. 2005
Watland of Wadi Gaza (W)	0.013	102.9	0.002	0.002	0.021	0.017	0.009		-	65.70	0.267	124.0		0.041	-	-	0.150	Shomar *et al*. 2005
Karanja Reservoir, India	-	-	-	-	-	0.211	0.585	-	-	-	0.225	-	0.778	1.103	-	-	0.210	Majagi *et al*. 2008
Sapanca Lake, Turkey	-		0.003		0.062	0.018	-	-	-		0.023		0.046	0.036	-	-	0.089	Duman *et al*. 2007
Nakambe watershed, Burkina Faso	5E-04	7.46	-	-	-	-	-	6.67	-	4.00		5.76	-	-	7E-05			Ouedraogo & Amyot, 2013
Bellandur Lake, India	-	-	0.001		0.006	0.012	1.09		-	-	-	-	0.003	0.009	-	-	0.132	Lokeshwari & Chandrapa 2006a
Lalbagh Tank, India	-	-			0.001	0.001	0.166		-	-	-		0.001	0.004	-	-	0.043	Lokeshwari & Chandrapa 2006b
Pandoh Lake, India (S)	-	7.990						1.91	-	1.17		3.87	-	-	-	-	-	Anshumali & Ramanathan, 2007
Pandoh Lake, India (W)	-	24.43	-	-	-	-	-	2.46	-	6.32	-	5.51	-	-	-	-	-	Anshumali & Ramanathan, 2007
Rawal Lake, Pakistan (S)	-	12.89	0.006	0.011	0.009	0.010	0.093	3.140	0.006	4.992	0.004	13.51	-	0.162	-	0.884	0.014	Iqbal *et al*. 2013
Rawal Lake, Pakistan (W)	-	17.72	0.025	0.204	0.097	0.017	0.076	2.559	0.012	11.34	0.013	13.72	-	0.223	-	0.688	0.022	Iqbal *et al*. 2013
Manchar Lake, Pakistan (S)	0.088	403.4	0.006	0.041	0.008	0.020	3.228	22.74	-	283.5	0.076	566.5	0.036	0.088	-	-	0.774	Arain *et al*. 2008
Manchar Lake, Pakistan (W)	0.072	261.6	0.004	0.035	0.007	0.018	2.78	20.38	-	183.2	0.065	501.2	0.031	0.079	-	-	0.683	Arain *et al*. 2008

(S) – Summer; (W) – Winter

While for Cd and Pb, 100% of the water samples during monsoon and >90% during pre-monsoon and post-monsoon exceeded the WHO, USEPA and Pak-EPA guidelines. Similarly, average concentrations of Co were higher than WHO guidelines, whereas mean levels of Cr during pre-monsoon and monsoon seasons were higher than WHO and Pak-EPA guidelines. Average concentrations of Ni during pre-monsoon, monsoon and post-monsoon were higher than WHO and Pak-EPA guidelines but below the USEPA guidelines. About 58% of the samples for Cr during pre-monsoon and monsoon, and >92% for Ni in all seasons exceeded the WHO and Pak-EPA guidelines. Measured concentrations of Fe in more than 90% samples were lower than the national and international guidelines in all seasons. Present mean values of pH during post-monsoon were higher than the national and international guidelines, whereas on the average, TA levels during pre-monsoon and monsoon were higher than WHO guidelines. Nevertheless, rest of the metals and water quality parameters (EC, TDS, SO_4^{2-}, F^-, Cl^-) were well within the national and international guidelines (Pak-EPA, 2008; USEPA, 2012; WHO, 2011). Therefore, As, Cd, Co, Cr, Ni and Pb were potential pollutants in the reservoir and they might pose health risks to the exposed population.

Average metal concentrations in the water samples from Mangla Lake were also compared with the reported levels from other reservoirs around the world as shown in Table 11. Average levels of Cd, Co, Cr, Ni and Pb in the present study were found to be considerably higher compared with other studies given in the Table (Iqbal and Shah, 2013; Jiang *et al.,* 2012; Kazi *et al.,* 2009; Li *et al.,* 2008a; Ochieng *et al.,* 2008; Oyewala and Musa, 2006; Pekey *et al.,* 2004; Samecka-Cymermana and Kempers, 2001 & 2004; Varol, 2013; Varol *et al.,* 2010 & 2013) except Co levels during post-monsoon, which were lower than those reported for Legnica Lake (Southwest Poland), Dil Deresi Stream (Turkey), Manchar Lake (Pakistan), Lake Gilow (Poland), Khanpur & Simly Lakes (Pakistan). Measured levels of As in the present study were significantly higher than the reported levels for Kralkizi Dam, Dicle Dam, Batman Dam & Tigris River (Turkey), Taihu Lake & Danjiangkou Reservoirs (China) (Varol, 2013; Varol *et al.,* 2010 & 2013; Jiang *et al.,* 2012; Li *et al.,* 2008a), the mean As levels were lower than those reported for Dil Deresi stream (Turkey), Great Salt Lake (USA), Manchar Lake (Pakistan) during the three seasons (Pekey *et al.,* 2004; Adam *et al.,* 2015; Kazi *et al.,* 2009). Mean levels of Ca, K, Li, Mg, Se and Sr were found to be noticeably lower than most of the reported level as shown in Table 11. Nonetheless, Cu exhibited higher concentrations than those reported for Kralkizi Dam, Dicle Dam, Batman Dam & Tigris River (Turkey), Taihu Lake &

Danjiangkou Reservoir (China), Kainji dam (Nigeria), Anthropogenic Lake (West Poland), Great Salt Lake (USA) and Khanpur Lake (Pakistan), but lower than those reported for Dil Deresi Stream (Turkey), Kanyaboli Lake (Kenya), Legnica Lake (Southwest Poland) and Lake Gilow (Poland) in all seasons.

Table 10. Comparison of mean metal levels (mg/L) and water quality parameters of the water samples during pre monsoon, monsoon and post monsoon with national and international guidelines

	Pre-monsoon	Monsoon	Post-monsoon	WHO (2011)	USEPA (2012)	Pak-EPA (2008)
As	0.019	0.013	0.010	0.01	0.01	0.05
Ca	26.13	22.45	20.27	100	-	200
Cd	0.036	0.031	0.018	0.003	0.005	0.01
Co	0.235	0.157	0.103	0.04	-	-
Cr	0.075	0.067	0.021	0.05	0.1	0.05
Cu	0.020	0.014	0.014	2	1.3	2
Fe	0.128	0.089	0.109	0.3	0.3	-
K	1.880	1.511	1.635	12	-	-
Li	0.008	0.010	0.011	-	-	-
Mg	4.832	4.536	4.772	50	-	-
Mn	0.013	0.008	0.019	0.1	0.05	0.5
Na	4.905	4.767	8.583	200	-	-
Ni	0.313	0.126	0.124	0.07	0.7	0.02
Pb	0.339	0.226	0.129	0.01	0.015	0.05
Se	0.002	0.001	0.001	0.04	0.05	0.01
Sr	0.200	0.187	0.155	-	-	-
Zn	0.031	0.008	0.012	3	5	5
pH	7.92	7.37	6.43	6.5-8.5	6.5-8.5	6.5-8.5
EC	183.8	278.9	158.7	1500	-	-
TDS	91.95	139.2	79.35	1200	500	1000
Cl^-	19.06	17.51	25.31	250	250	250
NO_3^-	20.23	18.07	12.02	50	10	50
SO_4^{2-}	12.64	15.90	20.15	-	250	-
F^-	0.237	0.116	0.320	1.5	4	1.5
TA	332	259	141	200	-	-

EC (μS/cm), TDS (mg/L), Cl^- (mg/L), NO_3^- (mg/L), SO_4^{2-} (mg/L), F^- (mg/L), TA (mg/L as $CaCO_3$)

Table 11. Comparison of mean metal levels (µg/L) in the water samples during pre-monsoon, monsoon and post-monsoon with the worldwide reported levels

	As	Ca	Cd	Co	Cr	Cu	Fe	K	Li	Mg	Mn	Na	Ni	Pb	Se	Sr	Zn	
Mangla Lake (Pre-monsoon)	18.5	26.1	36.3	75.1	235	20.3	128	1.88	7.74	4.83	13.1	4.91	313	339	1.91	200	31.2	Present study
Mangla Lake (Monsoon)	12.8	22.5	31.1	67.2	157	14.4	88.5	1.51	8.99	4.54	8.16	4.77	126	226	1.22	187	7.84	Present study
Mangla Lake (Post-monsoon)	9.84	20.3	18.3	21.0	103	13.7	109	1.64	11.3	4.77	18.9	8.58	124	129	1.15	155	11.7	Present study
Kralkızı Dam Reservoir, Turkey	2.39	-	0.036	-	22.06	2.83	58.63	-	-	-	-	-	15.75	2.56	-	-	5.02	Varol, 2013
Dicle Dam Reservoir, Turkey	1.61	-	0.030	-	18.58	2.12	62.07	-	-	-	-	-	15.86	1.84	-	-	4.12	Varol, 2013
Batman Dam Reservoir, Turkey	0.71	-	0.044	-	16.5	-	57.66	-	-	-	-	-	15.96	1.56	-	-	4.09	Varol, 2013
Tigris River, Turkey	12.32	46.61	-		48.58	4.52	159.5	1.44	-	9.14		6.43	17.32	22.03	-	-	3.62	Varol *et al.* 2010 & 2013
Taihu Lake, China	1.86	-	0.06	-	0.99	5.81	-	-	-	-	-	-	5.34	2.74	-	-	15.86	Jiang *et al.* 2012
Danjiangkou Reservoir, China	11.08	-	1.17	1.08	6.29	13.32	19.14	-	-	-	5.69	-	1.73	10.59	15.36	231.8	2.02	Li *et al.* 2008
Dil Deresi stream, Turkey	50	-	8	21	42	37	4030	-	-	-	-	-	-	120	-	-	700	Pekey *et al.* 2004
Kanyaboli Lake, Kenya	-	-	4.4	6.06	21.54	23.95	-	-	-	-	284.3	-	16.38	20.65	-	-	32.79	Ochieng *et al.* 2008
Kainji dam, Nigeria	-	-	-	1.2	2.2	1.3	13	-	-	-	9	-	0.90	1.2	-	-	0.90	Oyewala & Musa, 2006
Anthropogenic lake, Poland	-	49	0.2	13	2.6	7	9000	12	-	28	130	-	-	2	-	-	86	Cymermana & Kempers, 2001
Legnica Lake, Poland	-	283	1.72	65	1.1	29	6	64	-	87	670	-	68.2	0.21	-	1100	204	Cymermana & Kempers, 2004
Lake Gilow, Poland	-	101	0.58	27	0.9	48	6	30	-	36	390	-	76	0.5	-	1400	167	Cymermana & Kempers, 2004
Great Salt Lake, USA	112	-	-	-	-	4.2	-	-	-	-	-	-	-	-	6	-	-	Adam *et al.* 2015
Khanpur Lake, Pakistan	-	20.42	20	114	46	9	51	1.573	11.4	10.55	11	6.466	-	221	-	740	15	Iqbal & Shah, 2013
Simly Lake, Pakistan	-	19.02	17	157	75	22	60	2.709	12.2	10.26	14	14.9	-	200	-	160	25	Iqbal & Shah, 2013
Manchar Lake, Pakistan	80.8	224.6	5.3	38.9	7.64	18.9	2960	21.48	-	151.8	72.6	445.3	35	82.4	52.8	-	730	Kazi *et al.* 2009

Ca, K, Mg and Na levels are expressed as mg/L

Higher mean levels of Fe were observed in the present study compared with the reported levels for Kralkizi Dam, Dicle Dam & Batman Dam (Turkey), Danjiangkou Reservoir (China), Kainji dam (Nigeria), Legnica Lake (Southwest Poland), Lake Gilow (Poland), Simly Lake and Khanpur Lake (Pakistan), however, present levels were lower than those reported for Tigris River (Turkey), Dil Deresi Stream (Turkey), Anthropogenic Lake (West Poland) and Manchar lake (Pakistan). Mean levels of Na were higher than the reported levels from Tigris River (Turkey) and Khanpur Lake (Pakistan) during post-monsoon season (Varol *et al.,* 2013; Iqbal and Shah, 2013). Manganese showed lower average levels than those reported for Kanyaboli Lake (Kenya), Anthropogenic Lake (West Poland), Legnica Lake (Southwest Poland), Lake Gilow (Poland) and Manchar Lake (Pakistan). Mean levels of Zn were higher than those reported for Kralkizi Dam, Dicle Dam, Batman Dam & Tigris River (Turkey), Danjiangkou Reservoir (China), Kainji dam (Nigeria), Simly Lake and Khanpur Lake (Pakistan) while lower than those reported for the Taihu Lake (China), Dil Deresi Stream (Turkey), Kanyaboli Lake (Kenya), Anthropogenic Lake (West Poland), Legnica Lake (Southwest Poland), Lake Gilow (Poland) and Manchar lake (Pakistan) (Varol, 2013; Varol *et al.,* 2010 & 2013; Jiang *et al.,* 2012; Li *et al.,* 2008a; Ochieng *et al.,* 2008; Oyewala and Musa, 2006; Samecka-Cymermana and Kempers, 2001 & 2004; Pekey *et al.,* 2004; Kazi *et al.,* 2009; Iqbal and Shah, 2013).

3.6 Spatial Distribution of Selected Metals in Water Samples

Spatial distribution of the metals in Mangle Lake was also evaluated during pre-monsoon, monsoon and post-monsoon seasons. Five major sampling sites (as shown in Figure 3) were selected to assess the spatial variability of the metals. These sites included entrance of Jhelum river (S-1), Poonch pocket (S-2), main Mangla (S-3), Khad (S-4) and Jari (S-5). During the study period, most of the metals showed significant spatial variations among the sampling sites ($p < 0.05$) as shown in Table 12. The highest concentrations of Ca, Cd, Co, Cr, Cu, Fe, Mn, Na, Ni, Pb, Se and Zn were found at S-4; Arsenic, K, Mg exhibited highest concentration at S-3 while Li showed highest levels at S-2. However As, Ca, Cd, Co, Cr, Cu, K, Li, Mn, Na, Ni, Pb and Sr revealed lowest concentration at S-2 while Fe, Mg, Se and Zn showed lowest concentration at S-1 in the water samples during pre-monsoon season. Almost similar trend was found during monsoon and post-monsoon; and most of metals exhibited highest concentration at S-4.

Table 12. Spatial variations in average metal levels (mg/L ± SE) in the water samples during pre-monsoon, monsoon and post-monsoon

			As	Ca	Cd	Co	Cr	Cu	Fe	K	Li	Mg	Mn	Na	Ni	Pb	Se	Sr	Zn
Pre-monsoon	S-1	Mean	0.018	25.67	0.032	0.211	0.064	0.018	0.057	1.717	0.004	4.381	0.010	4.409	0.266	0.315	0.002	0.195	0.027
		SE	0.002	0.155	0.008	0.047	0.015	0.003	0.012	0.045	0.001	0.540	0.003	0.413	0.048	0.070	0.000	0.009	0.006
	S-2	Mean	0.016	19.89	0.031	0.182	0.025	0.014	0.128	1.731	0.013	3.929	0.011	4.204	0.263	0.246	0.002	0.165	0.031
		SE	0.002	0.515	0.007	0.043	0.008	0.004	0.023	0.044	0.003	0.263	0.003	0.223	0.053	0.068	0.000	0.012	0.007
	S-3	Mean	0.020	26.62	0.041	0.295	0.095	0.024	0.120	2.174	0.008	6.226	0.011	5.188	0.335	0.397	0.002	0.223	0.032
		SE	0.003	0.692	0.012	0.024	0.012	0.006	0.021	0.136	0.002	0.366	0.003	1.594	0.075	0.135	0.000	0.013	0.007
	S-4	Mean	0.020	30.29	0.045	0.297	0.143	0.028	0.187	1.898	0.009	4.954	0.023	5.405	0.404	0.459	0.002	0.198	0.038
		SE	0.002	1.189	0.008	0.030	0.036	0.005	0.035	0.042	0.002	0.218	0.006	0.390	0.075	0.115	0.000	0.018	0.007
	S-5	Mean	0.019	28.16	0.032	0.189	0.049	0.018	0.147	1.878	0.005	4.671	0.011	5.319	0.298	0.277	0.002	0.221	0.028
		SE	0.002	1.080	0.007	0.040	0.008	0.006	0.017	0.018	0.001	0.027	0.003	1.296	0.040	0.098	0.000	0.027	0.007
Monsoon	S-1	Mean	0.012	21.53	0.028	0.100	0.042	0.025	0.045	1.458	0.009	4.023	0.008	3.978	0.124	0.234	0.001	0.181	0.005
		SE	0.001	1.361	0.004	0.017	0.007	0.006	0.010	0.071	0.001	0.183	0.002	0.070	0.021	0.046	0.000	0.010	0.001
	S-2	Mean	0.013	22.59	0.026	0.075	0.066	0.015	0.062	1.491	0.007	4.221	0.006	4.017	0.085	0.203	0.002	0.203	0.009
		SE	0.001	1.390	0.003	0.015	0.013	0.005	0.009	0.061	0.001	0.231	0.001	0.167	0.022	0.026	0.000	0.016	0.001
	S-3	Mean	0.011	22.85	0.032	0.170	0.083	0.010	0.090	1.550	0.011	4.707	0.011	4.215	0.149	0.246	0.001	0.204	0.016
		SE	0.001	1.092	0.003	0.060	0.017	0.001	0.022	0.070	0.002	0.358	0.002	0.480	0.035	0.035	0.000	0.018	0.007
	S-4	Mean	0.014	22.67	0.037	0.263	0.070	0.010	0.122	1.576	0.009	5.742	0.010	7.310	0.154	0.271	0.001	0.206	0.006
		SE	0.001	1.425	0.003	0.052	0.016	0.002	0.022	0.083	0.002	0.307	0.002	0.228	0.028	0.045	0.000	0.014	0.002
	S-5	Mean	0.014	22.62	0.033	0.175	0.075	0.013	0.125	1.482	0.008	3.986	0.007	4.314	0.118	0.175	0.001	0.142	0.004
		SE	0.001	1.051	0.002	0.034	0.021	0.002	0.029	0.081	0.001	0.049	0.001	0.275	0.022	0.026	0.000	0.016	0.001
Post-monsoon	S-1	Mean	0.010	18.23	0.016	0.060	0.018	0.016	0.135	1.390	0.011	4.225	0.018	2.912	0.098	0.135	0.001	0.113	0.005
		SE	0.001	1.712	0.003	0.017	0.005	0.003	0.031	0.038	0.002	0.240	0.001	0.489	0.009	0.016	0.000	0.015	0.001
	S-2	Mean	0.009	20.53	0.016	0.091	0.012	0.010	0.147	1.420	0.011	3.055	0.017	1.865	0.105	0.100	0.001	0.156	0.010
		SE	0.001	0.399	0.004	0.014	0.004	0.002	0.042	0.080	0.002	0.028	0.003	0.037	0.019	0.029	0.000	0.008	0.001
	S-3	Mean	0.011	22.23	0.016	0.098	0.017	0.016	0.047	1.485	0.012	7.890	0.019	12.86	0.117	0.093	0.001	0.143	0.013
		SE	0.001	2.602	0.002	0.022	0.006	0.003	0.011	0.066	0.002	1.324	0.002	0.429	0.015	0.021	0.000	0.015	0.001
	S-4	Mean	0.011	20.44	0.025	0.139	0.025	0.013	0.149	2.206	0.012	5.122	0.023	22.03	0.163	0.164	0.001	0.199	0.017
		SE	0.001	0.332	0.004	0.018	0.005	0.002	0.031	0.143	0.002	0.083	0.005	4.455	0.031	0.014	0.000	0.010	0.003
	S-5	Mean	0.008	19.95	0.018	0.127	0.034	0.014	0.068	1.675	0.012	3.568	0.019	3.243	0.138	0.152	0.001	0.166	0.015
		SE	0.001	0.614	0.003	0.018	0.005	0.002	0.017	0.015	0.002	0.254	0.002	0.510	0.023	0.023	0.000	0.009	0.001

Generally, the maximum levels of the metals were observed at sites S-3, S-4 and S-5; and these sites were located near to highly urbanized areas (Mirpur city). Commonly, these sites received untreated sewage, agricultural, urban & industrial wastes and automobile emissions from urbanized (Mirpur city) and semi-urban (Chakswari, Islamghar, Kharak, Dhok Choudrian) catchments areas. However, the lowest concentrations were found at sampling sites S-1 and S-2 which were close to the less populated/remote areas of the Lake. Moreover, elevated metal levels at sites S-4 and S-5 might also be due to greater retention of water that agglutinated the sampling points, while at sites S-1 and S-2 the continuous flow of water could not provide enough time for the metals accumulation. The lowest metal levels found at sites S-1 and S-2 might also be due to reduced anthropogenic intrusions around these sites. Overall, relative variations of total mean metal concentrations remained similar during monsoon and post-monsoon seasons; S-4 > S-3 > S-5 > S-2 > S-1 while the order was slightly different during pre-monsoon season; S-4 > S-3 > S-5 > S-1 > S-2.

3.7 Correlation Study of Physicochemical Parameters and Selected Metals in Water Samples

Spearman correlation coefficient matrix related to the physicochemical parameters and selected metals in the water samples during summer and winter are shown in Tables 13 & 14, respectively. Numerous significant and strong correlations were observed between the variables. Among the physicochemical parameters, NO_3^- was strongly correlated with SO_4^{2-} (r = 0.668) while F^- was significantly correlated with NO_3^- (r = 0.486), SO_4^{2-} (r = 0.552) and TA (r = 0.365). Besides, some inverse correlations were also noted, such as, pH was inversely correlated with EC (r = -0.500) and TDS (r = -0.503); which were quite obvious as at higher pH, mostly precipitation takes place and the dissolved contents were minimized in the reservoir. Chloride was also inversely correlated with SO_4^{2-} (r = -0.432). Among the metals, As exhibited significant positive correlation with Ni (r = 0.462), Li (r = 0.429) and significant inverse relationship with Ca (r = -0.851), Mg (r = -0.529) and Cr (r = -0.426), while Ca showed significant positive correlation with Mg (r = 0.504) and inverse relationships with Ni (r = -0.449) and Li (r = -0.447). A number of positive significant relationships were noted between other pairs, such as, Mg-Na (r = 0.707), Na-Mn (r = 0.601), Mg-Mn (r = 0.577), Fe-Sr (r = 0.485), Li-Ni (r = 0.449), Cr-Fe (r = 0.437) and Fe-Zn (r = 0.425) alongside some negative relationships, such as, Cr-Li (r = -0.514), Cd-K (r = -0.484), Co-Na (r = -0.480), Fe-Li (r = -0.480), and Cd-Sr (r = 0.427). These mutual associations among the metals indicated their probably common origin in the water.

Table 13. Correlation coefficient (r)* matrix for physicochemical parameters in the water samples during summer and winter

		T	pH	EC	TDS	DO	Cl^-	NO_3^-	SO_4^{2-}	F^-	TA
Summer (n = 150)	T	1									
	pH	-0.079	1								
	EC	-0.248	-0.500	1							
	TDS	-0.255	-0.503	0.996	1						
	DO	-0.013	-0.116	0.205	0.205	1					
	Cl^-	-0.073	0.078	0.008	0.006	0.011	1				
	NO_3^-	-0.002	0.017	-0.035	0.001	0.251	-0.212	1			
	SO_4^{2-}	0.144	0.227	-0.123	-0.105	-0.167	-0.432	0.668	1		
	F^-	0.345	-0.038	-0.007	0.018	0.250	-0.154	0.486	0.552	1	
	TA	0.178	0.113	-0.115	-0.111	0.247	-0.130	0.197	-0.021	0.365	1
Winter (n = 150)	T	1									
	pH	0.118	1								
	EC	0.024	0.060	1							
	TDS	0.022	0.062	1.000	1						
	DO	-0.144	-0.249	-0.158	-0.156	1					
	Cl^-	0.156	0.125	0.605	0.606	0.126	1				
	NO_3^-	0.197	0.289	-0.007	-0.001	-0.175	0.520	1			
	SO_4^{2-}	-0.245	0.103	0.150	0.154	-0.007	0.251	0.467	1		
	F^-	-0.062	0.372	0.332	0.337	-0.508	0.157	0.440	0.535	1	
	TA	-0.280	-0.088	0.543	0.544	-0.089	0.365	-0.164	0.203	0.289	1

*r-values > 0.300 or < -0.300 are significantly correlated at $p < 0.05$

Table 14. Correlation coefficient (r)* matrix for selected metal levels in the water samples during summer (below the diagonal) and winter (above the diagonal)

	As	Ca	Cd	Co	Cr	Cu	Fe	K	Li	Mg	Mn	Na	Ni	Pb	Se	Sr	Zn
As	1	-0.008	0.105	-0.261	0.309	0.150	0.020	-0.084	-0.163	0.055	-0.014	-0.017	0.078	-0.058	0.039	0.039	-0.107
Ca	-0.851	1	-0.097	-0.310	-0.168	0.145	-0.038	-0.089	0.244	0.594	0.139	0.773	0.004	-0.080	0.438	-0.026	-0.116
Cd	0.106	0.014	1	-0.111	-0.004	-0.196	-0.121	0.001	0.178	-0.262	-0.155	-0.232	0.099	-0.087	-0.421	-0.169	0.442
Co	0.327	-0.155	0.054	1	-0.211	-0.042	0.121	-0.117	-0.189	-0.377	-0.083	-0.314	-0.112	0.042	-0.061	-0.254	0.125
Cr	-0.426	0.276	0.027	-0.242	1	0.392	0.014	0.006	-0.120	0.307	-0.070	0.137	-0.144	0.300	-0.362	0.578	-0.041
Cu	0.027	-0.109	0.052	0.174	-0.112	1	-0.046	-0.121	-0.060	0.253	-0.015	0.293	0.040	0.027	-0.156	0.130	-0.236
Fe	-0.397	0.363	0.252	-0.152	0.437	-0.009	1	0.114	0.089	0.132	-0.166	0.064	-0.175	0.081	-0.146	0.285	-0.233
K	0.036	-0.141	-0.484	-0.053	-0.340	-0.142	-0.293	1	0.337	0.358	-0.148	-0.285	-0.315	0.217	-0.219	0.119	0.136
Li	0.429	-0.447	-0.227	0.259	-0.514	0.349	-0.480	0.140	1	0.258	0.018	0.052	-0.101	-0.008	0.039	-0.068	0.179
Mg	-0.529	0.504	-0.007	-0.306	0.317	-0.113	0.296	0.063	-0.088	1	-0.122	0.676	-0.234	0.259	0.100	0.487	-0.140
Mn	-0.265	0.246	0.113	-0.122	0.211	-0.188	0.411	-0.150	-0.026	0.577	1	0.139	-0.117	-0.249	0.419	-0.149	-0.374
Na	-0.308	0.130	-0.145	-0.407	0.222	-0.139	0.129	0.118	0.063	0.707	0.601	1	-0.048	0.017	0.383	0.163	-0.276
Ni	0.462	-0.449	-0.036	0.136	-0.116	0.185	-0.171	0.220	0.449	-0.086	-0.190	-0.105	1	0.036	0.053	-0.348	0.095
Pb	0.083	-0.057	-0.138	-0.114	-0.155	0.205	0.153	0.187	0.123	0.070	-0.105	0.095	0.203	1	-0.089	0.196	0.146
Se	0.020	-0.062	0.116	-0.210	0.281	-0.144	0.296	-0.117	-0.208	0.190	0.348	0.263	0.231	-0.242	1	-0.293	-0.275
Sr	-0.338	0.284	0.427	-0.175	0.204	-0.056	0.485	-0.242	-0.325	0.092	0.108	-0.017	-0.329	0.042	0.198	1	-0.172
Zn	0.099	-0.019	0.251	-0.005	-0.018	-0.267	0.425	-0.034	-0.219	0.010	0.225	-0.030	0.174	-0.072	0.339	0.321	1

*r-values > 0.300 or < -0.300 are significantly correlated at $p < 0.05$

The correlation coefficient matrix for the physicochemical parameters and selected metals in the water samples during winter are also shown in Tables 13 & 14, respectively. Among the physicochemical parameters, EC and TDS were directly associated with each other, while Cl^- was positively correlated with TDS (r = 0.606), EC (r = 0.605) and NO_3^- (r = 0.520). Similarly, TA was found to be positively correlated with TDS (r = 0.544), EC (r = 0.543) and chloride (r = 0.365) during winter. Moreover, F^- exhibited significant positive association with SO_4^{2-} (r = 0.535) and NO_3^- (r = 0.440); while inverse association with DO (r = -0.508). Nitrate also showed positive association with SO_4^{2-} (r = 0.467). Among the metals, Ca showed positive relationship with Na (r = 0.773), Mg (r = 0.594) and Se (r = 0.438). In addition, Mg revealed strong correlations with Na (r = 0.773), Sr (r = 0.487), and Se (r = 0.419); Cd was found to be positively correlated with Zn (r = 0.442) and inversely correlated with Se (r = -0.421); and Co was positively correlated with Sr (r = 0.578). Though, the correlation findings for winter season were nearly comparable to those observed in summer, nonetheless, some considerable differences in the mutual relationship were also observed which may be attributed to the seasonal effects.

Correlation coefficient matrix for the physicochemical parameters and selected metals in water samples during pre-monsoon is shown in Tables 15 & 16, respectively. Among the physicochemical parameters, EC and TDS exhibited significant and similar associations with NO_3^- (r = 0.328), while F^- levels showed inverse relationships with DO (r = -0.492) and T (r = -0.487). Some inverse associations were also found between T & NO_3^- (r = -0.552), and pH & SO_4^{2-} (r = -0.361). Among the metals, Mn exhibited positive correlation with Fe (r = 0.435) and Ca (r = 0.348); while Na revealed positive correlation with Cu (r = 0.412) and inverse correlation K (r = -0.349) in the water samples. Positive correlations were also observed between Co-Cu (r = 0.420), K-Mg (r = 0.383), Li-Se (r = 0.326) and Pb-Zn (r = 0.344).

The correlation findings for the physicochemical parameters and selected metals in the water samples during monsoon season are shown in Tables 15 & 17, respectively. Among the physicochemical parameters, EC and TDS showed direct relationship as found in other seasons, while pH was positively correlated with EC (r = 0.534) and TDS (r = 0.528). In addition, F^- exhibited significant positive correlations with pH (r = 0.555), TDS (r = 0.532), EC (r = 0.533) and SO_4^{2-} (r = 0.467) whereas inverse correlation were observed with T (r = -0.403), which exhibited positive association with NO_3^- (r = 0.393). Among the metals, Cd revealed significant positive relationship with Co (r = 0.501), Mg (r = 0.450), and Ca (r = 0.410), and negative association with Cu (r = -0.338).

Table 15. Correlation coefficient (*r*)* matrix for physicochemical parameters in the water samples during pre-monsoon, monsoon and post-monsoon

		T	pH	EC	TDS	DO	Cl^-	NO_3^-	SO_4^{2-}	F^-	TA
Pre-monsoon ($n = 150$)	T	1									
	pH	-0.105	1								
	EC	-0.213	-0.303	1							
	TDS	-0.210	-0.301	1.000	1						
	DO	0.087	-0.204	-0.191	-0.190	1					
	Cl^-	0.122	-0.139	0.155	0.154	-0.180	1				
	NO_3^-	-0.552	0.299	0.328	0.328	-0.242	0.052	1			
	SO_4^{2-}	0.060	-0.361	0.212	0.215	0.131	0.029	-0.187	1		
	F^-	-0.487	0.034	0.266	0.261	-0.492	-0.040	0.211	-0.026	1	
	TA	-0.001	-0.231	0.024	0.023	0.013	0.292	-0.310	-0.073	-0.036	1
Monsoon ($n = 150$)	T	1									
	pH	-0.171	1								
	EC	-0.037	0.534	1							
	TDS	-0.040	0.528	1.000	1						
	DO	-0.089	-0.046	-0.172	-0.175	1					
	Cl^-	-0.191	-0.084	0.044	0.046	-0.207	1				
	NO_3^-	0.393	-0.001	-0.090	-0.091	-0.013	0.058	1			
	SO_4^{2-}	-0.244	-0.052	-0.280	-0.281	-0.147	-0.162	0.025	1		
	F^-	-0.403	0.555	0.533	0.532	-0.071	0.160	0.014	0.467	1	
	TA	-0.154	-0.075	-0.182	-0.183	-0.310	0.293	0.158	0.047	0.053	1
Post-monsoon ($n = 150$)	T	1									
	pH	-0.031	1								
	EC	0.130	0.053	1							
	TDS	0.138	0.027	0.994	1						
	DO	-0.093	-0.127	0.087	0.092	1					
	Cl^-	0.129	-0.198	0.034	0.053	0.132	1				
	NO_3^-	0.050	0.365	0.322	0.264	0.050	-0.359	1			
	SO_4^{2-}	0.104	0.538	0.248	0.185	-0.268	-0.102	0.563	1		
	F^-	-0.071	0.366	0.423	0.396	-0.155	-0.294	0.152	0.386	1	
	TA	0.252	-0.113	0.109	0.140	-0.120	0.287	-0.320	-0.101	0.177	1

**r*-values > 0.300 or < -0.300 are significantly correlated at $p < 0.05$

Table 16. Correlation coefficient (r)* matrix for selected metal levels in the water samples during pre-monsoon ($n = 150$)

	As	Ca	Cd	Co	Cr	Cu	Fe	K	Li	Mg	Mn	Na	Ni	Pb	Se	Sr	Zn
As	1																
Ca	0.142	1															
Cd	-0.124	-0.076	1														
Co	0.107	0.237	0.012	1													
Cr	0.108	0.083	0.024	0.110	1												
Cu	-0.135	0.250	-0.001	0.420	0.193	1											
Fe	0.025	0.188	0.139	0.033	0.136	0.062	1										
K	0.295	0.056	-0.008	-0.145	-0.330	-0.144	-0.086	1									
Li	0.015	0.321	0.075	0.181	-0.076	0.220	0.028	-0.141	1								
Mg	-0.068	0.085	-0.216	-0.082	-0.334	-0.050	0.168	0.383	0.096	1							
Mn	-0.032	0.348	0.114	-0.208	-0.112	0.067	0.435	0.018	0.285	0.184	1						
Na	-0.228	0.017	-0.095	0.022	0.016	0.412	0.127	-0.349	0.123	-0.109	0.030	1					
Ni	0.112	0.133	0.149	-0.005	0.073	0.083	0.187	0.018	0.060	-0.098	0.211	-0.070	1				
Pb	-0.116	-0.024	0.282	0.074	0.154	-0.168	0.123	-0.117	-0.118	0.016	-0.037	-0.123	-0.027	1			
Se	-0.051	0.144	0.119	0.167	-0.032	-0.047	-0.068	-0.057	0.326	0.072	-0.053	-0.068	-0.044	0.418	1		
Sr	-0.029	0.198	0.140	-0.284	-0.110	0.020	-0.001	0.257	0.231	0.191	0.141	-0.017	0.088	-0.059	0.022	1	
Zn	-0.022	0.141	0.181	-0.005	0.090	-0.086	0.114	0.081	-0.116	0.069	0.099	-0.046	0.266	0.344	-0.007	0.268	1

*r-values > 0.300 or < -0.300 are significantly correlated at $p < 0.05$

Table 17. Correlation coefficient (*r*)* matrix for selected metal levels in the water samples during monsoon (*n* = 150)

	As	Ca	Cd	Co	Cr	Cu	Fe	K	Li	Mg	Mn	Na	Ni	Pb	Se	Sr	Zn
As	1																
Ca	-0.529	1															
Cd	-0.044	0.410	1														
Co	-0.088	0.321	0.501	1													
Cr	0.047	0.215	-0.190	-0.064	1												
Cu	0.039	-0.257	-0.338	-0.052	-0.210	1											
Fe	-0.143	0.116	0.169	0.198	-0.142	-0.260	1										
K	0.279	-0.065	0.109	0.060	-0.233	0.005	-0.064	1									
Li	-0.184	0.334	0.282	0.316	-0.038	-0.243	0.260	-0.234	1								
Mg	0.203	0.025	0.450	0.419	-0.178	-0.151	0.020	0.201	0.188	1							
Mn	0.185	-0.127	-0.063	0.082	0.072	0.036	-0.140	0.123	-0.060	0.267	1						
Na	0.256	-0.057	0.181	0.160	0.201	-0.086	0.147	0.133	-0.100	0.451	0.094	1					
Ni	0.217	-0.191	0.098	0.099	0.195	-0.020	-0.261	0.101	-0.200	0.180	0.097	0.285	1				
Pb	0.071	-0.031	0.089	-0.094	0.005	-0.125	0.031	0.134	0.203	0.300	0.131	0.161	-0.039	1			
Se	-0.154	0.306	0.103	-0.017	-0.104	-0.262	-0.078	0.258	0.023	0.024	-0.144	0.093	-0.194	0.202	1		
Sr	0.112	-0.229	-0.160	-0.094	0.005	-0.143	-0.081	0.139	0.045	0.173	0.254	0.147	0.091	0.321	0.008	1	
Zn	0.163	-0.033	-0.048	0.026	0.318	0.072	-0.126	0.038	-0.001	-0.119	-0.003	0.127	-0.019	-0.143	-0.148	-0.075	1

**r*-values > 0.300 or < -0.300 are significantly correlated at $p < 0.05$

Table 18. Correlation coefficient (*r*)* matrix for selected metal levels in the water samples during post-monsoon ($n = 150$)

	As	Ca	Cd	Co	Cr	Cu	Fe	K	Li	Mg	Mn	Na	Ni	Pb	Se	Sr	Zn
As	1																
Ca	-0.003	1															
Cd	0.044	0.090	1														
Co	0.108	-0.177	0.445	1													
Cr	-0.057	0.012	0.133	0.228	1												
Cu	0.126	0.180	-0.134	-0.250	-0.018	1											
Fe	0.067	-0.105	0.069	0.064	0.052	-0.161	1										
K	0.200	0.062	0.275	0.402	0.207	-0.138	0.145	1									
Li	-0.065	0.143	-0.031	-0.051	0.165	-0.160	0.181	-0.039	1								
Mg	0.167	-0.032	-0.079	-0.077	0.064	0.082	-0.176	0.089	0.120	1							
Mn	0.127	0.013	-0.031	0.010	0.107	0.134	0.231	0.233	-0.186	0.037	1						
Na	0.203	0.070	0.251	0.220	0.049	0.069	-0.056	0.481	0.202	0.284	-0.024	1					
Ni	-0.099	-0.073	0.079	0.057	0.086	0.063	-0.070	0.175	0.250	0.129	0.165	0.314	1				
Pb	0.032	-0.128	0.043	-0.041	0.209	-0.283	0.125	0.277	0.264	0.175	-0.048	0.154	0.263	1			
Se	-0.103	-0.025	-0.101	-0.211	-0.233	0.051	-0.180	-0.046	-0.018	0.060	0.148	0.045	0.012	-0.153	1		
Sr	-0.022	0.057	0.228	0.153	0.284	-0.083	0.039	0.293	0.069	0.000	0.095	0.425	0.418	0.170	-0.116	1	1
Zn	0.149	0.101	0.005	0.411	0.261	-0.158	0.084	0.535	-0.022	0.011	0.363	0.097	0.208	-0.051	-0.080	0.248	

**r*-values > 0.300 or < -0.300 are significantly correlated at $p < 0.05$

In addition, Mg revealed a significant correlation with Na (r = 0.451) and Co (r = 0.419) while Li was found to be positively correlated with Ca (r = 0.334) and Co (r = 0.316). Moreover, Pb was significantly correlated with Sr (r = 0.321) while Ca was inversely correlated with As (r = -0.529) in the water samples.

The correlation findings related to the physicochemical parameters and selected metals in the water samples during post-monsoon season are shown in Tables 15 & 18, respectively. Among the physicochemical parameters, F^- was positively correlated with TDS (r = 0.396), EC (r = 0.423) and SO_4^{2-} (r = 0.386). Similarly, pH was found to be positively correlated with SO_4^{2-} (r = 0.538), NO_3^- (r = 0.365) and F^- (r = 0.366). In addition, NO_3^- exhibited significant positive association with SO_4^{2-} (r = 0.563) and inverse association with Cl^- (r = -0.359). Among the metals, Co showed positive relationship with Cd (r = 0.445), Zn (r = 0.411) and K (r = 0.402); K revealed strong correlation with Zn (r = 0.535) and Na (r = 0.481), and Sr was positively correlated with Na (r = 0.425) and Ni (r = 0.418). Generally, the metals exhibiting positive mutual associations were believed to be contributed by common sources, which would be further explored by multivariate statistical methods.

3.8 Multivariate Analysis of Selected Metals in Water Samples

One of the most important aspects of the present study was apportionment and identification of the sources of metal pollutants in the freshwater reservoir. For this purpose, multivariate statistical methods comprising of principle components analysis (PCA) and cluster analysis (CA) were employed. The principle component loadings of the metals in water samples during summer are shown in Table 19 where five principle components (PCs) were extracted with eigenvalues greater than one, together explaining more than 67% of the total variance of the data. The CA related to the metal levels during summer is shown in Figure 11 as a dendrogram, which exhibited three significant clusters of the metals during summer. PC 1 exhibiting 25.87 % of the total variance, revealed highest loadings for Ca, K, Mg, Na and Mn, while PC 2 showed significant loadings for Fe, Li, Sr, Se and Zn. These metals also showed strong clustering among them in CA and they were mostly originated by natural processes including the corrosion, erosion and weathering of the parent rocks/soil in the upstream/catchments areas. PC 3 revealed higher loadings in favour of Cr and Ni, while PC 4 exhibited highest loadings for Cu and Co which were mainly contributed by industrial emissions. Last PC showed highest loadings for As, Cd and Pb which were mainly contributed by automobile emissions and agricultural run-offs. The CA was in very good agreement with the PCA results and mostly the clusters were formulated by the metals contributed by common sources.

Table 19. Principal component analysis of selected metal levels in the water samples during summer

	PC 1	PC 2	PC 3	PC 4	PC 5
Eigen value	4.397	2.347	1.994	1.453	1.320
Total Variance (%)	25.87	13.80	11.73	8.546	7.765
Cumulative Eigen value	4.397	6.744	8.738	10.19	11.51
Cumulative Variance (%)	25.87	39.67	51.40	59.95	67.71
As	-0.349	0.030	0.039	-0.109	0.849
Ca	0.821	-0.028	-0.117	0.071	0.033
Cd	-0.077	0.268	-0.015	-0.022	0.677
Co	-0.132	-0.238	0.295	0.482	0.140
Cr	0.323	0.199	0.450	-0.180	0.186
Cu	-0.043	-0.366	0.173	0.566	0.149
Fe	0.268	0.604	-0.396	0.265	0.291
K	0.824	-0.050	0.177	0.132	0.022
Li	0.121	0.684	0.187	0.226	0.028
Mg	0.824	-0.004	-0.300	0.122	-0.085
Mn	0.788	0.158	-0.076	-0.143	0.177
Na	0.871	-0.039	-0.057	0.024	-0.207
Ni	0.054	0.149	0.740	0.210	-0.090
Pb	-0.006	0.078	0.075	-0.238	0.847
Se	0.231	0.550	0.191	-0.304	0.097
Sr	-0.038	0.543	-0.419	0.205	0.302
Zn	0.021	0.808	0.144	-0.065	0.025

The PC loadings related to selected metals in the water samples during winter are shown in Table 20 where six PCs were extracted with eigenvalues greater than one, and cumulatively explaining more than 70% of the total variance of data. The CA is shown as dendrogram in Figure 12 where four clusters of the metals were noted. The natural contribution of the metals in water was shown by PC 1 with maximum loadings of Ca, Mg and Na, while PC 2 revealed significant loadings of Co, Cr and Ni which were mainly contributed by industrial activities. The PC 3 exhibited higher loadings of Li and Sr, while PC 4 showed significant loadings for Mn, Se and Zn, which were mostly geogenic in origin. Similarly, PC 5 revealed higher loadings in favour of As, Cd, K and Pb which were mostly contributed by agriculture runoffs and automobile emissions. Last PC showed elevated loadings of Fe and Cu, which were associated with natural contributions.

Table 20. Principal component analysis of selected metal levels in the water samples during winter

	PC 1	PC 2	PC 3	PC 4	PC 5	PC 6
Eigenvalue	3.270	2.670	1.933	1.723	1.302	1.046
Total Varinace (%)	19.24	15.71	11.37	10.14	7.659	6.152
Cumulative Eigenvalue	3.270	5.940	7.873	9.596	10.90	11.94
Cumulative Variance (%)	19.24	34.94	46.31	56.45	64.11	70.26
As	-0.008	-0.411	-0.196	-0.033	0.542	0.087
Ca	0.908	0.143	-0.020	-0.089	-0.069	0.025
Cd	-0.164	0.146	0.061	0.165	0.767	0.110
Co	-0.336	0.619	-0.220	0.014	-0.153	0.109
Cr	-0.042	0.888	0.045	0.063	-0.064	0.051
Cu	0.224	-0.003	-0.301	-0.058	0.041	0.525
Fe	0.043	-0.028	0.089	0.036	0.043	0.873
K	-0.063	-0.056	0.142	0.149	0.821	0.026
Li	0.342	0.285	0.563	0.215	-0.166	0.008
Mg	0.754	-0.415	0.370	0.010	0.152	-0.097
Mn	0.004	0.146	0.075	0.757	-0.211	0.264
Na	0.878	-0.159	-0.177	-0.193	0.032	-0.090
Ni	0.081	0.597	-0.144	0.305	-0.051	0.313
Pb	0.057	-0.105	0.137	0.298	0.677	0.186
Se	0.118	0.073	-0.127	0.584	0.124	0.239
Sr	0.084	0.087	0.694	-0.034	0.036	-0.361
Zn	-0.124	0.199	0.138	0.719	0.064	0.311

The CA results (Figure 12) showed four main clusters of the metals in water samples; cluster-1 (Cr, Co, Ni) and cluster-III (As, Cd, Pb, K) were mostly associated with anthropogenic activities in the water reservoir, while cluster-II (Cu, Fe, Sr, Zn, Li) and cluster-IV (Ca, Na, Mg, Mn, Se) were mainly contributed by natural sources. The PCA and CA results were in close agreement with each other.

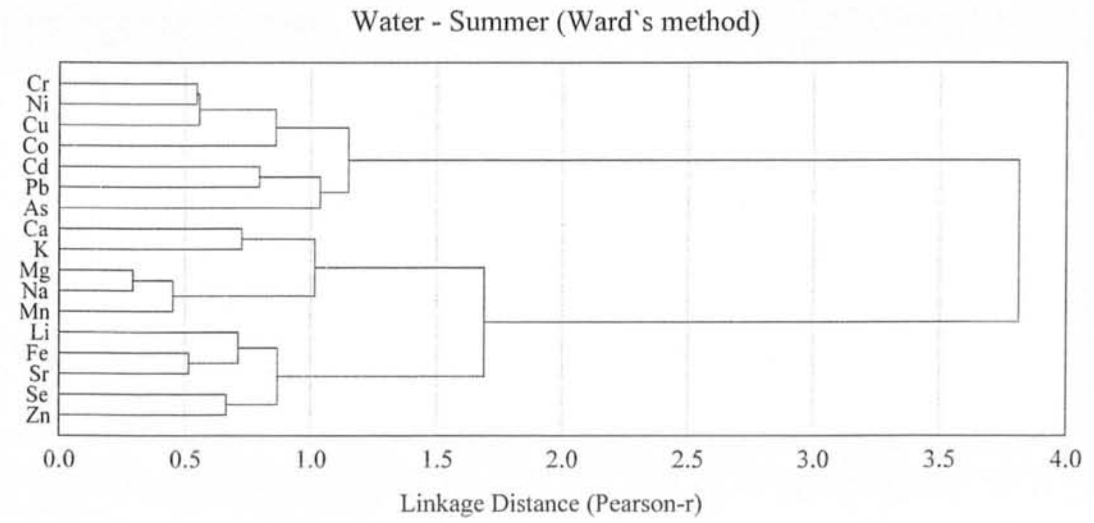

Figure 11. Cluster analysis of selected metal levels in the water samples during summer

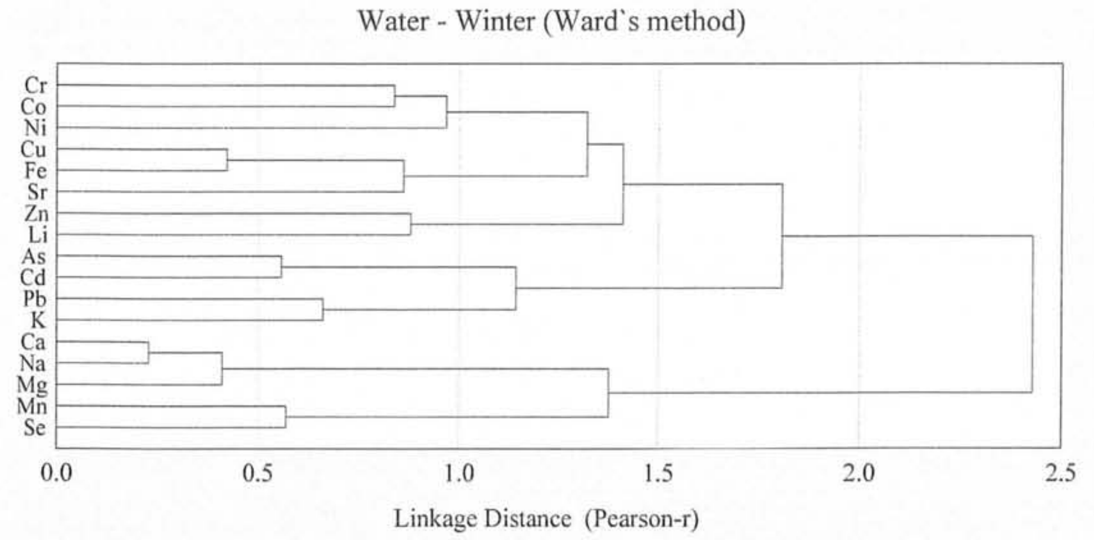

Figure 12. Cluster analysis of selected metal levels in the water samples during winter

The PC loadings of selected metals in the water samples during pre-monsoon are shown in Table 21 where seven PCs were extracted with eigen values greater than one, together explaining more than 69% of the total variance of data. The dendrogram of the CA related to the metal levels during pre-monsoon is shown in Figure 13. PC 1 exhibiting 13.43% of the total variance showed highest loadings for Ca, Fe, Li and Mn, which were mostly contributed by natural sources. PC 2 showed significant loadings of Cr and Ni which were likely to be contributed by the industrial activities. PC 3 exhibited higher loadings in favour of Pb and Co which were believed to be originated from automobile activities. PC 4 showed highest loadings for As and Cd which are mainly contributed by agricultural runoffs. PC 5 revealed higher loadings of K, Mg and Na, while PC 6 revealed highest loadings for Se and Sr. These metals were mostly originated from natural processes including corrosion, erosion and weathering of the parent rocks/soil in the upstream areas. Last PC, showed highest loadings of Cu and Zn which were believed to be originated from domestic and municipal wastes. The CA results were in very good agreement with the PCA results and mostly the clusters were formulated by the metals showing shared loadings to a particular PC. Cluster-I (Zn-Cu), cluster-II (As-Cd-Ni-Cr) and cluster-III (Pb-Co) were associated with anthropogenic activities, while, cluster-IV (K-Mg), cluster-V (Ca-Li-Fe-Mn) and cluster-VI (Sr-Se-Na) might be associated with natural contributions.

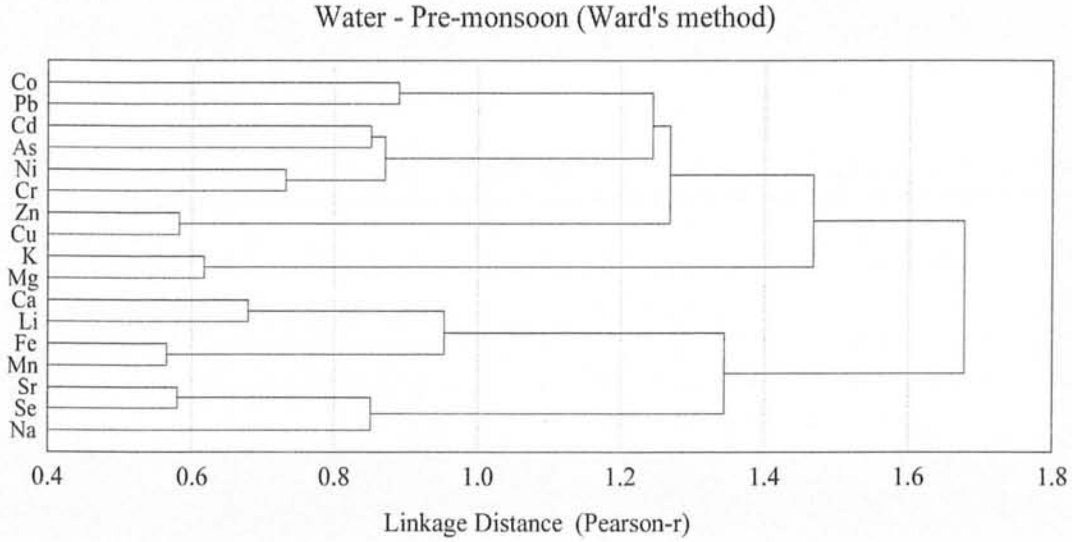

Figure 13. Cluster analysis of selected metal levels in the water samples during pre-monsoon

Table 21. Principal component analysis of selected metal levels in the water samples during pre-monsoon

	PC 1	PC 2	PC 3	PC 4	PC 5	PC 6	PC 7
Eigen value	2.283	2.242	1.874	1.574	1.509	1.185	1.101
Total Variance (%)	13.43	13.19	11.02	9.257	8.875	6.968	6.477
Cumulative Eigen value	2.283	4.524	6.399	7.972	9.481	10.67	11.77
Cumulative Variance (%)	13.43	26.61	37.64	46.90	55.77	62.74	69.22
As	0.046	0.170	-0.201	0.770	-0.082	-0.046	0.201
Ca	0.556	-0.104	-0.022	0.314	-0.166	0.223	0.145
Cd	0.070	0.083	0.372	0.583	0.034	0.384	-0.247
Co	-0.124	0.111	0.778	0.071	-0.069	-0.201	0.092
Cr	0.099	0.597	0.096	-0.241	-0.032	-0.026	0.305
Cu	0.018	0.108	-0.243	0.122	0.416	0.116	0.680
Fe	0.839	0.012	0.111	-0.129	0.064	-0.038	0.084
K	-0.109	-0.055	-0.136	-0.098	0.609	0.318	-0.063
Li	0.843	-0.021	-0.015	0.103	0.067	0.076	0.208
Mg	0.221	0.004	0.090	-0.031	0.850	0.039	0.052
Mn	0.792	-0.103	-0.094	0.295	0.032	0.149	-0.126
Na	0.081	0.084	-0.230	0.026	0.728	-0.031	0.221
Ni	0.127	0.592	-0.095	-0.001	-0.214	0.042	0.061
Pb	0.070	0.059	0.880	-0.157	0.025	0.056	-0.004
Se	-0.132	-0.087	-0.084	0.113	-0.049	0.695	0.118
Sr	-0.045	-0.234	-0.097	0.249	0.056	0.762	-0.101
Zn	0.137	-0.004	0.358	-0.369	-0.017	0.034	0.664

The PC loadings of selected metals in the water samples during monsoon are shown in Table 22 where seven PCs were extracted with eigenvalues greater than one, together explaining more than 70% of the total variance of data. The dendrogram of CA related to the metals during monsoon is shown in Figure 14, which exhibited four significant clusters of the metals in water. First PC exhibiting 16.40% of the total variance, revealed highest loadings for Cd, Mn and Pb; PC 2 showed significant loadings for Cu, Mg and Na; PC 3 indicated higher loading for As; PC 4 displayed highest loadings for Cr, Ni and Co; PC 5 exhibited higher loadings in favour of K and Se; PC 6 showed highest loadings for Fe, Li and Sr; and the last PC revealed highest loadings for Ca and Zn.

Overall, PC 1, PC 3 and PC 4 were believed to be originated by anthropogenic activities including agricultural runoffs, untreated poultry discharge, municipal/industrial wastes, atmospheric deposition, land cultivation, reservoir up gradation and vehicular emissions. Overall, the CA was in good agreement with the PCA results and both methods indicated significant anthropogenic pollution in the water reservoir.

Table 22. Principal component analysis of selected metal levels in the water samples during monsoon

	PC 1	PC 2	PC 3	PC 4	PC 5	PC 6	PC 7
Eigen value	2.788	2.519	1.692	1.519	1.350	1.124	1.041
Total Variance (%)	16.40	14.82	9.956	8.938	7.941	6.615	6.126
Cumulative Eigen value	2.788	5.307	7.000	8.519	9.869	10.99	12.03
Cumulative Variance (%)	16.40	31.22	41.17	50.11	58.05	64.67	70.79
As	0.000	0.159	0.762	-0.030	0.042	-0.046	0.209
Ca	0.393	0.014	-0.167	0.274	-0.328	0.022	0.664
Cd	0.788	-0.053	-0.104	0.078	-0.192	0.168	-0.097
Co	0.023	-0.108	-0.094	0.844	0.099	0.008	0.087
Cr	-0.165	-0.083	0.024	0.792	0.137	-0.173	0.372
Cu	-0.157	0.603	-0.194	-0.051	0.271	-0.394	0.121
Fe	0.155	0.014	-0.059	-0.023	0.106	0.848	-0.066
K	0.164	0.096	0.073	-0.271	0.601	-0.171	0.082
Li	0.265	-0.379	0.320	0.006	0.139	0.594	0.173
Mg	0.110	0.780	0.087	-0.015	-0.035	-0.011	-0.119
Mn	0.589	0.092	0.139	-0.094	0.215	-0.409	0.137
Na	0.320	0.658	0.115	0.126	-0.094	0.128	0.055
Ni	0.113	0.099	-0.085	0.547	0.104	-0.041	-0.140
Pb	0.711	0.024	0.101	0.048	-0.252	0.140	-0.061
Se	-0.003	-0.173	0.082	0.073	0.857	0.012	-0.087
Sr	-0.130	0.142	0.019	0.091	0.008	0.726	-0.125
Zn	-0.017	0.152	-0.141	0.144	0.053	-0.061	0.868

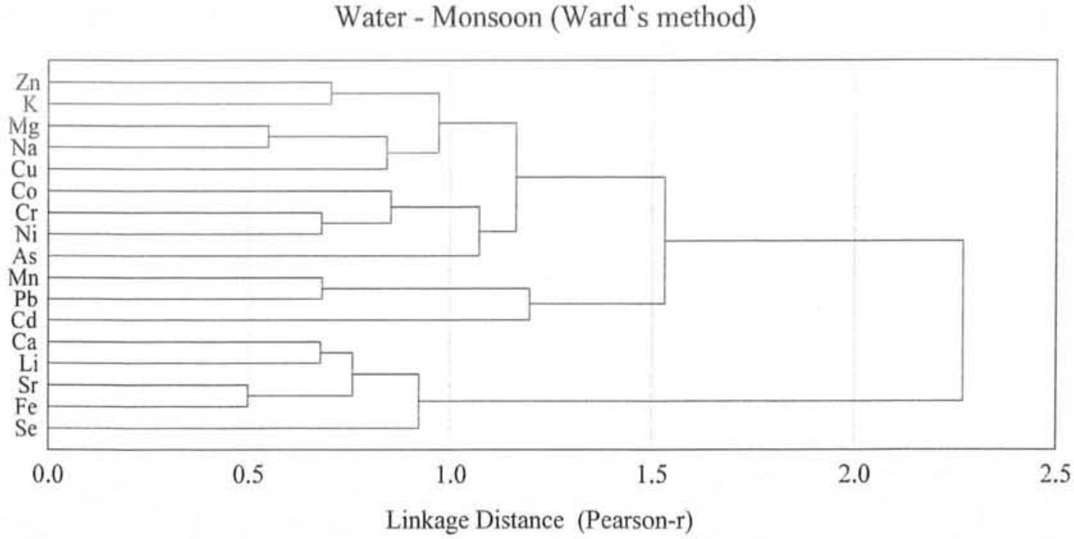

Figure 14. Cluster analysis of selected metal levels in the water samples during monsoon

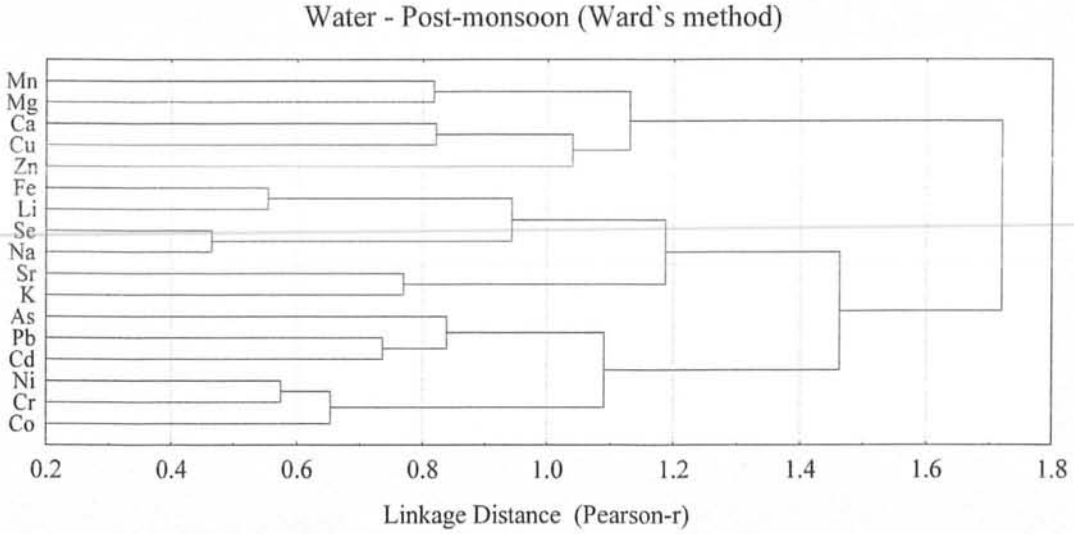

Figure 15. Cluster analysis of selected metal levels in the water samples during post-monsoon

The PC loadings of selected metals in the water samples during post-monsoon are shown in Table 23, where seven PCs were extracted with eigenvalues > 1, together explaining more than 67% of the total variance of data. The dendrogram of CA related to the metal levels in the water samples during post-monsoon season is shown in Figure 15 which exhibited three major clusters of the metals. PC 1 exhibiting 18.19% of the total variance revealed highest loadings for Mg, Mn and Zn; PC 2 showed significant loadings for K, Na, Sr and Se; PC 3 indicated higher loadings for Ca and Cu; PC 4 displayed higher loadings for Cd and Pb; PC 5 exhibited highest loadings for As and Co; PC 6 demonstrated higher loadings in favour of Cr and Ni; and PC 7 showed highest loadings for Fe and Li. Overall, PC 1, PC 2, PC 3 and PC 7 were mainly contributed by natural processes including corrosion, erosion and weathering of the parent rocks/soil in the upstream/catchments areas, while PC 4, PC 5 and PC 6 were predominantly contributed by automobile emissions, agricultural run-offs and industrial activities, respectively. The CA findings were in very good agreement with the PCA results and mostly the clusters were formulated by the metals showing common sources in the water reservoir.

Table 23. Principal component analysis of selected metal levels in the water samples during post monsoon

	PC 1	PC 2	PC 3	PC 4	PC 5	PC 6	PC 7
Eigen value	3.092	1.781	1.706	1.391	1.290	1.192	1.062
Total Variance (%)	18.19	10.47	10.03	8.184	7.588	7.014	6.248
Cumulative Eigen value	3.092	4.873	6.578	7.969	9.259	10.45	11.51
Cumulative Variance (%)	18.19	28.66	38.70	46.88	54.47	61.48	67.73
As	0.280	-0.387	-0.052	0.134	0.673	0.047	0.064
Ca	0.010	0.023	0.871	0.047	-0.067	0.037	0.052
Cd	-0.108	0.058	-0.110	0.761	-0.075	0.030	0.023
Co	0.177	-0.003	0.266	0.047	0.741	0.250	-0.107
Cr	0.168	0.307	-0.002	0.039	-0.014	0.724	0.023
Cu	0.069	-0.001	0.638	-0.120	0.245	0.011	-0.261
Fe	0.172	-0.268	0.010	0.047	-0.145	0.055	0.689
K	0.170	0.609	0.010	0.063	0.190	0.040	0.151
Li	-0.243	0.322	-0.211	-0.089	0.067	0.062	0.661
Mg	0.781	0.200	0.084	0.055	-0.136	0.018	-0.067
Mn	0.836	0.071	-0.034	-0.155	0.033	-0.104	-0.025
Na	-0.030	0.689	-0.197	0.023	0.125	-0.169	0.083
Ni	0.142	-0.039	0.064	-0.016	0.086	0.788	0.068
Pb	-0.105	0.303	0.313	0.629	0.305	0.209	0.049
Se	0.089	0.776	0.031	-0.038	-0.032	0.083	-0.126
Sr	0.156	0.639	-0.100	0.104	-0.015	0.179	0.049
Zn	0.707	0.188	0.012	0.267	-0.008	0.219	-0.039

3.9 Drinking/Irrigation Water Quality Assessment

Suitability of the water for drinking and irrigation purposes depends upon its composition and mineral constituents, such as, pH, DO, TA, EC, TDS, TH, Cl^-, HCO_3^-, Na, K, Ca, Mg, etc. (WHO, 2008). Elevated pH generally decreased the solubility of most of the metals while lower pH solubilized the metals thereby releasing free ions into the water column. In the present study, the pH mostly ranged from 6.89 to 8.29 and the measured levels were within the permissible limits for drinking water as per WHO, USEPA and Pak-EPA guidelines (USEPA, 2009, WHO, 2008; Pak-EPA, 2008). The reservoir water was thus classified under no problem category with respect to pH, indicating that the water samples were suitable for irrigation use during summer, winter, pre-monsoon and monsoon seasons (Ayers and Westcot, 1994). However, the pH ranged from 6.21 to 6.83 with an average value of 6.43 during post-monsoon season, thus suggesting that pH of most of the water samples was not within the permissible limits for drinking water quality guidelines (Pak-EPA 2008; USEPA 2009, WHO 2008). Hence, the water samples during post-monsoon season were categorized as unsuitable for drinking and irrigation purposes (Ayers and Westcot, 1994).

To support the diversified biota in an aquatic ecosystem, water should have at least 5 mg/L concentrations of DO (Radojevic and Bashkin, 1999). In the present study, the DO contents were below 5 mg/L during summer, winter and pre-monsoon seasons; consequently the aquatic ecosystem was under little stress due to low DO contents. However, there was no problem for biota regarding DO levels during monsoon and post-monsoon seasons. In the present study, mean value of TA was found to be 143.8, 93.86, 332.1, 259.0, and 140.9 mg $CaCO_3$/L during summer, winter, pre-monsoon, monsoon and post-monsoon seasons, respectively, indicating that average levels of TA during pre-monsoon and monsoon seasons were higher than the permissible limits for drinking water set by WHO (2011).

The EC and TDS of water represented its salts contents, which affected the growth of the plants directly as well as indirectly by disturbing the soil structure, permeability and aeration. Therefore, TDS and EC were used for water classification for irrigation purpose. In the present study, the minimum to maximum EC values were noted between 119.6 to 771 μS/cm in the water samples during all seasons which were well below than the WHO (2011) guideline value. Consequently, water sample were suitabile for the drinking and irrigation practises on basis of EC (Wilcox, 1955; Appendix G). The lowest to highest levels of TDS found in water samples were observed to be 60.10-385.0 mg/L with an average value of 121.9 mg/L which were well within the acceptable levels set by international and national authorities; as a result water can be used for drinking use without any risk regarding TDS.

Suitability of the water for drinking purpose was also assessed by Total Hardness (TH) measured during all seasons (Table 24). Highest level of TH recorded in the present study was 449.1 mg $CaCO_3$/L which was found in winter, these levels were within the permissible limit for drinking use set by WHO guidelines (WHO, 2008). Generally, water is considered as soft, moderately hard, hard and very hard with respect to TH values (Adhikary *et al.,* 2012, Appendix G). Based on the mean TH levels, the water samples were categorized as moderately hard during summer and pre-monsoon seasons; and soft during monsoon and post-monsoon seasons, indicating suitability of the water for agricultural use (Simsek and Gunduz, 2007). However, during winter season, water was classified as hard and was not very suitable for agricultural use.

Table 24. Descriptive statistics for various quality parameters in the water samples

		TH	SAR	PS	KR	Mg/Ca	MAR	HCO_3^-	RSBC	PI
Summer	Min	47.50	0.081	4.512	0.035	0.113	10.13	1.020	-1.037	26.82
	Max	133.8	0.154	12.94	0.112	0.356	26.27	4.990	3.615	161.1
	Mean	122.4	0.096	5.508	0.044	0.133	11.67	2.875	0.707	62.48
Winter	Min	120.2	0.114	4.662	0.041	0.062	5.862	0.600	-4.855	12.37
	Max	449.1	0.718	17.75	0.213	0.162	13.91	3.894	0.009	48.04
	Mean	218.1	0.188	6.450	0.062	0.104	9.364	1.877	-2.086	26.40
Pre-monsoon	Min	61.29	0.113	8.158	0.061	0.186	15.65	5.505	4.002	148.3
	Max	106.1	1.017	39.58	0.628	0.715	41.70	9.854	8.457	254.2
	Mean	85.20	0.233	13.20	0.129	0.312	23.40	6.641	5.320	182.4
Monsoon	Min	55.79	0.092	6.220	0.047	0.221	18.13	4.000	2.526	110.2
	Max	95.11	0.445	24.17	0.286	0.680	40.49	8.518	7.503	293.2
	Mean	74.79	0.241	14.17	0.141	0.344	25.17	5.180	4.085	174.3
Post-monsoon	Min	40.85	0.092	7.586	0.055	0.179	15.21	1.807	0.661	59.37
	Max	133.0	2.259	57.96	1.339	1.699	62.94	5.677	4.760	188.3
	Mean	70.32	0.438	19.44	0.259	0.411	27.42	2.183	1.798	100.0

TH – mg $CaCO_3$/L; PS – %; HCO_3^- – meq/L; RSBC – meq/L; PI – %

Chloride toxicity is most common in irrigation water. It can move easily from water to soil, taken up by the crops, moves in the transpiration stream and accumulates in the leaves (Ayers and Westcot, 1994). In the present study, the Cl^- levels ranged from 9.927 to 14.89 mg/L during summer; 4.999 to 15.00 mg/L during winter; 9.007 to 37.23 mg/L during pre-monsoon; 11.03 to 28.79 mg/L during monsoon; and 14.09 to 47.15 mg/L during post-monsoon. Based on the observed Cl^- levels, the water samples were categorized in the 'no problem' class for irrigation purpose in all seasons (Ayers and Westcot, 1994; Appendix G). Moreover, the chloride concentrations were within the permissible limits, indicating that water samples were suitable for the drinking purpose as well (USEPA, 2009, WHO, 2008; Pak-EPA, 2008).

Water having high levels of HCO_3^- contents tends to precipitate insoluble Ca and Mg in the soil when used for irrigation, and sodium adsorption ratio (SAR) increases due to their precipitates which ultimately leave higher Na proportion in the soil (Michael, 1978). It was defined that higher HCO_3^- concentration (>2 meq/L) in the water may cause severe Zn deficiency in the crops when used for irrigation purpose (Ayers and Westcot, 1994). In the present study, HCO_3^- levels ranged from 1.020 to 4.990, 0.600 to 3.894, 5.505 to 9.854, 4.000 to 8.518 and 1.807 to 5.677 meq/L during summer, winter, pre-monsoon, monsoon and post-monsoon seasons, respectively. Consequently, most of the water samples were found to be unsuitable for irrigation with respect to HCO_3^- levels except in winter (Ayers and Westcot, 1994). Mean value of RSBC during summer, winter, pre-monsoon, monsoon and post-monsoon were 0.707, 2.086, 5.320, 4.085 and 1.798 meq/L, respectively. On the average basis, the water samples were evaluated as unsuitable for irrigation purpose with respect to RSBC except in winter (Gupta and Gupta, 1987).

Higher levels of Na in the water are objectionable because it can adsorb on the soil cation-exchange sites, causing soil aggregates to break down (deflocculating) by the sealing pores of soil and making it impermeable to water flow (Gayman, 1995). Sodium adsorption ratio (SAR) is an important parameter, which is a measure of alkali/sodium hazard to the crops. Generally, Na causes damage to the soil structure which becomes compact and impervious by replacing adsorbed Ca and Mg (Ayers and Westcot, 1994). SAR categorizes water as excellent, good, doubtful and unsuitable water (Richards, 1954; Appendix G). The calculated range and mean levels of SAR in the water samples during all the seasons were clearly less than 10, therefore, the water was classified as excellent for irrigation use with respect to SAR. Similarly, based on percent sodium (PS), the water is categorised as; PS = 0–20% indicates excellent water; PS = 20–40% indicates good water;

PS = 40–60% shows permissible water; PS = 60–80% shows doubtful water and PS >80% demonstrates unsuitable water (Wilcox, 1955). In the present study PS of the water samples ranged from 4.512 to 12.94, 4.662 to 17.75, 8.158 to 39.58, 6.220 to 24.17 and 7.586 to 57.96 during summer, winter, pre-monsoon, monsoon and post-monsoon seasons, respectively. Consequently, most of the water samples were categorized as excellent for irrigation purpose although some water samples were found in good and permissible water categories during pre-monsoon and post-monsoon seasons, respectively.

Kelly's ratio (KR) was also used to classify the water samples for irrigation purpose. Water samples with KR < 1 are considered as suitable for irrigation, while the water samples having KR > 1 are unsuitable (Deshpande and Aher, 2012). The lowest, mean and highest KR values were less than unity in the present study during all the seasons, thus revealing suitability of the water for irrigation purpose (Kelly, 1963).

Based on Mg/Ca ratio, the water samples were classified as given by Kumar *et al.,* (2007; Appendix G). In this study, ranges and mean values of Mg/Ca ratio were less than 1.5, indicating no harmful effects as far as Mg/Ca ratio was concerned, hence the water samples were classified as safe for irrigation use during all the seasons. Paliwal (1972) introduced an important ratio called magnesium adsorption ratio (MAR) to assess the water for irrigation purpose. MAR > 50% would adversely affect the crop yield as the soils become more alkaline (Obiefuna and Sheriff, 2011). In the present study, the water samples from the lake during different seasons showed less than 50% MAR values, indicating their suitability irrigation use (Paliwal, 1972).

The soil permeability is normally affected by Na, Ca, Mg and HCO_3^- contents of the soil. Donean (1964) proposed a criterion for evaluating suitability of the water for irrigation based on permeability index (PI). According to PI values, the water samples can be classified as Class-I, Class-II and Class-III. Class-I and Class-II water samples are categorized as good for irrigation with 50-75% or more of the maximum permeability, while Class-III water samples are supposed as unsuitable with 25% of the maximum permeability. In the present study, mean values of PI in the water samples during summer, winter, pre-monsoon, monsoon and post-monsoon seasons were measured as 62.48, 26.40, 182.4, 174.3 and 100.0 %, respectively. As a result, the mean PI values in the water samples were found to be higher than 50%, indicating suitability of the water for irrigation purpose in all the seasons except winter, during which mean PI level was found near to 25%, indicating water was unsuitable for irrigation in that particular period.

The irrigation water quality (IWQ) index is an integrated method, based on the linear combination of the five irrigation water quality parameters that have potential negative impacts or hazards on the soil quality and crop yield (Simsek and Gunduz, 2007). The water quality parameters from these groups were designated based on the guidelines presented by Ayers and Westcot (1994). The proposed IWQ index was then calculated as given by Simsek and Gunduz (2007). Generally, IWQ index indicates low suitability, medium suitability and high suitability of the water for irrigation purpose (Simsek and Gunduz, 2007; Appendix G). When the computed index value is higher than 37, the corresponding area is considered to have minimum problems with respect to irrigation quality. When the computed index value is between 22 and 37, the corresponding water demonstrates moderate suitability for irrigation purposes. Within this range, values higher than 30 are considered to represent water that could be easily used on resistant crops. These water samples generally obtain high scores from the most important parameters including salinity, infiltration and permeability hazards. On the other hand, values below 30 indicate water that should only be used with caution and better be avoided, particularly for sensitive crops, if a better alternative is available. These areas generally have low scores from the most important parameters including salinity and infiltration hazards. Under extreme conditions, water from these locations could be used with caution. Finally, areas with IWQ index values of less than 22 are considered to be poor quality water and are not suitable for irrigating agricultural fields. Such water could impair soil quality and results in yield loss. As a rule of thumb, water from such areas should be avoided.

In the present study, the minimum to maximum values of IWQ index in the water samples were observed as 35.1 to 36.7, 37.0 to 39.1, 36.3 to 38.4, 36.2 to 37.8 and 36.0 to 39.3 during summer, winter, pre-monsoon, monsoon and post-monsoon seasons, respectively, indicating that the water exhibited medium/high suitability for irrigation use (Simsek and Gunduz, 2007). On the mean basis, water exhibited high suitability for irrigation purpose during winter and monsoon and medium suitability during rest of the seasons. However, there were numerous factors that may decline the current status including intrusion of agricultural runoffs and uncontrolled sewage disposals from the nearby areas. Overall, based on the mean levels of Cl^-, SAR, KR, PS, MAR Mg/Ca and permeability index, water samples were suitable and safe for drinking/irrigation purpose. These samples were found to be moderately hard during summer and pre-monsoon; soft during monsoon and post-monsoon seasons indicating suitability of the water for agricultural use. IWQ index showed high to medium suitability for irrigation purpose. Most of the water samples were found to be unsuitable for irrigation with respect to bicarbonate and RSBC levels. Generally, IWQ index is an appropriate tool for agricultural management plans and in measuring the most suitable site for evaluating the water quality.

3.10 Evaluation of Water Pollution Indices

Overall pollution status of the water samples from Mangla Lake was evaluated by using two well-known methods; (i) heavy metal evaluation index (*HEI*) & (ii) degree of contamination (C_d) (Edet and Offiong, 2002). The pollution evaluation indices for selected metals in the water samples during different seasons are shown in Table 25. Maximum admissible concentrations (MAC) as given in Table 25 were used to calculate *HEI* and C_d. The results were inferred using proposed classification scheme for the surface waters as suggested by Bhuiyan *et al.,* (2010, Appendix H). In the present study, mean values of *HEI* and C_d were found to be 274.5, 243.0, 256.6, 169.9, 99.83 and 265.3, 233.9, 247.2, 160.3, 90.64 during summer, winter, pre-monsoon, monsoon and post-monsoon seasons, respectively. It revealed that water samples were assessed to have medium degree of pollution by heavy metals in all the seasons except post-monsoon during which HEI and C_{deg} were less than 150, indicating low contamination in the water samples. Overall, according to the pollution indices, the water samples in different seasons showed contamination in the following order; summer > pre-monsoon > winter > monsoon > post-monsoon. The decreasing level of the pollutants during monsoon and post-monsoon might be due to the dilution caused by substantial precipitation in rainy monsoon season.

In *HEI*, the highest contribution was shown by Pb, followed by, Cd, Ni and Cr; these metals exhibited the maximum contribution during summer and minimum contribution during post-monsoon. On the other hand, the highest contributing metal for C_d was also Pb, followed by, Cd, Ni and Cr; these metals showed highest contribution during summer season and least contribution during post-monsoon except Ni which was higher during summer while lower during winter. Overall, relatively higher heavy metals pollution was observed in the water samples during summer and pre-monsoon which may be due to high evaporation and intense anthropogenic activities (agriculture, recreational, industrial and municipal activities) in the catchments areas during these seasons. Moreover, Cd, Cr, Ni and Pb emerged as major contributors towards heavy metals contamination in the water samples; therefore attention should be focused to manage these toxic pollutants in the study area.

Table 25. Description of pollution evaluation indices for selected metal levels (mg/L) in the water samples during different seasons

	MAC	*HEI*					C_d				
		Summer	Winter	Pre-monsoon	Monsoon	Post-monsoon	Summer	Winter	Pre-monsoon	Monsoon	Post-monsoon
As	0.05	0.225	0.131	0.371	0.257	0.197	-0.775	-0.869	-0.629	-0.743	-0.803
Cd	0.003	11.01	9.067	12.09	10.37	6.107	10.01	8.067	11.09	9.373	5.107
Cr	0.05	1.550	1.499	1.501	1.344	0.420	0.550	0.499	0.501	0.344	-0.580
Cu	1	0.018	0.022	0.020	0.014	0.014	-0.982	-0.978	-0.980	-0.986	-0.986
Fe	0.2	0.741	0.671	0.639	0.443	0.546	-0.259	-0.329	-0.361	-0.558	-0.454
Mn	0.05	0.273	0.362	0.262	0.163	0.378	-0.727	-0.638	-0.738	-0.837	-0.622
Ni	0.02	6.427	5.354	15.67	6.292	6.216	5.427	4.354	14.67	5.292	5.216
Pb	0.0015	254.1	225.8	225.8	150.5	85.84	253.1	224.8	224.8	149.5	84.84
Se	0.01	0.132	0.083	0.191	0.122	0.115	-0.868	-0.917	-0.809	-0.878	-0.885
Zn	5	0.006	0.006	0.006	0.002	0.002	-0.994	-0.994	-0.994	-0.998	-0.998
$\sum HEI/C_d$		274.5	243.0	256.6	169.5	99.83	265.3	233.9	247.2	160.3	90.64

MAC = Maximum admissible concentrations; *HEI* = Heavy metal evaluation index; C_d = degree of contamination

3.11 Health Risk Assessment for Selected Metals in Water Samples

There are three main pathways for the exposure of pollutants to human beings; (a) ingestion, (b) inhalation (c) dermal absorption. Ingestion and dermal absorption pathways played the most significant role in case of the metals in hydrogeoenvironment (Kim *et al.*, 2004). Tables 26 and 27 show the hazard quotient (*HQ*), hazard index (*HI*) and reference values for oral and dermal exposures of the metals for children and adults during summer, winter, pre-monsoon, monsoon and post-monsoon seasons, whereas the description of used parameters for exposure assessment of metals in the water through ingestion pathway and dermal absorption is shown in Appendix J.

During summer, the mean HQ_{ing} values via ingestion route for adults were found in the order of; Co > Pb > Cd > As > Cr > Ni > Li > Mn > Cu > Sr > Se > Fe > Zn. The results demonstrated Co, Pb, Cd, As, Cr and Ni as major contributors towards non-carcinogenic risks while Zn, Fe, Se and Sr were the minor contributors. Consequently, As, Cd, Co and Pb ($HQ >> 1.0$) might pose severe adverse health hazard to the adults. Moreover, there was higher risk for adults via ingestion route. Alternatively, the average HQ_{derm} values were found in the sequence of; Cr > Co > Cd > Pb > As > Mn > Ni > Se > Li > Cu > Sr > Fe > Zn. The results revealed that Cr, Co, Cd and Pb were the main contributors while Fe and Zn were the minor contributors for the adults through dermal contact. However, the mean HQ_{derm} values were very less than unity, showing that the metals could pose little or no adverse risks to the local population via dermal absorption. Non-carcinogenic health risk assessment was also evaluated for the most sensitive population (children). The mean HQ_{ing} values were found in the following order; Co > Pb > Cd > As > Cr > Ni > Li > Mn > Cu > Sr > Se > Fe > Zn. The calculated HQ_{ing} values of Co, Pb, As, Cd and Cr were higher than safety limit unity, revealing that these metals were the priority pollutants through oral ingestion of the water for children. On the contrary, the HQ_{derm} values were found in the order of; Cr > Co > Cd > Pb > As > Mn > Ni > Se > Li > Cu > Sr > Fe > Zn. It revealed that Cr, Cd, Co, Pb and As were the major participants whereas Sr, Fe and Zn were the least. However, the HQ_{derm} values were found to be lower than unity, indicating that there was little or no risk for children through dermal route. Hazard index (*HI*) was also calculated to evaluate the overall non-carcinogenic risk posed by the metals via ingestion and dermal routes as a whole. In case of adults, Cd, Cr, Pb and Co were found to be the major contributors towards HI (3.79E+01), suggesting that these metals deserved serious health concern via ingestion route. For children, the HI value was noted to be 1.38E+02. Overall, Cd, Cr, Co, As and Pb were the major pollutants through ingestion route during summer.

Table 26. Summary of non-carcinogenic health risk assessment for selected metals in the water for adults and children via ingestion/dermal routes during summer and winter

	Metal	RfD_{ing}	RfD_{derm}	HQ_{ing}		HQ_{derm}		$HI = \sum HQs$	
		(µg/kg-day)	(µg/kg-day)	Child	Adults	Child	Adults	Child	Adults
Summer	As	0.3	0.285	4.30E+00	1.10E+00	1.70E-05	5.70E-06	4.30E+00	1.10E+00
	Cd	0.5	0.025	7.60E+00	1.99E+00	5.57E-04	1.89E-04	7.60E+00	1.99E+00
	Co	0.3	0.06	9.73E+01	2.55E+01	7.13E-04	2.42E-04	9.73E+01	2.55E+01
	Cr	3	0.075	2.97E+00	7.78E-01	8.72E-04	2.96E-04	2.97E+00	7.79E-01
	Cu	40	8	5.26E-02	1.38E-02	9.64E-07	3.27E-07	5.26E-02	1.38E-02
	Fe	700	140	2.44E-02	6.38E-03	4.47E-07	1.51E-07	2.44E-02	6.38E-03
	Li	2	1	5.78E-02	1.25E-01	3.51E-06	1.19E-06	5.78E-02	1.25E-01
	Mn	24	0.96	5.78E-02	1.71E-02	6.00E-06	2.03E-06	5.78E-02	1.72E-02
	Ni	20	5.4	6.16E-01	1.94E-01	4.02E-06	1.36E-06	6.16E-01	1.94E-01
	Pb	1.4	0.42	2.47E+01	8.21E+00	1.53E-04	5.19E-05	2.47E+01	8.21E+00
	Se	5	0.15	3.00E-02	8.00E-03	3.70E-06	1.30E-06	3.00E-02	8.00E-03
	Sr	600	120	3.67E-02	9.62E-03	6.74E-07	2.28E-07	3.67E-02	9.62E-03
	Zn	300	60	1.23E-02	3.22E-03	1.35E-07	4.59E-08	1.23E-02	3.22E-03
Winter	As	0.3	0.285	2.5E+00	6.6E-01	9.7E-06	3.3E-06	2.51E+00	6.59E-01
	Cd	0.5	0.025	6.3E+00	1.6E+00	4.6E-04	1.6E-04	6.26E+00	1.64E+00
	Co	0.3	0.06	6.1E+01	1.6E+01	4.5E-04	1.5E-04	6.13E+01	1.61E+01
	Cr	3	0.075	2.9E+00	7.5E-01	8.4E-04	2.9E-04	2.88E+00	7.53E-01
	Cu	40	8	6.4E-02	1.7E-02	1.2E-06	4.0E-07	6.39E-02	1.67E-02
	Fe	700	140	2.2E-02	5.8E-03	4.0E-07	1.4E-07	2.21E-02	5.78E-03
	Li	2	1	4.9E-01	1.3E-06	3.8E-06	1.3E-06	4.85E-01	2.57E-06
	Mn	24	0.96	7.7E-02	2.3E-02	8.0E-06	2.7E-06	7.66E-02	2.27E-02
	Ni	20	5.4	5.1E-01	1.6E-01	3.3E-06	1.1E-06	5.13E-01	1.61E-01
	Pb	1.4	0.42	2.2E+01	7.3E+00	1.4E-04	4.6E-05	2.20E+01	7.29E+00
	Se	5	0.15	1.9E-02	5.0E-03	2.3E-06	7.9E-07	1.91E-02	5.00E-03
	Sr	600	120	4.2E-02	1.1E-02	7.7E-07	2.6E-07	4.19E-02	1.10E-02
	Zn	300	60	1.2E-02	3.1E-03	1.3E-07	4.5E-08	1.20E-02	3.14E-03

In winter, the mean HQ_{ing} values for adults were found as; Co > Pb > Cd > Cr > As > Ni > Mn > Cu > Sr > Fe > Se > Zn > Li. It showed that Co, Pb, Cd, Cr, As and Ni were the major contributors towards non-carcinogenic risks, whereas, Fe, Zn, Li and Se were the least contributors. Among the metals, Cd, Co, Pb ($HQ >> 1.0$) and Cr, As (near to unity) might pose severe adverse health effects for the adults during winter. On the other hand, average HQ_{derm} values were found in the sequence of; Cr > Cd > Co > Pb > As > Mn > Li > Ni > Se > Cu > Sr > Fe > Zn. The average HQ_{derm} values were significantly less than unity, exhibiting that the metals might pose little or no adverse risks to the local population via dermal absorption. Similarly, non-carcinogenic health risk assessment was also computed for children. The mean HQ_{ing} values were found in order of; Co > Pb > Cd > Cr > As > Ni > Li > Mn > Cu > Sr > Fe > Se > Zn. The calculated HQ_{ing} values for Co, Pb, Cd, As and Cr were higher than safe limit unity, indicating that these metals were the priority pollutants through oral ingestion for children. On the contrary, through dermal contact of surface water, the HQ_{derm} values were found in the order of Cr > Cd > Co > Pb > As > Mn > Li > Ni > Cu > Sr > Fe > Zn. However, these values were found to be lower than unity, indicating that there was little or no risk for children through dermal route. HI was also calculated to assess the overall non-carcinogenic risk posed by the metals via ingestion and dermal contact as a whole. For adults, As, Cd, Cr, Pb and Co were found to be the major contributors towards HI (2.66E+01), suggesting that these metals might have serious health concerns. For children, the HI value was noted to be 9.62E+01. Overall, As, Cd, Cr, Co and Pb were the major pollutants through ingestion route for both groups.

During pre-monsoon season, HQ_{ing} for children was more than 1 for As, Cd, Co, Cr, Ni and Pb, indicating that they might cause adverse health effects. In case of adults, HQ_{ing} for As, Cd, Co and Pb were found much higher than unity while that of Cr was nearing unity (0.75), indicating serious health concerns by these metals. However, HQ_{ing} of the remaining metals for children and adults were less than unity, suggesting that these metals posed little/no hazard through direct intake of the Lake water. The HQ_{derm} for all the metals for adults and children were below unity, indicating that these metals posed little/no hazards via dermal absorption. For children, the largest values of HQ_{derm} were 0.84, 0.66 and 0.61 for Cr, Co and Cd, respectively, demonstrating that these metals could cause potential adverse health effects via dermal absorption in future. Overall, HI for As, Cd, Co, Cr and Pb in case of adults and children exceeded safe limit (1) and HI of Ni for children was higher than unity. It can be concluded that the highest contributors towards chronic risks were As, Cd, Co, Cr, Ni and Pb for both adults and children.

Table 27. Summary of non-carcinogenic health risk assessment for selected metals in the water for adults and children via ingestion/dermal routes during pre-monsoon, monsoon and post-monsoon

	Metal	RfD_{ing}	RfD_{derm}	HQ_{ing}		HQ_{derm}		$HI = \sum HQs$	
		(µg/kg-day)	(µg/kg-day)	Child	Adults	Child	Adults	Child	Adults
Pre-monsoon	As	0.3	0.285	7.1E+00	1.9E+00	2.7E-05	9.3E-06	7.1E+00	1.9E+00
	Cd	0.5	0.025	8.3E+00	2.2E+00	6.1E-01	2.1E-01	9.0E+00	2.4E+00
	Co	0.3	0.06	9.0E+01	2.4E+01	6.6E-01	2.2E-01	9.1E+01	2.4E+01
	Cr	3	0.075	2.9E+00	7.5E-01	8.4E-01	2.9E-01	3.7E+00	1.0E+00
	Cu	40	8	5.8E-02	1.5E-02	1.1E-03	3.6E-04	5.9E-02	1.6E-02
	Fe	700	140	2.1E-02	5.5E-03	3.9E-04	1.3E-04	2.1E-02	5.6E-03
	Li	2	1	4.5E-01	1.2E-01	3.3E-06	1.1E-06	4.5E-01	1.2E-01
	Mn	24	0.96	5.6E-02	1.6E-02	5.8E-03	2.0E-03	6.1E-02	1.8E-02
	Ni	20	5.4	1.5E+00	4.7E-01	9.8E-03	3.3E-03	1.5E+00	4.8E-01
	Pb	1.4	0.42	2.2E+01	7.3E+00	1.4E-01	4.6E-02	2.2E+01	7.3E+00
	Se	5	0.15	4.4E-02	1.2E-02	5.4E-06	1.8E-06	4.4E-02	1.2E-02
	Sr	600	120	3.8E-02	1.0E-02	7.0E-07	2.4E-07	3.8E-02	1.0E-02
	Zn	300	60	1.2E-02	3.1E-03	1.3E-04	4.5E-05	1.2E-02	3.2E-03
Monsoon	As	0.3	0.285	4.9E+00	1.3E+00	1.9E-05	6.5E-06	4.9E+00	1.3E+00
	Cd	0.5	0.025	7.2E+00	1.9E+00	5.3E-01	1.8E-01	7.7E+00	2.1E+00
	Co	0.3	0.06	6.0E+01	1.6E+01	4.4E-01	1.5E-01	6.1E+01	1.6E+01
	Cr	3	0.075	2.6E+00	6.7E-01	7.6E-01	2.6E-01	3.3E+00	9.3E-01
	Cu	40	8	4.1E-02	1.1E-02	7.6E-04	2.6E-04	4.2E-02	1.1E-02
	Fe	700	140	1.5E-02	3.8E-03	2.7E-04	9.0E-05	1.5E-02	3.9E-03
	Li	2	1	5.2E-01	1.4E-01	3.8E-06	1.3E-06	5.2E-01	1.4E-01
	Mn	24	0.96	3.5E-02	1.0E-02	3.6E-03	1.2E-03	3.8E-02	1.1E-02
	Ni	20	5.4	6.0E-01	1.9E-01	3.9E-03	1.3E-03	6.1E-01	1.9E-01
	Pb	1.4	0.42	1.5E+01	4.9E+00	9.1E-02	3.1E-02	1.5E+01	4.9E+00
	Se	5	0.15	2.8E-02	7.4E-03	3.4E-06	1.2E-06	2.8E-02	7.4E-03
	Sr	600	120	3.6E-02	9.4E-03	6.6E-07	2.2E-07	3.6E-02	9.4E-03
	Zn	300	60	3.0E-03	7.9E-04	3.3E-05	1.1E-05	3.0E-03	8.0E-04
Post-monsoon	As	0.3	0.285	3.8E+00	9.9E-01	1.5E-05	4.9E-06	3.8E+00	9.9E-01
	Cd	0.5	0.025	4.2E+00	1.1E+00	3.1E-01	1.0E-01	4.5E+00	1.2E+00
	Co	0.3	0.06	3.9E+01	1.0E+01	2.9E-01	9.8E-02	4.0E+01	1.0E+01
	Cr	3	0.075	8.1E-01	2.1E-01	2.4E-01	8.0E-02	1.0E+00	2.9E-01
	Cu	40	8	3.9E-02	1.0E-02	7.2E-04	2.4E-04	4.0E-02	1.1E-02
	Fe	700	140	1.8E-02	4.7E-03	3.3E-04	1.1E-04	1.8E-02	4.8E-03
	Li	2	1	6.5E-01	1.7E-01	4.8E-06	1.6E-06	6.5E-01	1.7E-01
	Mn	24	0.96	8.0E-02	2.4E-02	8.3E-03	2.8E-03	8.8E-02	2.7E-02
	Ni	20	5.4	6.0E-01	1.9E-01	3.9E-03	1.3E-03	6.0E-01	1.9E-01
	Pb	1.4	0.42	8.4E+00	2.8E+00	5.2E-02	1.8E-02	8.4E+00	2.8E+00
	Se	5	0.15	2.6E-02	6.9E-03	3.2E-06	1.1E-06	2.6E-02	6.9E-03
	Sr	600	120	3.0E-02	7.8E-03	5.5E-07	1.8E-07	3.0E-02	7.8E-03
	Zn	300	60	4.5E-03	1.2E-03	4.9E-05	1.7E-05	4.5E-03	1.2E-03

During monsoon season, the HQ_{ing} for As, Cd, Co, Cr and Pb in case of children were higher than unity, while in case of adults, HQ_{ing} for As, Cd, Co and Pb were higher than 1 and Cr was near to one. Consequently, As, Cd, Co, Cr and Pb were the major contributors towards adverse health effects. However, HQ_{derm} values were lower than unity for both population groups, demonstrating that these metals posed no significant adverse health effects via dermal absorption. Generally, HI of As, Cd, Co and Pb for children and adults exceeded 1, while HI of Cr was higher than unity for children therefore these metals emerged as major pollutants in the water reservoir in this season.

During post-monsoon season, the HQ_{ing} for As, Cd, Co and Pb were higher than unity for children, and Cr was near to one, while in case of adults, HQ_{ing} for As, Cd, Co and Pb were higher than 1. However, HQ_{derm} were lower than unity for both children and adults, demonstrating that dermal exposure posed little/no adverse health effects. The highest value of HQ_{derm} was less than 0.31 which was for Cd in case of children. Generally, HI for As, Cd, Co and Pb for children and adults exceeded 1, and HI of Cr was higher than unity and Ni was 0.60 for children only.

Overall, among the selected metals, As, Cd, Co, Cr, Ni and Pb emerged as priority pollutants for both adults and children through ingestion intake of the lake water. However, the extent of adverse health risks was relatively higher for children than adults. Therefore, special attention should be focused to As, Cd, Co, Cr, Ni and Pb particularly for the children, and measures needed to be taken for sustaining the healthy aquatic ecosystem. However, there were some uncertainties for risk characterization, which were emphasized by USEPA and other documents. Uncertainties in some methodological aspects, such as, water and dermal contact factor (K_p), varied exposure condition due to different age and receptor, temporal and spatial variations in contaminant concentrations could not be quantified. In addition, the exposure parameters employed in the study (Appendix J) were adopted from USEPA, WHO and elsewhere, which might not be specific to local conditions/population. Therefore, further precise risk characterization should be defined and risk assessment approaches may be modified through the investigation on the risk levels in the Mangla Lake.

Section-II: SEDIMENTS

3.12 Sampling Progress

Sampling of the surface sediments was carried out during summer and winter 2011 and a total of 180 (90 in each season) composite samples (1–15 cm top layer) were collected during both seasons. Each sample was composed of 5–10 sub-samples collected from an area of 50–100 m^2. Broadly, the samples were collected from three parts of the lake shown as ‘A’, ‘B’ and ‘C’ in the location map (Figure 16) and 30 samples were collected from each part during each season. Similarly, a total of 375 (125 in each season) composite surface sediment samples (1-15 cm top layer) were collected during pre-monsoon (May 2012), monsoon (August 2012) and post-monsoon (October/November 2012) seasons from ten different sites of Mangla Lake, as shown in Figure 17. About 10-15 composite samples were collected from each site and every sample was composed of 3–5 sub-samples.

Figure 16. Map of the study area showing sediments sampling locations during summer and winter

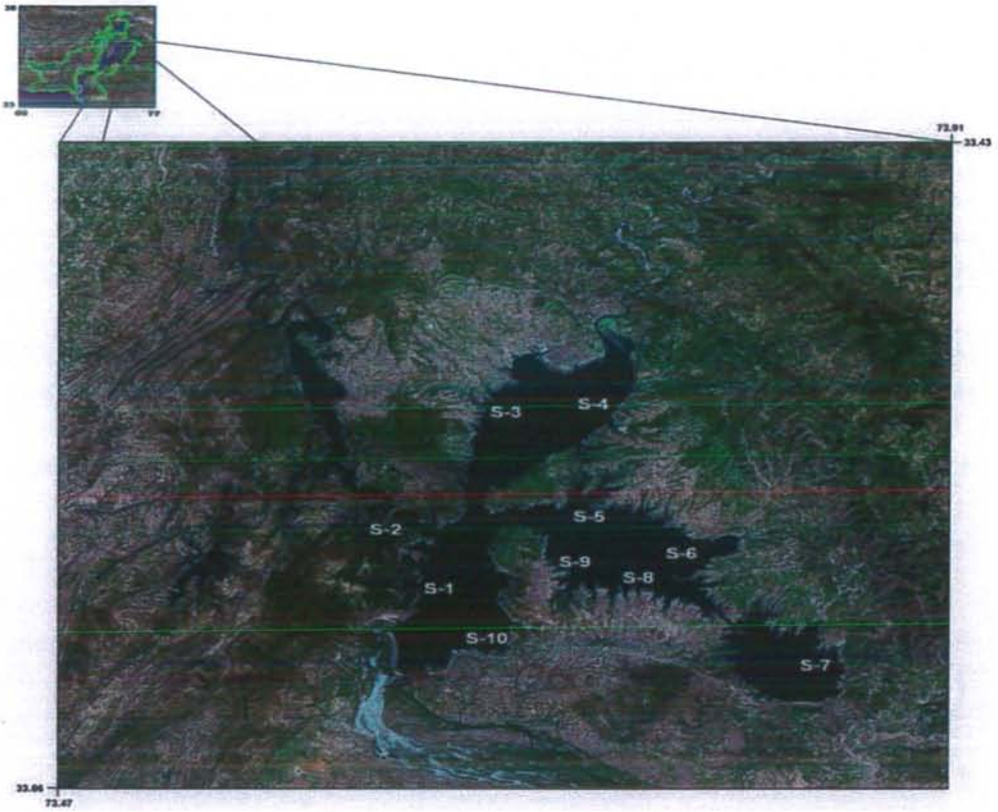

Figure 17. Map of the study area showing sediments sampling locations during pre-monsoon, monsoon and post-monsoon seasons

3.13 Distribution of Physicochemical Parameters in Sediment Samples

As reported earlier, physicochemical parameters were estimated in the water-extract of sediment samples. Statistical summary for physicochemical parameters in water-extract of the sediment samples collected during summer is shown in Table 28. Temperature was ranging from 27.5 to 27.9°C with an average value of 27.7°C and pH was found to be slightly acidic ranging from 6.31 to 6.90 with mean and median values of 6.58 and 6.55, respectively. The minimum-maximum & average values of EC were recorded as 3.020-20.08 & 10.66 mS/cm, respectively, and it was associated with random dispersion as shown by SD and SE values. Likewise, TDS revealed the minimum value of 1.508 g/L to a maximum value of 10.10 g/L. The mean and median values of TDS were recorded as 5.320 and 5.555 g/L, respectively. Generally, the large values of EC and TDS were associated with very high concentration of soluble ions. Total alkalinity ranged from 0.060 to 0.180 mg/g as $CaCO_3$ with mean value of 0.113 mg/g as $CaCO_3$, while the average moisture contents and organic matter (OM) were recorded as 18.38% and 4.947%, respectively.

During winter season (Table 28), the average temperature was recorded as 15.7°C with very small variations. The pH of sediment samples was once again found to be slightly acidic with an average value of 6.61. Generally, acidic pH displayed higher solubility of the metallic cations. This is also evident by large values of EC and TDS in the sediments. The mean values of EC and TDS were measured as 10.26 mS/cm and 5.119 g/L, respectively. Total alkalinity of the sediments exhibited almost similar levels as note in the previous season (0.104 mg/g as $CaCO_3$). Moisture contents of the sediments exhibited large variations during both seasons, although the average value was much higher during winter season. It could be loss of water due to evaporation during summer (dry and hot season). Organic matter varied from 3.805 to 9.953% with an average value 7.716%. Overall, most of sediment samples showed acidic characteristic, associated with large concentration of the soluble species during both summer and winter seasons.

Table 28. Statistical distribution of physicochemical parameters in the sediment samples during summer and winter

		Min	Max	Mean	Median	SD	SE	Skew	Kurt
Summer (*n* = 90)	T (°C)	27.5	27.9	27.7	27.8	0.144	0.028	-0.484	-1.142
	pH	6.31	6.90	6.58	6.55	0.187	0.037	0.136	-1.404
	EC (mS/cm)	3.020	20.08	10.66	11.12	5.128	1.006	0.154	-0.697
	TDS (g/L)	1.508	10.10	5.320	5.555	2.566	0.503	0.165	-0.674
	TA (mg/g as $CaCO_3$)	0.060	0.180	0.113	0.120	0.049	0.010	0.224	-1.453
	MC (%)	6.897	37.28	18.38	17.59	7.209	1.414	0.605	0.612
	OM (%)	2.568	6.786	4.947	5.456	1.374	0.307	-0.417	-1.109
Winter (*n* = 90)	T (°C)	15.5	15.8	15.7	15.65	0.107	0.020	-0.003	-1.214
	pH	6.30	6.95	6.61	6.63	0.187	0.034	0.063	-1.073
	EC (mS/cm)	1.608	16.85	10.26	13.65	6.045	1.104	-0.523	-1.714
	TDS (g/L)	0.802	8.42	5.119	6.800	3.016	0.551	-0.521	-1.713
	TA (mg/g as $CaCO_3$)	0.060	0.180	0.104	0.120	0.044	0.008	0.480	-0.972
	MC (%)	27.04	75.97	44.78	43.19	11.58	2.114	1.039	1.266
	OM (%)	3.805	9.953	7.176	7.606	1.934	0.432	-0.383	-1.040

The statistical distribution of physicochemical parameters in water-extract of the sediments during pre-monsoon, monsoon and post-monsoon seasons is shown in Table 29. During pre-monsoon season, the temperature remained between 31.3 to 32.7°C with an average value of 31.7°C while pH was found between 6.90 to 7.95 with mean and median values of 7.36 and 7.29, respectively. Very large and fluctuating values of EC were recorded during this season exhibiting extreme values of 2.279 to 8.395 mS/cm. The average value of EC was recorded as 4.671 mS/cm, associated with large and random dispersion as exhibited by SD and SE values. Likewise, TDS also revealed minimum value of 1.140 g/L to a maximum value of 4.198 g/L. The mean and median values of TDS were recorded as 2.335 and 2.358 g/L, respectively. Total alkalinity ranged from 0.139 to 0.206 mg/g as $CaCO_3$ with the mean value of 0.174 mg/g as $CaCO_3$; whereas average moisture contents and OM were recorded as 27.99% and 5.960%, respectively.

Table 29. Statistical distribution of physicochemical parameters in the sediment samples during pre-monsoon, monsoon and post monsoon

		Min	Max	Mean	Median	SD	SE	Skew	Kurt
Pre-monsoon (*n* = 125)	T (°C)	31.3	32.7	31.7	31.7	0.349	0.055	1.093	0.747
	pH	6.90	7.95	7.36	7.29	0.298	0.047	0.725	-0.632
	EC (mS/cm)	2.279	8.395	4.671	4.716	14.09	2.228	0.238	-0.033
	TDS (g/L)	1.140	4.198	2.335	2.358	7.051	1.115	0.237	-0.034
	TA (mg/g as $CaCO_3$)	0.139	0.206	0.174	0.178	0.014	0.002	-0.283	0.702
	MC (%)	19.04	35.95	27.99	28.11	4.581	0.724	-0.081	-0.952
	OM (%)	3.094	8.175	5.960	6.574	1.656	0.370	-0.417	-1.109
Monsoon (*n* = 125)	T (°C)	21.6	22.5	22.1	22.1	0.215	0.034	-0.142	-0.330
	pH	7.37	8.03	7.65	7.61	0.155	0.025	0.575	-0.331
	EC (mS/cm)	2.513	6.321	4.435	4.399	9.603	1.518	-0.066	-0.367
	TDS (g/L)	1.257	3.161	2.218	2.200	4.804	1.060	-0.067	-0.368
	TA (mg/g as $CaCO_3$)	0.149	0.198	0.173	0.170	0.010	0.002	0.275	0.600
	MC (%)	15.19	31.16	24.12	24.49	3.440	0.544	-0.384	0.121
	OM (%)	3.998	7.380	5.264	5.059	0.945	0.211	0.783	0.284
Post-monsoon (*n* = 125)	T (°C)	13.6	14.6	14.2	14.2	0.256	0.040	-0.435	-0.370
	pH	7.43	8.10	7.79	7.76	0.175	0.028	0.330	-0.760
	EC (mS/cm)	1.674	4.917	2.976	2.632	9.630	15.23	0.772	-0.650
	TDS (g/L)	0.837	2.459	1.488	1.316	4.816	7.614	0.772	-0.649
	TA (mg/g as $CaCO_3$)	0.149	0.216	0.181	0.182	0.014	0.002	0.399	0.440
	MC (%)	10.97	42.50	26.84	26.59	7.877	1.245	-0.148	-0.750
	OM (%)	3.197	9.372	6.141	5.829	1.903	0.425	0.170	-1.220

During monsoon season (Table 29), average temperature was recorded at 22.1°C with very small variations. The pH of sediments was found between 7.37 to 8.03 with an average value of 7.65 and an almost matching median value (7.61). Mean levels of EC and TDS in the sediments were relatively higher in monsoon season which could be due to heavy inputs of dissolved ions during wet season. Total alkalinity ranged from 0.149 to 0.198 mg/g as $CaCO_3$ with the mean value of 0.173 mg/g as $CaCO_3$. Total alkalinity levels were almost comparable during pre-monsoon and monsoon seasons, while the average moisture contents and OM were found at 24.12% and 5.264%, respectively.

During post-monsoon season (Table 29), temperature varied from 13.6 to 14.6°C with an average value of 14.2°C; while pH of the sediments was varying between 7.43 to 8.10 with mean and median values of 7.79 and 7.76, respectively. During post-monsoon, EC exhibited minimum to maximum range as 1.674 to 4.917 mS/cm with average value of 2.976 mS/cm. It was mostly associated with random dispersion as revealed by SD and SE values. Likewise, TDS exhibited minimum-maximum levels as 0.837-2.459 g/L with mean and median values of 1.488 and 1.316 g/L, respectively. Total alkalinity ranged from 0.149 to 0.216 mg/g as $CaCO_3$ with mean value of 0.181 mg/g as $CaCO_3$; and average moisture contents and OM were recorded at 26.84% and 6.141%, respectively.

3.14 Distribution of Selected Metals in Calcium Nitrate Extract of Sediment Samples

Concentrations of selected metals in calcium nitrate extract of the sediment samples were measured in order to assess the soluble and bio-available fraction of the metals. Basic statistical parameters related to the distribution of selected metals in calcium nitrate extract of the sediments are given in Tables 30 to 34. The statistical distribution of the metals in calcium nitrate extract of the sediments during summer is shown in Table 30. On the average basis, Ca, Na, Mg and K were the major components with mean levels of 99.42, 14.67, 10.83 and 6.332 mg/kg, respectively. However, Cu, Zn, Cd, Li and Hg were found to be minor contributors with mean levels of 0.096, 0.091, 0.086, 0.052 and 0.010 mg/kg, respectively. Among the remaining metals, Pb, Fe, As, Co, Ni, Sr, Cr, Se and Mn exhibited average levels of 0.899, 0.804 0.742, 0.677, 0.359, 0.311, 0.239, 0.168 and 0.129 mg/kg, respectively. Overall, the metals exhibited following increasing concentration order in the sediments during summer: Hg < Li < Cd < Zn < Cu < Mn < Se < Cr < Sr < Ni < Co < As < Fe < Pb < K < Mg < Na < Ca. Some of the metals (Ca, K, Na and Mg) showed predominantly random distribution as supported by large range and elevated SD and SE values. Relatively asymmetric distribution was shown by Mn, K, Mg, and Se, as indicated by their skewness and kurtosis values. The quartile distribution of selected metals in calcium nitrate extract of sediments during summer is shown in Figure 18 where most of the metals exhibited broad range with appreciable variations; however, Ca, Hg and Se displayed relatively narrow distribution in the examined sediments. The highest asymmetry was observed for Ni, Cd, Li, K and Mn in calcium nitrate extract of the sediments.

Table 30. Statistical distribution of selected metal levels (mg/kg) in calcium nitrate extract of the sediments during summer (*n* = 90)

	Min	Max	Mean	Median	SD	SE	Skew	Kurt
As	0.321	1.752	0.742	0.437	0.492	0.096	0.820	-1.129
Ca	65.66	161.3	99.42	85.21	28.86	5.661	0.823	-0.482
Cd	0.004	0.180	0.086	0.092	0.049	0.010	0.014	-0.788
Co	0.040	1.500	0.677	0.556	0.403	0.079	0.476	-0.628
Cr	0.022	0.486	0.239	0.228	0.141	0.028	0.089	-1.093
Cu	0.022	0.162	0.096	0.087	0.037	0.007	0.109	-0.858
Fe	0.162	1.672	0.804	0.717	0.432	0.085	0.505	-0.465
Hg	0.005	0.017	0.010	0.010	0.004	0.001	0.263	-1.189
K	1.542	29.18	6.332	3.897	6.591	1.293	2.404	5.750
Li	0.002	0.120	0.052	0.047	0.030	0.006	0.606	-0.008
Mg	3.806	23.84	10.83	10.50	4.281	0.840	1.107	2.270
Mn	0.010	1.060	0.129	0.081	0.202	0.040	4.274	19.84
Na	4.512	24.41	14.67	14.20	5.513	1.081	-0.335	-0.604
Ni	0.014	0.926	0.359	0.286	0.275	0.054	0.679	-0.612
Pb	0.170	1.582	0.899	0.884	0.332	0.065	-0.082	-0.081
Se	0.117	0.279	0.168	0.156	0.037	0.007	1.132	1.608
Sr	0.026	0.756	0.311	0.284	0.183	0.036	0.369	-0.048
Zn	0.006	0.204	0.091	0.075	0.064	0.013	0.456	-1.162

Statistical distribution of selected metals in calcium nitrate extract of the sediments during winter is shown in Table 31. Among the metals, average concentration of Ca (104.1 mg/kg) was the highest, followed by, Na (16.03 mg/kg), Mg (11.89 mg/kg), K (3.690 mg/kg), Fe (1.706 mg/kg) and Mn (1.209 mg/kg). The mean concentrations of Pb, Sr and

Co were noted at 0.657, 0.625 and 0.620 mg/kg, respectively. However, the lowest average concentrations were shown by Zn, Li and Hg. Overall, following increasing concentration order was noted for selected metals in the sediments during winter: Hg < Li < Zn < Cd < Se < Cu < Ni < Cr < As < Co < Sr < Pb < Mn < Fe < K < Mg < Na < Ca. Considerably random distribution was observed for Ca, Mg, Mn and Na; duly supported by their higher SD and SE values. Moreover, Hg, Mn and Mg showed relatively asymmetric variations associated with relatively higher skewness and kurtosis values. Compared with the summer results, less dispersion/asymmetry was noted during winter, which may be associated with the seasonal characteristics. Box and whisker plot showing the quartile distribution of selected metals in the sediments during winter is shown in Figure 19, which revealed broad range and predominantly asymmetrical distribution of Cd, Co, Cr, Pb, Ni and Mn in the sediment samples. Nevertheless, relatively symmetric distribution pattern was shown by Sr, Li, Se, Hg, Zn and Fe.

Table 31. Statistical distribution of selected metal levels (mg/kg) in calcium nitrate extract of the sediments during winter (*n* = 90)

	Min	Max	Mean	Median	SD	SE	Skew	Kurt
As	0.108	0.766	0.454	0.549	0.274	0.050	-0.249	-1.684
Ca	55.74	154.3	104.1	104.9	25.12	4.587	0.001	-0.283
Cd	0.008	0.244	0.127	0.131	0.057	0.010	-0.052	-0.106
Co	0.024	1.440	0.620	0.638	0.346	0.063	0.337	-0.387
Cr	0.044	1.062	0.409	0.390	0.282	0.052	0.762	0.030
Cu	0.034	0.310	0.148	0.134	0.073	0.013	0.336	-0.608
Fe	0.606	3.646	1.706	1.677	0.665	0.121	0.592	0.983
Hg	0.006	0.021	0.010	0.009	0.003	0.001	2.745	10.41
K	2.146	5.29	3.690	3.664	0.741	0.135	0.068	-0.291
Li	0.002	0.070	0.024	0.021	0.018	0.003	0.969	0.275
Mg	7.790	16.98	11.89	11.54	2.227	0.407	0.471	-0.242
Mn	0.150	3.994	1.209	0.890	1.108	0.202	1.123	0.342
Na	5.496	38.23	16.03	12.96	6.925	1.264	1.346	2.449
Ni	0.010	0.868	0.399	0.370	0.247	0.045	0.226	-0.909
Pb	0.012	1.700	0.657	0.569	0.482	0.088	0.747	-0.275
Se	0.068	0.209	0.129	0.122	0.035	0.006	0.731	0.076
Sr	0.256	1.136	0.625	0.608	0.178	0.033	0.563	1.147
Zn	0.004	0.218	0.098	0.085	0.057	0.010	0.498	-0.567

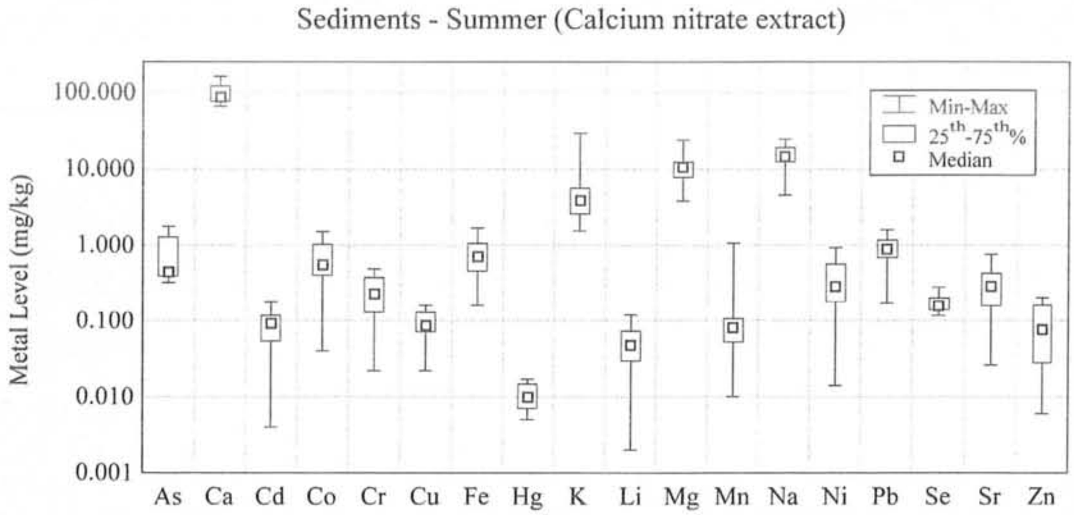

Figure 18. Quartile distribution of selected metal levels (mg/kg) in calcium nitrate extract of the sediments during summer

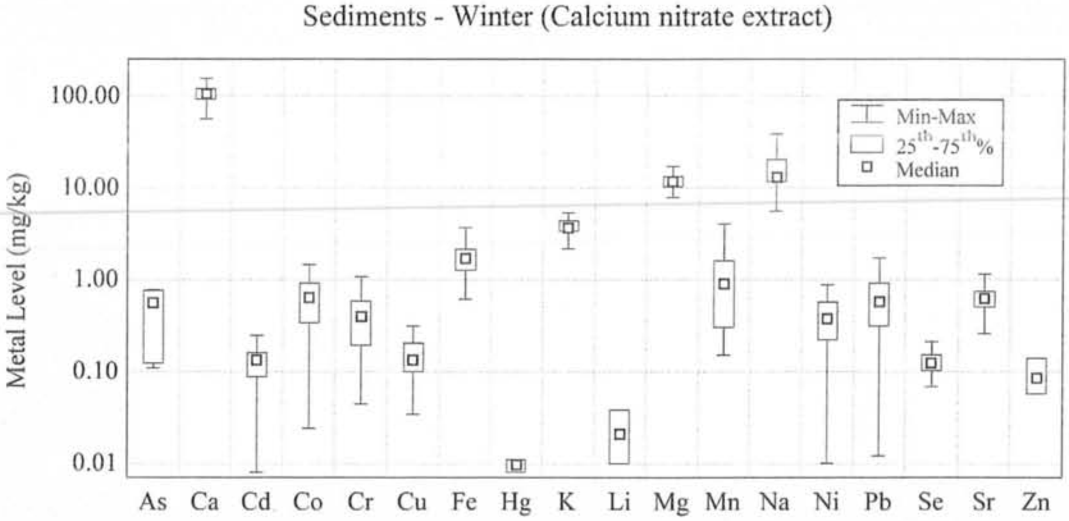

Figure 19. Quartile distribution of selected metal levels (mg/kg) in calcium nitrate extract of the sediments during winter

Comparison of the average metal levels in calcium nitrate extract of the sediments during summer and winter is shown in Figure 20. Almost comparable mean levels were found for Hg, Ca, Mg and Zn during the two seasons, however, average concentrations of Cd, Cr, Cu, Fe, Na, Ni, Sr and Mn were comparatively higher in winter than summer, which might be attributed to the reduced water flow and enrichment/precipitation of the pollutants on the sediment bed in winter season. Nonetheless, average levels of As, K, Pb, Li and Se were significantly higher in summer than winter (F > F*crit*), which might be due to excessive anthropic intrusions during summer.

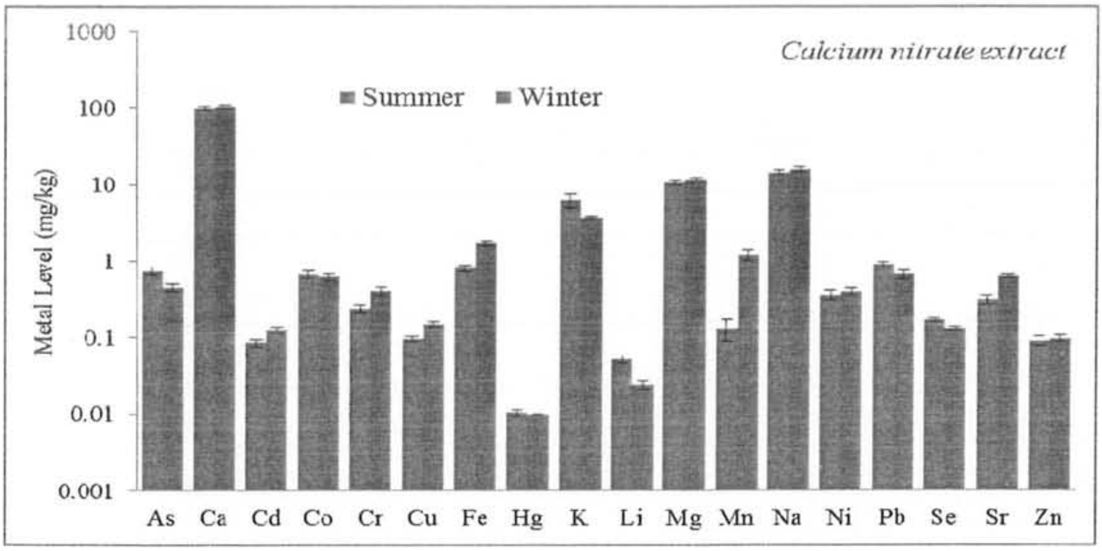

Figure 20. Comparison of average metal concentrations (mg/kg, ±SE) in calcium nitrate extract of the sediments during summer and winter

Basic statistical parameters related to distribution of selected metals in calcium nitrate extract of the sediments during pre-monsoon are given in Table 32. On the average basis, Ca, Na, Mg, K, Sr and Co were noted to be the major contributors with mean levels of 467.7, 66.80, 47.07, 35.16, 9.824 and 2.362 mg/kg, respectively. However, relatively lower contributions were noted for Mn, Cu, Se, Zn, Li and Hg with mean values of 0.510, 0.332, 0.286, 0.125, 0.111 and 0.015 mg/kg, respectively. Mean levels of remaining metals including Ni, As, Cr, Pb, Cd and Fe were measured at 1.046, 0.968, 0.935, 0.861, 0.768 and 0.763 mg/kg, in that order. Overall, the metals exhibited following increasing trend of their concentrations: Hg < Li < Zn < Se < Cu < Mn < Fe < Cd < Pb < Cr < As < Ni < Co < Sr < K < Mg < Na < Ca. Among the metals, Ca, Co, K, Mg, Na and Sr showed random dispersion as supported by relatively larger SD and SE values, while predominately asymmetric distribution was noted for Cd, Co, Cr, Li, Se and Zn as indicated by skewness values. Quartile distribution of selected metals in calcium nitrate extract of the sediments during pre-monsoon is shown in Figure 21 as box-whisker plot. Very broad spread was noted for Ni, Cd, Co and Fe, whereas, Zn, K, Cu and As indicated asymmetrical pattern. On the other hand, Sr, Na, Se, Mg, Hg and Ca showed very narrow distribution as shown by nearly overlapping upper and lower quartiles, while relatively symmetrical distribution was observed for Li and Cr in the sediments.

Table 32. Statistical distribution of selected metal levels (mg/kg) in calcium nitrate extract of the sediments during pre-monsoon (*n* = 125)

	Min	Max	Mean	Median	SD	SE	Skew	Kurt
As	0.407	2.225	0.968	0.583	0.646	0.144	0.817	-1.167
Ca	266.6	630.6	467.7	459.3	116.6	26.06	-0.046	-1.438
Cd	0.030	2.950	0.768	0.398	0.858	0.192	1.420	0.859
Co	0.010	7.890	2.362	1.590	2.191	0.490	1.063	0.583
Cr	0.250	2.450	0.935	0.720	0.597	0.134	1.351	1.408
Cu	0.040	0.780	0.332	0.265	0.219	0.049	0.765	-0.428
Fe	0.040	1.990	0.763	0.395	0.675	0.151	0.620	-1.187
Hg	0.008	0.023	0.015	0.015	0.005	0.001	0.151	-1.451
K	9.840	57.12	35.16	35.12	12.43	2.780	-0.351	0.419
Li	0.030	0.260	0.111	0.100	0.069	0.015	1.170	0.723
Mg	27.65	82.91	47.07	48.35	12.52	2.800	0.992	2.334
Mn	0.060	0.960	0.510	0.525	0.246	0.055	0.018	-0.435
Na	38.36	107.9	66.80	61.69	22.67	5.069	0.540	-1.036
Ni	0.010	2.770	1.046	0.720	0.935	0.209	0.806	-0.708
Pb	0.140	2.019	0.861	0.775	0.532	0.119	0.919	0.258
Se	0.216	0.454	0.286	0.266	0.061	0.014	1.174	1.529
Sr	5.430	15.61	9.824	9.200	2.914	0.652	0.250	-0.890
Zn	0.009	0.840	0.125	0.060	0.182	0.041	3.460	13.63

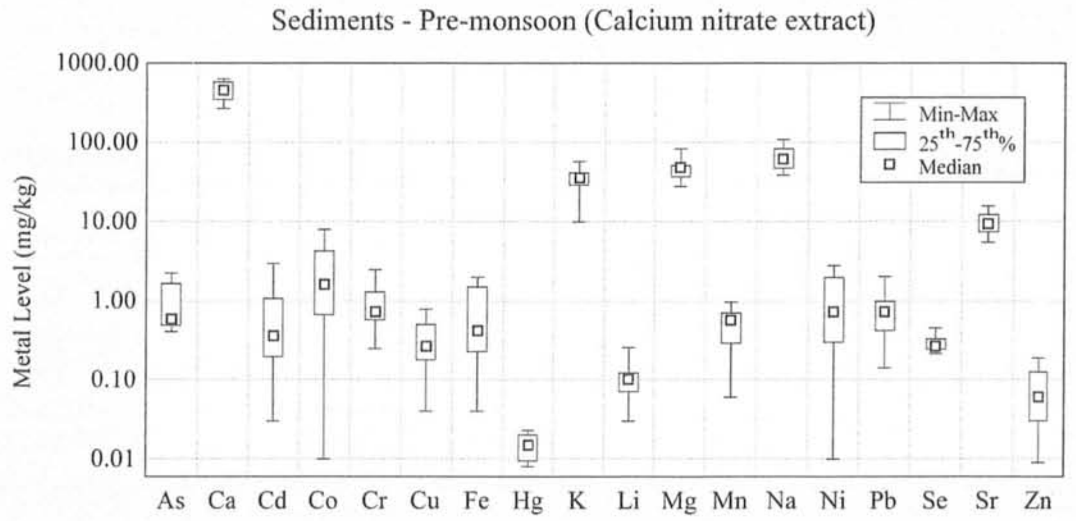

Figure 21. Quartile distribution of selected metal levels (mg/kg) in calcium nitrate extract of the sediments during pre-monsoon

Table 33. Statistical distribution of selected metal levels (mg/kg) in calcium nitrate extract of the sediments during monsoon ($n = 125$)

	Min	Max	Mean	Median	SD	SE	Skew	Kurt
As	0.238	1.579	0.676	0.450	0.423	0.067	0.747	-1.106
Ca	251.0	629.1	417.7	404.6	106.1	16.77	0.236	-1.044
Cd	0.030	2.225	0.601	0.430	0.564	0.089	1.272	0.903
Co	0.845	8.455	4.118	3.495	2.283	0.361	0.396	-1.091
Cr	0.630	3.368	1.597	1.462	0.782	0.124	0.610	-0.520
Cu	0.130	0.928	0.327	0.301	0.160	0.025	1.934	5.187
Fe	0.230	3.606	1.299	1.266	0.670	0.106	1.211	3.170
Hg	0.010	0.023	0.016	0.015	0.004	0.001	0.255	-0.930
K	18.46	53.43	37.02	37.41	8.068	1.276	-0.025	-0.221
Li	0.045	0.351	0.147	0.136	0.077	0.012	0.647	-0.152
Mg	30.75	77.35	49.30	48.26	9.787	1.547	0.435	0.368
Mn	0.140	1.733	0.611	0.598	0.316	0.050	1.398	3.709
Na	36.83	90.50	62.98	62.03	14.08	2.226	0.043	-0.959
Ni	0.810	7.075	3.045	2.982	1.388	0.219	0.669	0.667
Pb	0.130	1.821	0.728	0.559	0.437	0.069	0.864	-0.054
Se	0.174	0.380	0.250	0.242	0.046	0.007	0.778	0.755
Sr	4.825	14.94	9.709	9.816	2.332	0.369	-0.007	-0.510
Zn	0.020	0.173	0.071	0.076	0.039	0.006	0.514	-0.495

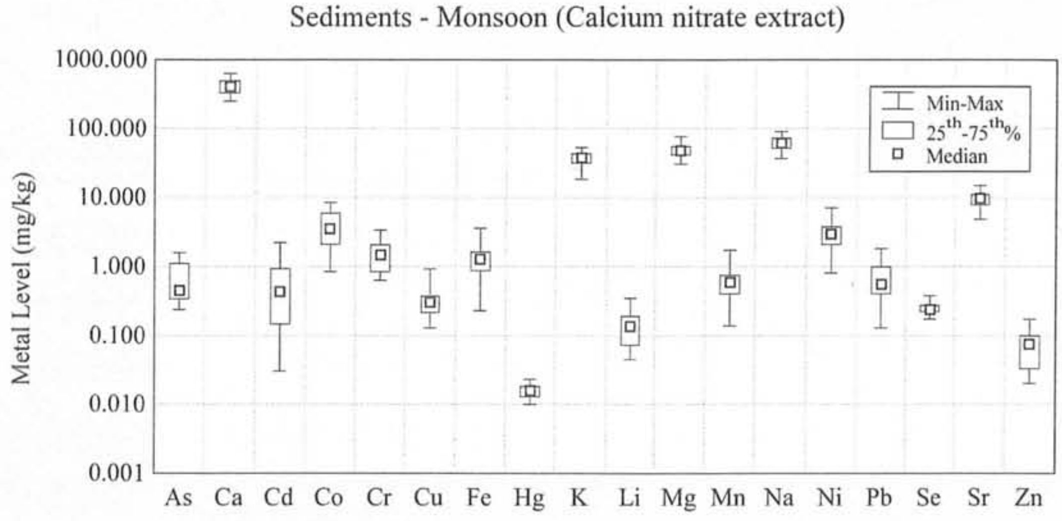

Figure 22. Quartile distribution of selected metal levels (mg/kg) in calcium nitrate extract of the sediments during monsoon

Table 34. Statistical distribution of selected metal levels (mg/kg) in calcium nitrate extract of the sediments during post-monsoon ($n = 125$)

	Min	Max	Mean	Median	SD	SE	Skew	Kurt
As	0.068	0.429	0.266	0.307	0.157	0.035	-0.356	-1.687
Ca	151.4	426.6	295.4	283.1	91.31	20.42	0.029	-1.512
Cd	0.020	1.250	0.472	0.360	0.384	0.086	0.732	-0.437
Co	0.630	12.550	5.110	4.820	2.962	0.662	0.673	0.591
Cr	0.630	4.430	1.999	1.640	1.168	0.261	0.844	-0.463
Cu	0.060	0.460	0.235	0.220	0.129	0.029	0.271	-1.083
Fe	0.140	3.290	1.514	1.285	0.817	0.183	0.806	0.119
Hg	0.011	0.015	0.013	0.013	0.001	0.000	-0.070	-0.900
K	13.11	48.42	32.45	32.34	9.048	2.023	-0.022	-0.058
Li	0.010	0.330	0.157	0.135	0.101	0.023	0.485	-0.872
Mg	28.70	64.55	42.97	42.19	9.067	2.027	0.461	0.091
Mn	0.120	2.222	0.623	0.545	0.460	0.103	2.373	7.451
Na	12.66	80.20	48.23	47.35	18.72	4.187	0.185	-0.689
Ni	0.340	11.88	4.191	4.215	2.734	0.611	1.155	2.067
Pb	0.009	0.645	0.170	0.096	0.195	0.044	1.513	1.019
Se	0.131	0.267	0.171	0.157	0.036	0.008	1.024	1.015
Sr	4.220	12.09	7.909	7.635	2.304	0.515	-0.016	-0.987
Zn	0.010	0.160	0.060	0.050	0.046	0.010	0.772	-0.146

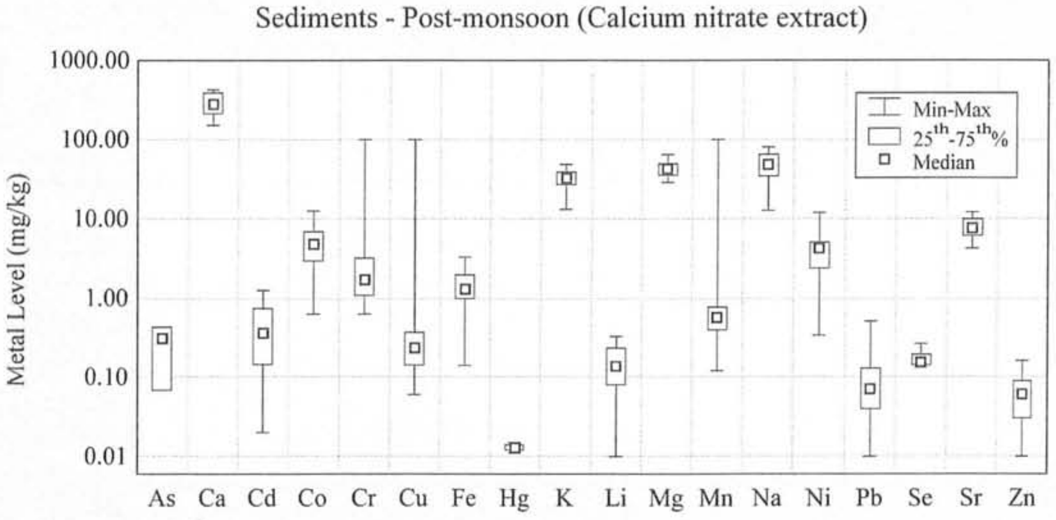

Figure 23. Quartile distribution of selected metal levels (mg/kg) in calcium nitrate extract of the sediments during post-monsoon

Statistical distribution of selected metals in calcium nitrate extract of the sediments during monsoon is given in Table 33. On the mean basis, Ca, Na, Mg, K, Sr and Co were noted to be the major components with mean levels of 417.7, 62.98, 49.30, 37.02, 9.709 and 4.118 mg/kg, respectively. However, Cd, Cu, Se, Li, Zn and Hg were found in smaller amounts with mean values of 0.601, 0.327, 0.250, 0.147, 0.071 and 0.016 mg/kg, respectively. Mean levels of Ni, Cr, Fe, Pb, As and Mn in the sediments were found at 3.045, 1.597, 1.299, 0.728, 0.676 and 0.611 mg/kg, respectively. Overall, the metals revealed following increasing trend of their concentrations: Hg < Zn < Li < Se < Cu < Cd < Mn < As < Pb < Fe < Cr < Ni < Co < Sr < K < Mg < Na < Ca. Mostly random distribution was observed for Ca, Co, K, Mg, Na, Ni and Sr as supported by relatively higher SD and SE values. Noticeable asymmetrical distribution was noted for Cd, Cu, Fe and Mn as indicated by skewness and kurtosis values. Box & Whisker plot manifesting the quartile distribution of selected metals in calcium nitrate extract of the sediments during monsoon is shown in Figure 22. Maximum spread and broad distribution was exhibited by Ni, Cd, Pb and Fe in the sediment samples, however, more or less symmetric distribution was shown by Ca, As, Hg, Mg, Na, Zn and Se. Highest asymmetry in the distribution was shown by Cu and K levels in the sediments during monsoon.

Statistical distribution parameters for selected metals in calcium nitrate extract the sediments during post-monsoon are shown in Table 34. Highest mean level was noted for Ca (295.4 mg/kg), followed by Na (48.23 mg/kg), Mg (42.97 mg/kg), K (32.45 mg/kg), Sr (7.909 mg/kg) and Co (5.110 mg/kg), while the lowest average concentrations were shown by Li (0.157 mg/kg), Zn (0.060 mg/kg) and Hg (0.013 mg/kg). Overall, following increasing concentration order was noted for selected metals in the sediments during post-monsoon: Hg < Zn < Li < Pb < Se < Cu < As < Cd < Mn < Fe < Cr < Ni < Co < Sr < K < Mg < Na < Ca. Generally, random distribution was observed for Ca, Co, Cr, K, Mg, Na, Ni and Sr levels in the sediments as shown by higher SD values. Moreover, Mn, Ni, Se and Pb showed relatively asymmetric dispersion as indicated by relatively higher skewness and kurtosis values. The quartile distribution of selected metals in calcium nitrate extract of the sediments during post-monsoon is illustrated in Figure 23. Very narrow distribution was shown by Hg and As with overlapping of lower and upper quartiles, while moderately narrow range was exhibited by Sr, Se, Mg, K and Ca in the sediments. More or less symmetrical distribution was noted for Mg, nevertheless, appreciable asymmetry with broad distribution and large spread was noted for Cd, Cr, Cu, Li, Mn, Ni and Pb in calcium nitrate extract of the sediments during post-monsoon.

Comparison of average metal levels in calcium nitrate extracts of the sediment samples collected during pre-monsoon, monsoon and post-monsoon is shown in Figure 24. Average concentrations of As, Ca, Cd, Cu, Hg, Na, Pb, Se, Sr and Zn were found to be relatively higher during pre-monsoon and lower during post-monsoon, which might be due to increased anthropogenic activities during pre-monsoon season. Almost comparable mean levels were observed for Cu, Sr and Hg during the pre-monsoon and monsoon seasons; while K and Mg showed almost comparable mean levels during pre-monsoon, monsoon and post-monsoon seasons. Conversely, average levels of Co, Cr, Fe, Li, Mn and Ni were observed to be higher during post-monsoon, which might be due to the enrichment of pollutants and/or mixing of the polluted water from surrounding areas in the vicinity of reservoir.

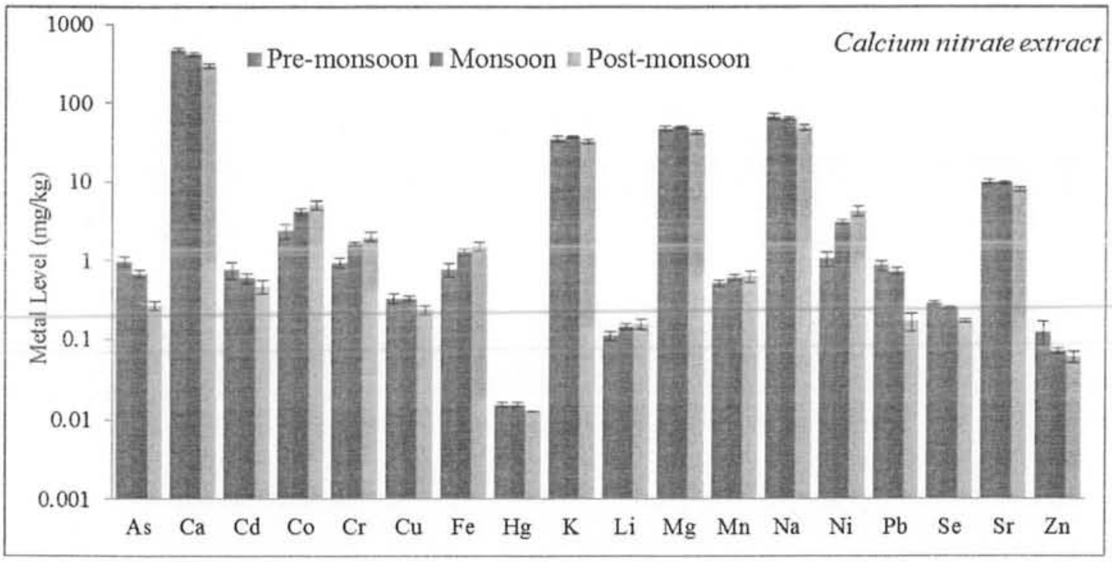

Figure 24. Comparison of average metal concentrations (mg/kg, ±SE) in calcium nitrate extract of the sediments during pre-monsoon, monsoon and post-monsoon

3.15 Distribution of Selected Metals in Acid Extract of Sediment Samples

Basic statistical parameters related to distribution of selected metals in acid-extract of the sediment samples during summer are given in Table 35. Most of the metals exhibited large variations as indicated by their minimum and maximum levels. Overwhelmingly higher mean concentration was recorded for Ca (44491 mg/kg), followed by Fe (3870 mg/kg) and Mg (3177 mg/kg). Preeminent concentration of Ca pointed out the fact that the secondary soil particles in the sediments are calcite in nature which also revealed the general characteristics of the soil in upstream area and around the water body. Moderate mean levels were found for K, Mn, Na, Sr, Ni, Zn, As and Cr at 815.2, 323.5, 156.5, 43.92, 38.73, 37.37, 23.67 and 21.34 mg/kg, respectively. The lowest mean levels were noted for Cd, Se and Hg at 1.328, 1.126 and 0.501 mg/kg, in that order. Overall, average metal contents in acid extract of the sediments exhibited following decreasing concentration order: Ca > Fe > Mg > K > Mn > Na > Sr > Ni > Zn > As > Cr > Co > Pb > Cu > Li > Cd > Se > Hg. Most of the metals showed random distribution as shown by their relatively higher SD and SE values except Cd, Hg and Se which exhibited rather lower dispersion. Some of the metals (As, Fe, Hg, Pb and Zn) exhibited asymmetrical distribution as shown by relatively higher skewness values.

Table 35. Statistical distribution of selected metal levels (mg/kg) in acid extract of the sediments during summer ($n = 90$)

	Min	Max	Mean	Median	SD	SE	Skew	Kurt
As	16.73	35.76	23.67	22.64	4.718	0.925	1.055	0.752
Ca	8538	69790	44491	42538	15431	3026	-0.341	0.249
Cd	0.049	3.621	1.328	1.143	0.934	0.183	0.625	-0.029
Co	5.938	32.55	18.81	19.16	7.762	1.522	-0.144	-0.876
Cr	12.57	35.18	21.34	21.90	5.923	1.162	0.299	-0.148
Cu	4.843	26.63	13.43	13.75	5.246	1.029	0.702	0.763
Fe	3724	4177	3870	3864	112.0	21.96	1.031	1.339
Hg	0.250	1.193	0.501	0.383	0.289	0.057	1.547	0.939
K	203.1	1837	815.2	639.0	550.5	108.0	0.399	-1.499
Li	3.914	17.93	10.73	10.54	4.390	0.861	-0.059	-1.379
Mg	2156	3872	3177	3249	546.7	107.2	-0.483	-1.140
Mn	32.63	493.2	323.5	337.4	86.84	17.03	-1.240	4.258
Na	2.431	281.1	156.5	173.0	75.22	14.75	-0.734	-0.052
Ni	3.350	111.0	38.73	39.66	27.77	5.445	0.792	0.465
Pb	2.512	49.85	17.15	12.05	12.48	2.448	1.139	0.596
Se	0.816	1.450	1.126	1.106	0.171	0.033	0.080	-0.654
Sr	13.09	85.39	43.92	45.74	14.76	2.894	0.230	2.043
Zn	2.016	150.4	37.37	31.52	27.41	5.375	2.979	11.69

The quartile distribution of selected metals in acid extract of the sediments during summer is presented in Figure 25 which revealed broad and asymmetrical distribution for Ca, Mn, Na, Ni, Pb and Zn, while very narrow distribution with overlapping lower and upper quartiles was shown by Cd and Fe in the sediments. Somewhat asymmetric distribution was noted for As, Co, Hg, Mg, Li and Sr, while Se, Cr and Cu displayed fairly narrow and symmetrical distribution in the sediment samples during summer.

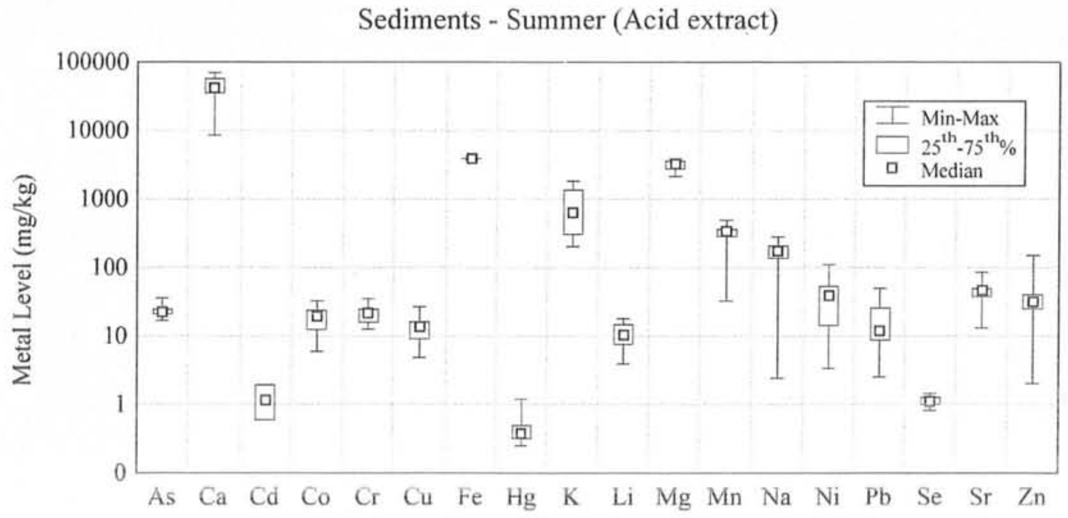

Figure 25. Quartile distribution of selected metal levels (mg/kg) in acid extract of the sediments during summer

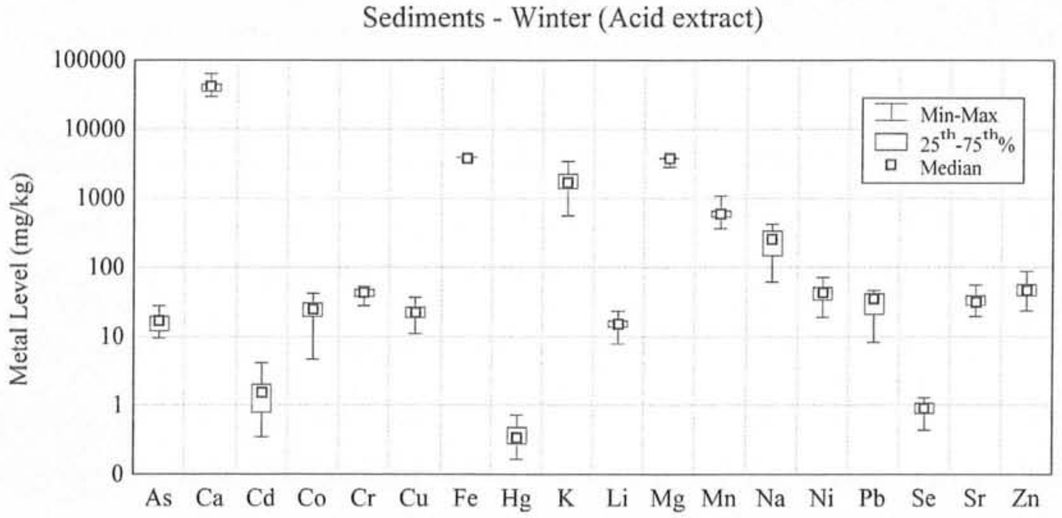

Figure 26. Quartile distribution of selected metal levels (mg/kg) in acid extract of the sediments during winter

Table 36. Statistical distribution of selected metal levels (mg/kg) in acid extract of the sediments during winter ($n = 90$)

	Min	Max	Mean	Median	SD	SE	Skew	Kurt
As	9.496	27.79	16.67	16.86	5.286	0.965	0.506	-0.755
Ca	29627	63792	41521	42484	8361	1527	0.650	0.257
Cd	0.347	4.085	1.520	1.546	0.909	0.166	0.996	1.207
Co	4.586	41.94	24.38	25.23	8.503	1.553	-0.393	0.272
Cr	27.92	52.72	41.96	43.99	7.577	1.383	-0.394	-0.906
Cu	11.02	36.90	23.29	22.29	6.58	1.202	0.595	-0.193
Fe	3589	3911	3796	3798	64.91	11.85	-0.830	2.492
Hg	0.166	0.719	0.374	0.335	0.159	0.029	0.873	-0.251
K	556.5	3416	1944	1684	818.6	149.4	0.809	-0.457
Li	7.761	23.27	15.35	15.31	3.681	0.672	0.038	-0.073
Mg	2828	3897	3678	3739	207.9	37.95	-2.845	9.815
Mn	364.6	1076	611.9	601.8	142.9	26.09	1.365	3.146
Na	61.59	423.7	248.3	255.0	117.2	21.40	-0.042	-1.485
Ni	19.06	71.85	43.06	42.66	14.07	2.569	0.175	-0.497
Pb	8.12	46.37	30.64	35.26	12.67	2.314	-0.524	-1.013
Se	0.436	1.287	0.910	0.899	0.206	0.038	0.004	-0.285
Sr	19.57	55.54	33.82	31.72	8.613	1.572	0.814	0.630
Zn	23.63	87.44	50.11	45.76	15.81	2.886	0.685	-0.248

Descriptive statistical parameters for selected metals distribution in acid-extract of the sediments during winter are shown in Table 36. Average levels of As, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Li, Mg, Mn, Na, Ni, Pb, Se, Sr and Zn in acid-extract of the sediments were found as 16.67, 41521, 1.520, 24.38, 41.96, 23.29, 3796, 0.374, 1944, 15.35, 3678, 611.9, 248.3, 43.06, 30.64, 0.910, 33.82 and 50.11 mg/kg, respectively. Highest average concentration was again shown by Ca, followed by Fe, Mg and K, whereas the lowest mean values were shown by Cd, Se and Hg. Overall, mean metal levels in acid-extract of the sediments exhibited following decreasing concentration pattern: Ca > Fe > Mg > K > Mn > Na > Zn > Ni > Cr > Sr > Pb > Co > Cu > As > Li > Cd > Se > Hg. Most of the metals exhibited comparable mean and median levels in the sediments during winter compared with summer where significant differences were observed in the central tendency of metal contents. Most of the metals exhibited non-Gaussian distribution as noted by their larger SD and SE values. The asymmetry in the metal distribution was found to be almost similar in both summer and winter seasons, thus, it supported the assumption that rate of discharge of pollutant levels in the water body was almost equivalent during the entire year. Box & Whisker plot showing quartile distribution of selected metals in acid-extract of the sediments during winter is depicted in Figure 26, which revealed relatively narrow distribution for most of the metals. However, Cd, Co, K, Na and Pb exhibited comparatively large spread and broad distribution. Meanwhile, Fe and Mg showed the narrowest distribution with overlapping of quartiles, while As, Cd, Mn and Sr showed relatively symmetrical distribution in the sediments during winter.

Comparison of average metal levels in acid-extracts of the sediments during summer and winter is shown in Figure 27. Most of the metals (Cd, Co, Cr, Cu, K, Li, Mg, Mn, Na, Ni, Pb and Zn) showed relatively higher concentrations during winter season, indicating enrichment/accumulation of the metal pollutants in sediments because of reduced inflow of water during winter (dry season). Rest of the metals showed almost comparable average concentrations in the sediments during both seasons.

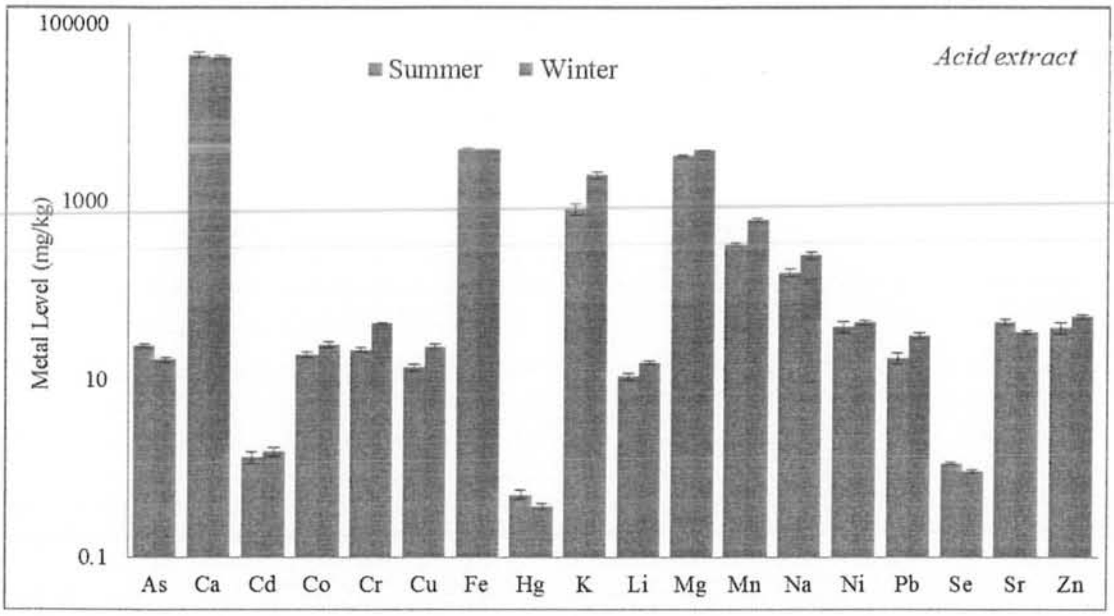

Figure 27. Comparison of average metal concentrations (mg/kg, ±SE) in acid extract of the sediments during summer and winter

Statistical parameters related to distribution of selected metals in acid-extract of the sediments during pre-monsoon are given in Table 37. In this season, average levels of As, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Li, Mg, Mn, Na, Ni, Pb, Se, Sr and Zn in acid-extract of the sediments were measured as 16.79, 52140, 5.641, 34.26, 32.10, 28.52, 4466, 0.344, 1351, 19.39, 1291, 398.5, 707.1, 43.69, 50.24, 2.497, 196.5 and 124.3 mg/kg, respectively.

Highest average concentration was once more shown by Ca, followed by Fe, K and Mg while the lowest values were shown by Cd, Se and Hg. Overall, mean metal levels in acid-extract of the sediments exhibited following decreasing pattern: Ca > Fe > K > Mg > Na > Mn > Sr > Zn > Pb > Ni > Co > Cr > Cu > Li > As > Cd > Se > Hg. Most of the metals showed random distribution in the sediments as shown by relatively higher SD and SE values except As, Cd, Hg, Li and Se which exhibited rather lower dispersion as evidenced by relatively lower SD and SE values. Most of the metals showed symmetrical dispersion supported by smaller skewness and kurtosis values except Ca and Ni which revealed fairly asymmetrical distribution. The corresponding quartile distribution of selected metals in acid-extract of the sediments during pre-monsoon is shown in Figure 28, which demonstrated that most of the metals showed narrow distribution. Nonetheless, Cd, Na, Ni, Sr and Zn showed relatively broad and asymmetric distribution, while As, Se, Co, Mn and Pb showed moderately symmetrical distribution in the sediments.

Table 37. Statistical distribution of selected metal levels (mg/kg) in acid extract of the sediments during pre-monsoon ($n = 125$)

	Min	Max	Mean	Median	SD	SE	Skew	Kurt
As	12.07	22.25	16.79	16.53	2.787	0.623	0.259	-0.746
Ca	36285	86300	52140	48607	12775	2857	1.022	1.272
Cd	1.191	9.570	5.641	5.150	2.319	0.519	0.057	-0.911
Co	14.70	68.14	34.26	34.22	13.69	3.061	0.786	0.652
Cr	22.86	39.02	32.10	33.05	4.223	0.944	-0.836	0.301
Cu	19.14	42.75	28.52	26.89	5.748	1.285	0.854	0.812
Fe	2932	5270	4466	4625	571.2	127.7	-0.968	1.159
Hg	0.195	0.639	0.344	0.267	0.149	0.033	0.839	-0.919
K	764.8	1707	1351	1360	232.7	52.03	-0.674	0.589
Li	14.17	25.05	19.39	19.34	3.027	0.677	0.013	-1.122
Mg	1074	1469	1291	1281	105.1	23.50	-0.041	-0.319
Mn	308.6	546.5	398.5	406.1	60.65	13.56	0.425	0.376
Na	246.9	1182	707.1	701.7	291.4	65.16	-0.168	-1.310
Ni	23.76	79.76	43.69	42.33	14.00	3.131	1.058	1.234
Pb	29.44	77.99	50.24	46.52	12.44	2.782	0.849	0.334
Se	1.675	3.767	2.497	2.446	0.553	0.124	0.725	0.106
Sr	99.35	304.5	196.5	194.1	56.07	12.54	0.113	-0.335
Zn	26.66	245.1	124.3	120.2	45.64	10.21	0.524	1.997

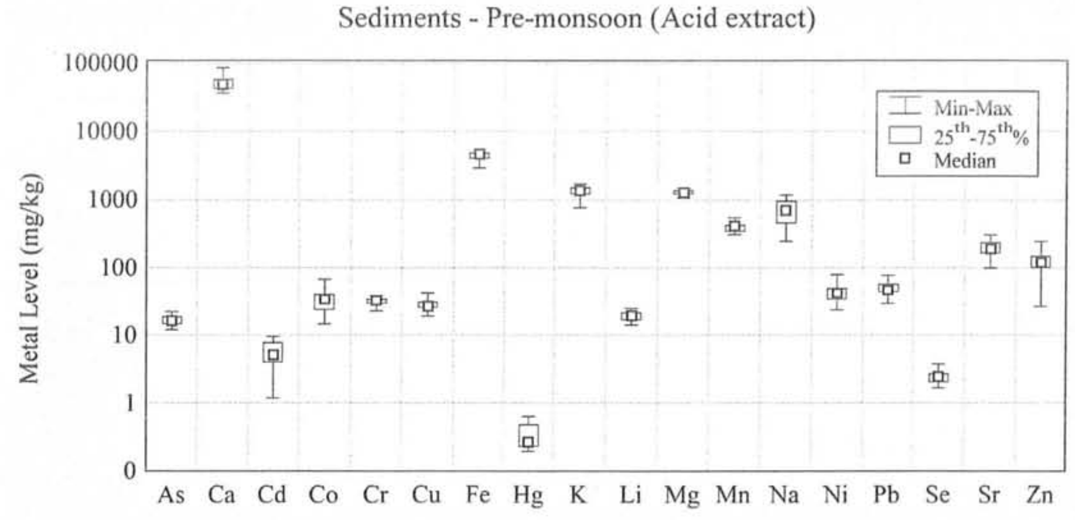

Figure 28. Quartile distribution of selected metal levels (mg/kg) in acid extract of the sediments during pre-monsoon

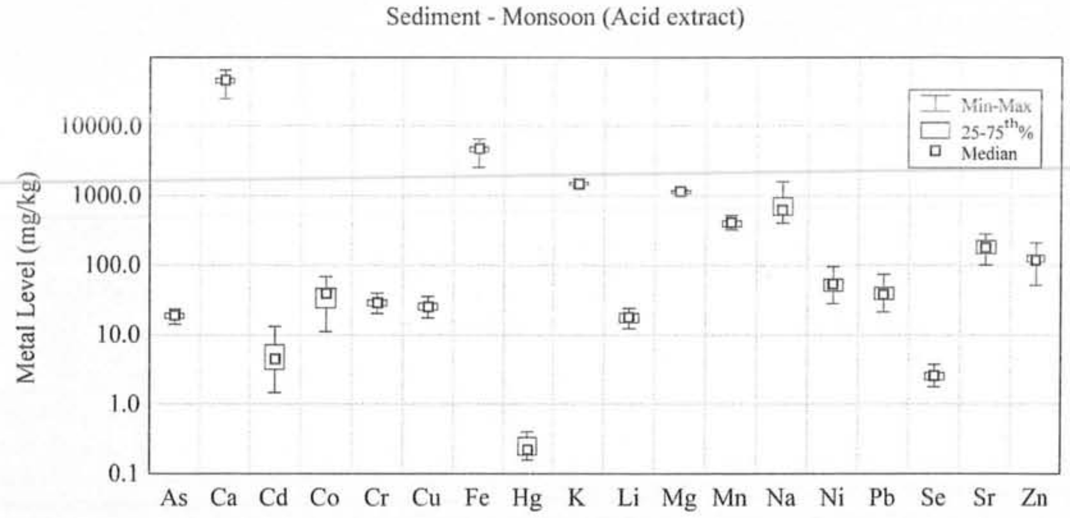

Figure 29. Quartile distribution of selected metal levels (mg/kg) in acid extract of the sediments during monsoon

Basic statistical parameters related to distribution of selected metals in acid-extract of the sediments during monsoon are given in Table 38. Most of the metals exhibited large variations as indicated by their lowest and highest levels. Overwhelmingly higher mean concentration was recorded for Ca (45501 mg/kg), followed by, Fe (4652 mg/kg), K (1497 mg/kg) and Mg (1131 mg/kg), while the lowest levels were found for Cd (5.153 mg/kg), Se (2.574 mg/kg) and Hg (0.253 mg/kg). Moreover, the mean levels of As, Co, Cr, Cu, Li, Mn, Na, Ni, Pb, Sr and Zn were found at 18.78, 36.92, 29.03, 25.54, 17.65, 405.6, 769.2, 56.28, 41.64, 182.9 and 122.8 mg/kg, respectively. Overall, mean metal levels in acid-extract of the sediments exhibited following decreasing pattern: Ca > Fe > K > Mg > Na > Mn > Sr > Zn > Ni > Pb > Co > Cr > Cu > As > Li > Cd > Se > Hg. Most of the metals showed random distribution in the sediments as shown by relatively higher SD and SE values except As, Cd, Li, Hg and Se which exhibited rather lower dispersion. In addition, most of the metals showed symmetrical distribution as indicated by smaller skewness and kurtosis values except Cd, Na and Pb, which revealed asymmetrical distribution.

Table 38. Statistical distribution of selected metal levels (mg/kg) in acid extract of the sediments during monsoon ($n = 125$)

	Min	Max	Mean	Median	SD	SE	Skew	Kurt
As	14.10	23.39	18.78	18.70	2.497	0.558	0.048	-0.756
Ca	24965	64691	45501	45835	7890	1764	-0.225	2.648
Cd	1.468	13.06	5.153	4.450	2.781	0.622	1.269	1.959
Co	11.01	68.07	36.92	39.17	15.24	3.408	0.142	-0.468
Cr	20.18	39.65	29.03	28.76	5.399	1.207	0.186	-0.403
Cu	17.45	35.53	25.54	25.33	5.144	1.150	0.359	-0.373
Fe	2568	6570	4652	4753	791.9	177.1	-0.313	2.767
Hg	0.158	0.401	0.253	0.218	0.079	0.018	0.560	-1.241
K	1328	1751	1497	1480	116.4	26.02	0.710	0.176
Li	12.18	23.90	17.65	17.99	3.337	0.746	-0.080	-0.683
Mg	1014	1250	1131	1146	74.60	16.68	-0.217	-0.999
Mn	323.5	521.1	405.6	415.4	55.19	12.34	0.417	-0.452
Na	404.7	1594.6	769.2	628.1	362.6	81.07	1.212	0.129
Ni	27.93	95.29	56.28	53.35	18.89	4.224	0.558	-0.387
Pb	21.20	74.05	41.64	37.88	13.89	3.106	1.018	0.731
Se	1.778	3.737	2.574	2.562	0.487	0.109	0.614	0.393
Sr	100.3	280.4	182.9	176.2	56.39	12.61	0.167	-0.874
Zn	51.10	209.8	122.8	118.0	36.78	8.22	0.201	0.787

Box & Whisker plot showing quartile distribution of selected metals in acid-extract of the sediments during monsoon is presented in Figure 29. Relatively narrow range and predominantly asymmetric distribution was shown by most of the metals. Among the selected metals, Zn, Co and Cd exhibited relatively broad range, while Mg and K showed very narrow range with overlapping of lower and upper quartiles. Moderately symmetric distribution in acid-extract of the sediments during monsoon was noted for Cu, Ni, Se and Pb, while rest of the metals displayed asymmetrical and random variations.

Statistical parameters related to distribution of selected metals in acid-extract of the sediments during post-monsoon are given in Table 39. Mean levels of As, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Li, Mg, Mn, Na, Ni, Pb, Se, Sr and Zn in the sediments during post-monsoon season were found at 15.87, 54921, 4.711, 39.91, 26.23, 22.79, 4879, 0.251, 1371, 16.06, 1223, 416.3, 1103, 69.38, 33.41, 2.183, 170.9 and 122.3 mg/kg, respectively. Highest average concentration was shown by Ca, followed by, Fe, K and Mg, while the lowest mean values were noted for Cd, Se and Hg. Overall, mean metal levels in acid-extract of the sediments exhibited following decreasing pattern: Ca > Fe > K > Mg > Na > Mn > Sr > Zn > Ni > Co > Pb > Cr > Cu > Li > As > Cd > Se > Hg. Highest concentration of Ca during all seasons pointed out the fact that the sediments are mostly composed of calcite particles which is also the general characteristics of the soil in catchments areas. Most of the metals showed random distribution in the sediments as shown by relatively higher SD and SE values except As, Cd, Hg and Se which exhibited small dispersion. Also, most of the metals showed symmetrical dispersion as evidenced by rather lower values of skewness and kurtosis except Cd, Hg, Na and Pb which revealed asymmetrical distribution.

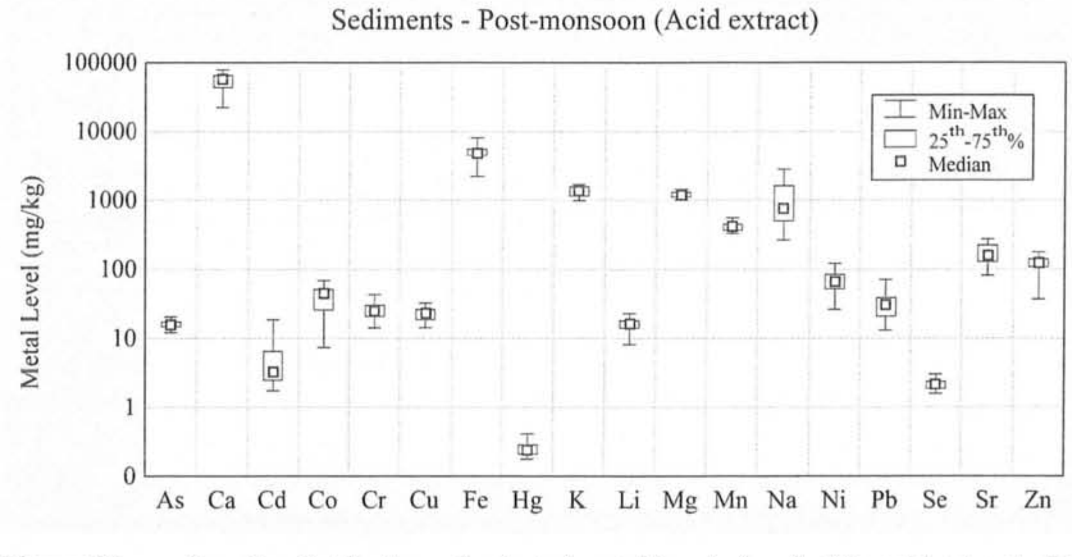

Figure 30. Quartile distribution of selected metal levels (mg/kg) in acid extract of the sediments during post-monsoon

Table 39. Statistical distribution of selected metal levels (mg/kg) in acid extract of the sediments during post-monsoon ($n = 125$)

	Min	Max	Mean	Median	SD	SE	Skew	Kurt
As	12.11	20.56	15.87	15.69	2.296	0.513	0.376	-0.249
Ca	22457	78596	54921	57424	15787	3530	-0.487	-0.483
Cd	1.758	18.68	4.711	3.241	3.845	0.860	2.731	9.202
Co	7.409	68.61	39.91	44.45	17.43	3.898	-0.265	-0.901
Cr	14.22	43.35	26.23	24.85	7.351	1.644	0.695	0.477
Cu	14.33	32.45	22.79	23.13	5.075	1.135	-0.037	-0.769
Fe	2226	8062	4879	4852	1098	245.5	0.521	4.233
Hg	0.176	0.411	0.251	0.236	0.059	0.013	1.197	1.405
K	988.6	1692	1371	1383	212.7	47.55	0.003	-1.103
Li	8.203	22.98	16.06	16.29	3.945	0.882	-0.207	-0.299
Mg	1014	1454	1223	1207	117.4	26.25	0.205	-0.699
Mn	329.6	555.8	416.3	422.2	62.10	13.89	0.438	-0.216
Na	265.2	2813	1103	770.2	855.2	191.2	1.093	-0.311
Ni	26.25	121.4	69.38	66.92	25.83	5.776	0.394	-0.448
Pb	13.15	70.77	33.41	30.29	16.17	3.615	1.001	0.809
Se	1.558	3.029	2.183	2.136	0.360	0.080	0.459	0.145
Sr	81.13	273.6	170.9	158.9	61.23	13.69	0.265	-1.089
Zn	36.99	176.3	122.3	122.0	32.80	7.33	-0.679	1.277

Box and whisker plot given in Figure 30 demonstrates quartile distribution of selected metals in acid-extract of the sediments during post-monsoon. Most of the metals showed narrow range and relatively asymmetrical distribution; however Cr, Mn and Se exhibited relatively symmetrical distribution in the sediments.

Overall, the metal data showed highest concentrations of essential metals (Ca, Mg, K, Fe, Na, Mn, & Zn) in the sediments from Mangla Lake, while the lowest concentrations were found for Se and Hg. Moreover, the measured levels of toxic metals (Cd, Co, Cr, Cu, Ni & Pb) were relatively elevated. Distribution of selected metals was mostly found to be non-Gaussian, as revealed by large SD and SE values. The asymmetry in metal distribution was found to be more or less similar in all seasons, thus supporting the assumption that the rate of discharge of metal pollutants in the water body was almost comparable during the entire year. This aspect of the study would be taken in detail by utilizing the multivariate statistical methods in the forthcoming sections.

Comparison of average metal levels in acid-extracts of the sediments during pre-monsoon, monsoon and post-monsoon is shown in Figure 31. Most of the metals showed almost comparable average concentrations and statistically insignificant differences during the three seasons. However, some of the metals, such as, Cd, Cr, Cu, Hg, Li, Mg, Pb, Sr and Zn showed relatively higher concentrations in pre-monsoon season, which might be attributed to excessive anthropogenic activities (agriculture, recreational and high degree of domestic/industrial activities) and decreased water level due to intense evaporation during pre-monsoon (Gupta *et al.,* 2009). Similarly, average levels of Ca, Co, Fe, Mn, Na and Ni were comparatively higher in post-monsoon, while As, K and Se levels were relatively higher in monsoon. It could be due to heavy precipitation during monsoon thereby carrying the pollutants from upstream areas to the water body resulting in increase of metal concentrations during post-monsoon season. Occasionally, the variations in metal concentrations might also be influenced by changes in lithological inputs, hydrological effects, geological features, cultural influences and type of vegetation cover (Collvin, 1985; Huang *et al.,* 2012; Jain *et al.,* 2007; Varol, 2011).

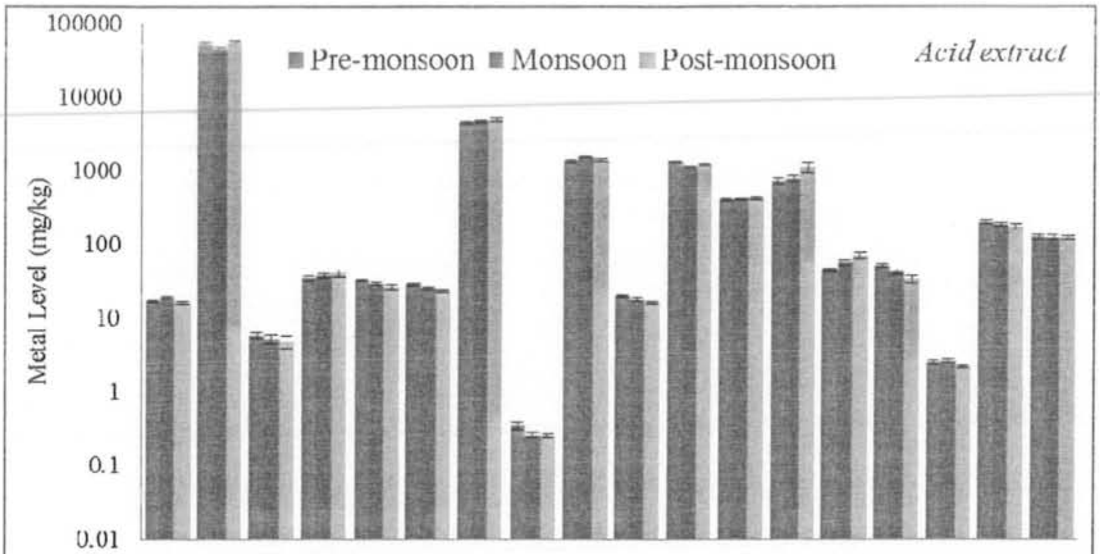

Figure 31 Comparison of average metal concentrations (mg/kg, ±SE) in acid extract of the sediments during pre-monsoon, monsoon and post-monsoon

3.16 Comparison of Present Metal Levels with Worldwide Reported Levels

Average concentrations of selected metals in the sediment during summer and winter in the present study were compared with the reported levels from other parts of the world as shown in Table 40. The measured levels of As in the present study were higher than the levels reported for Caizi Lake (Cheng *et al.,* 2015), Honghu Lake (Cheng *et al.,* 2015), Dongting Lake (Cheng *et al.,* 2015), Taihu Lake (Fu *et al.,* 2013) and Algeciras Bay (Diaz-de Alba *et al.,* 2011). Similarly, present mean levels of Ca were higher than the reported levels for Chaohu Lake (Liu *et al.,* 2012) while mean levels of Cd were noted to be higher than those of Caizi Lake, Honghu Lake, Dongting Lake, Skadar Lake (Vemic *et al.,* 2014), Taihu Lake, Nasser Lake (Goher *et al.,* 2014), Algeciras Bay (Diaz-de Alba *et al.,* 2011) and Sungai Buloh, Malaysia (Nemati *et al.,* 2011) but lower than the reported levels for Khanpur Lake (Iqbal and Shah, 2014b) during both seasons. Mean levels of Co were comparatively higher than Mighan Lake (Ghadimi F, 2014), Algeciras Bay and Sungai Buloh, Malaysia. Likewise, average levels of Cr were found to be higher than the reported levels for Mighan Lake, Nasser Lake, Sungai Buloh, Malaysia and Khanpur Lake during winter season but lower than those of Caizi Lake, Honghu Lake, Dongting Lake, Chaohu Lake, Skadar Lake, Taihu Lake and Algeciras Bay during both seasons. The measured mean levels of Hg were higher than the levels reported for Caizi Lake, Honghu Lake, Dongting Lake and Taihu Lake. Similarly, present mean levels of Mn were also higher than the levels reported for Skadar Lake, Nasser Lake, Algeciras Bay and Khanpur Lake. However, present levels were lower than that of Chaohu Lake. Present mean levels of Ni were noted to be greater than those of Mighan Lake, Caizi Lake, Chaohu Lake, Taihu Lake, and Nasser Lake while lower than the reported levels for Honghu Lake, Dongting Lake, Skadar Lake and Algeciras Bay during both seasons. Moreover, current Pb levels were found to be higher than those of Skadar Lake, Nasser Lake, Khanpur Lake (winter) and Algeciras Bay during winter season while lower than the levels reported for Caizi Lake, Honghu Lake, Dongting Lake, Chaohu Lake, Taihu Lake, Khanpur Lake (summer) and Sungai Buloh, Malaysia during both seasons. Nevertheless, average concentrations of Cu, Fe, K, Mg, Na, Sr and Zn were found to be lower than most of the reported studies given in Table 40.

Average metal concentrations in the sediment samples from Mangla Lake during pre-monsoon, monsoon and post-monsoon seasons were also compared with the reported studies from other parts of the world as shown in Table 41. Present mean levels of As were higher than the reported levels for Dalonghu Lake (Cheng *et al.*, 2015), Fuxian Lake (Cheng *et al.*, 2015), Hongze Lake (Cheng *et al.*, 2015), Akkulam Veli Lake (Swarnalatha *et al.*, 2015) and Lake Nakaumi (Ahmed *et al.*, 2010) while lower than that of Dongting Lake (Li *et al.*, 2013a) during all seasons. The measured levels of Ca and Co were comparatively higher than those of Kurang Nallah (Zahra *et al.*, 2014) and Rawal Lake (Iqbal *et al.*, 2013b & 2015), whereas, Cd levels were higher than the reported levels for Skadar Lake (Vemic *et al.*, 2014), Dalonghu Lake, Fuxian Lake, Hongze Lake, Akkulam Veli Lake, Dongting Lake, Kurang Nallah (during Pre-monsoon), Kurang Nallah (during Post-monsoon) and Rawal Lake. Mean levels of Cr were higher than the levels reported for Dalonghu Lake, Kurang Nallah (during Pre-monsoon), Kurang Nallah (during Post-monsoon) and Rawal Lake (Iqbal *et al.*, 2013b) while lower than those of Skadar Lake, Fuxian Lake, Hongze Lake, Akkulam Veli Lake, Dongting Lake, Rawal Lake (Iqbal *et al.*, 2015) and Lake Nakaumi during all seasons. Mean levels of Cu were higher than those of Skadar Lake, Dalonghu Lake, Kurang Nallah (during Pre-monsoon), Kurang Nallah (during Post-monsoon) and Rawal Lake, but lower than the reported levels for Fuxian Lake, Hongze Lake, Akkulam Veli Lake, Dongting Lake and Lake Nakaumi during all seasons. Average levels of Fe in the present study were higher than those of Kurang Nallah and Rawal Lake (Iqbal *et al.*, 2015) but lower than the levels reported for Skadar Lake and Rawal Lake (Iqbal *et al.*, 2013b). Mean levels of Hg were also higher than the reported levels for Dalonghu Lake, Fuxian Lake, Hongze Lake and Dongting Lake. Mean concentrations of K, Li, Mg, Mn and Na were considerably higher than the levels reported for Kurang Nallah and Rawal Lake. Mean levels of Ni were higher than the reported levels for Dalonghu Lake, Fuxian Lake, Hongze Lake, Kurang Nallah and Lake Nakaumi while lower than those of Skadar Lake and Akkulam Veli Lake. The measured levels of Pb were higher than the reported levels for Skadar Lake, Dalonghu Lake, Hongze Lake, Kurang Nallah, Rawal Lake (Iqbal *et al.*, 2013b) and Lake Nakaumi, however, the present levels were lower than those of Fuxian Lake, Akkulam Veli Lake, Dongting Lake and Rawal Lake (Iqbal *et al.*, 2015). In addition, present mean levels of Zn were found to be higher than the levels reported for Skadar Lake, Dalonghu Lake, Fuxian Lake, Hongze Lake, Akkulam Veli Lake, Kurang Nallah and Rawal Lake, whereas the current levels were lower than the reported levels for Dongting Lake and Lake Nakaumi during pre-monsoon, monsoon and post-monsoon seasons.

Table 40. Average metal concentrations (mg/kg, dry weight) in the sediment during summer and winter in comparison with the worldwide reported levels

	As	Ca	Cd	Co	Cr	Cu	Fe	Hg	K	Li	Mg	Mn	Na	Ni	Pb	Se	Sr	Zn	
Mangla Lake (Summer)	23.67	44491	1.328	18.81	21.34	13.43	3870	0.501	815.2	10.73	3177	323.5	156.5	38.73	17.15	1.126	43.92	37.37	Present study
Mangla Lake (Winter)	16.67	41521	1.520	24.38	41.96	23.29	3796	0.374	1944	15.35	3678	611.9	248.3	43.06	30.64	0.910	33.82	50.11	Present study
Mighan Lake	-	-	-	4.93	19.28	3.01	-	-	-	-	-	-	-	29.9	-	-	2136	69.69	Ghadimi, 2014
Caizi Lake	10.3	-	0.202	-	80	32.5	-	0.051	-	-	-	-	-	36.5	38.3	-	-	98	Cheng *et al.*, 2015
Honghu Lake	11.4	-	0.301	-	104	44.4	-	0.071	-	-	-		-	49.6	33.1	-	-	110	Cheng *et al.*, 2015
Dongting Lake	14.4	-	0.501	-	102	53.9	-	0.092	-	-	-		-	48.2	39	-	-	127	Cheng *et al.*, 2015
Chaohu Lake	-	5520	-	-	81.9	28.9	36500	-	17100	-	6480	1120	9310	37.2	52.4	-	121	152	Liu *et al.*, 2012
Skadar Lake	-	-	0.5	-	63.5	26.8	17400	-	13200	-	12300	529	-	88.9	18.1	-	-	53.2	Vemic *et al.*, 2014
Taihu Lake	9.82	-	0.14	-	68.09	34.14	-	0.11	-	-	-	-	-	36.23	33.55	-	-	105.6	Fu *et al.*, 2013
Nasser Lake	-	-	0.175	-	30.79	21.78	12418	-	-	-	-	279.6	-	27.56	10.91	-	-	35.38	Goher *et al.*, 2014
Khanpur Lake (Summer)	-	-	1.883	-	34.66	36.84	-	-	-	-	-	447.5	-	-	33.71	-	-	86.09	Iqbal and Shah, 2014
Khanpur Lake (Winter)	-	-	2.457	-	37.65	28.05	3791	-	-	-	-	321.4	-	-	18.24	-	-	61.9	Iqbal and Shah, 2014
Algeciras Bay	11	-	0.3	11	112	17	28129	-	-	-	-	534	-	65	24	-	-	73	Diaz-de Alba *et al.* 2011
Sungai Buloh, Malaysia	-	-	0.316	4.01	39.51	34.73	-	-	-	-	-	-	-	16.99	37.27	-	-	93.98	Nemati *et al.*, 2011

Table 41. Average metal concentrations (mg/kg, dry weight) in the sediment during pre-monsoon, monsoon and post-monsoon in comparison with the worldwide reported levels

	As	Ca	Cd	Co	Cr	Cu	Fe	Hg	K	Li	Mg	Mn	Na	Ni	Pb	Se	Sr	Zn	
Mangla Lake (Pre monsoon)	16.79	52140	5.641	34.26	32.10	28.52	4466	0.344	1351	19.39	1291	398.5	707.1	43.69	50.24	2.50	196.5	124.3	Present Study
Mangla Lake (Monsoon)	18.78	45501	5.153	36.92	29.03	25.54	4652	0.253	1497	17.65	1131	405.6	769.2	56.28	41.64	2.57	182.9	122.8	Present Study
Mangla Lake (Post monsoon)	15.87	54921	4.711	39.91	26.23	22.79	4879	0.251	1371	16.06	1223	416.3	1103	69.38	33.41	2.18	170.9	122.3	Present Study
Skadar Lake	-	-	0.40	-	52.9	21.1	14100	-	11100	-	11700	392	-	69.2	11.7	-	-	33.8	Vemic *et al.*, 2014
Dalonghu Lake	5.4	-	0.085	-	23	9.7	-	0.014	-	-	-	-	-	10.4	19.1	-	-	26	Cheng *et al.*, 2015
Fuxian Lake	9.2	-	0.490	-	109	59.6	-	0.054	-	-	-	-	-	39.8	34.8	-	-	99	Cheng *et al.*, 2015
Hongze Lake	15.2	-	0.16	-	90	34.0	-	0.033	-	-	-		-	48.2	28.9	-	-	86	Cheng *et al.*, 2015
AkkulamVeli Lake	1.43	-	0.27	-	183.2	53.8	-	-	-	-	-		-	83.77	59.05	-	-	123.4	Swarnalatha *et al.*, 2015
Dongting Lake	29.71	-	4.65	-	88.29	47.48	-	0.157	-	-	-		-		60.99	-	-	185.3	Li *et al.*, 2013
Kurang Nallah (Pre monsoon)	-	1164	0.42	1.26	1.67	0.17	235.1	-	911	0.09	106	26.7	227.5	6.8	0.3	-	-	58.57	Zahra *et al.*, 2014
Kurang Nallah (Post monsoon)	-	1410	0.09	0.45	1.69	0.14	185.5	-	378.3	0.07	88.91	38.4	227.1	28.42	0.69	-	-	54.25	Zahra *et al.*, 2014
Rawal Lake	-	18400	3.93	34.0	40.6	18.8	3400	-	1060	12.0	3790	303	278.0	-	52.8	-	216	57	Iqbal *et al.*, 2015
Rawal Lake	-	22933	2.13	3.901	12.15	7.16	14979	-	502.5	4.938	2343	306.4	507.7	-	16.94	-	114	18.18	Iqbal *et al.*, 2013
Lake Nakaumi	12	-	-	-	46	32	-	-	-	-	-	-	-	21	25	-	-	135	Ahmed *et al.*, 2010

3.17 Distribution of Selected Metals in Sequentially Extracted Fractions of Sediment Samples

Measurement of total metal contents in the sediments provided little information about their bioavailability, mobility, toxicity and reactivity; however, it could be useful as an indicator of metal contamination in aquatic ecosystems (Hooda, 2010; Sundaray *et al.*, 2011). Fractionation of the metals in sediments provided much useful information regarding chemical nature or potential mobility and bioavailability of a particular element (Yang *et al.*, 2009). The bio-availability and prospective toxicity of metals to biota depends on their chemical forms (Ahlf *et al.*, 2009; Arnason and Fletcher, 2003). Therefore, researchers are interested in determining the associations of metals with different geochemical phases, which could be assessed by sequentially extracting the sediments for various fractions (Rauret, 1998). Though sequential extraction procedure is complicated and lengthy, it provides adequate information related to the origin, occurrence, biological/physicochemical aspects, mobilization and transport of various metals (Passos *et al.*, 2010). Therefore, sequential extraction of the sediment samples was carried out during summer and winter seasons to determine the associations of metals with different geochemical phases and to assess their bioavailability and toxicity.

3.17.1 Distribution of Selected Metals in Exchangeable Fraction of Sediments

Statistical description of selected metals concentrations (mg/kg) in exchangeable fraction of the sediments during summer is shown in Table 42. Most of the metals exhibited relatively larger spread as shown by their minimum and maximum levels. Average levels of As, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Li, Mg, Mn, Na, Ni, Pb, Se, Sr and Zn in exchangeable fraction of the sediments were found at 1.105, 48160, 1.345, 4.754, 2.751, 2.170, 20.11, 0.017, 196.1, 2.272, 257.2, 80.33, 253.5, 7.300, 22.22, 0.270, 134.2 and 0.367 mg/kg, respectively. Highest average concentration was shown by Ca, followed by, Mg, Na and K, while the lowest values were shown by Zn, Se and Hg. Overall, average metal levels in exchangeable fraction of the sediments during summer displayed following decreasing order: Ca > Mg > Na > K > Sr > Mn > Fe > Pb > Ni > Co > Cr > Li > Cu > Cd > As > Zn > Se > Hg. Comparatively higher dispersion was noted for Ca, Na, Mg, K, Sr, Mn, Pb and Fe as indicated by their SD and SE values. Appreciably higher skewness and kurtosis values for Ca, Ni, As, Zn and Se indicated their asymmetric and random distribution in the sediments.

Table 42. Statistical distribution of selected metal levels (mg/kg) in the exchangeable fraction of sediments during summer ($n = 90$)

	Min	Max	Mean	Median	SD	SE	Skew	Kurt
As	0.465	2.540	1.105	0.666	0.737	0.165	0.817	-1.167
Ca	33337	82702	48160	44651	12588	2815	1.137	1.566
Cd	0.149	2.600	1.345	1.422	0.770	0.172	-0.039	-1.167
Co	0.398	9.581	4.754	4.458	2.450	0.548	0.183	-0.582
Cr	0.299	5.389	2.751	2.490	1.633	0.365	0.240	-1.378
Cu	0.498	4.246	2.170	2.114	1.173	0.262	0.176	-1.069
Fe	5.450	34.33	20.11	18.79	7.159	1.601	0.100	-0.251
Hg	0.008	0.029	0.017	0.016	0.006	0.001	0.321	-0.885
K	94.55	281.9	196.1	179.0	53.51	11.96	-0.003	-1.101
Li	0.800	4.133	2.272	2.291	0.998	0.223	0.069	-0.879
Mg	133.4	358.6	257.2	266.2	62.17	13.90	-0.155	-0.836
Mn	41.15	90.77	80.33	82.29	10.87	2.431	-2.621	8.904
Na	37.25	457.6	253.5	296.1	188.4	42.14	-0.081	-2.100
Ni	1.996	15.20	7.300	6.683	3.320	0.742	0.943	1.448
Pb	9.600	39.36	22.22	23.36	8.248	1.844	0.223	-0.297
Se	0.192	0.404	0.270	0.263	0.056	0.012	0.768	0.189
Sr	80.45	219.6	134.2	128.8	36.88	8.247	0.517	-0.127
Zn	0.024	1.099	0.367	0.200	0.356	0.080	0.798	-0.696

Statistical distribution of selected metals concentrations (mg/kg) in exchangeable fraction of the sediments during winter is shown in Table 43. In this season, average levels of As, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Li, Mg, Mn, Na, Ni, Pb, Se, Sr and Zn in exchangeable fraction of the sediments were measured as 0.689, 51193, 1.276, 9.738, 1.346, 2.464, 40.68, 0.015, 225.3, 1.462, 247.9, 83.74, 211.6, 10.31, 11.44, 0.206, 125.0 and 1.679 mg/kg, respectively. Highest average concentration was shown by Ca, followed by, Mg, K, Na, Sr and Mn while lowest levels were observed for Cd, As, Se and Hg. Overall, average metal levels in exchangeable fraction of the sediments during winter revealed following decreasing order: Ca > Mg > K > Na > Sr > Mn > Fe > Pb > Ni > Co > Cu > Zn > Li > Cr > Cd > As > Se > Hg. Among the selected metals, Cr, Cd, Cu, Li, As, Se and Hg showed somewhat normal distribution pattern as evidenced by very small values of SD and SE while higher dispersion was noted for Ca, Na, K, Mg, Sr and Fe in the sediment samples. Moreover, considerable asymmetry in distribution of Zn, Mn, Cr, Co, Na and Fe was evidenced by relatively higher skewness and kurtosis values.

Table 43. Statistical distribution of selected metal levels (mg/kg) in the exchangeable fraction of sediments during winter ($n = 90$)

	Min	Max	Mean	Median	SD	SE	Skew	Kurt
As	0.177	1.110	0.689	0.795	0.407	0.091	-0.356	-1.687
Ca	20498	74969	51193	52562	15775	3527	-0.383	-0.651
Cd	0.150	3.144	1.276	0.948	0.812	0.182	0.703	-0.413
Co	1.996	24.88	9.738	8.163	6.264	1.401	1.000	0.554
Cr	0.398	3.942	1.346	1.021	0.943	0.211	1.359	1.573
Cu	0.349	3.700	2.464	2.399	0.806	0.180	-0.561	1.112
Fe	11.93	89.92	40.68	32.02	24.02	5.370	0.811	-0.369
Hg	0.011	0.020	0.015	0.015	0.002	0.000	0.386	-0.300
K	100.4	363.8	225.3	187.3	89.03	19.91	0.428	-1.310
Li	0.500	3.047	1.462	1.223	0.781	0.175	0.686	-0.577
Mg	86.88	373.9	247.9	277.1	88.21	19.72	-0.184	-1.424
Mn	51.50	91.67	83.74	88.56	11.71	2.618	2.158	3.737
Na	30.20	499.8	211.6	145.4	177.8	39.76	0.851	-0.922
Ni	1.844	25.05	10.31	9.951	5.876	1.314	0.669	0.526
Pb	1.447	27.17	11.44	10.80	6.608	1.478	0.432	0.235
Se	0.148	0.303	0.206	0.197	0.042	0.009	0.810	0.294
Sr	49.45	189.5	125.0	127.7	43.49	9.724	-0.149	-0.954
Zn	0.087	10.36	1.679	0.899	2.294	0.513	3.084	11.38

3.17.2 Distribution of Selected Metals in Reducible Fraction of Sediments

Statistical distribution of selected metals levels (mg/kg) in reducible fraction of the sediments during summer is shown in Table 44. Mean levels of As, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Li, Mg, Mn, Na, Ni, Pb, Se, Sr and Zn in reducible fraction of the sediments during summer were noted as 4.107, 2545, 0.828, 10.38, 3.246, 3.931, 2010, 0.057, 142.5, 1.128, 284.8, 84.62, 39.10, 6.681, 15.61, 0.844, 34.10 and 8.985 mg/kg, respectively. Highest average concentration was shown by Ca, followed by Fe, Mg, K, and Mn, while lowest levels were shown by Li, Se, Cd and Hg. Overall, average metal levels in reducible fraction of the sediments revealed following decreasing order: Ca > Fe > Mg > K > Mn > Na > Sr > Pb > Co > Zn > Ni > As > Cu > Cr > Li > Se > Cd > Hg. Most of the metals showed random distribution pattern as evidenced by relatively high SD and SE values, while some of the metals (As, Cd, Hg, Li and Se) exhibited relatively normal distribution pattern. Moreover, predominantly asymmetrical distribution was shown by Ni, followed by Fe, Zn, Se and Pb as evidenced by higher skewness and kurtosis values.

Table 44. Statistical distribution of selected metal levels (mg/kg) in the reducible fraction of sediments during summer ($n = 90$)

	Min	Max	Mean	Median	SD	SE	Skew	Kurt
As	3.084	5.396	4.107	4.058	0.655	0.146	0.254	-0.807
Ca	913.2	4353	2545	2420	1054	235.8	0.239	-0.969
Cd	0.050	1.643	0.828	0.924	0.442	0.099	-0.113	-0.933
Co	0.649	21.36	10.38	9.593	6.602	1.476	0.002	-1.502
Cr	0.996	5.700	3.246	3.192	1.413	0.316	-0.036	-1.144
Cu	0.548	6.524	3.931	3.967	1.781	0.398	-0.184	-0.862
Fe	536.5	2667	2010	2187	519.6	116.2	1.215	1.871
Hg	0.015	0.096	0.057	0.068	0.031	0.007	-0.417	-1.648
K	52.30	245.3	142.5	134.5	55.95	12.51	0.169	-1.172
Li	0.299	1.594	1.128	1.274	0.369	0.082	-0.893	-0.165
Mg	123.8	371.9	284.8	295.3	64.02	14.32	-1.114	1.271
Mn	36.53	141.5	84.62	80.39	31.03	6.937	0.364	-0.830
Na	5.045	84.80	39.10	40.11	19.31	4.318	0.293	0.717
Ni	1.452	26.010	6.681	5.123	5.237	1.171	2.819	10.09
Pb	7.285	29.32	15.61	12.53	7.352	1.644	0.739	-0.906
Se	0.431	1.608	0.844	0.648	0.380	0.085	0.820	-0.837
Sr	3.150	67.56	34.10	33.97	23.44	5.242	0.091	-1.882
Zn	3.593	16.33	8.985	8.671	2.935	0.656	0.760	1.242

Distribution of selected metal concentrations in terms of basic statistical parameters in reducible fraction of the sediments during winter is shown in Table 45. Most of the metals exhibited large variation in their minimum and maximum levels. Mean levels of As, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Li, Mg, Mn, Na, Ni, Pb, Se, Sr and Zn in reducible fraction of the sediments during winter were found at 3.841, 2254, 0.718, 12.48, 4.274, 3.522, 2489, 0.109, 172.2, 1.861, 304.2, 80.84, 43.72, 10.84, 10.88, 0.714, 20.58 and 12.76 mg/kg, respectively. Highest average concentration was shown by Fe, followed by Ca, Mg, K, and Mn, while lowest levels were shown by Li, Cd, Se and Hg in reducible fraction of the sediments. Overall, average metal levels in this fraction during winter revealed following decreasing order: Fe > Ca > Mg > K > Mn > Na > Sr > Zn > Co > Pb > Ni > Cr > As > Cu > Li > Cd > Se > Hg. Most of the metals revealed random distribution pattern, however, comparatively higher dispersion was noted for Ca, Fe, K, Mg, Mn, Na and Sr as shown by their large SD and SE values. Large skewness and kurtosis values for Cd, Cu, Fe, Mn and Zn showed their asymmetric dispersion in reducible fraction of the sediments during winter.

Table 45. Statistical distribution of selected metal levels (mg/kg) in the reducible fraction of sediments during winter (*n* = 90)

	Min	Max	Mean	Median	SD	SE	Skew	Kurt
As	2.882	4.879	3.841	3.790	0.527	0.118	0.121	-0.419
Ca	303.1	4865	2254	2454	1327	296.8	0.058	-1.032
Cd	0.012	2.495	0.718	0.654	0.621	0.139	1.354	2.523
Co	0.324	32.03	12.48	12.26	7.958	1.780	0.648	0.413
Cr	1.447	7.143	4.274	4.013	1.743	0.390	0.197	-1.340
Cu	1.645	6.986	3.522	3.440	1.249	0.279	1.169	2.282
Fe	719.4	5578	2489	2427	950.0	212.4	1.518	5.640
Hg	0.038	0.233	0.109	0.081	0.067	0.015	0.658	-1.197
K	61.34	300.4	172.2	158.9	80.31	17.96	0.442	-1.291
Li	0.100	3.200	1.861	2.221	1.085	0.243	-0.315	-1.529
Mg	171.5	378.4	304.2	308.0	53.491	11.96	-0.967	1.291
Mn	41.54	186.7	80.84	71.24	33.41	7.470	1.945	4.634
Na	12.33	72.08	43.72	42.94	19.55	4.372	-0.033	-1.254
Ni	0.748	22.50	10.84	10.73	5.835	1.305	0.351	-0.268
Pb	1.249	28.47	10.88	10.21	7.205	1.611	0.846	0.546
Se	0.464	1.040	0.714	0.683	0.163	0.036	0.359	-0.722
Sr	0.449	60.38	20.58	14.63	18.32	4.097	0.993	-0.262
Zn	7.910	22.38	12.76	11.84	4.272	0.955	1.257	0.674

3.17.3 Distribution of Selected Metals in Oxidiseable Fraction of Sediments

Basic statistical parameters for distribution of selected metals levels (mg/kg) in oxidiseable fraction of the sediments during summer are given in Table 46. An examination of the data revealed relatively higher mean levels for Fe (205.7 mg/kg), Mg (176.0 mg/kg), Ca (81.46 mg/kg) and K (78.38 mg/kg), followed by, Na (24.59 mg/kg) and Mn (16.82 mg/kg), while Se (0.936 mg/kg), Cu (0.826 mg/kg), As (0.744 mg/kg) and

Hg (0.010 mg/kg) demonstrated the lowest concentrations. The metals exhibited following decreasing order based on average concentration in oxidiseable fraction of the sediments during summer: Fe > Mg > Ca > K > Na > Mn > Ni > Sr > Cr > Pb > Co > Li > Zn > Cd > Se > Cu > As > Hg. Comparatively lower SD and SE values for Hg, Se, As, Li, Cu, Zn and Cr indicated somewhat normal distribution pattern of these metals in the sediments, however, Cd, Na and K showed relatively asymmetrical and random dispersion as shown by relatively higher skewness values.

Table 46. Statistical distribution of selected metal levels (mg/kg) in the oxidiseable fraction of sediments during summer ($n = 90$)

	Min	Max	Mean	Median	SD	SE	Skew	Kurt
As	0.229	1.182	0.744	0.867	0.362	0.081	-0.424	-1.631
Ca	7.650	208.6	81.46	73.91	51.91	11.607	0.739	0.375
Cd	0.149	6.000	2.108	1.296	2.022	0.452	1.097	-0.532
Co	0.100	5.329	2.441	2.796	1.751	0.392	0.056	-1.358
Cr	0.649	6.150	3.841	4.169	1.468	0.328	-0.616	-0.229
Cu	0.050	1.948	0.826	0.750	0.543	0.121	0.584	-0.498
Fe	142.7	275.8	205.7	213.2	41.67	9.317	-0.045	-0.772
Hg	0.003	0.025	0.010	0.004	0.008	0.002	0.814	-1.257
K	30.01	252.9	78.38	71.61	46.21	10.33	2.977	11.40
Li	1.450	3.443	2.387	2.439	0.561	0.125	0.097	-0.644
Mg	140.6	223.3	176.0	174.3	21.63	4.837	0.579	0.209
Mn	12.09	22.10	16.82	17.13	2.340	0.523	-0.056	0.706
Na	1.984	72.80	24.59	13.45	23.90	5.345	1.068	-0.390
Ni	2.450	33.78	14.36	14.04	7.990	1.787	0.750	0.669
Pb	0.199	7.300	3.604	3.182	2.219	0.496	0.348	-1.228
Se	0.673	1.299	0.936	0.947	0.158	0.035	0.575	0.283
Sr	0.598	22.27	8.631	7.261	5.698	1.274	0.669	0.178
Zn	0.248	5.000	2.267	1.974	1.222	0.273	0.560	0.236

Statistical evaluation of selected metal levels in oxidiseable fraction of the sediments during winter (Table 47) showed the highest mean level of Ca (339.0 mg/kg), followed by, Mg (164.9 mg/kg), Fe (156.7 mg/kg), K (57.44 mg/kg), Na (23.03 mg/kg) and Ni (17.82 mg/kg), while Se (0.874 mg/kg), Cd (0.865 mg/kg), As (0.725 mg/kg) and Hg (0.019 mg/kg) demonstrated fairly lower concentrations. The metals exhibited following decreasing order based on average concentration in oxidiseable fraction of the sediments during winter: Ca > Mg > Fe > K > Na > Ni > Mn > Sr > Co > Pb > Cr > Zn > Li > Cu > Se > Cd > As > Hg. Most of the metals showed large dispersion and non-Gaussian distribution as shown by relatively higher SD and SE values. Some of the metals (Ca, Cr, Cu, Na, Sr and Zn) exhibited significant asymmetry in their distribution as shown by skewness and kurtosis values.

Table 47. Statistical distribution of selected metal levels (mg/kg) in the oxidiseable fraction of sediments during winter (*n* = 90)

	Min	Max	Mean	Median	SD	SE	Skew	Kurt
As	0.318	1.121	0.725	0.793	0.252	0.056	-0.350	-1.164
Ca	11.70	1386	339.0	52.37	536.4	119.9	1.298	-0.255
Cd	0.149	1.496	0.865	0.910	0.438	0.098	-0.288	-1.277
Co	0.349	7.300	4.174	4.623	2.300	0.514	-0.271	-1.430
Cr	0.125	8.832	2.564	2.524	2.136	0.478	1.242	2.588
Cu	0.249	3.436	0.960	0.747	0.745	0.167	2.080	5.657
Fe	66.27	227.6	156.7	163.1	44.79	10.016	-0.437	-0.121
Hg	0.009	0.028	0.019	0.020	0.006	0.001	-0.383	-1.197
K	25.67	95.37	57.44	51.57	23.97	5.361	0.265	-1.527
Li	0.699	2.390	1.619	1.699	0.468	0.105	-0.158	-0.483
Mg	119.4	214.4	164.9	167.5	25.46	5.693	0.031	0.065
Mn	7.050	14.17	11.35	11.24	1.682	0.376	-0.635	0.810
Na	3.490	108.8	23.03	12.23	26.63	5.954	2.354	5.547
Ni	3.742	37.20	17.82	17.17	11.09	2.479	0.305	-1.263
Pb	0.032	7.635	3.318	2.573	2.385	0.533	0.452	-0.504
Se	0.577	1.315	0.874	0.871	0.197	0.044	0.699	0.070
Sr	0.100	29.75	8.857	4.656	8.982	2.008	1.027	-0.033
Zn	0.100	7.984	1.998	1.661	1.627	0.364	2.826	10.02

3.17.4 Distribution of Selected Metals in Residual Fraction of Sediments

Table 48 shows basic statistical distribution parameters for selected metal levels (mg/kg) in residual fraction of the sediments during summer. Highest mean concentration was noted for Fe (2229 mg/kg), followed by, K (899.2 mg/kg), Ca (886.2 mg/kg), Mg (525.8 mg/kg), Na (323.1 mg/kg), Mn (216.3 mg/kg) and Zn (112.3 mg/kg), while relatively lower mean levels were found for As (10.07 mg/kg), Sr (9.751 mg/kg), Pb

(8.283 mg/kg), Cd (0.690 mg/kg), Se (0.272 mg/kg) and Hg (0.249 mg/kg). The increasing trend in average metal levels exhibited following pattern: Hg < Se < Cd < Pb < Sr < As < Li < Ni < Co < Cu < Cr < Zn < Mn < Na < Mg < Ca < K < Fe. Comparatively lower SD and SE values for As, Cd, Cr, Co, Hg, Pb, Li and Se indicated their small dispersion in the residual fraction of the sediments. Most of the metals exhibited relatively symmetrical distribution as indicated by rather lower skewness and kurtosis values except Cd and Pb which showed asymmetric distribution.

Table 48. Statistical distribution of selected metal levels (mg/kg) in the residual fraction of sediments during summer ($n = 90$)

	Min	Max	Mean	Median	SD	SE	Skew	Kurt
As	6.602	14.45	10.07	9.734	2.240	0.501	0.359	-0.729
Ca	274.3	1303	886.2	894.7	277.9	62.131	-0.353	-0.481
Cd	0.150	1.984	0.690	0.599	0.403	0.090	1.995	5.200
Co	7.600	26.14	15.49	15.53	4.104	0.918	0.602	1.277
Cr	17.15	25.30	21.48	21.59	2.391	0.535	-0.066	-1.190
Cu	12.90	35.32	21.39	20.16	5.380	1.203	0.987	1.134
Fe	2111	2337	2229	2238	67.75	15.15	-0.391	-0.827
Hg	0.093	0.582	0.249	0.141	0.181	0.040	0.805	-1.247
K	566.2	1067	899.2	903.2	131.7	29.46	-0.977	0.937
Li	9.400	17.63	13.49	13.39	2.323	0.519	-0.001	-0.822
Mg	378.7	601.4	525.8	537.7	55.78	12.47	-1.061	1.126
Mn	157.1	298.4	216.3	215.2	43.43	9.712	0.333	-1.011
Na	6.972	660.2	323.1	375.1	197.9	44.25	-0.217	-1.139
Ni	6.444	25.60	14.33	12.12	6.306	1.410	0.721	-0.798
Pb	1.245	22.82	8.283	8.745	4.889	1.093	1.092	3.003
Se	0.159	0.397	0.272	0.266	0.071	0.016	0.121	-1.101
Sr	0.645	20.65	9.751	8.342	5.891	1.317	0.322	-0.740
Zn	15.15	230.5	112.5	109.2	44.73	10.00	0.467	2.048

Basic statistical parameters related to distribution of selected metal concentrations (mg/kg) in residual fraction of the sediments during winter are given in Table 49. Among the metals, highest mean level was noted for Fe (2230 mg/kg), followed by K (883.3 mg/kg), Ca (840.8 mg/kg), Na (776.2 mg/kg), Mg (465.8 mg/kg), Mn (239.7 mg/kg) and Zn (109.5 mg/kg), while relatively lower mean values were found for Li (11.38 mg/kg), As (10.14 mg/kg), Pb (4.814 mg/kg), Cd (1.499 mg/kg), Se (0.256 mg/kg) and Hg (0.097 mg/kg). Overall, average metal levels exhibited following increasing concentration order in the residual fraction of the sediments: Hg < Se < Cd < Pb < As < Li < Sr < Co < Cu < Cr < Ni < Zn < Mn < Mg < Na < Ca < K < Fe. Most of the metals showed significant difference between mean and median levels as well as considerably higher SD and SE values, thus indicating predominantly non-Gaussian distribution. Higher skewness and kurtosis were noted for Cd, Fe, Sr and Zn, revealing their asymmetric variations in the residual fraction of the sediments.

Table 49. Statistical distribution of selected metal levels (mg/kg) in the residual fraction of sediments during winter ($n = 90$)

	Min	Max	Mean	Median	SD	SE	Skew	Kurt
As	7.570	12.96	10.14	9.973	1.465	0.328	0.331	-0.466
Ca	73.51	1940	840.8	884.8	689.2	154.1	0.204	-1.643
Cd	0.010	16.12	1.499	0.712	3.508	0.784	4.218	18.29
Co	6.014	25.57	15.09	14.79	4.639	1.037	0.228	0.331
Cr	10.63	22.73	16.56	17.21	3.226	0.721	0.011	-0.671
Cu	4.790	22.93	15.61	16.97	5.228	1.169	-0.444	-0.763
Fe	1396	2508	2230	2270	216.2	48.35	-3.197	12.72
Hg	0.053	0.154	0.097	0.091	0.031	0.007	0.337	-1.039
K	719.7	1011	883.3	890.9	81.45	18.21	-0.257	-0.925
Li	4.541	17.53	11.38	11.03	3.380	0.756	-0.001	-0.555
Mg	386.9	549.6	465.8	469.7	46.46	10.39	-0.090	-0.517
Mn	152.0	407.8	239.7	232.6	66.03	14.76	0.851	0.591
Na	101.4	2440	776.2	351.1	845.2	189.0	1.175	-0.336
Ni	14.62	51.15	31.70	28.97	10.16	2.273	0.166	-0.812
Pb	0.298	11.59	4.814	3.030	3.583	0.801	0.609	-1.043
Se	0.169	0.361	0.256	0.257	0.050	0.011	0.267	-0.292
Sr	5.473	32.84	14.53	13.47	6.938	1.551	0.888	0.923
Zn	29.59	152.1	109.5	111.9	29.43	6.581	-1.055	1.707

3.17.5 Comparison of Selected Metal Levels in the Sequentially Extracted Fractions of Sediments

Mean metal levels in different sequentially extracted fractions of the sediments during summer and winter were compared in order to assess their relative contribution and mobility. Mean concentrations of the metals in each fraction of sediments during summer and winter are shown in Figure 32, for comparative evaluation. During summer, highest average level of As was found in residual fraction (10.07 mg/kg), followed by, 4.107 mg/kg in reducible fraction, 1.105 mg/kg in exchangeable fraction and 0.744 mg/kg in oxidiseable fraction, however, during winter the metal levels were noted as 10.14 mg/kg in residual fraction, 3.841 mg/kg in reducible fraction, 0.725 mg/kg in oxidiseable fraction and 0.689 mg/kg in exchangeable fraction. Highest levels of As were observed in the residual fraction, followed by the reducible fraction in both seasons; consequently most of the metal contents were immobilized in the sediments. In case of Ca, during summer, mean level was found at 48160 mg/kg in exchangeable fraction, 2545 mg/kg in reducible fraction, 81.46 mg/kg in oxidiseable fraction and 886.2 mg/kg in residual fraction, while during winter, mean Ca levels were 51193 mg/kg in exchangeable fraction, 2254 mg/kg in reducible fraction, 339.0 mg/kg in oxidiseable fraction and 840.8 mg/kg in residual fraction. Overall, highest Ca concentrations were found in exchangeable fractions, followed by, reducible fractions, while lowest contents were found in oxidiseable fraction. Relatively lower contribution of Ca in oxidizable fraction indicated insignificant association with the organic matter while higher metal levels in exchangeable fraction showed its predominant inorganic contributions. Hence, most of the metal contents were mobile in the sediments during both seasons.

Highest mean level of Cd was found at 2.108 mg/kg in oxidiseable fraction, followed by, 1.345 mg/kg in exchangeable fraction, 0.828 mg/kg in reducible fraction and 0.690 mg/kg in residual fraction during summer. Similarly, during winter the metal levels were found at 1.499 mg/kg in residual fraction, 1.276 mg/kg in exchangeable fraction, 0.865 mg/kg in oxidiseable fraction and 0.718 mg/kg in reducible fraction. Overall, oxidiseable and exchangeable fractions showed higher Cd contents during summer while residual and exchangeable fraction revealed the elevated levels during winter. Consequently, significantly large levels of Cd were bioavailable in the sediments and the elevated levels could be associated with adverse effects to the aquatic biota. Average levels of Co in various fractions during summer were 4.754 mg/kg in exchangeable fraction, 10.38 mg/kg in reducible fraction, 2.441 mg/kg in oxidiseable fraction and 15.49

mg/kg in residual fraction. In comparison, the average metal levels during winter were 9.738 mg/kg in exchangeable fraction, 12.48 mg/kg in reducible fraction, 4.174 mg/kg in oxidiseable fraction and 15.09 mg/kg in residual fraction. Overall, Co showed the following decreasing concentration order during the both seasons: Residual > Reducible > Exchangeable > Oxidiseable. However, considerable metal contents were bioavailable in the sediments during both seasons.

Mean concentrations of Cr in exchangeable reducible, oxidiseable and residual fractions of the sediments were recorded at 2.751, 3.246, 3.841 and 21.48 mg/kg, during summer and 1.346, 4.274, 2.564 and 16.56 mg/kg, during winter, respectively. On comparative basis, highest Cr levels were found in residual fraction, followed by, oxidiseable and reducible fractions. Average levels of Cu extracted in various fractions of the sediments during summer revealed the mean levels at 2.170 mg/kg in exchangeable fraction, 3.931 mg/kg in reducible fraction, 0.826 mg/kg in oxidiseable fraction and 21.39 mg/kg in residual fraction. However, during winter, the metal levels were 2.464 mg/kg in exchangeable fraction, 3.522 mg/kg in reducible fraction, 0.960 mg/kg in oxidiseable fraction and 15.61 mg/kg in residual fraction. Highest concentration of Cu was found in residual fraction, while the lowest concentration was observed in oxidiseable fraction during both seasons. Mean levels of Fe in exchangeable, reducible, oxidiseable and residual fractions were 20.11, 2010, 205.7 and 2229 mg/kg during summer, and 40.68, 2489, 156.7 and 2230 mg/kg during winter, respectively. Comparatively, higher Fe concentrations were observed during winter than summer as indicated in first three fractions, while comparable Fe concentrations were noted in residual fraction during both seasons. Overall, significantly higher Fe levels were found in reducible and residual fractions, while the lowest levels were noted in exchangeable fraction during both seasons. Thus, Fe exhibited considerable bioavailable levels in the sediments.

Average levels of Hg during summer were 0.017 mg/kg in exchangeable fraction, 0.057 mg/kg in reducible fraction, 0.010 mg/kg in oxidiseable fraction and 0.249 mg/kg in residual fraction. During winter, average metal levels were 0.015 mg/kg in exchangeable fraction, 0.109 mg/kg in reducible fraction, 0.019 mg/kg in oxidiseable fraction and 0.097 mg/kg in residual fraction. The highest Hg level was observed in residual fraction, followed by, reducible and exchangeable fractions during summer, while Hg levels were noted to be higher in reducible fraction, followed by residual and oxidiseable fractions during winter. Consequently, significant Hg levels were bioavailable in the water reservoir and the elevated levels may affect the aquatic biota.

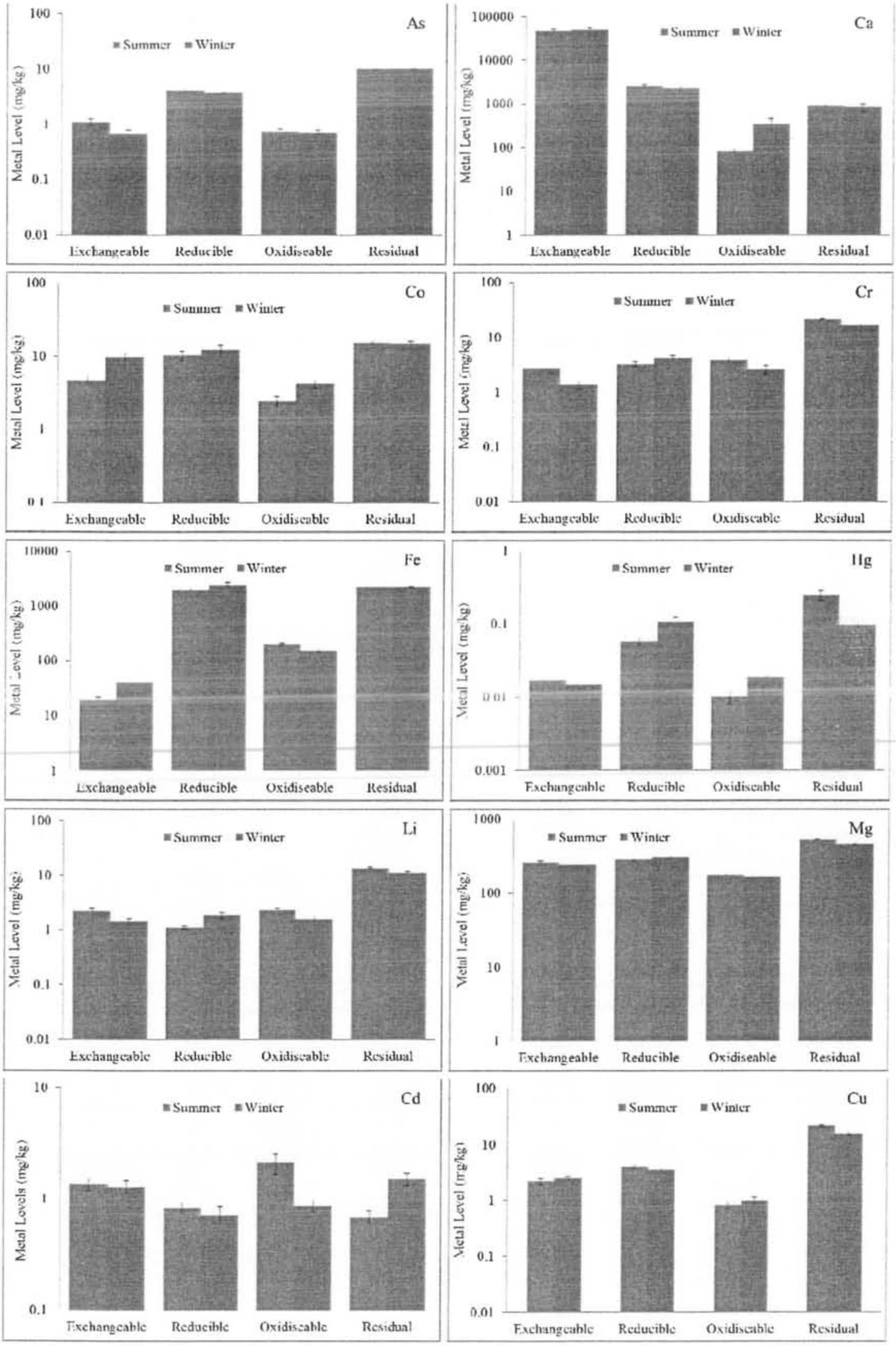

Figure 32. (Contd........)

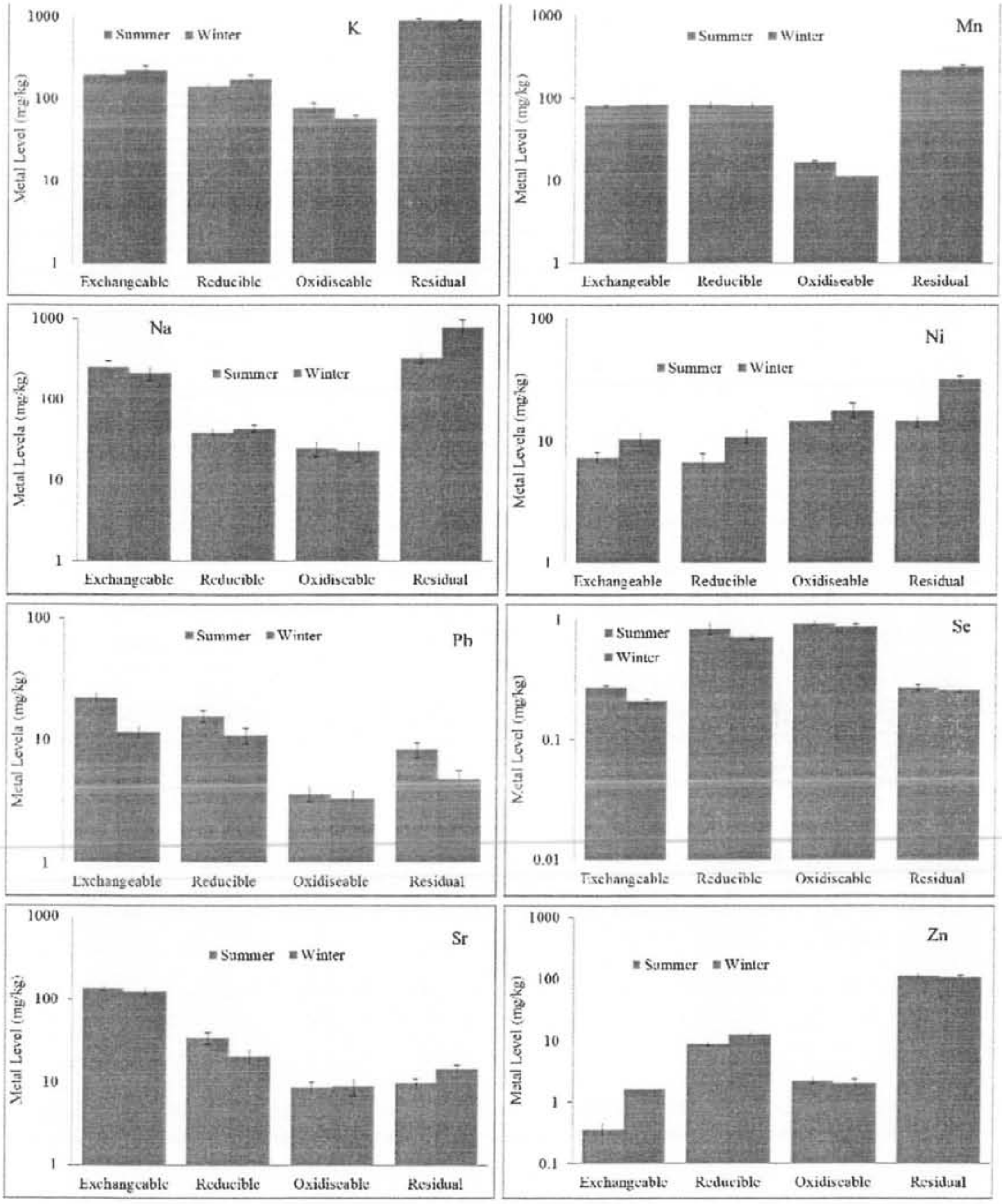

Figure 32. Comparison of selected metal levels (mg/kg, ±SE) in various geochemical fractions of the sediments during summer and winter

Among different fractions of the sediments during summer, mean levels of K were 196.1, 142.5, 78.38 and 899.2 mg/kg in exchangeable, reducible, oxidiseable and residual fractions, respectively. During winter, mean levels were 225.3 mg/kg in exchangeable fraction, 172.2 mg/kg in reducible fraction, 57.44 mg/kg in oxidiseable fraction and 883.3

mg/kg in residual fraction. Hence, K showed following decreasing pattern during both seasons: residual > exchangeable > reducible > oxidiseable. Mean levels of Li during summer were 2.272 mg/kg in exchangeable fraction, 1.128 mg/kg in reducible fraction, 2.387 mg/kg in oxidiseable fraction and 13.49 mg/kg in residual fraction. However, during winter Li showed mean levels at 1.462 mg/kg in exchangeable fraction, 1.861 mg/kg in reducible fraction, 1.619 mg/kg in oxidiseable fraction and 11.38 mg/kg in residual fraction. Residual and oxidiseable fractions exhibited higher Li levels during summer, while residual and reducible fractions showed its elevated levels during winter.

Average levels of Mg were found at 257.2 mg/kg in exchangeable fraction, 284.8 mg/kg in reducible fraction, 176.0 mg/kg in oxidiseable fraction and 525.8 mg/kg in residual fraction during summer. In comparison, the average metal levels during winter were 247.9 mg/kg in exchangeable fraction, 304.2 mg/kg in reducible fraction, 164.9 mg/kg in oxidiseable fraction and 465.8 mg/kg in residual fraction. Mean levels of Mn in sediments were noted at 80.33 mg/kg in exchangeable fraction, 84.62 mg/kg in reducible fraction, 16.82 mg/kg in oxidiseable fraction and 216.3 mg/kg in residual fraction during summer. The data during winter exhibited the mean levels at 83.74 mg/kg in exchangeable fraction, 80.84 mg/kg in reducible fraction, 11.35 mg/kg in oxidiseable fraction and 239.7 mg/kg in residual fraction. On comparative basis, Mn mean levels were highest in residual fractions, followed by significant levels in reducible and exchangeable fractions.

Average levels of Na in exchangeable, reducible, oxidiseable and residual fractions were noted at 253.5, 39.10, 24.59 and 323.1 mg/kg during summer and 211.6, 43.72, 23.03 and 776.2 mg/kg during winter, respectively. Highest contribution of Na was found in residual fraction, while significant levels were observed in exchangeable fraction of the sediments. Average levels of Ni extracted in various fractions of sediments during summer were 7.300 mg/kg in exchangeable fraction, 6.681 mg/kg in reducible fraction, 14.36 mg/kg in oxidiseable fraction and 14.33 mg/kg in residual fraction. During winter, mean concentrations of Ni were found at 10.31 mg/kg in exchangeable fraction, 10.84 mg/kg in reducible fraction, 17.82 mg/kg in oxidiseable fraction and 31.70 mg/kg in residual fraction. Overall, higher concentration of Ni was observed in oxidiseable and residual fractions during both seasons. Highest mean level of Pb during summer was recorded in exchangeable fraction (22.22 mg/kg), followed by, reducible fraction (15.61 mg/kg), residual fraction (8.283 mg/kg) and oxidiseable fraction (3.604 mg/kg). However, the metal levels during winter were found at 11.44 mg/kg in exchangeable fraction, 10.88 mg/kg in reducible fraction, 4.814 mg/kg in residual fraction and 3.318 mg/kg in oxidiseable fraction. Overall, highest Pb levels were found in exchangeable fraction, followed by reducible fraction. As a consequence, it revealed significantly higher bioavailability during both seasons and a number of ecological/health effects may be associated with its elevated concentrations.

Different fractions of the sediment during summer showed average Se levels at 0.270 mg/kg in exchangeable fraction, 0.844 mg/kg in reducible fraction, 0.936 mg/kg in oxidiseable fraction and 0.272 mg/kg in residual fractions. In comparison during winter, the average levels were 0.206 mg/kg in exchangeable fraction, 0.714 mg/kg in reducible fraction, 0.874 mg/kg in oxidiseable fraction and 0.256 mg/kg in residual fractions. On comparative basis, higher concentration of Se was observed during summer than winter. Overall, elevated Se levels were found in oxidiseable and reducible fractions, followed by, residual and exchangeable fractions during both seasons. Similarly, mean levels of Sr in the sediments during summer were noted at 134.2 mg/kg in exchangeable fraction, 34.10 mg/kg in reducible fraction, 8.631 mg/kg in oxidiseable fraction and 9.751 mg/kg in residual fraction. During winter, mean levels were observed at 125.0 mg/kg in exchangeable fraction, 20.58 mg/kg in reducible fraction, 8.857 mg/kg in oxidiseable fraction and 14.53 mg/kg in residual fraction. On comparative basis, higher Sr levels were noted in exchangeable and reducible fractions during both seasons, representing its higher bioavailability during both seasons. The distribution pattern of Zn in various fractions during winter and summer followed the same order: residual > reducible > oxidiseable > exchangeable. Overall, higher concentration of Zn in residual fraction indicated its low extractability, mobility and bioavailability in the sediments.

Generally, predominantly higher contributions of As, Cr, Cu, Hg, K, Li, Mn, Na and Zn were found in the residual fraction while highest mean levels of Na, Ca, Sr and Pb were noted in the exchangeable fraction of the sediments. Significant levels of Cd, Mg, Ni and Co were observed in all fractions; however, excessive levels of Fe were noted in the reducible and residual fractions. Arsenic was mostly retained (60-67%) in the residual fraction, followed by, the reducible fraction (25-26%), while < 9% of As was found in the remaining fractions. Similarly, Cr (60-77%), Cu (64-85%), K (63-74%), Li (61-74%), Mn (48-59%), Hg (53-82%) and Zn (87-95%) were mostly found in the residual fraction, while significant amounts of Cu (22%) and Hg (34%) were noted in the reducible fraction. Likewise, highest percentages of Ca (90-96%) and Sr (56-85%) were noted in the exchangeable fraction. Cadmium contents in the sediments were critically evaluated due to its high toxicity. It was found in oxidiseable fraction (10-70%), followed by, exchangeable

(6-48%), reducible (11-27%) and residual (7-27%) fractions. Maximum proportion of Pb was found in the exchangeable fraction (33-52%) and reducible fraction (21-52%), showing higher mobility and toxicity in the sediments (Zhao *et al.*, 2012a). Consequently, there might be a significant store of contaminant metals which are hazardous to health for both aquatic biota and humans, building up in the sediments. Excessive amounts of Pb are available in an exchangeable form showing higher mobility and toxicity.

It is recognized that sequential extraction method enables prediction of possible metal impact on the aquatic biota. Generally, metal fractions introduced by human activities remained in the exchangeable fraction and bounded to carbonates which are weakly retained. These fractions may equilibrate with aqueous phase thus become readily bioavailable and cause environmental toxicity. The metal fractions bound to Fe–Mn oxides and organic matter can be mobilized when environmental conditions become increasingly reducing or oxidizing (Karbassi and Shankar, 2005; Sundaray *et al.*, 2011). The metal present in inert phase, being of detrital and lattice origin or primary mineral phases, can be regarded as a measure of contribution by natural sources (Salmonas and Forstner, 1980). In the residual fraction, metals are mostly bounded to silicates and are therefore unavailable to the aquatic biota (Tuzen, 2003). The bioavailable fraction refers to the fraction that when the appropriate pH and redox conditions are maintained, the metal can be solubilized and taken up by the aquatic plants or ingested by the animals, causing environmental toxicity. The potential level of bioavailability based on the sum of first three fractions (Passos *et al.*, 2010) during summer revealed following order of mobility (from most to least bioavailable) was: Ca > Sr > Se > Cd > Pb > Ni > Mg > Co > Na > Fe > Mn > As > Cr > K > Li > Hg > Cu > Zn. Generally, Ca, Mg, Na, Fe and Mn were predominant metals in the sediments and their higher contents in bioavailable fraction might be attributed to the formation of metal carbonates and oxides (Carrol *et al.*, 2002; Choque *et al.*, 2013; Sundaray *et al.*, 2011). High proportions of exchangeable and Fe/Mn oxides–bound fractions of the metals in surface sediments could be indicative of their anthropogenic origins and high potential availability (Farkas *et al.*, 2007; Filgueiras *et al.*, 2004). Sedimentary geochemical data of the metals suggested that among non-residual fractions (F1 + F2 + F3), higher concentrations of Ca, Sr, Cd, Pb, Ni and Co might adversely affect the aquatic biota in the Lake. Elevated concentrations of these metals might be contributed by anthropogenic activities, such as, agricultural runoffs, atmospheric deposition, urban runoffs, automobile exhausts and untreated domestic/industrial wastes (Farkas *et al.*, 2007; Filgueiras *et al.*, 2004).

3.18 Spatial Variations of Selected Metals in Sediment Samples

3.18.1 Spatial Variations of Selected Metals during Summer and Winter

Metals data in the sediments were evaluated for spatial variations at three sites (Figure 16) during summer and winter as shown in Figure 33. The statistical data showed insignificant spatial variability of most of the metal levels at three sites of the lake ('A', 'B' and 'C') during both seasons. Hence, more or less similar metal levels were noted in the entire reservoir, which may partially be attributed to the composite sampling methodology and the biological or physical mixing of sediment in the shallow water of the Lake. Therefore, variability in the metal levels was most likely due to seasonal variations rather than spatial disparities.

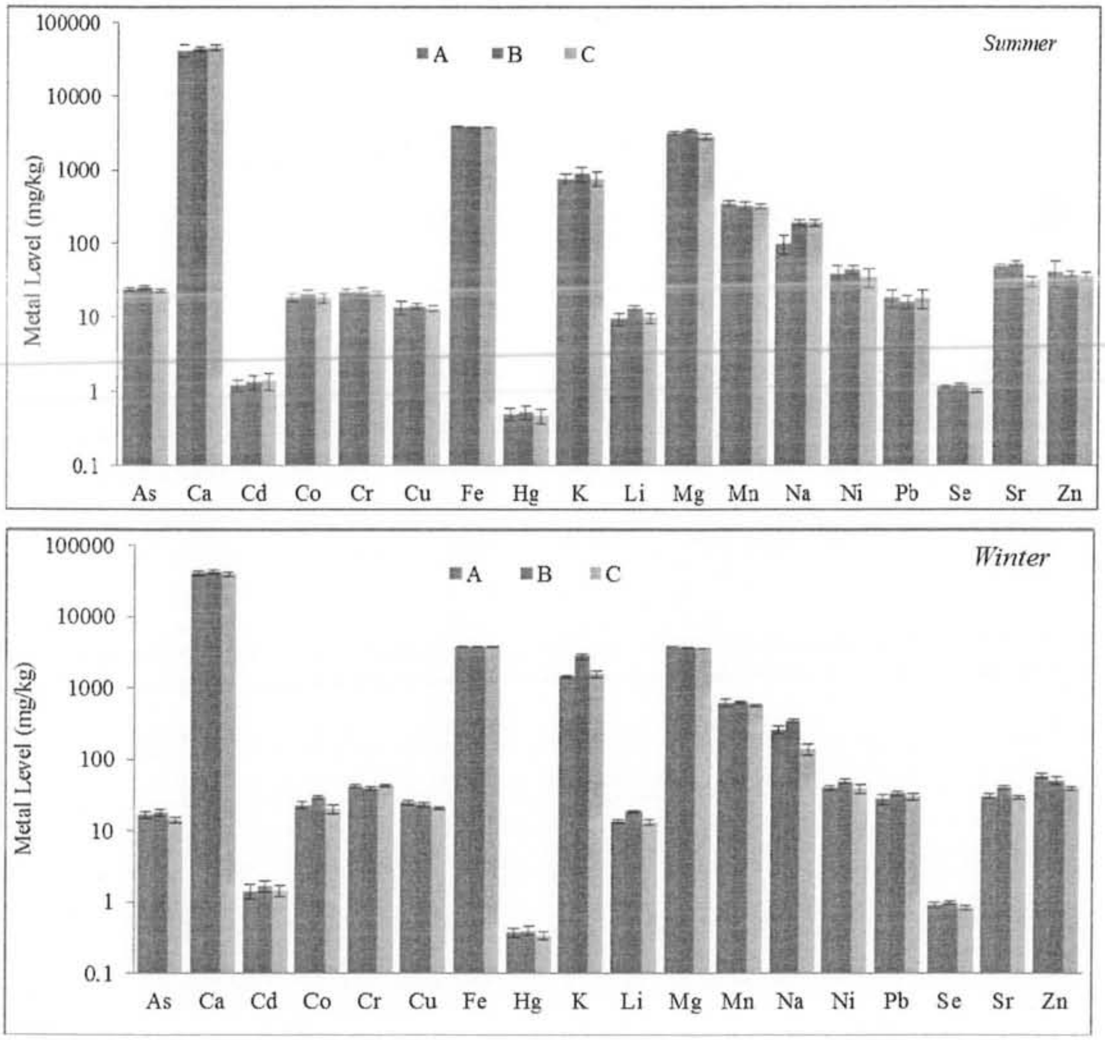

Figure 33. Spatial variations of selected metal levels (mg/kg ± SE) in the acid extract of sediments during summer and winter

3.18.2 Spatial Variations of Selected Metals during Pre-monsoon, Monsoon and Post-monsoon

Metal levels in acid-extract of the sediments were evaluated for spatial variations during pre-monsoon, monsoon and post-monsoon seasons. In order to measure the spatial variability of the metal levels in detail, sediments samples were collected from ten sites of the lake (Figure 17) during three seasons. Average metal levels ± standard error in the sediment samples collected from ten major sites during pre-monsoon are summarized in Table 50. The results revealed significant spatial variations in the metal levels ($p < 0.05$). The minimum to maximum variations of As, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Li, Mg, Mn, Na, Ni, Pb, Se, Sr and Zn in the sediments during pre-monsoon at different sites were noted as 12.74-19.61, 36800-70484, 2.585-8.986, 16.19-61.96, 23.25-37.66, 19.93-39.79, 3422-5107, 0.210-0.471, 1015-1670, 14.89-23.74, 1222-1447, 318.0-502.5, 294.6-1107, 26.81-74.88, 33.42-75.59, 1.972-3.140, 114.4-297.1 and 55.44-198.4 mg/kg, respectively. On comparative basis, highest concentrations of Cd, Co, Cr, Cu, Hg, Li, Mn, Ni, Pb, Se, Sr and Zn were found at site 10 (S-10); As, Ca, K and Mg at site 9 (S-9); and Fe at site 8 (S-8), while most of the metals showed lowest concentrations at site 1 and 2 (S-1 & S-2) during pre-monsoon.

In case of the sediment samples collected during monsoon, the ranges of As, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Li, Mg, Mn, Na, Ni, Pb, Se, Sr and Zn at the ten sites were assessed as 15.14-22.14, 36413-56830, 2.203-10.12, 13.52-63.76, 20.58-37.62, 17.73-35.00, 3226-5903, 0.171-0.328, 1377-1610, 12.51-22.90, 1045-1195, 339.9-486.0, 476.0-1405, 29.95-91.38, 23.45-72.30, 2.108-3.257, 101.5-279.0 and 70.72-184.6 mg/kg, respectively (Table 51). Comparative assessment at different sites revealed that highest mean concentrations of the metals were found at site 10 (S-10) except Ca, Cd, K, Mg and Na which exhibited highest concentrations at sites S-2, S-9, S-1, S-4 and S-6, respectively, during monsoon.

During post-monsoon season, the sediment samples collected from different sites showed significant variations in the concentrations of As, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Li, Mg, Mn, Na, Ni, Pb, Se, Sr and Zn which exhibited lowest–highest levels as 13.43-19.40, 30547-65684, 1.842-12.45, 10.97-66.13, 18.10-37.93, 15.69-30.54, 3060-6762, 0.193-0.302, 1066-1598, 10.23-22.27, 1076-1317, 331.5-473.9, 344.4-2641, 33.37-108.7, 13.69-69.66, 1.740-2.781, 89.57-263.5 and 62.32-172.5 mg/kg, respectively (Table 52).

Table 50. Comparison of average levels of selected metals (mg/kg ± SE) in the sediments from various sites during pre-monsoon

Sites		As	Ca	Cd	Co	Cr	Cu	Fe	Hg	K	Li	Mg	Mn	Na	Ni	Pb	Se	Sr	Zn
S-1	Mean	12.74	36800	2.585	16.19	30.37	19.93	3422	0.316	1504	16.04	1264	379.8	1107	26.81	33.42	2.093	118.6	79.76
	SE	0.387	297.5	0.805	0.860	0.856	0.456	282.5	0.065	7.760	0.135	58.19	8.135	43.24	1.761	2.302	0.241	11.13	5.758
S-2	Mean	15.29	70484	3.164	18.57	23.25	25.58	4016	0.210	1228	14.89	1263	380.9	797.3	34.37	41.45	2.337	114.4	55.44
	SE	0.312	9131	0.214	0.084	0.222	0.461	168.9	0.009	103.1	0.418	43.44	4.293	119.4	1.260	2.123	0.246	1.186	16.62
S-3	Mean	15.35	42567	3.721	26.62	30.18	24.76	4042	0.343	1360	18.25	1222	318.0	794.0	39.53	44.26	1.972	181.4	115.3
	SE	1.195	1635	0.369	1.592	1.481	1.156	20.3	0.074	1.063	1.068	36.66	0.150	122.9	4.201	1.559	0.075	2.565	8.119
S-4	Mean	14.62	44141	4.687	25.95	29.83	26.46	4442	0.369	1670	21.53	1447	319.6	908.8	31.65	44.93	2.386	176.1	120.4
	SE	0.078	2125	0.030	0.993	1.716	0.396	227.5	0.083	21.39	0.135	12.79	6.342	20.46	2.675	0.028	0.217	9.683	5.829
S-5	Mean	17.55	53595	4.814	33.47	33.24	28.06	4639	0.238	1584	17.28	1246	367.1	939.2	39.81	47.56	2.653	185.2	118.3
	SE	0.839	2789	0.402	0.755	0.832	0.635	23.7	0.003	15.56	0.203	2.98	23.35	30.99	2.418	0.735	0.208	5.903	3.302
S-6	Mean	17.53	65433	5.855	35.40	32.57	28.04	4393	0.382	1347	19.57	1358	424.8	828.9	39.60	45.68	2.215	222.4	108.8
	SE	1.761	4279	0.017	1.003	0.917	0.993	149.1	0.075	53.23	0.774	61.61	9.734	63.33	1.016	0.626	0.133	11.20	4.336
S-7	Mean	16.56	52598	6.335	36.31	34.07	26.48	4610	0.409	1395	18.10	1273	411.8	633.7	47.53	49.72	2.693	197.5	123.2
	SE	0.504	4030	0.892	0.054	0.026	0.196	30.28	0.084	116.6	0.274	37.05	4.088	29.12	2.444	4.125	0.313	7.149	12.91
S-8	Mean	19.54	48608	8.398	40.32	33.72	29.93	5107	0.265	1287	22.46	1298	417.0	425.8	50.18	55.15	2.949	233.6	149.1
	SE	0.604	6343	0.276	0.504	0.247	0.889	94.13	0.008	18.17	0.296	15.03	0.901	76.42	2.425	2.681	0.291	15.82	5.779
S-9	Mean	19.61	53506	7.872	47.81	36.08	36.14	4890	0.435	1015	22.05	1241	463.6	294.6	52.53	64.64	2.534	238.7	174.1
	SE	1.522	5178	0.182	3.177	0.074	0.329	9.075	0.094	144.2	0.066	96.31	3.626	27.55	2.572	2.966	0.108	8.567	2.028
S-10	Mean	19.11	53668	8.986	61.96	37.66	39.79	5098	0.471	1123	23.74	1296	502.5	340.9	74.88	75.59	3.140	297.1	198.4
	SE	0.581	3012	0.337	3.567	0.785	1.713	22.72	0.097	24.68	0.754	11.31	25.39	15.31	2.813	1.385	0.362	4.257	26.95

Table 51. Comparison of average levels of selected metals (mg/kg ± SE) in the sediments from various sites during monsoon

Sites		As	Ca	Cd	Co	Cr	Cu	Fe	Hg	K	Li	Mg	Mn	Na	Ni	Pb	Se	Sr	Zn
S-1	Mean	15.14	36413	2.203	13.52	24.26	17.73	3226	0.228	1610	13.50	1117	354.1	703.9	29.95	23.45	2.108	107.8	70.72
	SE	0.604	6610	0.424	1.450	1.620	0.164	380.2	0.034	81.34	0.762	58.25	3.510	6.828	1.169	1.302	0.191	0.698	4.413
S-2	Mean	16.89	56830	2.636	18.60	20.58	22.21	4035	0.171	1464	12.51	1142	373.2	670.6	37.59	34.34	2.371	101.5	71.62
	SE	0.471	4539	0.171	0.968	0.232	1.058	206.4	0.008	66.22	0.153	0.130	5.562	46.57	1.709	1.162	0.179	0.709	11.85
S-3	Mean	16.54	43454	3.133	26.38	24.45	21.45	4179	0.245	1377	16.26	1063	339.9	581.8	44.94	30.19	2.111	155.8	125.3
	SE	0.609	3405	0.301	1.380	0.618	1.567	25.61	0.041	11.13	1.209	27.96	9.475	72.10	2.285	1.063	0.090	5.104	1.698
S-4	Mean	17.29	46676	3.661	28.73	27.12	22.51	4575	0.264	1505	18.62	1195	359.7	532.6	45.64	35.12	2.408	155.4	114.2
	SE	0.237	4071	0.000	2.084	0.741	0.073	124.1	0.046	36.37	0.375	7.950	10.96	0.593	0.145	1.923	0.158	3.938	0.374
S-5	Mean	19.17	47930	3.938	37.11	29.26	24.67	4567	0.194	1544	15.86	1045	375.8	577.7	48.53	38.90	2.699	163.7	117.0
	SE	0.025	2466	0.277	0.596	0.939	0.630	14.27	0.003	12.12	0.218	14.78	21.82	51.18	2.983	2.563	0.131	0.870	2.091
S-6	Mean	18.77	40792	4.527	40.97	28.41	26.15	4852	0.274	1443	17.50	1124	429.8	1405	58.44	36.78	2.378	195.4	111.4
	SE	1.090	2167	0.026	0.208	0.412	0.260	18.89	0.040	8.934	0.323	14.76	7.249	109.7	3.139	0.309	0.155	4.674	2.242
S-7	Mean	19.50	45511	5.505	41.52	30.88	25.33	4771	0.295	1570	17.79	1165	428.2	1392	61.44	42.30	2.711	202.6	126.2
	SE	0.707	1150	0.219	0.766	0.325	0.163	31.70	0.045	94.25	0.129	0.318	5.872	1.830	0.486	1.848	0.246	6.219	7.725
S-8	Mean	21.36	45238	7.653	46.09	31.46	28.28	5259	0.217	1562	20.29	1159	442.4	805.9	69.71	46.96	3.004	222.0	142.3
	SE	0.408	2396	0.202	0.488	0.560	0.002	37.17	0.008	33.37	0.103	52.50	7.976	188.4	3.076	1.676	0.207	13.15	1.873
S-9	Mean	20.97	48259	10.115	52.52	36.28	32.05	5149	0.310	1437	21.25	1138	466.7	476.0	75.20	56.04	2.694	245.6	164.1
	SE	0.728	1115	1.699	1.863	0.940	0.246	54.33	0.052	62.71	0.337	59.33	21.74	41.19	6.169	0.908	0.125	0.624	2.148
S-10	Mean	22.14	43908	8.159	63.76	37.62	35.00	5903	0.328	1460	22.90	1167	486.0	546.7	91.38	72.30	3.257	279.0	184.6
	SE	0.719	828.4	0.222	2.489	1.169	0.303	384.9	0.015	17.67	0.580	8.945	20.30	19.22	2.257	1.008	0.278	0.784	14.51

Table 52. Comparison of average levels of selected metals (mg/kg ± SE) in the sediments from various sites during post-monsoon

Sites		As	Ca	Cd	Co	Cr	Cu	Fe	Hg	K	Li	Mg	Mn	Na	Ni	Pb	Se	Sr	Zn
S-1	Mean	13.60	48879	1.842	10.97	18.38	15.69	3060	0.220	1422	11.09	1218	331.5	549.1	33.37	13.69	1.740	97.98	62.32
	SE	0.664	15255	0.048	2.053	2.399	0.785	481.3	0.017	155.6	1.666	71.25	1.083	27.17	4.110	0.315	0.105	9.728	14.62
S-2	Mean	14.07	63234	2.133	18.81	18.10	19.04	4089	0.193	1433	10.23	1274	368.9	780.6	41.15	27.54	1.975	89.57	88.45
	SE	1.132	1548	0.130	1.861	0.245	1.664	245.7	0.010	17.34	0.110	43.73	6.882	229.0	2.173	0.210	0.080	2.610	7.187
S-3	Mean	13.43	59678	2.573	26.38	18.94	18.33	4354	0.234	1144	14.42	1140	365.0	574.8	50.75	16.38	1.866	131.6	136.5
	SE	0.137	6376	0.235	1.181	0.238	1.992	71.72	0.023	21.29	1.361	25.48	19.19	46.80	0.389	0.577	0.088	7.688	4.707
S-4	Mean	15.46	65684	2.667	31.77	24.65	18.75	4749	0.253	1066	15.88	1207	403.0	344.4	60.04	25.63	1.992	136.2	109.1
	SE	0.334	7454	0.029	3.194	0.227	0.249	21.80	0.025	44.73	0.619	4.879	15.68	19.07	2.966	3.891	0.071	1.772	5.077
S-5	Mean	15.80	59181	3.097	41.08	25.55	21.50	4535	0.219	1224	14.58	1076	387.9	420.1	57.68	30.60	2.255	143.6	116.8
	SE	0.882	8591	0.154	1.953	1.054	0.630	4.928	0.005	37.59	0.235	35.82	20.48	89.43	3.575	4.414	0.030	4.155	0.898
S-6	Mean	15.11	30547	3.241	46.91	24.50	24.49	5354	0.262	1276	15.58	1140	438.6	2476	77.82	28.20	2.108	170.1	115.1
	SE	0.135	819	0.069	1.421	0.088	0.472	111.2	0.020	36.98	0.125	28.81	4.830	194.8	5.291	0.005	0.149	1.805	0.169
S-7	Mean	17.35	54487	4.725	47.11	27.97	24.41	4975	0.284	1459	17.64	1317	448.4	2641	75.89	35.26	2.237	209.6	130.3
	SE	0.726	6737	0.451	1.486	0.680	0.130	33.40	0.021	54.76	0.015	37.75	15.89	24.82	3.420	0.413	0.135	5.344	2.610
S-8	Mean	17.62	57833	6.976	52.26	29.47	26.89	5458	0.246	1554	18.31	1278	471.8	1470	89.88	39.19	2.513	212.4	136.9
	SE	1.314	706	0.130	1.485	0.878	0.884	19.46	0.011	78.84	0.089	101.6	16.92	366.8	3.755	0.687	0.085	10.59	2.016
S-9	Mean	16.87	60044	12.449	57.70	36.80	28.25	5454	0.295	1598	20.64	1288	473.9	825.5	98.55	47.93	2.364	254.7	155.7
	SE	0.256	2554	3.596	0.565	1.815	0.165	118.2	0.029	30.22	0.611	35.53	47.31	69.37	9.821	1.143	0.119	9.820	6.344
S-10	Mean	19.40	49644	7.406	66.13	37.93	30.54	6762	0.302	1532	22.27	1297	473.8	945.5	108.71	69.66	2.781	263.5	172.5
	SE	0.669	4962	0.108	1.432	3.133	1.105	750.5	0.063	56.80	0.411	31.19	15.38	29.92	7.347	0.639	0.143	5.832	2.193

On comparative basis, highest concentrations of the metals during post-monsoon were found at site 10 (S-10) except Ca, Cd, K, Mg and Na which showed highest concentrations at S-9, S-9, S-4, S-7 and S-9, respectively. Overall, concentrations of most of the metals were found to be significantly higher at sampling sites S-6 to S-10 which were located in close vicinity to highly urbanized (Mirpur city) and semi-urban areas (Chakswari and Islamghar). Numerous anthropogenic activities around these sites alongside untreated sewage, agricultural, urban & industrial wastes as well as automobile emissions were the major contributing sources towards elevated metal levels. However, the lowest metal levels were found at sites S-1 and S-2 owing of less anthropogenic disruption around these sites. Nonetheless, higher metal concentrations at sites S-6 to S-10 might be due to greater retention of water that agglutinates the metals at these sites, while the constant/continuous water flow could not provide enough time for the metal's precipitation at sites S-1 and S-2 in the reservoir.

3.19 Sediments Texture and Particle Size Distribution

Sediment texture is one of the most important characteristics, affecting many of the physical and chemical characteristics, such as, water/nutrient holding capacities, surface area, retention capability and hydraulic conductivity. Spatial distribution and variability of various sediment texture fractions (coarse sand, fine sand, silt and clay) is increasingly required for input into the ecological, hydrologic, climatic and other environmental models. A sound approach to the textural characteristic of the sediment is to obtain a detailed particle size distribution by using sieves and sedimentation of dispersed particles in a liquid. In this way, a more accurate description of texture can be obtained. Commonly, particle size distributions are reported as cumulative distributions and different functions have been proposed to fit the experimental data. Particle size distribution for the sediments estimated in the present study during summer is shown in Table 53 where average percentages of finest particles/clay (1-5 μm) were 20.31%. Among the silt particles (5-75 μm), highest mean percentage was shown by the particles in range of 30-75 μm (9.647%). Coarse particles were classified as fine sand ranging from 75-200 μm, and higher mean percentage was shown by the particles in range of 100-200 μm (12.95%). However, highest contribution was shown by the particles in range of 200-400 μm (9.889 to 25.38%) with mean value of 16.08%. Medium sand (400-2000 μm) percentage ranged from 8.472 to 20.70% with a mean value of 14.56%.

Table 53. Statistical distribution parameters for various particle size fractions (%) in the sediments during summer

	Min	Max	Mean	Median	SD	SE	Skew	Kurt
1-1.35 µm	7.470	19.59	12.60	11.63	3.276	0.732	0.662	-0.288
1.35-5 µm	2.020	18.18	7.707	7.535	3.625	0.811	1.110	2.505
5-10 µm	3.920	11.22	5.819	5.000	2.096	0.469	1.511	1.721
10-20 µm	1.980	10.10	5.621	5.925	2.205	0.493	0.433	0.239
20-30 µm	0.750	6.110	2.907	2.525	1.477	0.330	0.940	0.425
30-75 µm	5.050	18.62	9.647	9.360	3.700	0.827	0.834	0.394
75-100 µm	3.728	15.78	9.701	10.01	3.595	0.804	-0.034	-0.918
100-200 µm	6.840	19.53	12.95	12.69	3.737	0.836	0.247	-0.752
200-400 µm	9.889	25.38	16.08	15.54	4.148	0.928	0.592	-0.172
400-2000 µm	8.472	20.70	14.56	14.57	3.167	0.708	-0.060	-0.499
> 2000 µm	0.398	4.328	1.448	1.058	1.116	0.250	1.788	2.199

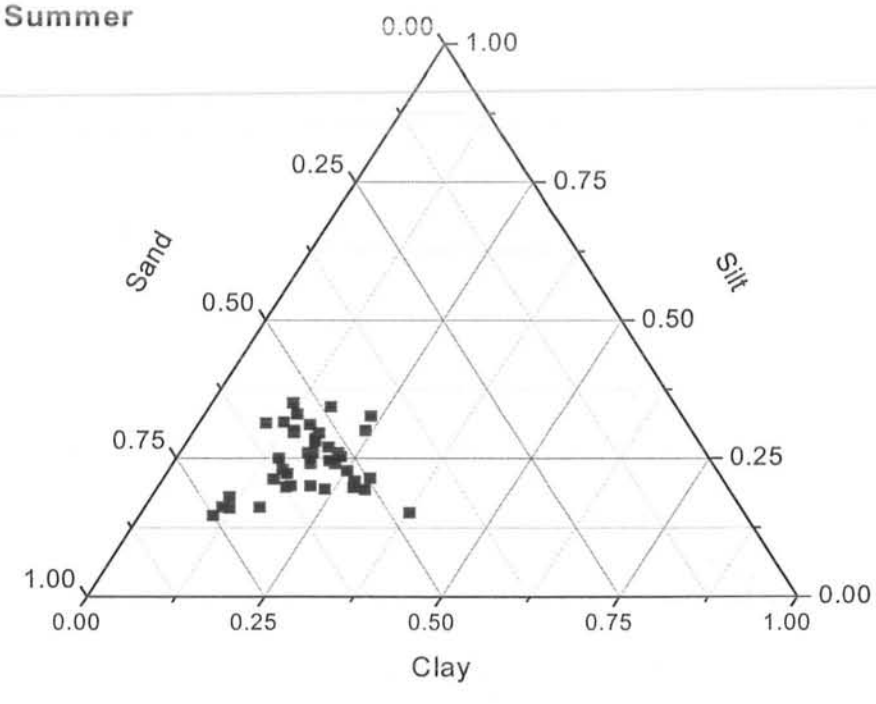

Figure 34. Ternary diagram showing texture of the sediment samples during summer

Table 54. Statistical distribution parameters for various particle size fractions (%) in the sediments during winter

	Min	Max	Mean	Median	SD	SE	Skew	Kurt
1-1.35 μm	4.848	22.44	11.63	10.56	4.891	1.094	1.149	0.794
1.35-5 μm	1.020	12.00	5.884	5.500	2.900	0.648	0.693	0.297
5-10 μm	2.000	11.22	5.206	4.580	2.227	0.498	1.003	1.291
10-20 μm	1.200	12.00	6.350	6.540	2.673	0.598	-0.120	0.126
20-30 μm	1.000	6.530	3.137	3.000	1.720	0.385	0.368	-1.093
30-75 μm	5.000	17.00	9.795	9.135	3.405	0.761	0.447	-0.467
75-100 μm	1.528	11.76	4.764	4.163	2.788	0.623	1.249	1.141
100-200 μm	4.348	20.91	11.69	10.60	5.067	1.133	0.439	-0.760
200-400 μm	13.45	56.47	31.57	31.83	12.32	2.755	0.340	-0.663
400-2000 μm	3.517	13.38	8.545	8.458	2.386	0.534	-0.072	0.014
> 2000 μm	0.111	1.421	0.524	0.414	0.366	0.082	1.297	1.009

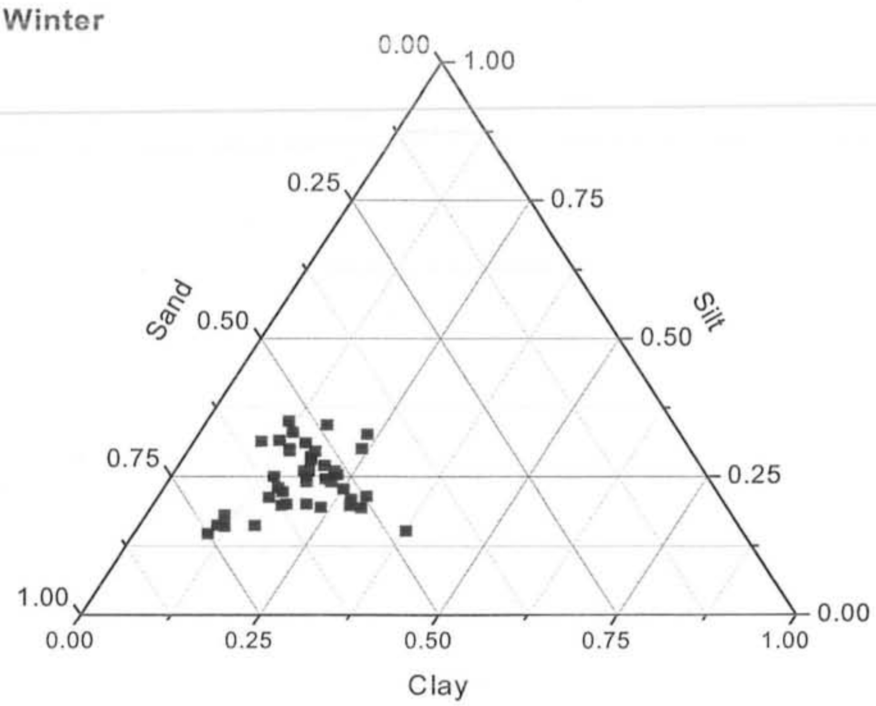

Figure 35. Ternary diagram showing texture of the sediment samples during winter

The coarse sand with the particles having diameter greater than 2000 µm showed average contribution of 1.448%, indicating quite low contents in the sediments during summer. Ternary diagram for the sediments' texture during summer (n = 40) is shown in Figure 34. The soil samples were fractionated into three main groups: fine particles represented by clay (1-5 µm), medium sized silt particles (5-75 µm), and coarse particles as shown by sand (> 75 µm). The sediments during summer mostly belonged to sandy loam (19% clay, 20% silt, & 61% sand) class of the texture.

During winter, as shown in Table 54, mean value of clay or fine particles in the range of 1-5 µm was 17.51%. Similarly, among silt particles in the range of 5-75 µm, highest mean percentage was shown by the particles in the range of 30-75 µm (9.795%). Coarse particles were classified as fine sand (75-200 µm), medium sand (200-400 µm) and coarse sand (400-2000 µm). Highest mean contribution was shown by the particles in the range of 200-400 µm (31.57%), while >2000 µm exhibited average percentage of 0.524%, which indicated fairly lower contents of coarse particles in the sediments during winter. Ternary diagram showing the prevailing texture of the sediments collected during winter is shown in Figure 35. The sediments contained high percentage of sand, and low percentages of silt and clay. All the samples belonged to the triangle of sandy loam, which contained about 17% clay, 20% silt and 63% sand. Higher percentage of sand in these sediments indicated their low bulk density, high porosity and low water holding capacity. On comparative basis, the sediments collected during winter and summer exhibited similar texture and no significant variations in the particle size distribution were observed.

3.20 Correlation Study of Physicochemical Parameters and Selected Metals in Sediment Samples

3.20.1 Correlation Study of Physicochemical Parameters in Sediment Samples

The correlation coefficient matrix for physiochemical parameters in the sediments during summer and winter is shown in Table 55. Among the physiochemical parameters, EC and TDS showed a direct strong relationship which is quite obvious. Likewise, pH and total alkalinity also revealed strong associations during summer (r = 0.936) and winter(r = 0.776), respectively. It is established fact that higher pH is always associated with higher alkalinity. During winter, pH showed inverse relationship with T (r = -0.370), while MC exhibited inverse correlation with TDS (r = -0.420). Other parameters showed weak or insignificant relationships with each another in the sediment samples during both seasons.

The correlation coefficient matrix pertaining to physiochemical parameters in the sediment during pre-monsoon, monsoon and post-monsoon seasons is also shown in Table 55. EC and TDS revealed positive correlation with T (r = 0.372), whereas TA showed inverse relationship with OM (r = 0.357) during post-monsoon season. Rest of the parameters exhibited independent variations as evidenced by weak or insignificant relationships with each other in the sediments during all three seasons.

Table 55. Correlation coefficient (r)* matrix of physicochemical parameters in the sediments during summer, winter, pre-monsoon, monsoon and post-monsoon

		T	pH	EC	TDS	TA	MC
Summer	pH	-0.187					
	EC	-0.120	-0.216				
	TDS	-0.121	-0.214	1.000			
	TA	-0.131	0.936	-0.128	-0.127		
	MC	0.203	0.010	0.029	0.025	-0.056	
	OM	0.346	-0.141	0.123	0.122	-0.122	-0.075
Winter	pH	-0.370					
	EC	-0.081	0.165				
	TDS	-0.081	0.167	1.000			
	TA	-0.205	0.776	-0.021	-0.020		
	MC	0.208	0.134	-0.419	-0.420	0.206	
	OM	-0.058	0.055	0.259	0.259	0.160	-0.120
Pre-monsoon	pH	0.097					
	EC	-0.073	-0.182				
	TDS	-0.073	-0.183	1.000			
	TA	0.053	-0.079	-0.112	-0.112		
	MC	0.279	0.070	0.289	0.289	0.019	
	OM	-0.068	-0.177	0.029	0.029	-0.021	-0.153
Monsoon	pH	0.034					
	EC	0.240	-0.253				
	TDS	0.239	-0.253	1.000			
	TA	-0.019	0.045	0.079	0.079		
	MC	0.182	-0.044	0.130	0.130	-0.114	
	OM	-0.271	-0.129	-0.266	-0.266	-0.314	0.149
Post-monsoon	pH	-0.137					
	EC	0.372	-0.139				
	TDS	0.372	-0.139	1.000			
	TA	-0.257	-0.079	0.068	0.068		
	MC	0.020	0.262	-0.193	-0.193	-0.271	
	OM	0.072	-0.113	-0.013	-0.013	-0.357	-0.217

*r-values > 0.350 or < -0.350 are significantly correlated at $p < 0.05$

3.20.2 Correlation Study of Selected Metals in Calcium Nitrate Extract of Sediment Samples

The correlation coefficient matrix pertaining to selected metal levels in calcium nitrate extract of the sediments during summer is shown in Table 56. Numerous strong and significant relationships were observed among the metals including K-Mg (r = 0.647), As-Hg (r = 0.591), K-Fe (r = 0.569), Na-Mg (r = 0.568), Cr-Se (r = 0.554) and Ni-Fe (r = 0.523). In addition, some significant positive correlations were found between Mg-Ca, Mn-Ca, Ni-Co, Mg-Co, Li-Co, K-Co, Fe-Co, Na-Cu, Mg-Cu, K-Cu, Zn-Fe, Na-K, Mn-K and Mn-Mg. Overall, Mg, Na, Mn, K and Cu exhibited parallel relationships with other metals which may be associated with their possibly common/shared source contribution in the aquatic system.

The correlation coefficient matrix for selected metal levels in calcium nitrate extract of the sediments during winter is also shown in Table 56. Among the metals, Hg exhibited strong correlation with Se (r = 0.725), while Ca was found to be strongly correlated with Cu (r = 0.590) and K (r = 0.573), and inversely related to Na (r = -0.639). Similarly, Cd revealed significant associations with Fe (r = 0.473), K (r = 0.339), Mn (r = 0.366) and Pb (r = 0.309), whereas Cu displayed considerable relationships with Mn (r = 0.459), K (r = 0.350) and Fe (r = 0.346) in addition to inverse association with Na (r = -0.458). Significant correlations were also found among other variables, such as, As-Se, Fe-Zn, Zn-Hg, Fe-Li, Mg-Mn and Na-Pb. Some significant inverse correlations were also found between Cd-Cr, K-Na, Fe-Sr and Li-Pb. Among the selected metals, K, Mn and Mg showed similar and strong mutual correlations, thus indicating their common origins and mutual variations in the sediments of Mangla Lake.

The correlation coefficient matrix of selected metal concentrations in calcium nitrate extract of the sediments during pre-monsoon is shown in Table 57. Very strong positive correlations were observed among As-Hg (r = 0.887), Cr-Fe (r = 0.787), Zn-Se (r = 0.668), Mg-K (r = 0.605), Ca-Sr (r = 0.603), Na-Li (r = 0.567), Cd-Cu (r = 0.560) and Se-Pb (r = 0.506). In addition, some significant correlations were also noted between Cu-Co, Mn-Cd, Mn-Co, Mn-Cu, Ca-Pb, Se-Ca, Se-Ni, Sr-Cu, Sr-Mg, Sr-Mn and Sr-Pb in the sediments. Nevertheless, significant inverse relationships were observed between Cr-Ca, As-Li, Na-Ca, Fe-Ni, Na-Ni, Na-Pb, Na-Se and Hg-Se, manifesting their opposing variations in calcium nitrate extract of the sediments during pre-monsoon season.

Table 56 Correlation coefficient (r)* matrix for selected metal levels in calcium nitrate extract of the sediments during summer (below the diagonal) and winter (above the diagonal)

	As	Ca	Cd	Co	Cr	Cu	Fe	Hg	K	Li	Mg	Mn	Na	Ni	Pb	Se	Sr	Zn
As	1	-0.079	-0.086	0.236	0.049	-0.035	-0.160	0.008	-0.226	0.181	-0.200	-0.045	0.143	-0.191	0.141	0.440	-0.067	-0.097
Ca	0.112	1	-0.157	-0.190	0.159	0.590	0.109	-0.047	0.573	-0.161	0.288	0.237	-0.639	-0.348	-0.245	-0.005	-0.160	0.161
Cd	-0.053	-0.052	1	0.298	-0.381	0.179	0.473	0.211	0.339	0.212	0.162	0.366	-0.050	0.145	0.309	-0.118	-0.181	0.222
Co	0.050	0.100	0.256	1	-0.266	-0.040	0.180	0.100	-0.005	0.304	0.042	0.305	0.276	-0.197	0.348	0.078	-0.118	-0.083
Cr	-0.059	0.304	0.165	0.108	1	0.258	-0.042	-0.133	-0.042	-0.343	-0.175	0.159	-0.119	0.042	0.037	0.302	0.123	-0.157
Cu	-0.123	-0.018	-0.321	0.029	-0.213	1	0.346	0.005	0.350	-0.176	0.163	0.459	-0.458	-0.225	-0.133	0.074	-0.301	0.180
Fe	-0.273	0.245	0.100	0.414	0.255	-0.185	1	0.162	0.179	0.396	-0.269	0.025	-0.145	-0.048	-0.076	-0.014	-0.493	0.472
Hg	0.591	0.004	-0.002	0.083	-0.001	0.093	-0.155	1	0.126	0.151	0.065	-0.046	-0.096	0.239	0.188	0.725	-0.011	0.460
K	-0.183	0.264	-0.048	0.390	-0.067	0.457	0.569	-0.022	1	-0.033	0.606	0.574	-0.438	0.057	-0.092	-0.029	-0.033	0.176
Li	0.077	-0.214	0.335	0.366	-0.061	-0.168	-0.049	0.255	-0.218	1	-0.229	-0.270	-0.084	-0.057	-0.405	-0.080	-0.047	0.161
Mg	0.108	0.399	-0.237	0.458	-0.314	0.391	0.288	0.103	0.647	-0.171	1	0.591	-0.188	0.068	0.039	-0.089	0.341	-0.045
Mn	-0.206	0.446	-0.026	0.064	0.305	0.280	0.127	-0.227	0.489	-0.089	0.367	1	-0.180	-0.080	0.208	-0.034	-0.080	-0.164
Na	0.128	-0.024	-0.235	-0.025	-0.282	0.401	0.011	0.139	0.364	-0.285	0.568	0.186	1	0.129	0.386	-0.028	0.183	-0.027
Ni	-0.038	0.123	0.328	0.404	0.288	-0.197	0.523	-0.255	0.199	0.105	0.046	-0.056	-0.038	1	0.131	0.094	-0.047	0.205
Pb	0.007	-0.014	0.299	0.279	-0.291	-0.147	0.328	0.005	0.268	0.198	0.240	0.050	0.043	0.197	1	0.215	0.144	-0.001
Se	0.014	0.422	0.279	-0.093	0.554	-0.271	0.157	-0.308	-0.052	-0.121	-0.369	0.149	-0.168	0.308	-0.222	1	-0.052	0.258
Sr	0.031	0.400	0.294	0.266	0.131	-0.067	-0.172	-0.110	-0.103	-0.007	0.293	0.249	-0.136	-0.018	-0.117	0.035	1	-0.164
Zn	-0.051	-0.268	0.192	0.300	0.316	-0.039	0.493	0.039	0.162	0.335	-0.292	-0.097	-0.120	0.447	0.186	0.222	-0.482	1

**r*-values > 0.350 or < -0.350 are significantly correlated at $p < 0.05$

Table 57. Correlation coefficient (r)* matrix for selected metal levels in calcium nitrate extract of the sediments during pre-monsoon

	As	Ca	Cd	Co	Cr	Cu	Fe	Hg	K	Li	Mg	Mn	Na	Ni	Pb	Se	Sr	Zn
As	1																	
Ca	0.071	1																
Cd	-0.229	-0.184	1															
Co	-0.035	0.110	0.618	1														
Cr	-0.108	-0.421	-0.237	-0.292	1													
Cu	-0.235	0.183	0.560	0.445	-0.302	1												
Fe	0.046	-0.329	-0.342	-0.304	0.787	-0.213	1											
Hg	0.887	-0.033	-0.133	0.089	-0.212	-0.244	-0.065	1										
K	0.199	0.206	-0.378	-0.142	0.007	-0.261	0.097	0.118	1									
Li	-0.379	-0.300	0.199	0.055	-0.029	0.044	-0.091	-0.226	-0.125	1								
Mg	-0.108	-0.033	-0.260	-0.013	0.137	-0.170	0.047	-0.090	0.605	0.041	1							
Mn	0.111	-0.097	0.488	0.467	0.320	0.419	0.172	0.109	-0.025	0.096	0.128	1						
Na	-0.082	-0.653	0.206	0.076	0.257	0.103	0.235	0.030	-0.059	0.567	0.256	0.280	1					
Ni	0.190	0.288	-0.206	0.150	-0.317	-0.427	-0.375	0.211	0.334	-0.118	-0.026	-0.197	-0.523	1				
Pb	0.086	0.407	-0.349	-0.286	0.166	-0.127	0.256	-0.084	0.346	-0.129	-0.061	0.026	-0.422	0.223	1			
Se	-0.173	0.379	-0.200	-0.018	0.125	-0.042	-0.033	-0.478	0.078	-0.184	-0.173	-0.149	-0.416	0.369	0.506	1		
Sr	-0.115	0.603	-0.060	0.094	-0.050	0.390	-0.052	-0.180	0.259	-0.020	0.378	0.444	-0.130	-0.028	0.362	0.113	1	
Zn	-0.190	0.192	-0.069	0.149	-0.011	-0.015	-0.125	-0.347	0.040	-0.077	0.030	-0.128	-0.159	0.268	0.187	0.668	-0.008	1

*r-values > 0.350 or < -0.350 are significantly correlated at $p < 0.05$

Table 58. Correlation coefficient (r)* matrix for selected metal levels in calcium nitrate extract of the sediments during monsoon

	As	Ca	Cd	Co	Cr	Cu	Fe	Hg	K	Li	Mg	Mn	Na	Ni	Pb	Se	Sr	Zn
As	1																	
Ca	-0.041	1																
Cd	-0.089	-0.295	1															
Co	-0.066	0.327	0.542	1														
Cr	-0.206	0.405	-0.160	0.428	1													
Cu	-0.383	0.159	0.595	0.583	0.210	1												
Fe	0.070	0.257	0.254	0.568	0.275	0.286	1											
Hg	0.802	0.059	0.038	0.054	-0.149	-0.249	-0.010	1										
K	0.025	0.499	-0.368	0.031	0.321	-0.106	0.214	0.085	1									
Li	-0.369	-0.155	0.501	0.150	-0.067	0.209	-0.022	-0.162	0.000	1								
Mg	-0.143	0.393	-0.168	-0.002	0.363	-0.093	-0.095	0.030	0.625	0.373	1							
Mn	0.121	0.335	0.163	0.620	0.655	0.325	0.267	0.038	0.299	-0.027	0.237	1						
Na	0.198	-0.077	0.181	0.104	0.288	-0.083	0.016	0.447	0.236	0.479	0.564	0.120	1					
Ni	0.111	-0.101	0.330	0.387	0.269	0.240	0.247	0.244	0.131	0.428	0.106	0.424	0.476	1				
Pb	0.007	0.075	-0.306	-0.089	0.280	-0.174	0.415	-0.145	0.036	-0.333	-0.061	-0.012	-0.138	-0.202	1			
Se	0.349	0.381	-0.072	0.308	0.087	0.062	0.628	0.172	0.266	-0.404	-0.053	0.100	-0.088	-0.049	0.381	1		
Sr	0.001	0.669	0.031	0.606	0.699	0.268	0.330	0.121	0.400	0.130	0.577	0.651	0.448	0.308	0.061	0.240	1	
Zn	0.137	-0.309	0.314	0.309	0.296	0.099	0.188	0.008	-0.117	0.055	-0.069	0.514	0.076	0.171	0.052	0.022	0.016	1

*r-values > 0.350 or < -0.350 are significantly correlated at $p < 0.05$

Table 59. Correlation coefficient (r)* matrix for selected metal levels in calcium nitrate extract of the sediments during post-monsoon

	As	Ca	Cd	Co	Cr	Cu	Fe	Hg	K	Li	Mg	Mn	Na	Ni	Pb	Se	Sr	Zn
As	1																	
Ca	-0.411	1																
Cd	-0.017	-0.206	1															
Co	-0.113	0.370	0.308	1														
Cr	-0.274	0.579	-0.191	0.674	1													
Cu	-0.302	0.181	0.377	0.247	-0.058	1												
Fe	-0.096	0.133	0.393	0.519	0.191	0.053	1											
Hg	0.243	0.001	0.028	0.023	0.011	-0.226	0.225	1										
K	-0.246	0.529	-0.199	0.004	0.070	0.227	-0.237	-0.250	1									
Li	-0.239	-0.127	0.060	-0.146	-0.005	-0.505	0.098	-0.335	-0.105	1								
Mg	-0.318	0.706	-0.236	0.016	0.338	-0.155	-0.129	-0.033	0.552	0.060	1							
Mn	0.058	0.535	-0.065	0.620	0.568	0.091	-0.005	-0.097	0.425	-0.239	0.304	1						
Na	0.027	0.314	-0.130	0.211	0.363	-0.169	0.217	0.554	-0.241	-0.196	0.416	-0.047	1					
Ni	0.154	-0.231	0.190	0.288	0.260	-0.287	0.053	-0.042	-0.110	0.490	-0.273	0.266	-0.237	1				
Pb	0.387	-0.563	0.053	-0.153	-0.360	-0.525	0.243	0.022	-0.380	0.445	-0.347	-0.400	-0.063	0.309	1			
Se	0.602	-0.095	0.285	0.173	-0.160	0.052	0.376	0.745	-0.258	-0.456	-0.249	0.043	0.401	0.023	0.147	1		
Sr	-0.233	0.584	0.273	0.603	0.528	0.087	0.416	0.302	0.129	-0.102	0.472	0.468	0.453	0.087	-0.248	0.289	1	
Zn	-0.051	0.320	-0.251	0.324	0.376	0.116	-0.395	-0.040	0.289	-0.318	0.105	0.474	-0.139	-0.031	-0.482	-0.153	0.187	1

**r*-values > 0.350 or < -0.350 are significantly correlated at $p < 0.05$

The data on metal-to-metal correlations in calcium nitrate extract of the sediments during monsoon are given in Table 58, wherein the *r*-values > 0.300 or < -0.300 are significant at $p < 0.05$. Strong positive correlations were observed between As-Hg (*r* = 0.802), Cr-Sr (*r* = 0.699), Ca-Sr (*r* = 0.669), Cr-Mn (*r* = 0.655), Mn-Sr (*r* = 0.651), Fe-Se (*r* = 0.628), K-Mg (*r* = 0.625), Co-Mn (*r* = 0.620), Co-Sr (*r* = 0.606), Cd-Cu (*r* = 0.595), Co-Cu (*r* = 0.583), Mg-Sr (*r* = 0.577), Fe-Co (*r* = 0.568), Mg-Na (*r* = 0.564), Cd-Co (*r* = 0.542), Mn-Zn (*r* = 0.514) and Cd-Li (*r* = 0.501). In addition, statistically significant correlations were found between Ca-Cr, Ca-K, Ca-Mg, Co-Cr, Co-Ni, Cr-Mg, Fe-Pb, Na-Hg, K-Sr, Li-Mg, Li-Na, Ni-Li, Mn-Ni, Na-Ni and Na-Sr. Conversely, some significant negative correlations were observed between Li-Se (*r* = -0.404) and As-Li (*r* = -0.369). The correlation study indicated mutual variations among most of the metals in calcium nitrate extract of the sediments during monsoon season. As-Hg and Cr-Sr showed strongest association in calcium nitrate extract of the sediments during monsoon season which pointed out that these metals might be originated from common sources.

The correlation coefficient matrix for selected metal levels in calcium nitrate extract of the sediments during post-monsoon is shown in Table 59. In this case, strong correlations were observed between Se-Hg (*r* = 0.745), Mg-Ca (*r* = 0.706), Cr-Co (*r* = 0.674), Co-Mn (*r* = 0.620), Sr-Co (*r* = 0.603), Se-As (*r* = 0.602), Sr-Ca (*r* = 0.584), Cr-Ca (*r* = 0.579), Mn-Cr (*r* = 0.568), Na-Hg (*r* = 0.554), K-Mg (*r* = 0.552), Mn-Ca (*r* = 0.535), K-Ca (*r* = 0.529), Sr-Cr (*r* = 0.528), Fe-Co (*r* = 0.519) and Ni-Li (*r* = 0.490). In addition, several significant positive correlations were also found between Ca-Co, Fe-Cd, K-Mn, Na-Cr, Na-Mg, As-Pb, Li-Pb, Fe-Se, Na-Se, Fe-Sr, Mg-Sr, Mn-Sr, Na-Sr, Zn-Cr and Zn-Mn. Nonetheless, significant negative correlations were observed between As-Ca, Li-Cu, Ca-Pb, Cr-Pb, Cu-Pb, K-Pb, Mn-Pb, Li-Se and Fe-Zn, thus manifesting inverse association of these metals during post-monsoon season. Consequently, the correlations among selected metals in the sediments were found to be significantly diverse during summer, winter, pre-monsoon, monsoon and post-monsoon seasons.

3.20.3 Correlation Study of Selected Metals in Acid-Extract of Sediment Samples

The correlation coefficient matrix pertaining to selected metal levels in acid extract of the sediments during summer is shown in Table 60. Many significant relationships were observed among the metals; Cr was found to be significantly associated with Fe (*r* = 0.742), Cu (*r* = 0.495), Mn (*r* = 0.461), Li (*r* = 0.415), Ni (*r* = 0.403) and Zn (*r* = 0.359); while inversely related to Sr (*r* = -0.382) and Pb (*r* = -0.345). Similarly, Cu was strongly correlated with Mg (*r* = 0.809), Fe (*r* = 0.774), Zn (*r* = 0.756), Li (*r* = 0.735), K (*r* = 0.654), Mn (*r* = 0.512) and Na (*r* = 0.405), while inversely associated with Pb (*r* = -388). Iron was also strongly correlated with Zn (*r* = 0.677), Mn (*r* = 0.645), Mg (*r* = 0.539), Li (*r* = 0.485), and Ni (*r* = 0.353), while negatively correlated with Pb (*r* = -0.309). Likewise, K was strongly correlated with Mg (*r* = 0.735), Li (*r* = 0.729), Zn (*r* = 0.473), Sr (*r* = 0.447) and Na (*r* = 0.402), whereas inversely associated with Pb (*r* = -0.304). Mg showed significant correlations with Li (*r* = 0.801), Zn (*r* = 0.488), Na (*r* = 0.394), Sr (*r* = 0.394) and Mn (*r* = 0.385), while inversely related to Pb (*r* = -0.336). Mn exhibited positive relationship with Zn (*r* = 0.344) and negative with Pb (*r* = -0.467). Li showed positive relationships with Na (*r* = 0.624) and Zn (*r* = 0.474) whilst negative relationship with Pb (*r* = -0.329). Some negative associations were also noted among Ni-Se, Pb-Zn, Cd-Na, As-Cr, As-Fe, As-Mn and As-Na, manifesting their opposing variations.

The correlation coefficient matrix for selected metal levels in acid extract of the sediments during winter is shown in Table 60. Many significant relationships were observed among selected metals; Ca was found to be significantly associated with Cd (*r* = 0.372) and Mg (*r* = 0.355), Cd was significantly correlated with Mn (*r* = 0.457); As with Se (*r* = 0.470) and Co showed positive association with Pb (*r* = 0.369) and negative with K (*r* = -0.461). Similarly, Cr showed negative associations with Na (*r* = -0.497), Cu exhibited strong relationships with Zn (*r* = 0.956), K (*r* = 0.819), Fe (*r* = 0.792), Mg (*r* = 0.705), Ni (*r* = 0.594), Li (*r* = 0.443) and Mn (*r* = 0.407), while negative correlation with Sr (*r* = -0.384). Likewise, Fe showed strong correlations with Zn (*r* = 0.787), Mg (*r* = 0.767), Mn (*r* = 0.580), K (*r* = 0.509) and Ni (*r* = 0.505), Hg was correlated with Se (*r* = 0.536), K exhibited direct relationship with Zn (*r* = 0.740), Li (*r* = 0.661), Mg (*r* = 0.636) and Ni (*r* = 0.517), whereas negative relationship with Sr (*r* = -0.466), Pb (*r* = -0.427) and Na (*r* = -0.393). Lithium showed positive relationship with Mg (*r* = 0.542), and negative relationships with Na (*r* = -0.470) and Pb (*r* = -0.455). Magnesium was found to be strongly associated with Zn (*r* = 0.673) and Mn (*r* = 0.309), Mn with Zn (*r* = 0.527) and Ni (*r* = 0.415), and Ni with Zn (*r* = 0.591). Strontium exhibited inverse association with Zn (*r* = -0.398). The correlation study thus revealed mutual variations in the selected metal contents which were indicative of their common origin in the sediments during winter season.

The correlation coefficients related to selected metal contents in acid extract of the sediments during pre-monsoon is shown in Table 61. Very strong relationships ($r > 0.750$) were observed between Pb-Co (*r* = 0.918), Ni-Co (*r* = 0.909), Pb-Cu (*r* = 0.906), Pb-Ni (*r*

= 0.901), Sr-Co (*r* = 0.893), Sr-Cd (*r* = 0.864), Pb-Sr (*r* = 0.856), Cu-Co (*r* = 0.855), Ni-Cu (*r* = 0.841), Sr-Zn (*r* = 0.841), Co-Cd (*r* = 0.836), Cu-Zn (*r* = 0.828), Li-Sr (*r* = 0.827), Ni-Cd (*r* = 0.826), Cu-Sr (*r* = 0.823), Ni-Sr (*r* = 0.822), Pb-Cd (*r* = 0.810), Cu-Cd (*r* = 0.803), Mn-Co (*r* = 0.787), Pb-Zn (*r* = 0.782), Mn-Ni (*r* = 0.776), Fe-Co (*r* = 0.770), Li-Co (*r* = 0.768), Cr-Zn (*r* = 0.763), Li-Zn (*r* = 0.759), Pb-Li (*r* = 0.755) and Cr-Sr (*r* = 0.751). A number of statistically significant correlations were observed between As-Cd, Co-As, Cr-As, Cr-Cd, Cr-Co, As-Cu, Cr-Cu, As-Fe, Fe-Cd, Fe-Cr, Fe-Cu, Hg-Co, Li-As, Li-Cr, Li-Cu, Li-Fe, Mg-K, Mn-As, Mn-Cd, Mn-Cr, Mn-Cu, Mn-Fe, Na-K, Ni-As, Ni-Cr, Ni-Fe, Ni-Li, Pb-As, Pb-Cr, Pb-Fe, Pb-Mn, Se-As, Cd-Se, Se-Cr, Se-Cu, Se-Fe, Se-Ni, Sr-As, Sr-Fe, Sr-Mn, Zn-As, Zn-Cd, Zn-Fe and Zn-Ni. However, various inverse relationships were also found, such as, K was negatively correlated with As, Ca, Cd, Co, Cu, Mn, Ni, Pb and Sr, while Na exhibited converse associations with As, Cd, Co, Cr, Cu, Fe, Li, Mn, Ni, Pb, Se, Sr and Zn in the sediment samples.

The correlation coefficient matrix pertaining to selected metal levels in acid extract of the sediments during monsoon is shown in Table 62. Several strong relationships were observed among the selected metals: As with Ni (*r* = 0.910), Se (*r* = 0.884), Cu (*r* = 0.867), Co (*r* = 0.834), Sr (*r* = 0.815), Pb (*r* = 0.795), Cr (*r* = 0.772), Fe (*r* = 0.764), Zn (*r* = 0.745), Li (*r* = 0.725) and Cd (*r* = 0.710); Cd with Cu (*r* = 0.849), Sr (*r* = 0.839), Mn (*r* = 0.814), Cr (*r* = 0.789), Li (*r* = 0.785), Pb (*r* = 0.785), Co (*r* = 0.778), Zn (*r* = 0.764), Ni (*r* = 0.755), Fe (*r* = 0.677), Se (*r* = 0.501) and Hg (*r* = 0.489); Co with Sr (*r* = 0.957), Ni (*r* = 0.935), Cu (*r* = 0.911), Pb (*r* = 0.910), Cr (*r* = 0.895), Fe (*r* = 0.886), Zn (*r* = 0.861), Li (*r* = 0.859), Mn (*r* = 0.818), Se (*r* = 0.587) and Hg (*r* = 0.447); Cr with Sr (*r* = 0.917), Li (*r* = 0.901), Cu (*r* = 0.896), Ni (*r* = 0.889), Pb (*r* = 0.851), Zn (*r* = 0.824), Mn (*r* = 0.788), Fe (*r* = 0.737), Se (*r* = 0.573) and Hg (*r* = 0.438). Similarly, Cu showed significant positive relationships with Ni (*r* = 0.939), Pb (*r* = 0.935), Sr (*r* = 0.914), Mn (*r* = 0.860), Li (*r* = 0.848), Fe (*r* = 0.836), Zn (*r* = 0.826) and Se (*r* = 0.681); Fe exhibited significantly strong associations with Sr (*r* = 0.829), Ni (*r* = 0.822), Pb (*r* = 0.802), Li (*r* = 0.776), Mn (*r* = 0.774), Zn (*r* = 0.666) and Se (*r* = 0.587); Hg was found to be significantly associated with Sr (*r* = 0.516), Mn (*r* = 0.488), Pb (*r* = 0.436), Zn (*r* = 0.428) and Li (*r* = 0.427); Li with Sr (*r* = 0.917), Zn (*r* = 0.863), Ni (*r* = 0.862), Pb (*r* = 0.828), Mn (*r* = 0.701) and Se (*r* = 0.505); and Mn with Sr (*r* = 0.826), Ni (*r* = 0.805), Pb (*r* = 0.790), Zn (*r* = 0.604) and Se (*r* = 0.513).

Table 60. Correlation coefficient (r)* matrix for selected metal levels in acid extract of the sediments during summer (below the diagonal) and winter (above the diagonal)

	As	Ca	Cd	Co	Cr	Cu	Fe	Hg	K	Li	Mg	Mn	Na	Ni	Pb	Se	Sr	Zn
As	1	-0.331	-0.344	-0.079	0.239	0.103	-0.023	-0.086	0.045	-0.158	-0.078	-0.178	-0.031	-0.149	-0.010	0.470	-0.249	0.073
Ca	-0.008	1	0.372	-0.033	0.135	0.109	0.194	0.274	0.044	0.192	0.355	0.206	0.010	-0.007	0.038	0.073	0.135	0.103
Cd	0.113	-0.092	1	-0.153	-0.016	0.205	0.283	-0.001	0.079	0.239	0.228	0.457	0.098	0.186	0.179	-0.188	0.212	0.211
Co	0.135	-0.287	-0.053	1	-0.098	-0.346	-0.212	0.093	-0.461	-0.318	-0.274	-0.170	0.311	-0.200	0.369	0.155	0.109	-0.311
Cr	-0.447	-0.206	0.081	0.058	1	0.164	0.234	0.039	0.112	0.113	0.242	0.054	-0.497	0.331	0.191	0.057	-0.256	0.041
Cu	-0.135	0.082	-0.114	0.206	0.495	1	0.792	0.172	0.819	0.443	0.705	0.407	-0.078	0.594	-0.235	0.073	-0.384	0.956
Fe	-0.371	-0.102	0.005	0.013	0.742	0.774	1	0.020	0.509	0.242	0.767	0.580	0.110	0.505	-0.097	-0.078	-0.163	0.787
Hg	0.181	0.021	-0.157	0.370	-0.193	0.085	-0.110	1	0.147	0.283	0.097	0.074	-0.070	0.189	-0.045	0.536	-0.149	0.171
K	0.231	0.064	-0.011	0.238	0.115	0.654	0.275	0.116	1	0.661	0.636	0.017	-0.393	0.517	-0.427	0.002	-0.466	0.740
Li	-0.139	0.045	-0.092	0.120	0.415	0.735	0.485	-0.016	0.729	1	0.542	-0.156	-0.470	0.207	-0.455	-0.075	-0.084	0.336
Mg	-0.099	0.139	0.139	0.003	0.263	0.809	0.539	-0.060	0.735	0.801	1	0.309	-0.191	0.253	-0.240	-0.087	-0.326	0.673
Mn	-0.488	0.273	-0.117	-0.035	0.461	0.512	0.645	-0.097	0.007	0.310	0.385	1	0.233	0.415	0.198	0.026	0.028	0.527
Na	-0.360	-0.179	-0.527	-0.036	0.132	0.405	0.260	0.082	0.402	0.624	0.394	0.094	1	-0.064	0.250	0.054	0.327	0.077
Ni	-0.095	-0.135	0.138	0.294	0.403	0.202	0.353	0.198	0.144	0.216	0.208	0.276	-0.115	1	-0.069	-0.084	-0.168	0.591
Pb	0.058	0.027	-0.120	-0.224	-0.345	-0.388	-0.309	-0.230	-0.304	-0.329	-0.336	-0.467	0.028	-0.244	1	0.209	-0.139	-0.195
Se	0.472	0.216	0.236	-0.121	-0.113	0.054	-0.124	-0.193	0.159	-0.019	0.133	-0.124	-0.368	-0.352	0.067	1	-0.204	0.101
Sr	0.220	0.360	-0.056	0.245	-0.382	0.294	-0.230	0.321	0.447	0.227	0.394	-0.036	0.040	-0.063	-0.112	0.225	1	-0.398
Zn	-0.105	-0.124	-0.324	0.318	0.359	0.756	0.677	0.240	0.473	0.474	0.488	0.344	0.456	0.154	-0.379	-0.247	0.033	1

*r-values > 0.350 or < -0.350 are significantly correlated at $p < 0.05$

Table 61. Correlation coefficient (r)* matrix for selected metal levels in acid extract of the sediments during pre-monsoon

	As	Ca	Cd	Co	Cr	Cu	Fe	Hg	K	Li	Mg	Mn	Na	Ni	Pb	Se	Sr	Zn
As	1																	
Ca	0.089	1																
Cd	0.741	0.055	1															
Co	0.662	0.058	0.836	1														
Cr	0.589	-0.122	0.749	0.733	1													
Cu	0.709	0.236	0.803	0.855	0.687	1												
Fe	0.635	0.303	0.728	0.770	0.590	0.739	1											
Hg	-0.251	0.027	0.195	0.401	0.186	0.185	0.095	1										
K	-0.359	-0.361	-0.513	-0.449	-0.278	-0.582	-0.330	-0.190	1									
Li	0.512	-0.126	0.764	0.768	0.646	0.706	0.707	0.371	-0.240	1								
Mg	0.039	-0.097	-0.024	0.051	-0.048	-0.005	0.183	-0.138	0.562	0.347	1							
Mn	0.520	0.230	0.641	0.787	0.562	0.691	0.508	0.319	-0.636	0.466	-0.111	1						
Na	-0.522	-0.194	-0.752	-0.783	-0.448	-0.749	-0.726	-0.347	0.637	-0.601	0.081	-0.624	1					
Ni	0.646	0.062	0.826	0.909	0.681	0.841	0.636	0.283	-0.554	0.676	-0.077	0.776	-0.717	1				
Pb	0.653	0.108	0.810	0.918	0.689	0.906	0.710	0.364	-0.476	0.755	0.025	0.699	-0.809	0.901	1			
Se	0.491	0.092	0.583	0.457	0.507	0.605	0.603	-0.362	-0.319	0.312	0.063	0.405	-0.478	0.535	0.454	1		
Sr	0.572	0.054	0.864	0.893	0.751	0.823	0.692	0.484	-0.401	0.827	0.044	0.597	-0.724	0.822	0.856	0.390	1	
Zn	0.628	-0.143	0.736	0.763	0.763	0.828	0.620	0.240	-0.256	0.759	0.120	0.454	-0.622	0.696	0.782	0.455	0.841	1

*r-values > 0.350 or < -0.350 are significantly correlated at $p < 0.05$

Table 62. Correlation coefficient (r)* matrix for selected metal levels in acid extract of the sediments during monsoon

	As	Ca	Cd	Co	Cr	Cu	Fe	Hg	K	Li	Mg	Mn	Na	Ni	Pb	Se	Sr	Zn
As	1																	
Ca	0.165	1																
Cd	0.710	0.060	1															
Co	0.834	-0.021	0.778	1														
Cr	0.772	-0.160	0.789	0.895	1													
Cu	0.867	0.146	0.849	0.911	0.869	1												
Fe	0.764	0.300	0.677	0.886	0.737	0.836	1											
Hg	0.009	-0.371	0.489	0.447	0.438	0.356	0.316	1										
K	-0.175	-0.543	-0.190	-0.077	0.087	-0.208	-0.293	0.119	1									
Li	0.725	-0.067	0.785	0.859	0.901	0.848	0.776	0.427	-0.040	1								
Mg	0.327	0.257	0.041	0.204	0.172	0.192	0.319	-0.134	0.076	0.297	1							
Mn	0.705	-0.007	0.814	0.818	0.788	0.860	0.774	0.488	-0.059	0.701	0.185	1						
Na	0.053	-0.097	-0.070	0.041	-0.036	-0.027	0.050	0.025	0.022	-0.081	-0.064	0.201	1					
Ni	0.910	-0.013	0.755	0.935	0.889	0.939	0.822	0.315	-0.093	0.862	0.338	0.805	0.015	1				
Pb	0.795	0.076	0.785	0.910	0.851	0.935	0.802	0.436	-0.057	0.828	0.259	0.790	-0.173	0.909	1			
Se	0.884	0.230	0.501	0.587	0.573	0.681	0.587	-0.162	-0.207	0.505	0.399	0.513	-0.055	0.744	0.615	1		
Sr	0.815	-0.093	0.839	0.957	0.917	0.914	0.829	0.516	-0.064	0.917	0.255	0.826	0.011	0.947	0.896	0.600	1	
Zn	0.745	-0.142	0.764	0.861	0.824	0.826	0.666	0.428	-0.053	0.863	0.110	0.604	-0.175	0.871	0.831	0.543	0.901	1

*r-values > 0.350 or < -0.350 are significantly correlated at $p < 0.05$

Table 63. Correlation coefficient (r)* matrix for selected metal levels in acid extract of the sediments during post monsoon

	As	Ca	Cd	Co	Cr	Cu	Fe	Hg	K	Li	Mg	Mn	Na	Ni	Pb	Se	Sr	Zn
As	1																	
Ca	0.043	1																
Cd	0.500	-0.012	1															
Co	0.672	-0.115	0.630	1														
Cr	0.657	-0.116	0.623	0.855	1													
Cu	0.680	-0.134	0.664	0.875	0.854	1												
Fe	0.644	0.083	0.508	0.841	0.751	0.798	1											
Hg	0.470	-0.472	0.522	0.452	0.348	0.358	0.161	1										
K	0.343	-0.366	0.537	0.361	0.570	0.514	0.223	0.251	1									
Li	0.628	-0.077	0.611	0.845	0.902	0.862	0.699	0.413	0.406	1								
Mg	0.531	0.453	0.213	0.205	0.299	0.270	0.361	-0.044	0.347	0.237	1							
Mn	0.657	-0.188	0.786	0.753	0.688	0.804	0.728	0.473	0.503	0.680	0.271	1						
Na	0.222	-0.374	0.100	0.371	0.140	0.423	0.310	0.193	0.187	0.222	0.094	0.405	1					
Ni	0.771	-0.101	0.551	0.895	0.822	0.829	0.743	0.490	0.374	0.845	0.362	0.663	0.324	1				
Pb	0.701	-0.019	0.633	0.858	0.833	0.836	0.772	0.434	0.506	0.782	0.383	0.666	0.125	0.783	1			
Se	0.856	0.134	0.401	0.743	0.655	0.727	0.640	0.267	0.286	0.691	0.466	0.513	0.191	0.854	0.758	1		
Sr	0.760	-0.026	0.679	0.919	0.901	0.883	0.794	0.449	0.472	0.901	0.429	0.756	0.324	0.935	0.823	0.772	1	
Zn	0.501	-0.121	0.529	0.810	0.783	0.722	0.641	0.446	0.330	0.868	0.049	0.536	0.130	0.785	0.719	0.609	0.791	1

*r-values > 0.350 or < -0.350 are significantly correlated at $p < 0.05$

In the same way, Ni showed significantly positive correlations with Sr (r = 0.947), Pb (r = 0.909), Zn (r = 0.871) and Se (r = 0.744); Pb with Sr (r = 0.896), Zn (r = 0.831) and Se (r = 0.615); Mg with Se (r = 0.399); Se with Sr (r = 0.600) and Zn (r = 0.543); and Sr exhibited significantly associations with Zn (r = 0.901). Calcium was inversely correlated with K (r = -0.543).

The correlation coefficient matrix pertaining to selected metal levels in acid extract of the sediments during post-monsoon is shown in Table 63. Numerous significant relationships were observed among the metals: As was found to be strongly associated with Se (r = 0.856), Ni (r = 0.771), Sr (r = 0.760), Pb (r = 0.701), Cu (r = 0.680), Co (r = 0.672), Cr (r = 0.657), Mn (r = 0.657), Fe (r = 0.644), Li (r = 0.628), Mg (r = 0.531), Zn (r = 0.501), Cd (r = 0.500) and Hg (r = 0.470). Calcium showed significant association with Mg (r = 0.453), and negative associations with K (r = -0.366), Na (r = -0.374), Hg (r = -0.472). Cadmium displayed strong correlations with Mn (r = 0.786), Sr (r = 0.679), Cu (r = 0.664), Pb (r = 0.633), Co (r = 0.630), Cr (r = 0.623), Li (r = 0.611), Ni (r = 0.551), K (r = 0.537), Zn (r = 0.529), Hg (r = 0.522), Fe (r = 0.508) and Se (r = 0.401). Cobalt revealed significantly correlations with Sr (r = 0.919), Ni (r = 0.895), Cu (r = 0.875), Pb (r = 0.858), Cr (r = 0.855), Li (r = 0.845), Fe (r = 0.841), Zn (r = 0.810), Mn (r = 0.753), Se (r = 0.743), Hg (r = 0.452), Na (r = 0.371) and K (r = 0.361). Chromium exhibited strong associations with Li (r = 0.902), Sr (r = 0.901), Cu (r = 0.854), Ni (r = 0.822), Pb (r = 0.800), Zn (r = 0.783), Fe (r = 0.751), Mn (r = 0.688), Se (r = 0.655) and K (r = 0.570); Cu with Li (r = 0.862), Pb (r = 0.836), Sr (r = 0.883), Ni (r = 0.829), Mn (r = 0.804), Fe (r = 0.798), Se (r = 0.727), Zn (r = 0.722), K (r = 0.514), Na (r = 0.423) and Hg (r = 0.358); Fe with Sr (r = 0.794), Pb (r = 0.772), Ni (r = 0.743), Mn (r = 0.728), Li (r = 0.699), Zn (r = 0.641), Se (r = 0.640) and Mg (r = 0.361); Hg with Ni (r = 0.490), Mn (r = 0.473), Sr (r = 0.449), Zn (r = 0.446), Pb (r = 0.434) and Li (r = 0.413); K with Pb (r = 0.506), Mn (r = 0.503), Sr (r = 0.472), Li (r = 0.406) and Ni (r = 0.374); and Li with Sr (r = 0.901), Zn (r = 0.868), Ni (r = 0.845), Pb (r = 0.782), Se (r = 0.691) and Mn (r = 0.680). In addition, Mg was significantly associated with Se (r = 0.466), Sr (r = 0.429), Pb (r = 0.383) and Ni (r = 0.362). Manganese exhibited significant correlations with Sr (r = 0.756), Pb (r = 0.666), Ni (r = 0.663), Zn (r = 0.536), Se (r = 0.513) and Na (r = 0.405). Nickel revealed strong correlations with Sr (r = 0.935), Se (r = 0.854), Zn (r = 0.785) and Pb (r = 0.783); Pb with Sr (r = 0.823), Se (r = 0.758) and Zn (r = 0.719); Se with Sr (r = 0.772) and Zn (r = 0.609); and Sr with Zn (r = 0.791). The correlation study, therefore showed mutual associations among the metals in sediments.

3.21 Multivariate Analyses of Selected Metals in Sediment Samples

Principle component analysis (PCA) and cluster analysis (CA) were employed in order to understand the complex nature of relationships among the metal contents in acid-extract of the sediments and their source apportionment. The PC loadings extracted by varimax normalized rotation of the data-set in acid-extract of the sediments during summer are shown in Table 64, whereas the corresponding CA of selected metals using Ward's method is shown in the form of dendrogram in Figure 36. Five PCs with eigenvalue greater than one were extracted for the metals during summer, yielding more than 75% of total variance of the data. PC 1 showed highest loadings for Cu, Fe, K, Mg, Na and Sr; while PC 2 showed highest loadings for Zn and Mn, which were supported by common clusters of these metals in CA. These metals were mostly contributed by lithogenic sources. PC 3 indicated highest loadings for Cd along with significant contributions of Hg, As and Pb, whereas PC 4 revealed higher contributions of Co, Cr, Ni and Se. CA also showed mutual cluster of Cd-Pb, As-Hg, Cr-Co-Ni-Se. These metals were believed to be associated with anthropogenic activities, particularly industrial, municipal sewage, atmospheric deposition, fuel combustion and recreational/agricultural activities. The last PC showed higher contributions of Li and Ca; these metals were believed to be associated with the mixed sources, natural as well as anthropogenic activities, particularly municipal sewage, urban runoffs and agricultural activities.

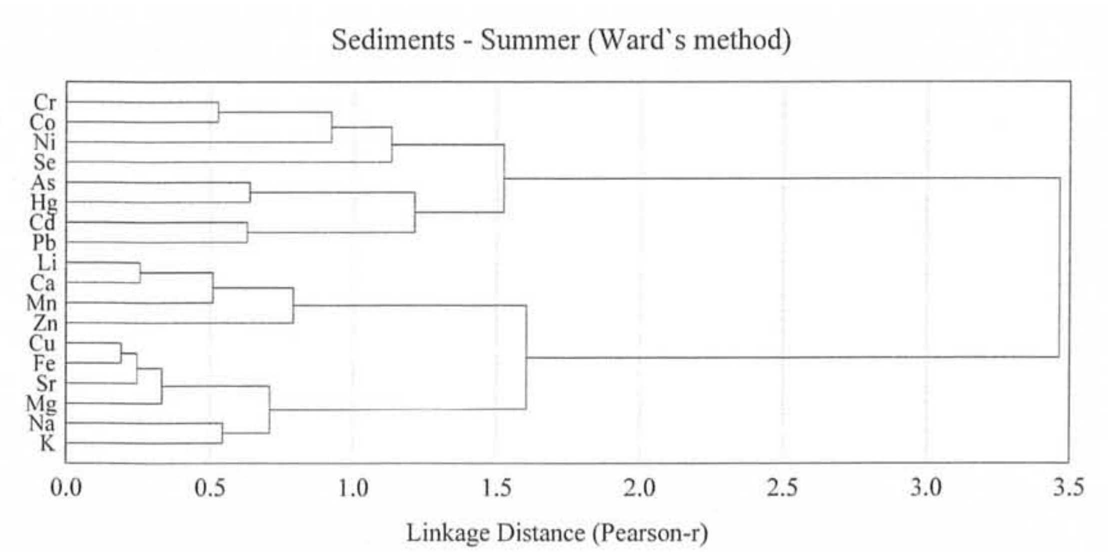

Figure 36. Cluster analysis of selected metal levels in the sediments during summer

Table 64. Principal component analysis of selected metal levels in the sediments during summer

	PC 1	PC 2	PC 3	PC 4	PC 5
Eigenvalue	5.472	2.722	2.025	1.881	1.423
Total Variance (%)	30.40	15.12	11.25	10.45	7.906
Cumulative Eigenvalue	5.472	8.194	10.22	12.10	13.52
Cumulative Variance (%)	30.40	45.52	56.77	67.23	75.13
As	0.089	-0.663	0.632	-0.223	0.015
Ca	0.003	0.070	0.032	0.171	0.879
Cd	-0.039	0.069	0.803	0.036	-0.146
Co	0.145	-0.088	0.010	0.755	-0.202
Cr	0.290	0.037	0.095	0.742	-0.371
Cu	0.850	0.377	-0.066	-0.138	0.099
Fe	0.735	0.215	-0.020	0.022	-0.191
Hg	-0.018	-0.161	0.760	0.192	-0.227
K	0.883	-0.172	0.047	-0.183	0.045
Li	-0.015	0.190	-0.141	0.000	0.864
Mg	0.884	0.213	0.092	0.032	0.172
Mn	0.188	0.825	-0.068	-0.011	0.350
Na	0.724	-0.009	-0.269	0.135	-0.172
Ni	0.267	0.058	0.170	0.722	-0.186
Pb	-0.290	-0.431	0.554	-0.193	-0.133
Se	0.221	-0.336	0.249	0.606	0.307
Sr	0.616	-0.373	0.026	-0.312	0.375
Zn	0.304	0.605	-0.344	-0.325	-0.129

The PC loadings of selected metal levels in the sediments during winter are shown in Table 65, while the corresponding CA in the form of dendrogram is shown in Figure 37. Overall, five PCs with eigenvalue greater than one were extracted for selected metals in the sediments during winter, yielding more than 73% of cumulative variance. PC 1 showed highest loadings for Fe, K, Li, Mg, Na and Sr; PC 2 for Ca, Cd, Mn and Se; PC 3 for Cu and Zn; PC 4 for Hg and As; and the last PC revealed significant contributions of Co, Cr, Ni and Pb. CA showed shared clusters of Ca-Cd-Mn; Se-Hg-As; and Co-Pb; Ni-Cr. These metals were believed to be associated with the anthropogenic activities, while other metals (Na-Sr-Cu-Zn-K-Fe-Mg-Li) were mostly associated with natural contributions. PCA findings were in good agreement with the CA results.

Table 65. Principal component analysis of selected metal levels in the sediments during winter

	PC 1	PC 2	PC 3	PC 4	PC 5
Eigenvalue	5.449	2.493	2.107	1.656	1.452
Total Variance (%)	30.27	13.85	11.71	9.199	8.066
Cumulative Eigenvalue	5.449	7.942	10.05	11.70	13.16
Cumulative Variance (%)	30.27	44.12	55.83	65.02	73.09
As	0.055	0.149	0.106	0.759	0.136
Ca	0.102	0.697	-0.018	0.058	0.130
Cd	0.310	0.699	0.099	-0.092	-0.003
Co	-0.117	0.015	-0.157	0.268	0.654
Cr	0.172	-0.019	0.149	0.000	0.881
Cu	-0.293	-0.073	0.910	0.122	0.048
Fe	0.891	0.133	-0.020	-0.054	0.018
Hg	0.067	0.158	-0.131	0.855	0.022
K	0.735	-0.130	-0.354	0.090	0.181
Li	0.781	0.261	0.212	0.182	0.215
Mg	0.688	0.204	-0.156	0.076	0.205
Mn	0.228	0.867	0.208	-0.037	-0.101
Na	0.755	0.042	0.299	0.019	0.119
Ni	0.181	0.074	-0.032	-0.043	0.660
Pb	-0.047	0.081	0.238	0.102	0.815
Se	0.025	0.822	0.207	-0.325	0.012
Sr	0.657	-0.046	0.059	-0.212	-0.437
Zn	-0.190	-0.074	0.945	0.135	-0.089

The PC loadings of selected metal contents in the sediments during pre-monsoon are shown in Table 66, where four PCs were extracted, cumulatively explaining more than 84% of the total variance. The corresponding dendrogram of CA for these metals is shown in Figure 38. PC 1 with maximum cumulative variance of data (57.55%) showed elevated loadings of As, Cd, Co, Cr, Hg, Ni, Pb and Se. The CA also showed similar clusters of these metals; As-Cd-Se and Co-Pb-Ni-Cr-Hg. These metals were mainly contributed by anthropogenic activities going on around the water reservoir. PC 2 showed higher loadings for K, Mg and Na; PC 3 for Ca, Fe, Li, Mn and Sr; and PC 4 for Cu and Na. These three PCs were believed to be associated with lithogenic contributions Overall, the PCA and CA results were in good agreement with each other.

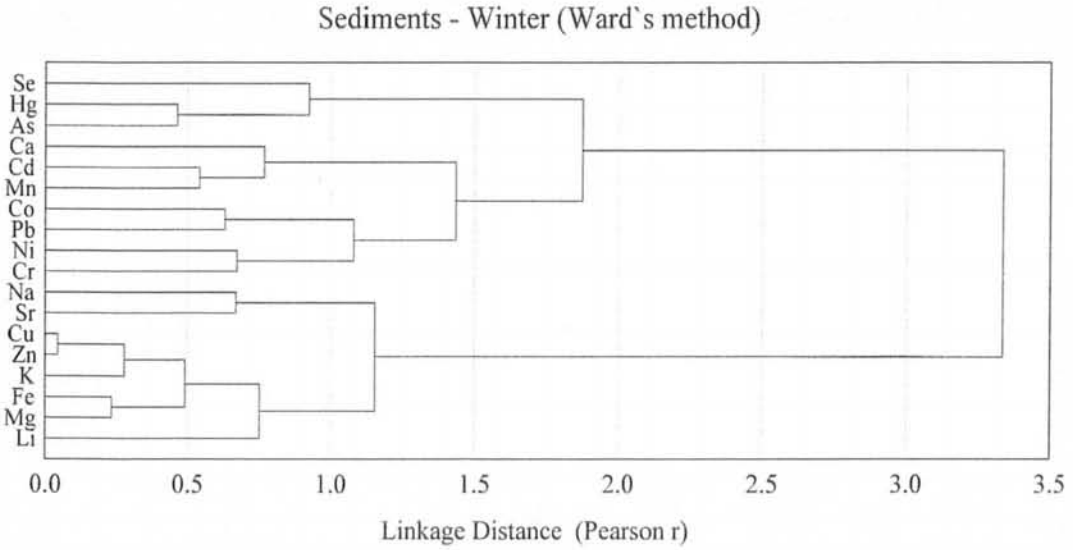

Figure 37. Cluster analysis of selected metal levels in the sediments during winter

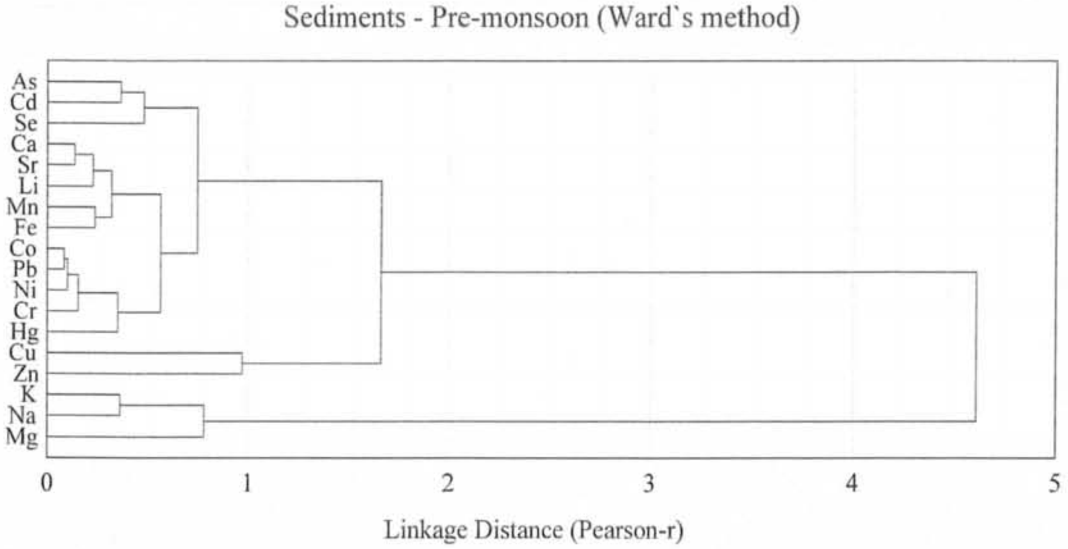

Figure 38. Cluster analysis of selected metal levels in the sediments during pre-monsoon

Table 66. Principal component analysis of selected metal levels in the sediments during pre-monsoon

	PC 1	PC 2	PC 3	PC 4
Eigenvalue	10.36	1.960	1.700	1.118
Total Variance (%)	57.55	10.89	9.443	6.210
Cumulative Eigenvalue	10.36	12.32	14.02	15.14
Cumulative Variance (%)	57.55	68.43	77.88	84.09
As	0.785	0.061	0.302	0.048
Ca	0.033	0.099	0.927	-0.011
Cd	0.900	0.134	0.176	0.037
Co	0.955	0.067	-0.045	0.097
Cr	0.806	0.107	0.162	-0.266
Cu	0.215	0.132	0.176	0.894
Fe	-0.175	0.231	0.778	0.217
Hg	0.902	0.114	0.267	0.043
K	0.228	0.783	-0.039	-0.374
Li	-0.122	-0.281	0.875	-0.062
Mg	0.107	0.934	0.062	0.047
Mn	-0.013	0.244	0.701	0.269
Na	-0.322	0.785	0.026	-0.198
Ni	0.889	0.235	0.064	0.068
Pb	0.933	0.087	-0.026	0.126
Se	0.791	0.059	0.308	0.118
Sr	-0.144	0.017	0.944	0.013
Zn	-0.201	-0.069	0.076	0.879

The PC loadings of selected metal concentrations in the sediments during monsoon are shown in Table 67, while the corresponding CA in the form of dendrogram is shown in Figure 39. Four PCs with eigenvalue greater than one were extracted, yielding more than 86% of cumulative variance. PC 1 showed highest loadings for As, Ca, Cd, Cr, Hg, Li, Se and Zn, whereas PC 2 exhibited elevated loadings for Co, Mn, Ni, Pb and Sr. Similar type of associations among these were observed in CA: As-Cd-Se-Hg, Mn-Sr-Co-Ni-Pb-Cr-Li-Zn-Ca. These metals were most likely contributed by anthropogenic activities, such as, industrial emissions, municipal sewage, urban runoffs, atmospheric deposition, coal combustion and agricultural runoffs. PC 3 indicated highest loadings for Cu and Mg, while last PC revealed higher loadings for Fe, K and Na, well supported by CA (Cu-Mg-Fe-K-Na). These metals were mainly associated with the natural contributions.

Table 67. Principal component analysis of selected metal levels in the sediments during monsoon

	PC 1	PC 2	PC 3	PC 4
Eigen value	10.85	2.194	1.283	1.153
Total Variance (%)	60.29	12.19	7.131	6.40
Cumulative Eigen value	10.85	13.05	14.33	15.48
Cumulative Variance (%)	60.29	72.48	79.61	86.02
As	0.830	-0.166	0.134	0.089
Ca	0.832	-0.038	0.299	-0.057
Cd	0.881	-0.139	-0.160	-0.049
Co	0.004	0.963	0.056	0.063
Cr	0.931	0.181	0.060	-0.022
Cu	0.088	-0.171	0.957	0.007
Fe	-0.290	0.109	0.141	0.848
Hg	0.712	0.299	-0.338	0.189
K	-0.099	-0.003	0.135	0.891
Li	0.912	0.085	0.071	-0.101
Mg	0.186	0.063	0.759	-0.035
Mn	-0.025	0.867	-0.021	0.286
Na	-0.020	0.047	-0.033	0.981
Ni	0.008	0.949	0.246	0.036
Pb	-0.027	0.934	0.099	-0.149
Se	0.714	-0.219	0.202	-0.092
Sr	0.066	0.982	0.040	0.019
Zn	0.894	-0.007	0.089	-0.219

The PC loadings of selected metal levels in the sediments during post-monsoon are shown in Table 68, while the matching CA is shown in Figure 40. Four PCs with eigen value greater than one were extracted, yielding more than 82% of cumulative variance. PC 1 exhibited highest loadings for Co, Cr, Ni, Se, Sr and Zn; PC 2 for Cu, Fe, K, Mn and Na; PC 3 for As, Ca, Cd, Hg and Pb; and PC 4 revealed higher contributions of Li and Mg. PC

1 and PC 3 were believed to be associated with the anthropogenic activities, while PC 2 and PC 4 were assumed to be derived from natural sources. The PCA results were in good agreement with the CA findings.

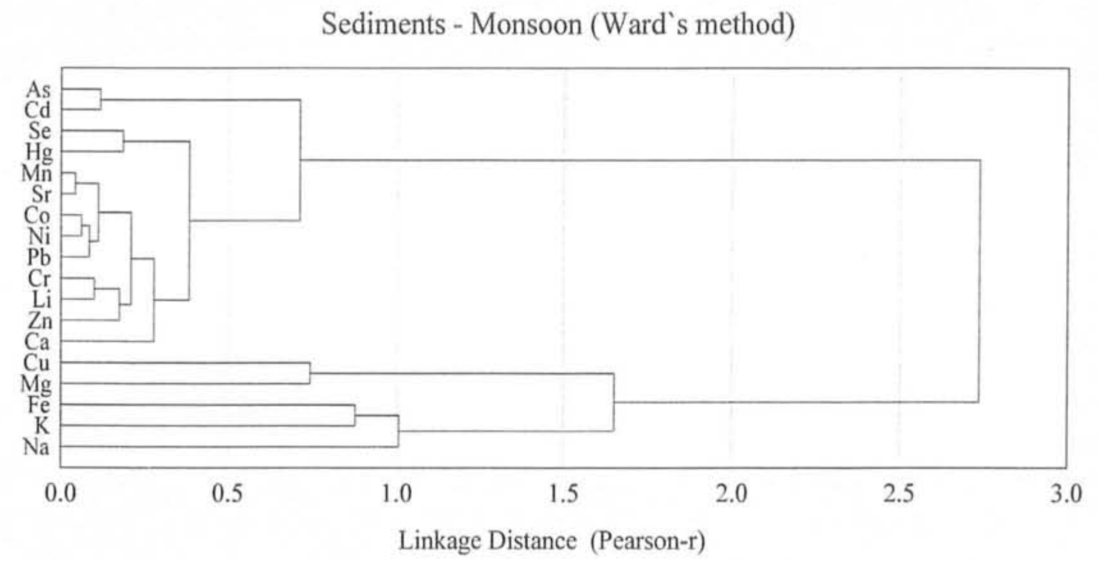

Figure 39. Cluster analysis of selected metal levels in the sediments during monsoon

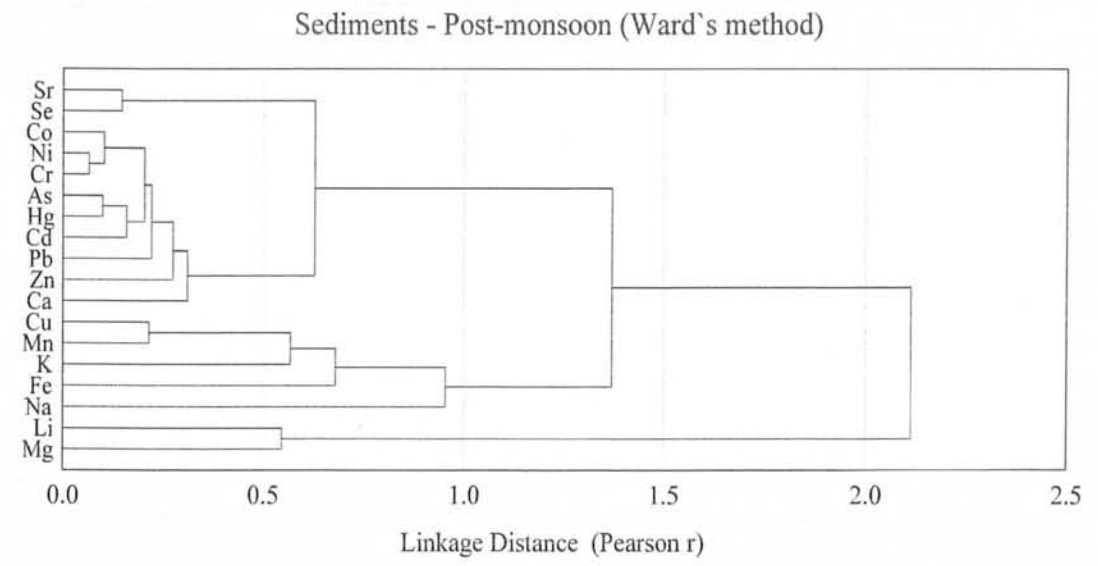

Figure 40. Cluster analysis of selected metal levels in the sediments during post-monsoon

Table 68. Principal component analysis of trace metal levels in the sediments during post-monsoon

	PC 1	PC 2	PC 3	PC 4
Eigen value	10.63	1.979	1.185	1.102
Total Variance (%)	59.05	11.00	6.586	6.122
Cumulative Eigen value	10.63	12.61	13.79	14.90
Cumulative Variance (%)	59.05	70.05	76.63	82.76
As	0.236	0.297	0.701	0.174
Ca	0.060	-0.379	0.717	-0.438
Cd	0.201	0.256	0.836	-0.221
Co	0.930	0.191	-0.057	0.179
Cr	0.846	0.380	0.019	-0.032
Cu	0.038	0.844	0.249	0.328
Fe	0.204	0.842	0.043	0.197
Hg	-0.132	0.293	0.666	0.086
K	0.187	0.864	0.089	0.115
Li	0.242	0.000	-0.061	0.899
Mg	0.214	0.278	0.099	0.867
Mn	0.030	0.738	0.322	0.285
Na	0.193	0.936	-0.060	0.051
Ni	0.902	0.204	0.058	0.179
Pb	0.126	0.369	0.828	-0.036
Se	0.808	0.080	0.329	0.107
Sr	0.898	0.320	0.124	0.135
Zn	-0.246	0.138	0.872	-0.111

3.22 Pollution Assessment of Selected Metals in Sediment Samples

Assessment of metal pollution in the sediment samples was carried out using different ecological risk indices, such as, enrichment factor (*EF*), geo-accumulation index (I_{geo}), contamination factor (*CF*), degree of contamination (C_{deg}), pollution load index (*PLI*), risk assessment code (*RAC*), individual contamination factor (*ICF*) and global contamination factor (*GCF*).

3.22.1 Enrichment Factor (*EF*) of Selected Metals in Sediment Samples

Comparative evaluation of metal levels in examined sediments with respect to the background reference levels is generally used to measure the enrichment of selected metals. Anthropogenic impact of the metals in sediments can be assessed from metal enrichment relative to the background/pre-industrial levels. Different methods to determine the metal enrichment have been reported (Loska *et al.,* 1997; Abrahim and Parker, 2008). The fundamental concept is to produce a numerical result comparing the measured metal levels with the background levels, such as, the average continental crust abundances. Enrichment factor (*EF*) estimates the anthropogenic impact on sediments using a normalization element in order to alleviate the variations produced by heterogeneity of the sediments. Mean *EF* values of the metals computed in the present study during summer and winter are shown in Figure 41. Overall, average *EF* values of the metals during summer followed the decreasing order; Se > As > Cd > Hg > Pb > Ca > Co > Li > Zn > Ni > Mn > Cu > Cr > Mg > Sr > K > Na, while during winter the order was; Se > Cd > As > Hg > Pb > Ca > Co > Li > Zn > Mn > Ni > Cr > Cu > Mg > K > Sr > Na. In the present study, Se, As, Cd and Hg showed extremely severe enrichment, whereas K, Mg, Na and Sr showed minor enrichment during summer and winter. However, Pb showed very severe enrichment during winter and severe enrichment during summer. Moreover, Ca, Co, Cr, Cu, Li, Mn, Ni and Zn exhibited significant enrichment during winter, while Ca, Co, Mn, Ni and Zn showed significant enrichment during summer. Overall, most of the metals showed higher enrichment during winter than summer.

Similarly, *EF* was also evaluated during pre-monsoon, monsoon and post-monsoon seasons. Average values of *EF* for selected metals in acid extract of the sediments during pre-monsoon, monsoon and post-monsoon are shown in Figure 42. Mean *EF* values of the metals during pre-monsoon showed following trend; Se > Cd > As > Hg > Pb > Zn > Co > Ca > Li > Sr > Ni > Cu > Mn > Cr > K > Mg > Na; while during monsoon and post-monsoon, the relative order was observed as; Se > Cd > As > Hg > Pb > Zn > Co > Ca > Li > Ni > Sr > Mn > Cu > Cr > K > Mg > Na. The results revealed almost similar order of *EF* values observed during pre-monsoon, monsoon and post-monsoon seasons. Overall, K, Mg and Na exhibited very low enrichment; Se, Cd, and As exhibited extremely severe enrichment; Hg and Pb showed severe to very severe enrichment; Zn, Co, Li and Ca revealed severe enrichment; and Ni, Mn, Cr, Sr and Mn revealed moderate to moderately severe enrichment in the sediment samples during three seasons. Comparative assessment showed that most of the metals (Se, Cd, Pb, Co, Zn and Ca) exhibited highest enrichment during pre-monsoon. These metals were mostly contributed by anthropogenic intrusions, such as, untreated municipal and domestic wastes, fossil fuel combustion, agriculture runoffs and automobile exhausts in the study area.

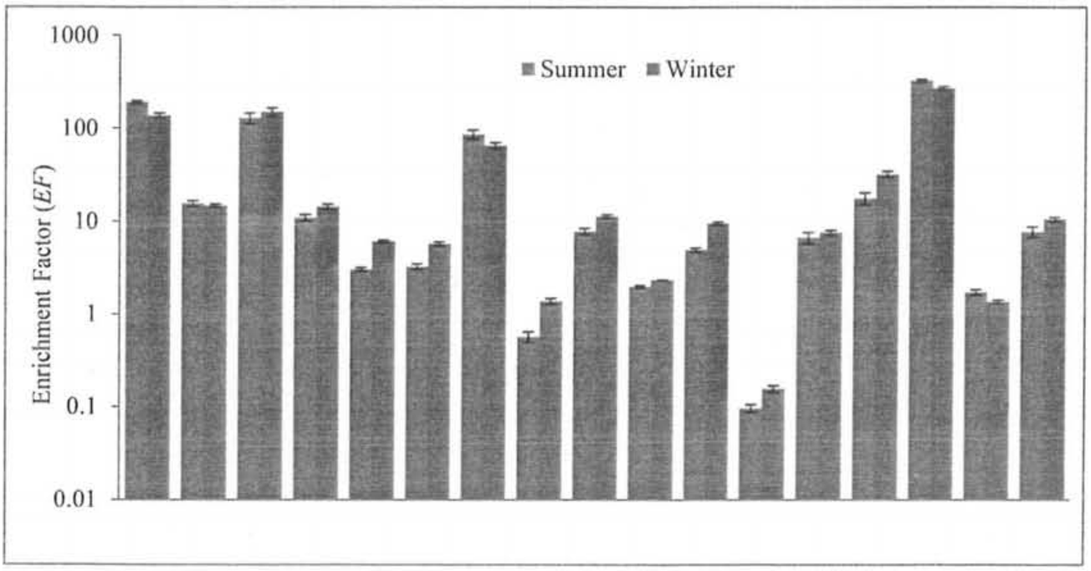

Figure 41. Average enrichment factors (*EF*) of selected metals in the acid extract of sediments during summer and winter

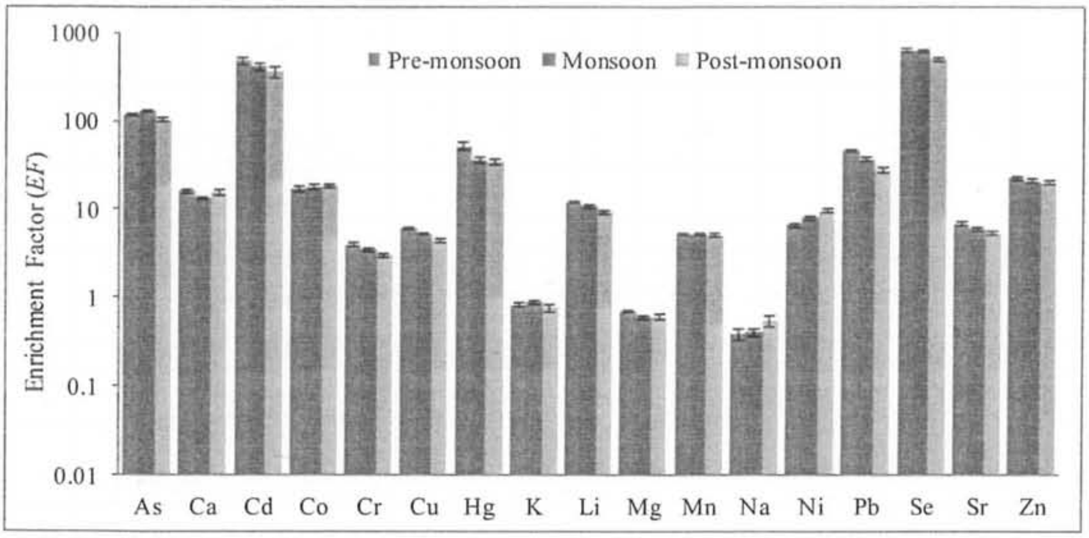

Figure 42. Average enrichment factors (*EF*) of selected metals in the acid extract of sediments during pre-monsoon, monsoon and post-monsoon

3.22.2 Geoaccumulation Index (I_{geo}) of Selected Metals in Sediment Samples

Geoaccumulation index has been used to explain the sediment quality, however, it is not readily comparable to the other indices of metal accumulation/enrichment due to the nature of its calculation, which involves a log function and a background multiplication of 1.5 (Karbassi *et al.,* 2008; Abrahim and Parker, 2008). Mean levels of selected metals in acid extract of the sediments were used to calculate the average I_{geo}. Mean I_{geo} values of the metals calculated in the present study during summer and winter seasons are represented in Figure 43. Average I_{geo} values of most of the metals revealed practically un-contamination during both seasons except As, Cd, Hg, Pb and Se. Among these metals, Se during both seasons and As during summer showed 'heavy contamination'; Cd during both seasons and As during winter exhibited 'moderate to heavy contamination'; Hg showed 'moderate contamination' during both seasons while Pb revealed 'un-contamination to moderate contamination' during winter season.

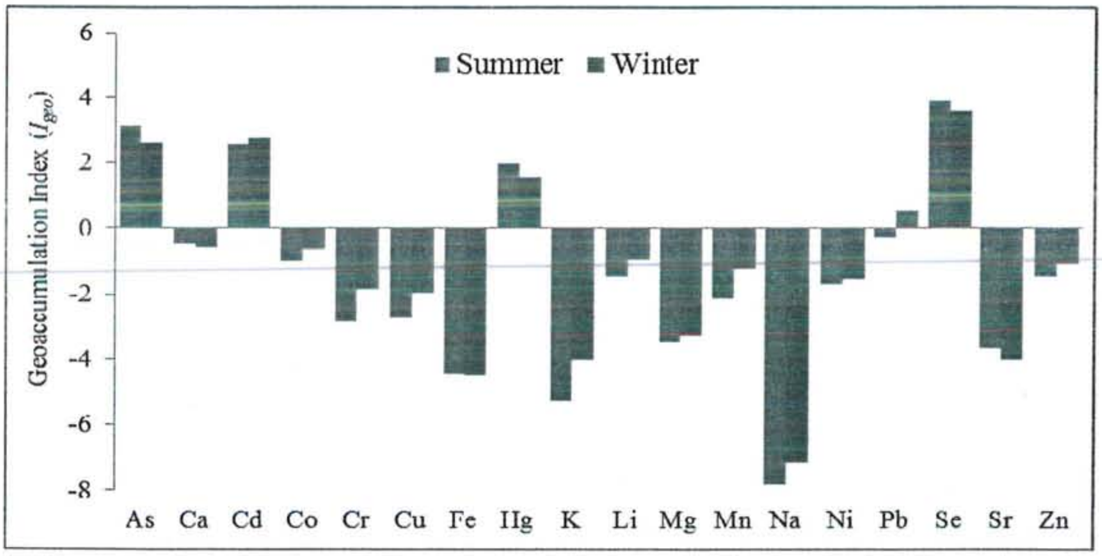

Figure 43. Average geo-accumulation indices (I_{geo}) for selected metals in acid extract of sediments during summer and winter

Figure 44 displayed I_{geo} for selected metals in acid extract of the sediment during pre-monsoon, monsoon and post-monsoon seasons. Among the selected metals, Se revealed 'extreme contamination' during pre-monsoon and monsoon; Cd during all seasons and Se during post-monsoon showed 'heavy to extreme contamination'. Arsenic showed 'moderate to heavy contamination' during the three seasons, while Hg and Pb exhibited 'moderate contamination' during pre-monsoon and 'un-contamination to moderate contamination' during monsoon and post-monsoon. The highest I_{geo} was shown by Se during monsoon, Pb and Cd during pre-monsoon and Hg & As during summer seasons. Overall, the I_{geo} study revealed that sediments were contaminated by As, Cd, Hg, Pb and Se while rest of metals showed un-contamination of the sediments.

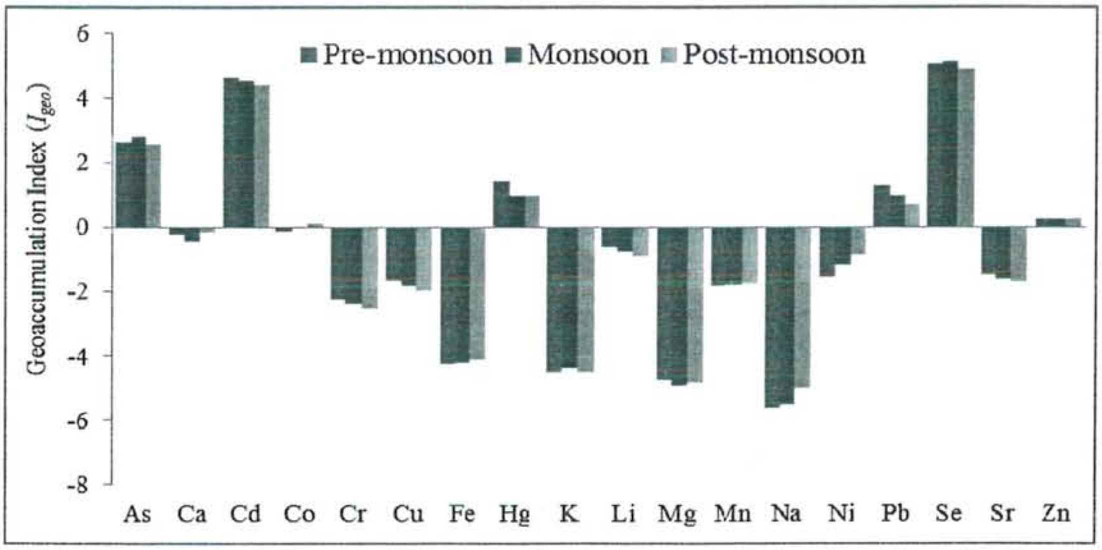

Figure 44. Average geo-accumulation indices (I_{geo}) for selected metals in acid extract of sediments during pre-monsoon, monsoon and post-monsoon

3.22.3 Contamination Factor (*Cf*), Degree of Contamination (C_{deg}) and Pollution Load Index (*PLI*) of Selected Metals in Sediment Samples

The sediment contamination was also evaluated by contamination factor (*Cf*), in which average metal levels in the sediments are compared with the reference value, while C_{deg} is the sum of individual *Cf*. A fundamental feature of C_{deg} is that it enables an assessment of the total degree of contamination based on the available contaminant levels. Besides, *PLI* is also widely used to assess the metal contamination and pollution in the sediments (Varol, 2011). It is determined as the nth root of the n CF_n multiplied together. Comparative assessment of average *Cf* of selected metals in acid extract of the sediments during summer and winter is shown in Figure 45. Mean values of *Cf* for Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, Sr and Zn were < 1 which exhibited low contamination of these metals in the sediment samples during summer and winter. However, *Cf* of Co during summer and winter was near to unity exceeding the low contamination level in sediment. Among rest of the metals, As, Cd, Se and Hg revealed very high contamination on the average basis during summer and winter, while Ca and Pb showed moderate contamination. Similarly, mean values of C_{deg} during summer and winter were 56.14 and 50.02, respectively, showing very high degree of contamination in the sediments during both seasons.

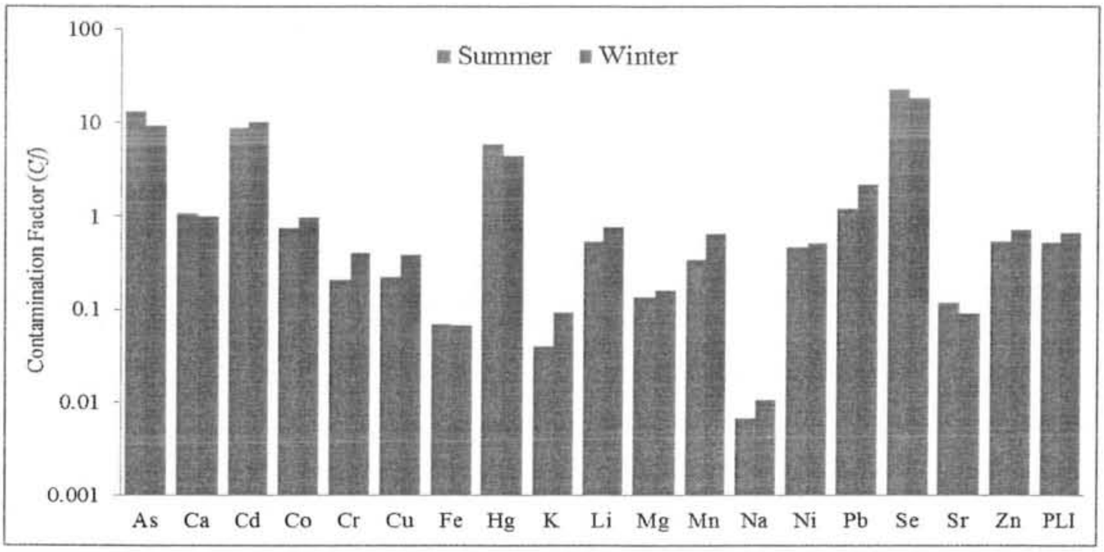

Figure 45. Average contamination factor (*Cf*) and pollution load index (*PLI*) for selected metals in the sediments during summer and winter

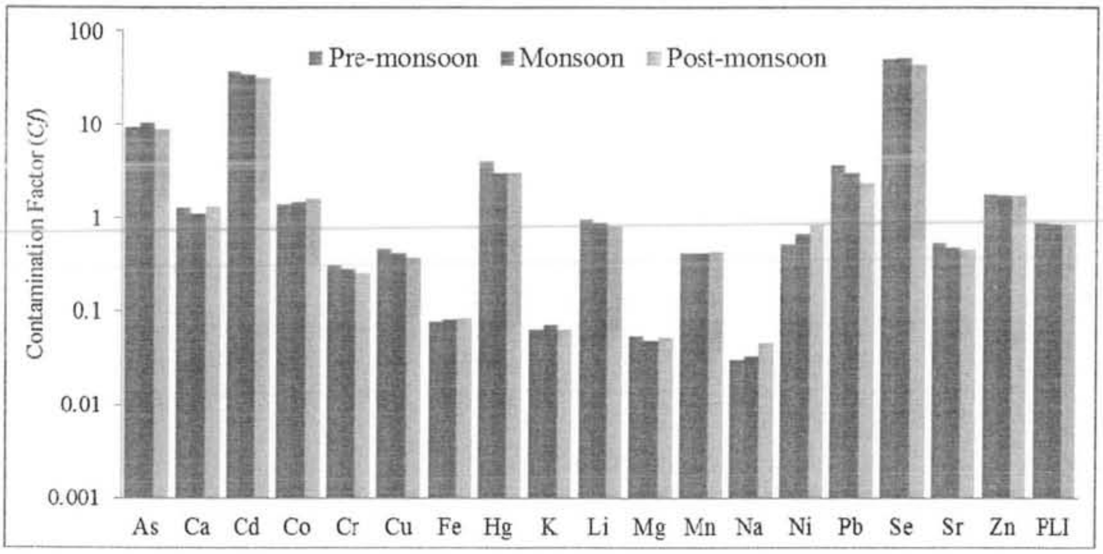

Figure 46. Average contamination factor (*Cf*) and pollution load index (*PLI*) for selected metals in the sediments during pre-monsoon, monsoon and post-monsoon

On the other hand, average values of *Cf* for selected metals in acid extract of the sediments during pre-monsoon, monsoon and post-monsoon are shown in Figure 46. Mean values of *Cf* for Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni and Sr were < 1 which exhibited low contamination of these metals in the sediment samples during pre-monsoon, monsoon and post-monsoon seasons. However, Ca, Co and Zn showed moderate contamination, whereas Pb and Hg showed considerable contamination during pre-monsoon and moderate contamination during monsoon and post-monsoon seasons. Nevertheless, As, Cd and Se revealed very high contamination on the average basis during pre-monsoon, monsoon and post-monsoon seasons. Overall, the cumulative index, C_{deg} (Figure 47) revealed very high degree of contamination during pre-monsoon (C_{deg} = 112.4), monsoon (C_{deg} = 110.0) and post-monsoon (C_{deg} = 97.31). According to the *PLI* values, the sediments were found to be non-polluted in the present study as the calculated values were 0.53, 0.65, 0.89, 0.86 and 0.85 during summer, winter, pre-monsoon, monsoon and post-monsoon, respectively. Outcomes of the C_{deg} assessment and PLI are different because degree of contamination (C_{deg}), a cumulative index, is computed as numeric sum of individual 'C_f' of each sample while PLI is a comparative index to determine the degree of metals pollution, computed as the nth root of n C_{fn} multiplied together. However, on comparative basis, sediments were most polluted during pre-monsoon and least polluted during summer as shown by *PLI*, which exhibited following trend; pre-monsoon > monsoon > post-monsoon > winter > summer.

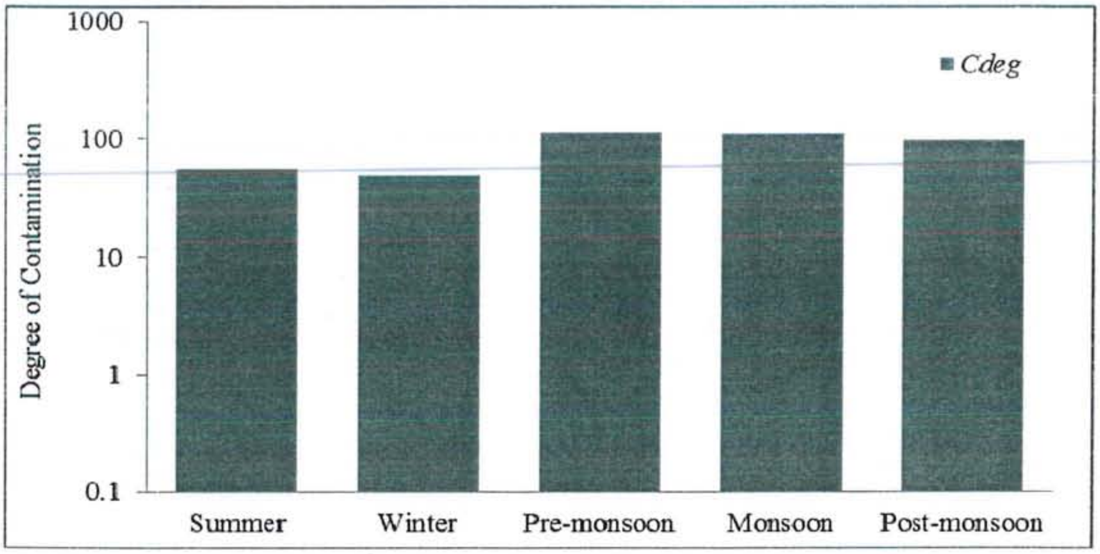

Figure 47. Average degree of contamination (C_{deg}) for selected metals in the sediments during summer, winter, pre-monsoon, monsoon and post-monsoon

Potential ecological risk factor (E_i) for selected metals in acid-extract of the sediments during summer, winter, pre-monsoon, monsoon and post-monsoon were also evaluated as shown in Figure 48. The results evidenced that Cr, Cu, Pb and Zn caused low risk, while As showed considerable risk during all seasons. Similarly, Hg showed considerable to great risk, whereas Cd revealed great to very great risk during all seasons.

Generally, As and Hg exhibited highest E_i during summer while Cd showed the elevated value during pre-monsoon. Overall, potential risk for selected metals in the sediments was assessed by potential ecological risk index (*RI*), which revealed very high risk for the metal contents in the sediments on cumulative basis during all seasons. On comparative basis, relatively higher pollution was observed during summer than winter and during pre-monsoon than other seasons (Figure 49). The classification related to E_i and *RI* were suggested by Hakanson (1980) as shown in Appendix-I.

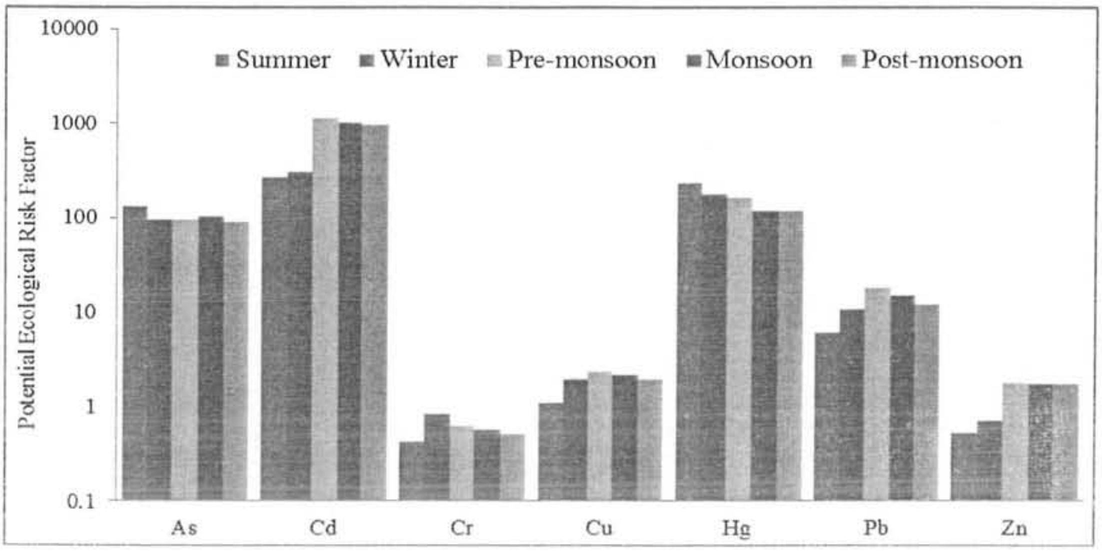

Figure 48. Potential ecological risk factor (E_i) for selected metals in the sediments during summer, winter, pre-monsoon, monsoon and post-monsoon

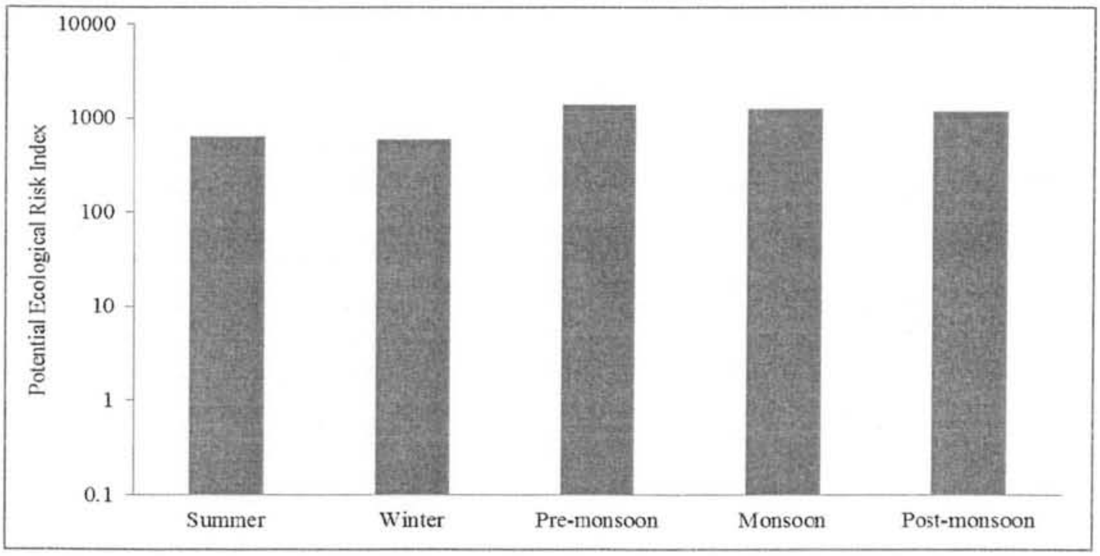

Figure 49. Potential ecological risk index (*RI*) for selected metals in the sediments during summer, winter, pre-monsoon, monsoon and post-monsoon

3.22.4 Risk Assessment Code (*RAC*), Individual Contamination Factor (*ICF*) and Global Contamination Factor (*GCF*) of Selected Metals in Sediment Samples

There are several sediment quality assessment methodologies that may be used to evaluate the effects of metals in an aquatic ecosystem. Typically, metals are bound to various sediment fractions, with varying binding strength, which determine their bioavailability and the risk associated with their contents in the aquatic environment. Therefore, different pollution indices, including *RAC*, *ICF* and *GCF* were applied to evaluate the metal mobility and toxicity in the sediment samples. The *RAC* is defined as the percentage of exchangeable fraction (F1) in the total metals contents (Passos *et al.*, 2010; Perin *et al.*, 1985; Yu *et al.*, 2011). The F1 fraction is considered the most important from an environmental point of view, since the metals contained are easily leached in neutral or slightly acidic water (Filgueiras *et al.*, 2004) and are thus available to the aquatic organisms. Several authors have proposed the F1 as the most potentially bioavailable fraction (Delgado *et al.*, 2011; Guillen *et al.*, 2012) in the environment, suggesting that it could be used to assess the potential ecological risk. A five-level classification was suggested; no risk (<1%), low risk (1–10%), medium risk (11–30%), high risk (31–50%), and very high risk (>50%), which is considered dangerous, with metals easily able to enter the food chain (Passos *et al.*, 2010; Perin *et al.*, 1985; Yu *et al.*, 2011).

Comparative evaluation of *RAC* (%), *ICF* and *GCF* in the sediments during summer and winter is described in Table 69. During summer, *RAC* exhibited no risk for Fe and Zn; low risk for As, Cr, Cu and Hg; low to medium risk for Co; medium risk for Mg, Se, K, Mn and Ni; medium to high risk for Ni; high to very high risk for Na; high risk for Pb and Cd and very high risk for Ca and Sr. Comparatively higher *RAC* values were found for Ca, Cd, Co, Ni, Pb and Sr in most of the sediment samples, consequently, these metals were considered dangerous for the aquatic flora and fauna during summer. Similarly, *ICF* is an important factor to assess the degree of risk by a particular metal and it indicated the relative retention time of the metal in sediments. The tabulated results for *ICF* showed the highest ability of Ca, Cd, Ni, Pb, Se, and Sr to be released from the sediments, whereas As, Co, Cr, Cu, Fe, Hg, K, Li, Mg, Mn, Na and Zn exhibited the lowest mobility during summer. Moreover, significantly higher *ICF* values for Na were observed at site 'B' (near urban areas). Generally, least mobile metals showed higher concentrations in the residual fraction, which is considered as non-mobile fraction and it plays an important part in influencing the mobility of the metals. The combined effects of metals, such as, Cd, Co, Ni, Sr and Pb at various sites together with high potential mobility demonstrated the increased possible risk of these metals to the surrounding environment and aquatic biota. *GCF* was calculated as sum of *ICF* of As, Cd, Cr, Co, Hg, Ni, Pb and Sr due to their toxic nature, whereas, the remaining metals (Ca, Cu, Fe, K, Li, Mg, Mn, Na, Se and Zn) were not included due to non-toxic or less toxic nature. As shown in the Table, *GCF* results revealed considerable to high risks to the surrounded environment at all sites.

Table 69. Description of individual contamination factors (*ICF*) and risk assessment code (*RAC*, %) for selected metals in the sediments during summer and winter

	Summer						Winter					
	A		B		C		A		B		C	
	ICF	*RAC*	*ICF*	*RAC*	*ICF*	*RAC*	*ICF*	*RAC*	*ICF*	*RAC*	*ICF*	*RAC*
As	0.586	6.700	0.646	8.995	0.583	6.628	0.557	6.006	0.511	4.018	0.519	4.809
Ca	36.80	94.00	73.54	95.81	55.61	92.37	210.1	97.14	294.5	93.95	57.64	93.90
Cd	2.754	34.77	12.78	39.33	4.931	46.27	1.310	35.85	4.685	43.66	5.471	31.52
Co	1.180	10.34	1.412	14.76	1.011	7.481	1.752	34.86	1.999	36.72	2.025	22.99
Cr	0.355	4.046	0.551	5.327	0.300	4.538	0.327	5.103	0.431	2.440	0.598	6.785
Cu	0.215	5.194	0.178	6.742	0.300	9.450	1.034	13.50	0.423	12.00	0.341	8.900
Fe	1.178	0.294	1.006	0.482	1.071	0.426	1.252	0.765	0.816	1.273	1.160	1.119
Hg	0.350	5.034	0.264	5.265	0.335	4.942	1.390	6.428	1.832	5.842	1.131	6.286
K	0.529	17.47	0.535	16.94	0.575	17.36	0.560	17.98	0.372	15.29	0.387	12.86
Li	0.357	10.55	0.629	21.71	0.385	10.49	0.422	6.548	0.402	7.750	0.300	8.222
Mg	1.524	24.95	1.682	23.36	1.350	21.97	1.472	24.31	1.345	15.27	1.402	13.56
Mn	0.696	18.48	0.840	18.40	1.001	19.93	1.001	24.94	0.711	22.86	0.765	16.89
Na	1.080	45.89	25.02	85.77	1.066	48.02	0.487	16.73	0.434	14.57	0.160	9.792
Ni	10.32	18.33	11.39	33.44	3.964	28.33	1.180	7.708	1.198	12.33	1.339	19.37
Pb	2.335	33.19	2.715	49.95	4.147	45.37	13.32	37.15	2.738	46.84	4.352	42.84
Se	7.364	11.77	9.012	10.07	7.392	11.78	6.776	10.40	7.082	10.07	6.938	9.628
Sr	37.50	67.20	21.48	69.29	13.52	56.23	10.25	82.62	8.427	78.79	6.330	68.57
Zn	0.134	0.624	0.106	0.092	0.090	0.543	0.161	2.573	0.122	1.693	0.146	1.066
GCF	55.37		51.24		28.79		30.08		21.82		21.76	

A, B, C stands for the sampling sites

Comparative evaluation of *RAC* values (%) in the sediments during winter is also given in Table 69. The *RAC* results revealed low risk for Fe, As, Cr, Hg, Li and Zn at all sites, low to medium risk for Na, Ni and Se, while medium risk was indicated by Mg, K, Mn and Cu. In addition, high risk was shown by Pb, Cd and Co, whereas Sr and Ca exhibited very high risk at all sites. Overall, RAC indicated that Cd, Co, Pb and Sr were highly mobile and bioavailable in the aquatic environment during winter. Therefore, significant remediation must be applied at the earliest as they might enter in the food chain and pose threat in the consumers. Similarly, the *ICF* results (Table 69) showed the highest ability of Ca, Cd, Co, Hg, Pb, Ni, Se, and Sr to be released from the sediments to overlying water, whereas As, Zn, K, Li, Na, Mg, Cr, Cu, Fe and Mn displayed the lowest mobility. Higher potential mobility demonstrated the increased risk of these metals to the surrounding environment and aquatic biota. The *GCF* results revealed considerable to high risks to the surrounded environment at all sites during winter on cumulative basis.

3.22.5 Ecotoxicological Evaluation of Selected Metals in Sediment Samples

Comparison of sediment quality guidelines (*SQGs*) with the measured levels of selected metals is very useful method to decide the sediments contamination and quality (Varol, 2011; MacDonald *et al.,* 2000). It was accomplished to envisage the detrimental biological effects and protect the aquatic organisms from polluted sediments. Various aspects, such as, designing monitoring programmes, assuming historical data, measuring the requirement for sediment quality evaluation, measuring the quality of potential dredged materials, accomplishing remedial examinations, ecological evaluations and developing sediment quality remedial goals have been achieved by these *SQGs* (MacDonald *et al.,* 2000; Zheng *et al.,* 2008; varol, 2011; Li *et al.,* 2013b). The ecotoxicological implications of the metal concentrations in sediments were measured by considering two sets of *SQGs*; i) lowest effect level (*LEL*)/severe effect level (*SEL*) and ii) the threshold effect level (*TEL*)/probable effect level (*PEL*) as reported in literature (MacDonald *et al.,* 2000; Iqbal *et al.,* 2013b; Saleem *et al.,* 2013). Metal levels below the *LEL* and *TEL* values are not likely to cause adverse effects, while levels more than the *SEL* and *PEL* values are likely to be very toxic. Furthermore, potential acute toxicity of the contaminants in sediments was calculated as the sum of the toxic units (*TUs*) which are defined as the ratio of the measured levels to *PEL* values (Pedersen *et al.,* 1998; Uluturhan *et al.,* 2011; Iqbal *et al.,* 2013b).

In the present study, average metal concentrations in the sediment samples during summer, winter, pre-monsoon, monsoon and post-monsoon were compared with *LEL*/*SEL* and *TEL*/*PEL* values as shown in Table 70. During summer, Hg, As, Cd, Ni, Cu, Cr, Pb and Zn were higher than the *LEL* in 100%, 93%, 73%, 60%, 27%, 19%, 12% and 4% of the samples, respectively. Moreover, Ni and As exceeded the *SEL* in 13% and 7% of the samples, respectively. Furthermore, As and Hg exceeded the *TEL* level while Cr and Cu levels were below the *TEL* in 100% of the samples. In addition, As, Ni, Hg and Cd were higher than *PEL* in 96%, 52%, 27% and 4% of the samples, respectively. During winter, it was observed that As, Cr and Ni were higher than the *LEL* in 100% of the samples, whereas Cu, Hg, Cd and Pb were higher than the *LEL* in 94%, 87%, 80% and 60% of the samples, respectively. Meanwhile, As and Ni concentrations were higher than the *TEL* in 100% of the samples, whereas, Hg, Cd, Cr, Pb, and Cu exceeded the *TEL* in 74%, 73%, 70%, 53% and 3% of the samples, respectively. Additionally, Ni, As, Hg and Cd contents were higher than the *PEL* in 70%, 50%, 23% and 7% of the samples, respectively.

During pre-monsoon, measured levels of As, Cd, Cu Ni and Pb were higher than the *LEL* in 100% of the samples, whereas Hg, Cr and Zn were higher than the *LEL* in 95%, 90% and 50% of the samples, respectively. Simialrly, As, Cd, Hg and Ni levels were found to be higher than the *TEL* in 100% of the samples, whereas, Pb, Zn, Cu and Cr contents were higher than the *TEL* in 90%, 40%, 20% and 10% of the samples, respectively. Furthermore, Cd, Ni, As and Hg exceeded the *PEL* in 80%, 70%, 45% and 25% of the samples. During monsoon season, mean levels of As and Cu were higher than the *LEL* in 100% of the samples, whereas Cd, Pb, Ni, Hg, Cr and Zn levels were higher than the *LEL* in 95%, 85%, 80%, 70%, 70% and 50% of the samples, respectively. Moreover, Ni and Cd exceeded the *SEL* in 20% and 5% of the samples, while As, Cd and Ni levels were higher than the *TEL* in 100% of samples. However, average contents of Hg, Pb, Zn, Cr and Cu were higher than the *TEL* in 85%, 65%, 40%, 10% and 5% of the samples, respectively. Besides, Ni, Cd, and As levels exceeded the *PEL* in 85%, 70% and 70% of the samples, correspondingly. During post-monsoon, As, Cd and Ni levels were higher than the *LEL* in 100% of the samples, whereas, Cu, Hg, Zn, Cr and Pb were higher than the *LEL* in 90%, 80%, 50%, 40% and 50% of the samples, respectively. Among the metals, Ni and Cd concentrations were higher than the *SEL* in 50% and 10%, respectively. When compared with *TEL-PEL*, average levels of As, Cd, Hg and Ni were higher than the *TEL* in 100% of the samples, while Zn, Pb and Cr were higher than the *TEL* in 50%, 40%, and 10% of the samples, respectively. Moreover, Ni, Cd and As exceeded the *PEL* in 90% 40% and 30% of the samples, which indicated that the concentrations of As, Cd, Hg, Ni and Pb are likely to result in frequently occurring harmful effects on the sediment-dwelling organisms during pre-monsoon, monsoon and post-monsoon seasons.

Table 70. Description of sediment quality guidelines (*SQGs*) and sediments samples (%) exceeding *SQGs* during summer, winter, pre-monsoon, monsoon and post-monsoon

		As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
SQGs	*LEL*	6	0.6	26	16	0.2	16	31	120
	SEL	33	10	110	110	2	75	250	820
	TEL	5.9	0.596	37.3	35.7	0.174	18	35	123
	PEL	17	3.53	90	197	0.486	36	91.3	315
Summer	< *LEL*	0	27	81	73	0	27	88	96
	LEL - SEL	93	73	19	27	100	60	12	4
	> *SEL*	7	0	0	0	0	13	0	0
	< *TEL*	0	23	100	100	0	40	88	96
	TEL - PEL	4	73	0	0	73	8	12	4
	> *PEL*	96	4	0	0	27	52	0	0
Winter	< *LEL*	0	20	0	6	13	0	40	100
	LEL - SEL	100	80	100	94	87	100	60	0
	> *SEL*	0	0	0	0	0	0	0	0
	< *TEL*	0	20	30	97	3	0	47	100
	TEL - PEL	50	73	70	3	74	30	53	0
	> *PEL*	50	7	0	0	23	70	0	0
Pre-monsoon	< *LEL*	0	0	10	0	5	0	0	50
	LEL - SEL	100	100	90	100	95	100	100	50
	> *SEL*	0	0	0	0	0	0	0	0
	< *TEL*	0	0	90	80	0	0	10	60
	TEL - PEL	55	20	10	20	75	30	90	40
	> *PEL*	45	80	0	0	25	70	0	0
Monsoon	< *LEL*	0	0	30	0	30	0	15	50
	LEL - SEL	100	95	70	100	70	80	85	50
	> *SEL*	0	5	0	0	0	20	0	0
	< *TEL*	0	0	90	95	15	0	35	60
	TEL - PEL	30	30	10	5	85	15	65	40
	> *PEL*	70	70	0	0	0	85	0	
Post-monsoon	< *LEL*	0	0	60	10	20	0	50	50
	LEL - SEL	100	90	40	90	80	50	50	50
	> *SEL*	0	10	0	0	0	50	0	0
	< *TEL*	0	0	90	100	0	0	60	50
	TEL - PEL	70	60	10	0	100	10	40	50
	> *PEL*	30	40	0	0	0	90	0	0

Lowest effect level (*LEL*); Severe effect level (*SEL*); Threshold effect level (*TEL*); Probable effect level (*PEL*)

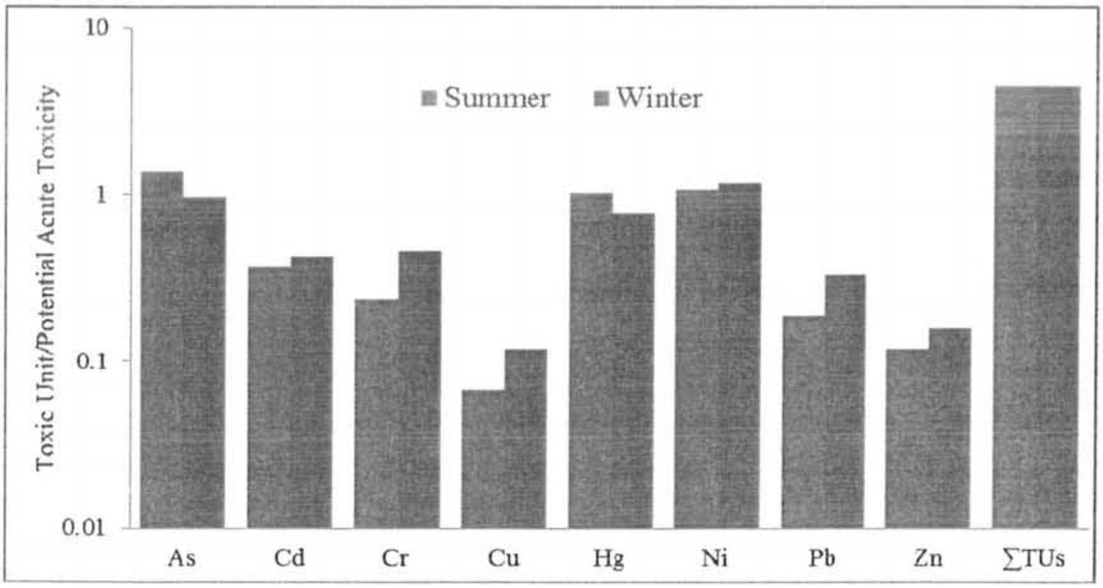

Figure 50. Average toxic units (*TUs*) and potential acute toxicity (Σ*TUs*) for selected metals in the sediments during summer and winter

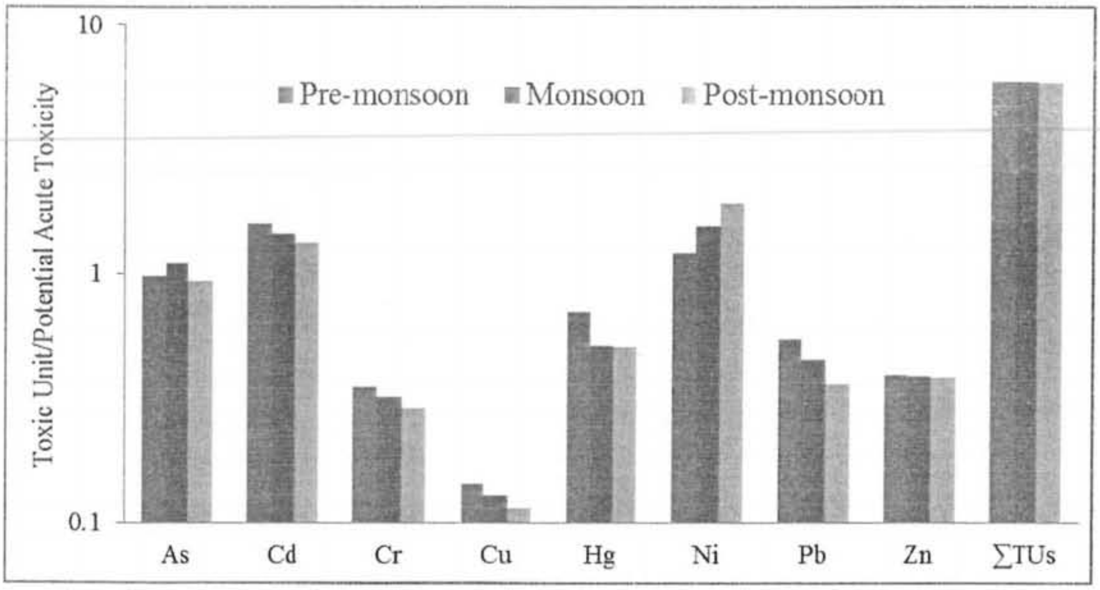

Figure 51. Average toxic units (*TUs*) and potential acute toxicity (Σ*TUs*) for selected metals in the sediments during pre-monsoon, monsoon and post-monsoon

The impending acute toxicity of the contaminants in sediments was also evaluated in terms of potential acute toxicity which is measured as toxic units (*TUs*) as shown in Figure 50. The results showed that *TUs* of Ni (summer and winter), As (summer) and Hg (summer) were found to be higher than the safe limit unity, while *TUs* of Cd and Ni were found to be higher than 1 during pre-monsoon, monsoon and post-monsoon. Ni was the only metal whose level is increasing with monsoon rains. High precipitation in monsoon might mix large volumes of Ni contaminated runoffs with water which resulted in increase of metal concentrations in water and eventually it settled down in sediment. Similarly, *TUs* for As, Hg and Pb were also reaching the safe limit during pre-monsoon, monsoon and post-monsoon. In addition, *TUs* for most of the metals were relatively higher during winter than summer season, whereas *TUs* for Cd, Cr, Cu, Hg, Pb and Zn were comparatively higher during pre-monsoon than monsoon and post-monsoon seasons (Figure 51). On cumulative basis, the results of sum of *TUs* revealed following decreasing order; pre-monsoon > monsoon > post-monsoon. Overall, the *TUs* of the metals showed that Cd, Cu, Pb and Zn were higher during pre-monsoon; As and Hg during summer; Ni during post-monsoon and Cr was higher during winter than other seasons.

3.23 Health Risk Assessment for Selected Metals in Sediment Samples

Descriptive summary for health risk assessment of selected metals in the sediments through oral and dermal pathways during summer and winter is given in Table 71, whereas details of other input parameters for exposure assessment through ingestion and dermal pathways are shown in Appendix K. During summer, average values of Exp_{ing} for selected metals showed following decreasing order; Ca > Fe > Mg > K > Mn > Na > Sr > Ni > Zn > As > Cr > Co > Pb > Cu > Li > Cd > Se > Hg, whereas during winter the order was; Ca > Fe > Mg > K > Mn > Na > Zn > Ni > Cr > Sr > Pb > Co > Cu > As > Li > Cd > Se > Hg. Thus, the results indicated major contributions of Ca, Fe, Mg and K, and minor contributions of Cd, Se and Hg through oral intake during both seasons. Hazard quotients (HQ_{ing} and HQ_{derm}) were used to calculate the non-carcinogenic health effects and the quotient value greater than 1 showed the probability of adverse health effects. Generally, the non-carcinogenic risk results exhibited relatively higher contributions by As, Co, Ca, Mn, Li, Pb, Cr, Mg, Fe and Ni, while minor contribution by Zn, K and Na during both seasons. However, the average values of HQ_{ing} and HQ_{derm} were significantly less than safety limit unity, indicating that the metals would not cause any adverse non-carcinogenic health risks during both seasons. Hazard index (*HI*) was also computed to evaluate the overall non-carcinogenic risk caused by the metals via ingestion route and dermal contact. The calculated HI_{ing} and HI_{derm} values during summer were noted to be 3.1E-01 and 1.4E-

02, while the mean values during winter were 3.4E-01 and 1.0E-02, respectively. Therefore, the results of hazard index revealed that the metals could not pose any adverse health effect to the local population during both seasons.

Health risk assessment through oral and dermal exposures was also assessed for selected metals in the sediments from Mangla Lake during pre-monsoon, monsoon and post-monsoon seasons as shown in Table 72. Average values of Exp_{ing} for selected metals during all seasons exhibited relatively higher contributions of Ca, Fe, K, Mg, Na, Sr and Zn while lowest contributions were noted for Li, As, Cd, Se and Hg. Similarly, average values of Exp_{derm} for selected metals showed comparatively higher exposure of Ca, Fe, K, Mg, Mn and As while least adsorption of Cu, Li, Cd, Se and Hg. Non-carcinogenic health effects were gauged in terms of HQ_{ing}, which revealed following order for selected metals during pre-monsoon; Co > As > Ca > Mn > Pb > Cr > Li > Fe > Cd > Ni > Hg > Cu > Se > Zn > Sr > Mg > K > Na. However, during monsoon average levels of HQ_{ing} showed following trend; Co > As > Ca > Mn > Pb > Cr > Li > Fe > Cd > Ni > Hg > Cu > Se > Zn > Sr > Mg > K > Na, while during post-monsoon the quotient exhibited following order; Co > Ca > As > Mn > Cr > Pb > Li > Fe > Cd > Ni > Hg > Cu > Se > Zn > Sr > Mg > Na > K. Consequently, the non-carcinogenic risk results exhibited relatively higher contributions by As, Co, Ca, Mn, Li, Pb, Cr, Fe, Cd, Ni in the sediment during pre-monsoon, monsoon and post-monsoon seasons. Nevertheless, mean values of HQ_{ing} and HQ_{derm} were noted to be lower than unity (safe limit), thus indicating no hazard associated with the metal contents in the sediment samples. In addition, HI_{ing} and HI_{derm} were noted to be 4.0E-01 and 1.0E-02; 4.0E-01 and 1.2E-02; and 4.1E-01 and 1.0E-02 during pre-monsoon, monsoon and post-monsoon seasons, respectively. Thus, the health risk assessment showed that the metal contents in the sediments could not pose any adverse health effect to the local population during all seasons. However, alteration in redox conditions or physically disturbance of the sediments could cause unwanted changes which may result in releases of toxic metals. Therefore, a regular monitoring of contamination levels in the lake should be assured.

Table 71. Description of health risk assessment for selected metals in acid-extract of the sediments during summer and winter

	RfD/RDA	Summer		Winter		Summer		Winter	
	(mg/kg/day)	Exp_{ing}	Exp_{derm}	Exp_{ing}	Exp_{derm}	HQ_{ing}	HQ_{derm}	HQ_{ing}	HQ_{derm}
As	3.0E-04	3.2E-05	3.9E-06	2.3E-05	2.7E-06	1.1E-01	1.3E-02	7.6E-02	9.1E-03
Ca	1.0E+00	6.1E-02	2.4E-04	5.7E-02	2.3E-04	6.1E-02	2.4E-04	5.7E-02	2.3E-04
Cd	1.0E-03	1.8E-06	7.3E-09	2.1E-06	8.3E-09	1.8E-03	7.3E-06	2.1E-03	8.3E-06
Co	3.0E-04	2.6E-05	1.0E-07	3.3E-05	1.3E-07	8.6E-02	3.4E-04	1.1E-01	4.4E-04
Cr	3.0E-03	2.9E-05	1.2E-07	5.7E-05	2.3E-07	9.7E-03	3.9E-05	1.9E-02	7.6E-05
Cu	4.0E-02	1.8E-05	7.3E-08	3.2E-05	1.3E-07	4.6E-04	1.8E-06	8.0E-04	3.2E-06
Fe	7.0E-01	5.3E-03	2.1E-05	5.2E-03	2.1E-05	7.6E-03	3.0E-05	7.4E-03	3.0E-05
Hg	3.0E-04	6.9E-07	2.7E-09	5.1E-07	2.0E-09	2.3E-03	9.1E-06	1.7E-03	6.8E-06
K	7.8E+01	1.1E-03	4.5E-06	2.7E-03	1.1E-05	1.4E-05	5.7E-08	3.4E-05	1.4E-07
Li	2.0E-03	1.5E-05	5.9E-08	2.1E-05	8.4E-08	7.4E-03	2.9E-05	1.1E-02	4.2E-05
Mg	5.8E+00	4.4E-03	1.7E-05	5.0E-03	2.0E-05	7.5E-04	3.0E-06	8.6E-04	3.4E-06
Mn	2.4E-02	4.4E-04	1.8E-06	8.4E-04	3.3E-06	1.8E-02	7.4E-05	3.5E-02	1.4E-04
Na	5.5E+01	2.1E-04	8.6E-07	3.4E-04	1.4E-06	3.9E-06	1.6E-08	6.2E-06	2.5E-08
Ni	2.0E-02	5.3E-05	2.1E-07	5.9E-05	2.4E-07	2.7E-03	1.1E-05	2.9E-03	1.2E-05
Pb	4.0E-03	2.3E-05	9.4E-08	4.2E-05	1.7E-07	5.9E-03	2.3E-05	1.0E-02	4.2E-05
Se	5.0E-03	1.5E-06	6.2E-09	1.2E-06	5.0E-09	3.1E-04	1.2E-06	2.5E-04	9.9E-07
Sr	6.0E-01	6.0E-05	2.4E-07	4.6E-05	1.8E-07	1.0E-04	4.0E-07	7.7E-05	3.1E-07
Zn	3.0E-01	5.1E-05	2.0E-07	6.9E-05	2.7E-07	1.7E-04	6.8E-07	2.3E-04	9.1E-07
					HI	3.1E-01	1.4E-02	3.4E-01	1.0E-02

Table 72. Description of health risk assessment for selected metals in acid-extract of the sediments during pre-monsoon, monsoon and post-monsoon

	RfD/RDA	Pre-monsoon				Monsoon				Post-monsoon			
	(mg/kg/day)	Exp_{ing}	Exp_{derm}	HQ_{ing}	HQ_{derm}	Exp_{ing}	Exp_{derm}	HQ_{ing}	HQ_{derm}	Exp_{ing}	Exp_{derm}	HQ_{ing}	HQ_{derm}
As	3.0E-04	2.3E-05	2.7E-06	7.7E-02	9.1E-03	2.6E-05	3.1E-06	8.6E-02	1.0E-02	2.2E-05	2.6E-06	7.2E-02	8.7E-03
Ca	1.0E+00	7.1E-02	2.3E-04	7.1E-02	2.3E-04	6.2E-02	2.5E-04	6.2E-02	2.5E-04	7.5E-02	3.0E-04	7.5E-02	3.0E-04
Cd	1.0E-03	7.7E-06	8.3E-09	7.7E-03	8.3E-06	7.1E-06	2.8E-08	7.1E-03	2.8E-05	6.5E-06	2.6E-08	6.5E-03	2.6E-05
Co	3.0E-04	4.7E-05	1.3E-07	1.6E-01	4.4E-04	5.1E-05	2.0E-07	1.7E-01	6.7E-04	5.5E-05	2.2E-07	1.8E-01	7.3E-04
Cr	3.0E-03	4.4E-05	2.3E-07	1.5E-02	7.6E-05	4.0E-05	1.6E-07	1.3E-02	5.3E-05	3.6E-05	1.4E-07	1.2E-02	4.8E-05
Cu	4.0E-02	3.9E-05	1.3E-07	9.8E-04	3.2E-06	3.5E-05	1.4E-07	8.7E-04	3.5E-06	3.1E-05	1.2E-07	7.8E-04	3.1E-06
Fe	7.0E-01	6.1E-03	2.1E-05	8.7E-03	3.0E-05	6.4E-03	2.5E-05	9.1E-03	3.6E-05	6.7E-03	2.7E-05	9.5E-03	3.8E-05
Hg	3.0E-04	4.7E-07	2.0E-09	1.6E-03	6.8E-06	3.5E-07	1.4E-09	1.2E-03	4.6E-06	3.4E-07	1.4E-09	1.1E-03	4.6E-06
K	7.8E+01	1.9E-03	1.1E-05	2.4E-05	1.4E-07	2.1E-03	8.2E-06	2.6E-05	1.0E-07	1.9E-03	7.5E-06	2.4E-05	9.6E-08
Li	2.0E-03	2.7E-05	8.4E-08	1.3E-02	4.2E-05	2.4E-05	9.6E-08	1.2E-02	4.8E-05	2.2E-05	8.8E-08	1.1E-02	4.4E-05
Mg	5.8E+00	1.8E-03	2.0E-05	3.0E-04	3.4E-06	1.5E-03	6.2E-06	2.7E-04	1.1E-06	1.7E-03	6.7E-06	2.9E-04	1.1E-06
Mn	2.4E-02	5.5E-04	3.3E-06	2.3E-02	1.4E-04	5.6E-04	2.2E-06	2.3E-02	9.2E-05	5.7E-04	2.3E-06	2.4E-02	9.5E-05
Na	5.5E+01	9.7E-04	1.4E-06	1.8E-05	2.5E-08	1.1E-03	4.2E-06	1.9E-05	7.6E-08	1.5E-03	6.0E-06	2.7E-05	1.1E-07
Ni	2.0E-02	6.0E-05	2.4E-07	3.0E-03	1.2E-05	7.7E-05	3.1E-07	3.9E-03	1.5E-05	9.5E-05	3.8E-07	4.8E-03	1.9E-05
Pb	4.0E-03	6.9E-05	1.7E-07	1.7E-02	4.2E-05	5.7E-05	2.3E-07	1.4E-02	5.7E-05	4.6E-05	1.8E-07	1.1E-02	4.6E-05
Se	5.0E-03	3.4E-06	5.0E-09	6.8E-04	9.9E-07	3.5E-06	1.4E-08	7.1E-04	2.8E-06	3.0E-06	1.2E-08	6.0E-04	2.4E-06
Sr	6.0E-01	2.7E-04	1.8E-07	4.5E-04	3.1E-07	2.5E-04	1.0E-06	4.2E-04	1.7E-06	2.3E-04	9.3E-07	3.9E-04	1.6E-06
Zn	3.0E-01	1.7E-04	2.7E-07	5.7E-04	9.1E-07	1.7E-04	6.7E-07	5.6E-04	2.2E-06	1.7E-04	6.7E-07	5.6E-04	2.2E-06
			HI	4.0E-01	1.0E-02			4.0E-01	1.2E-02			4.1E-01	1.0E-02

Section-III: SOIL

3.24 Sampling Progress

Soil samples were collected during summer (May) and winter (December) 2011. A total of 180 composite surface (1–15 cm top layer) soil samples were collected from ten major sampling sites as shown in Figure 52. Each composite soil sample was composed of five to ten sub-samples within an area of 10–15 m^2 from same locations during both seasons. Composite surface soil samples were also collected during pre-monsoon (May 2012), monsoon (August 2012) and post-monsoon (October-November 2012) seasons. A total of 300 (n = 100 in each season) composite surface (1–15 cm top layer) soil samples were collected.

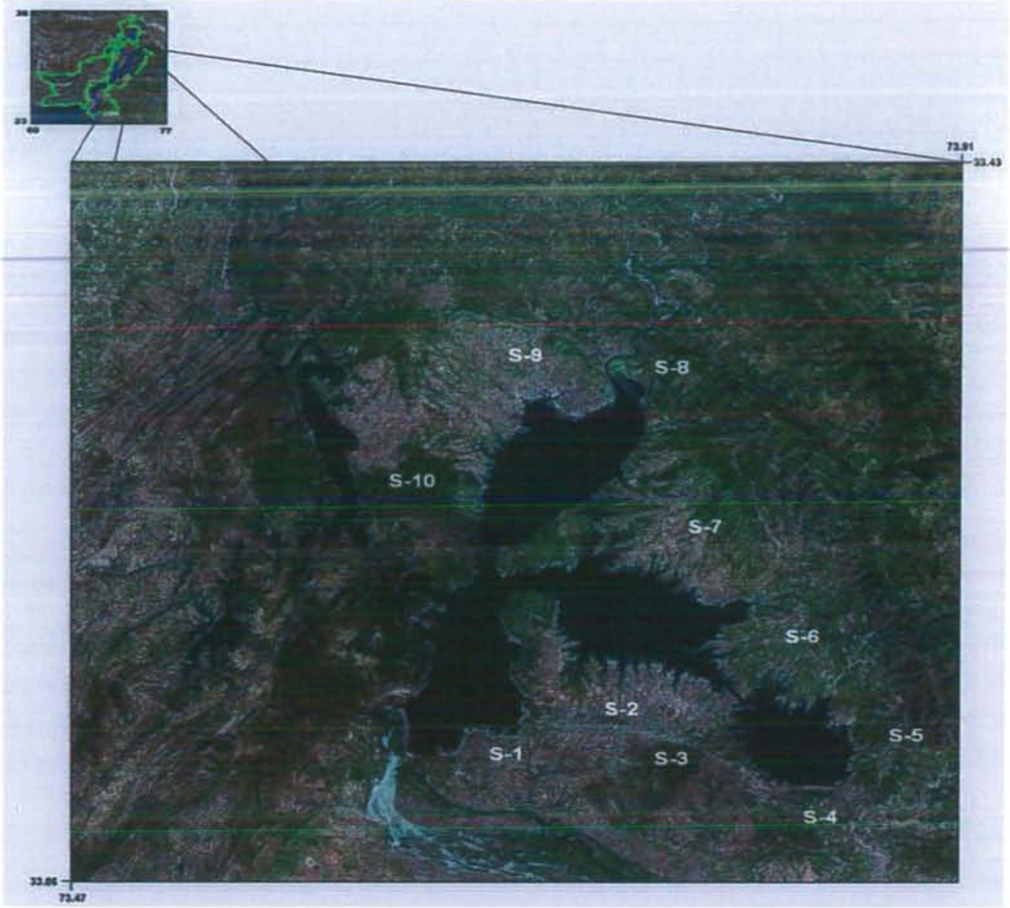

Figure 52. Location map of the study area showing major soil sampling sites

3.25 Distribution of Physicochemical Parameters in Soil Samples

Statistical summary related to distribution of physicochemical parameters in water-extract of the soil samples collected during summer is shown in Table 73. The temperature remained between 27.7 to 28.1°C with an average value of 27.9°C, whereas pH was found to be slightly acidic ranging from 6.35 to 7.45, with mean and median values of 6.77 and 6.66, respectively. Similarly, EC ranged from 1.703 to 13.15 mS/cm with mean value of 6.639 mS/cm and it was mostly associated with random distribution as shown by SD and SE values. Likewise, TDS revealed a minimum value of 0.853 g/L to a maximum value of 6.574 g/L, with the mean and median values of 3.449 and 3.139 g/L, respectively. Generally, large values of the EC and TDS were associated with very high concentration of soluble ions in the soil. Total alkalinity estimated in the soil samples ranged from 0.060 to 0.240 mg/g as $CaCO_3$ with mean value of 0.152 mg/g as $CaCO_3$, while average moisture contents and OM were recorded as 8.833% and 6.097 %, respectively.

During winter season (Table 73), average temperature was recorded as 15.9°C with rather small variations. The pH of soil was once again found to be slightly acidic with an average value of 6.76. Generally, acidic pH exhibited more solubility of the metallic cations, which was also supported by large values of EC and TDS for the soil samples. Average levels of EC and TDS were measured as 7.04 mS/cm and 3.542 g/L, respectively. Generally, large differences were associated with EC and TDS as shown by relatively higher SD and SE values. Total alkalinity of the soil showed almost comparable levels during summer (0.152 mg/g as $CaCO_3$) and winter (0.154 mg/g as $CaCO_3$). The moisture contents of the soil exhibited considerable variations during both seasons, although the magnitude on average basis was higher during summer season. Organic matter varied from 3.524 to 11.58% with an average value 7.103%. Overall, the physiochemical parameters in soil samples displayed acidic characteristic, associated with large variations of soluble species during summer and winter seasons.

Statistical distribution of physicochemical parameters pertaining to water-extracts of the soil samples during pre-monsoon, monsoon and post-monsoon is also shown in Tables 73. During pre-monsoon, temperature was noted between 31.2 to 32.9°C, with an average value of 31.7°C, while pH was varying between 6.80 to 7.64 with mean and median value of 7.27 and 7.25, respectively. Very large variations were observed for EC during pre-monsoon; extremum levels were 2.082 and 8.681 mS/cm, with an average value of 3.582 mS/cm. Likewise, TDS showed a minimum value of 1.041 g/L to a maximum value of 4.341 g/L, with mean and median values of 1.791 and 1.711 g/L, respectively. Both EC and TDS were associated with large dispersion and random distribution as revealed by SD and SE values. Total alkalinity ranged from 0.130 to 0.241 mg/g as $CaCO_3$ with the mean value of 0.180 mg/g as $CaCO_3$. Average moisture contents and organic matter were recorded at 1.876% and 8.415%, respectively.

Table 73. Statistical distribution of physicochemical parameters in the soil samples during summer, winter, pre-monsoon, monsoon and post-monsoon

		Min	Max	Mean	Median	SD	SE	Skew	Kurt
Summer (*n* = 90)	T (°C)	27.7	28.1	27.9	27.9	0.100	0.018	0.255	-0.143
	pH	6.35	7.45	6.77	6.66	0.330	0.060	1.063	-0.080
	EC (mS/cm)	1.703	13.15	6.639	6.030	3.253	0.594	0.324	-1.108
	TDS (g/L)	0.853	6.574	3.449	3.139	1.637	0.299	0.195	-1.213
	TA (mg/g as $CaCO_3$)	0.060	0.240	0.152	0.150	0.060	0.011	0.011	-1.010
	MC (%)	1.695	14.84	8.833	8.616	2.775	0.507	-0.483	1.118
	OM (%)	3.063	9.316	6.097	6.020	1.586	0.355	0.048	-0.337
Winter (*n* = 90)	T (°C)	15.6	16.1	15.9	15.9	0.132	0.024	-0.203	-0.325
	pH	6.54	7.15	6.76	6.71	0.164	0.030	0.771	-0.054
	EC (mS/cm)	2.35	11.5	7.04	5.130	3.656	0.668	0.106	-1.978
	TDS (g/L)	1.17	5.75	3.542	2.495	1.833	0.335	0.113	-1.984
	TA (mg/g as $CaCO_3$)	0.060	0.240	0.154	0.180	0.054	0.010	-0.214	-0.569
	MC (%)	1.745	7.867	3.868	3.604	1.299	0.237	0.932	1.602
	OM (%)	3.524	11.58	7.103	6.927	1.959	0.438	0.281	0.062
Pre-monsoon (*n* = 100)	T (°C)	31.2	32.9	31.7	31.6	0.410	0.065	1.426	1.428
	pH	6.8	7.64	7.27	7.25	0.186	0.029	-0.111	-0.160
	EC (mS/cm)	2.082	8.681	3.582	3.421	12.58	19.90	2.113	6.401
	TDS (g/L)	1.041	4.341	1.791	1.711	6.294	9.952	2.113	6.401
	TA (mg/g as $CaCO_3$)	0.130	0.241	0.180	0.178	0.017	0.003	0.243	0.057
	MC (%)	1.033	3.561	1.876	1.837	0.605	0.096	0.946	0.965
	OM (%)	5.446	12.43	8.415	8.661	2.152	0.481	0.095	-1.104
Monsoon (*n* = 100)	T (°C)	26.1	27.4	26.5	26.4	0.300	0.047	1.286	1.689
	pH	7.96	8.44	8.21	8.20	0.140	0.022	0.053	-0.988
	EC (mS/cm)	2.860	7.074	4.416	4.336	9.858	1.559	0.683	0.519
	TDS (g/L)	1.429	3.537	2.208	2.168	4.926	1.009	0.681	0.517
	TA (mg/g as $CaCO_3$)	0.171	0.268	0.208	0.206	0.021	0.003	0.748	0.926
	MC (%)	4.301	9.450	6.931	7.027	1.246	0.197	-0.140	-0.354
	OM (%)	4.046	8.925	7.015	7.358	1.450	0.324	-0.489	-0.789
Post-monsoon (*n* = 100)	T (°C)	13.8	14.7	14.3	14.3	0.212	0.033	-0.086	-0.218
	pH	6.72	7.49	7.01	6.95	0.165	0.026	0.963	0.789
	EC (mS/cm)	2.255	9.102	4.098	4.030	14.90	2.355	1.167	1.703
	TDS (g/L)	1.128	4.551	2.049	2.015	7.450	1.178	1.166	1.700
	TA (mg/g as $CaCO_3$)	0.119	0.269	0.196	0.182	0.025	0.004	1.122	1.766
	MC (%)	6.155	15.10	10.18	10.45	2.183	0.345	0.063	-0.192
	OM (%)	4.196	13.79	8.694	8.246	2.640	0.590	0.371	-0.546

During monsoon season (Table 73), average temperature was recorded as 26.5°C. The pH of soil was found between 7.96 to 8.47 with an average value of 8.21 and an almost matching median value (8.20). Comparatively large values of EC (4.412 mS/cm) and TDS (2.201 g/L) were found in the soil samples during monsoon, which were higher than the recorded values during pre-monsoon. Total alkalinity ranged from 0.171 to 0.268 mg/g as $CaCO_3$, with a mean value of 0.208 mg/g as $CaCO_3$, while the moisture contents and organic matter contents were recorded at 6.931% and 7.015%, respectively.

During post-monsoon (Table 73), temperature was noted between 13.8 to 14.7°C, with an average value of 14.3°C. Similarly, pH was varying between 6.72 to 7.49 with the mean and median values of 7.01 and 6.95, respectively. During post-monsoon, EC exhibited minimum-maximum levels as 2.255-9.102 mS/cm with average contents of 4.098 mS/cm. Likewise, TDS exhibited minimum-maximum levels as 1.128-4.551 g/L with mean and median values of 2.049 and 2.015 g/L, respectively. EC, TDS were mostly associated with random distribution as shown by large SD and SE values. Total alkalinity ranged from 0.119 to 0.269 mg/g as $CaCO_3$, with a mean value of 0.196 mg/g as $CaCO_3$. On comparative basis, total alkalinity of the soil was observed at nearly comparable levels during the pre-monsoon, monsoon and post-monsoon seasons. Average moisture contents and organic matter contents were recorded at 10.18% and 8.694%, respectively.

3.26 Distribution of Selected Metals in Calcium Nitrate Extract of Soil Samples

Concentrations of selected metals in calcium nitrate extract of the soil samples were analysed in order to assess the soluble and bio-available fraction of the metals. Basic statistical parameters related to distribution of selected metals in calcium nitrate extract of the soil samples during summer are given in Table 74. On the average basis, Ca, Na, Mg, K and Fe were noted to be the major components with mean levels of 67.37, 28.34, 9.067, 4.355 and 1.005 mg/kg, respectively. On the other hand, Li, Cu, Mn and Hg were found to be the minor contributors with mean values of 0.019, 0.032, 0.031 and 0.019 mg/kg, respectively. Overall, the metals exhibited following increasing concentration order: Hg < Li < Mn < Cu < Cd < Cr < Zn < Co < Se < Sr < Ni < As < Pb < Fe < K < Mg < Na < Ca. Some of the metals (Ca, K, Mg and Na) showed significant randomness in their distribution as supported by large SD and SE values. Relatively asymmetric distribution was noted for Ca, Cr, Cu, Hg, K, Mg, Mn and Se, as indicated by their higher skewness and kurtosis values. The quartile distribution of selected metals in calcium nitrate extract of the soil samples during summer is shown in Figure 53. Most of the metals exhibited broad range with appreciable variations; however, Hg, K, Mg, Na and Se showed relatively narrow distribution in the examined soil samples. Nonetheless, highest asymmetry in the quartile distribution was noted for Zn, Mn, Cr and Co in calcium nitrate extract of the soil samples.

Table 74. Statistical distribution of selected metal levels (mg/kg) in calcium nitrate extract of the soil during summer (*n* = 90)

	Min	Max	Mean	Median	SD	SE	Skew	Kurt
As	0.243	1.524	0.617	0.372	0.420	0.077	0.883	-0.953
Ca	3.710	364.4	67.37	52.54	64.72	11.82	3.571	15.75
Cd	0.010	0.152	0.085	0.091	0.035	0.006	-0.438	-0.277
Co	0.022	0.590	0.221	0.166	0.181	0.033	0.954	-0.384
Cr	0.002	0.358	0.095	0.066	0.089	0.016	1.498	2.102
Cu	0.004	0.138	0.032	0.019	0.035	0.006	1.984	3.236
Fe	0.100	3.170	1.005	0.697	0.812	0.148	0.945	0.213
Hg	0.014	0.045	0.019	0.019	0.006	0.001	2.866	10.53
K	1.280	19.86	4.355	3.816	3.475	0.634	3.278	13.82
Li	0.002	0.042	0.020	0.016	0.011	0.002	0.477	-0.778
Mg	2.424	25.62	9.067	8.271	4.823	0.881	1.671	3.911
Mn	0.002	0.098	0.031	0.027	0.021	0.004	1.465	2.895
Na	7.207	49.20	28.34	29.54	12.55	2.291	0.032	-0.940
Ni	0.042	1.264	0.433	0.375	0.297	0.054	0.922	0.589
Pb	0.152	1.498	0.801	0.789	0.331	0.061	0.086	-0.618
Se	0.166	0.673	0.287	0.255	0.126	0.023	1.902	3.845
Sr	0.116	0.730	0.369	0.361	0.171	0.031	0.459	-0.768
Zn	0.004	0.252	0.122	0.138	0.074	0.014	-0.082	-1.224

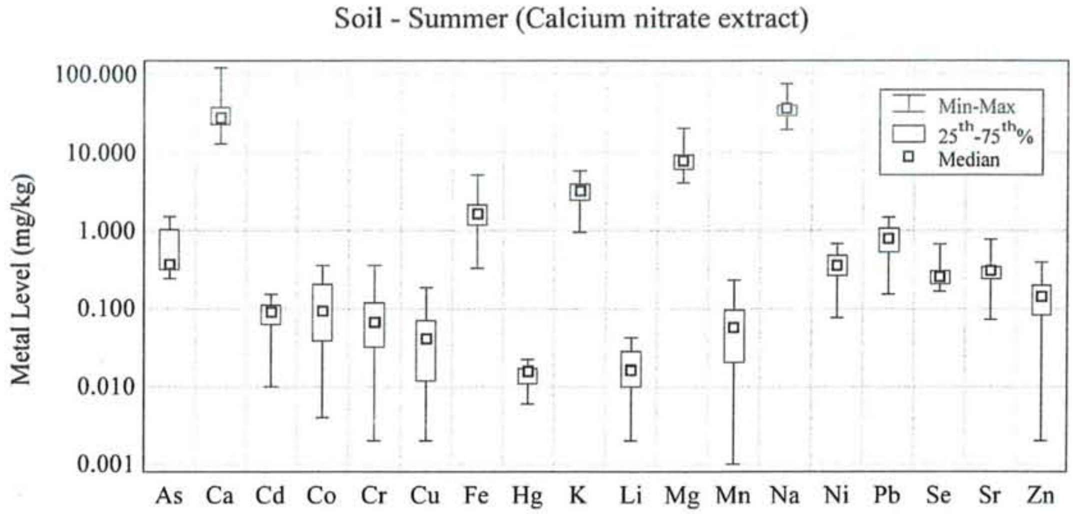

Figure 53. Quartile distribution of selected metal levels (mg/kg) in calcium nitrate extract of the soil during summer

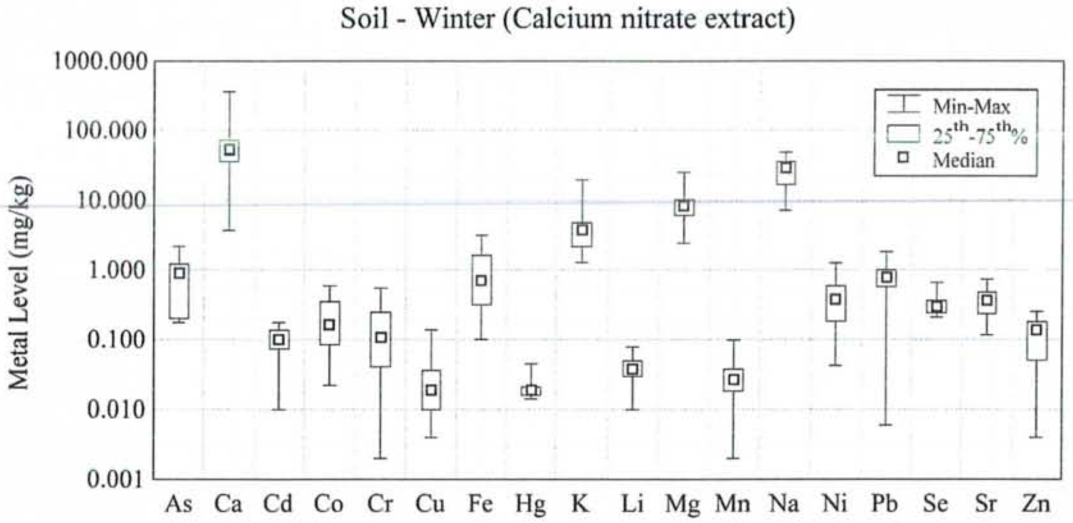

Figure 54. Quartile distribution of selected metal levels (mg/kg) in calcium nitrate extract of the soil during winter

Distribution of selected metals in calcium nitrate extract of the soil samples during winter is shown in Table 75, in terms of basic statistical parameters. Among the metals, on mean basis, Na (38.37 mg/kg) and Ca (32.61 mg/kg) were the dominant contributors, followed by, Mg (8.504 mg/kg), K (3.208 mg/kg) and Fe (1.803 mg/kg). Similarly, mean concentrations of As, Pb, Ni, Se, Sr, Cr, Zn and Co were found at 0.878, 0.806, 0.363, 0.322, 0.313, 0.151, 0.144 and 0.129 mg/kg, respectively. However, the lowest average concentrations were shown by Cd, Mn, Cu, Li and Hg at 0.104, 0.068, 0.050, 0.041 and 0.014 mg/kg, in that order. Overall, following increasing concentration order was noted for selected metals in the soil samples during winter: Hg < Li < Cu < Mn < Cd < Co < Zn < Cr < Sr < Se < Ni < Pb < As < Fe < K < Mg < Ca < Na. Predominantly random distribution was shown by Ca, Na, Mg and K as supported by their higher SD and SE values. Moreover, Ca, Cr, Cu, Fe, Mg, Mn, Na, Se and Sr showed relatively asymmetric dispersion as evidenced by relatively higher skewness and kurtosis values. Box and whisker plot showing the quartile distribution of selected metals in calcium nitrate extract of the soil samples during winter is shown in Figure 54, which revealed broad range and mostly asymmetrical distribution for Ca, Co, Cr, Pb, Ni and Zn. Nevertheless, relatively narrow distribution pattern was shown by Hg, Li, Na, Se and Sr in the soil samples.

Table 75. Statistical distribution of selected metal levels (mg/kg) in calcium nitrate extract of the soil during winter (*n* = 90)

	Min	Max	Mean	Median	SD	SE	Skew	Kurt
As	0.176	2.185	0.878	0.894	0.644	0.118	0.652	-0.485
Ca	13.11	122.2	32.61	27.77	19.63	3.580	3.506	15.33
Cd	0.010	0.176	0.104	0.099	0.041	0.007	-0.018	-0.486
Co	0.004	0.358	0.129	0.094	0.102	0.019	0.809	-0.366
Cr	0.002	0.548	0.151	0.108	0.136	0.025	1.258	1.426
Cu	0.002	0.186	0.050	0.040	0.048	0.009	1.263	1.012
Fe	0.330	5.228	1.803	1.646	0.935	0.171	1.708	5.152
Hg	0.006	0.022	0.014	0.016	0.004	0.001	-0.387	-0.691
K	0.960	5.90	3.208	3.242	1.191	0.217	0.043	-0.241
Li	0.010	0.078	0.041	0.038	0.018	0.003	0.398	-0.293
Mg	4.150	20.84	8.504	7.965	3.277	0.598	2.026	6.154
Mn	0.001	0.232	0.068	0.056	0.059	0.011	1.190	1.051
Na	19.89	75.90	38.37	36.90	13.06	2.384	1.380	2.036
Ni	0.076	0.684	0.363	0.359	0.159	0.029	0.016	-0.418
Pb	0.006	1.826	0.806	0.774	0.406	0.074	0.397	0.476
Se	0.209	0.656	0.322	0.299	0.103	0.019	1.467	2.503
Sr	0.072	0.778	0.313	0.306	0.126	0.023	1.679	5.750
Zn	0.002	0.396	0.144	0.142	0.093	0.017	0.567	0.395

Average metal levels in calcium nitrate extract of the soil samples during summer and winter are shown in Figure 55, for comparative evaluation. Average concentration of As, Cd, Cr, Cu, Fe, Li, Mn, Na, Se and Zn were found to be relatively higher during winter than summer, however, mean levels of Ca, Co, Hg, K, Ni and Sr were comparatively higher during summer than winter. Approximately equivalent mean levels were noted for Pb and Mg during both seasons.

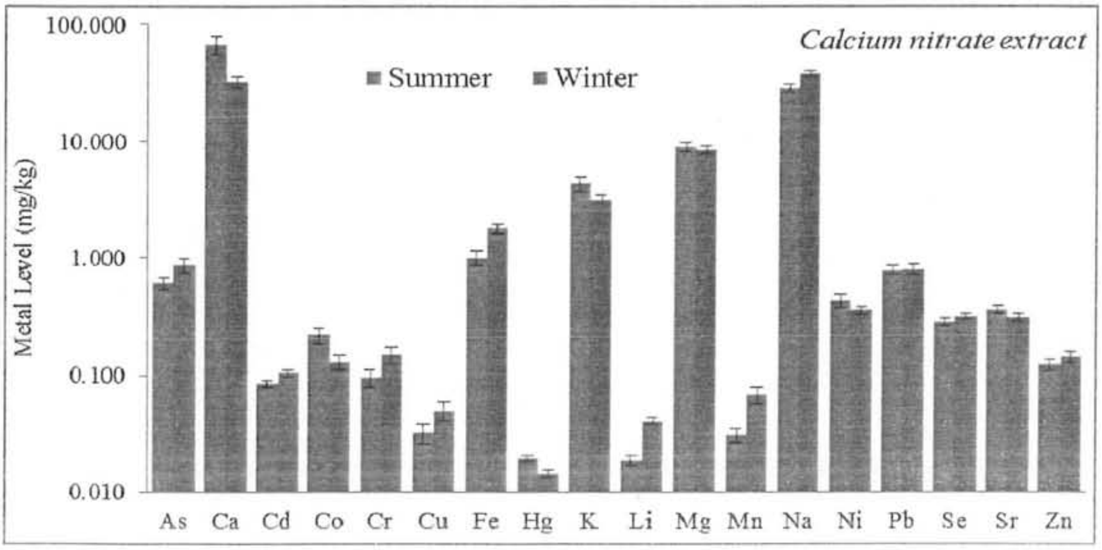

Figure 55. Comparison of average metal levels (mg/kg, ±SE) in calcium nitrate extract of the [illegible]ng summer and winter

Basic statistical parameters related to the distribution of selected metals in calcium nitrate extracts of the soil during pre-monsoon are given in Table 76. On the average basis, Ca, Na, Mg, K, Fe and As were the major components with mean levels of 368.6, 43.78, 9.620, 4.265, 1.423 and 1.384 mg/kg, respectively, while Zn, Cd, Hg and Li were the minor contributors with mean value of 0.120, 0.054, 0.021 and 0.017 mg/kg, respectively. Overall, selected metals displayed following increasing trend of concentrations: Li < Hg < Cd < Zn < Cu < Sr < Se < Pb < Cr < Ni < Mn < Co < As < Fe < K < Mg < Na < Ca. Random distribution was noted for Ca, Fe, K, Mg, Mn and Na as supported by relatively large SD and SE values. Most of the metals exhibited predominately asymmetric distribution in the soil samples as indicated by the skewness and kurtosis values. Quartile distribution of selected metals in calcium nitrate extract of the soil during pre-monsoon is shown in Figure 56. Most of the metals exhibited very broad range and relatively asymmetrical dispersion in calcium nitrate extract of the soil, however, As, Cd, Hg and Se showed moderately narrow distribution.

Table 76. Statistical distribution of selected metal levels (mg/kg) in calcium nitrate extract of the soil during pre-monsoon ($n = 100$)

	Min	Max	Mean	Median	SD	SE	Skew	Kurt
As	0.583	3.182	1.384	0.834	0.911	0.144	0.784	-1.176
Ca	5.906	5086	368.6	203.1	798.1	126.2	5.551	33.27
Cd	0.014	0.154	0.054	0.042	0.035	0.006	1.530	1.785
Co	0.024	2.628	0.938	0.924	0.672	0.106	0.600	-0.261
Cr	0.012	2.170	0.537	0.348	0.553	0.087	1.706	2.452
Cu	0.002	0.464	0.169	0.127	0.127	0.020	0.812	-0.173
Fe	0.122	4.960	1.423	1.044	1.112	0.176	1.489	1.920
Hg	0.011	0.032	0.021	0.020	0.007	0.001	0.145	-1.424
K	0.746	16.94	4.265	2.618	3.722	0.588	1.696	2.900
Li	0.002	0.066	0.017	0.016	0.015	0.002	1.506	2.317
Mg	1.468	28.89	9.620	7.236	6.466	1.022	1.337	1.408
Mn	0.020	5.488	0.666	0.254	1.265	0.200	2.906	7.557
Na	4.606	315.6	43.78	24.99	54.89	8.678	3.345	15.06
Ni	0.064	1.332	0.580	0.622	0.329	0.052	0.258	-0.560
Pb	0.028	1.084	0.463	0.450	0.238	0.038	0.374	-0.052
Se	0.160	0.336	0.212	0.197	0.044	0.007	1.127	1.175
Sr	0.004	1.160	0.193	0.154	0.211	0.033	3.167	12.37
Zn	0.008	0.432	0.120	0.067	0.107	0.017	1.253	1.211

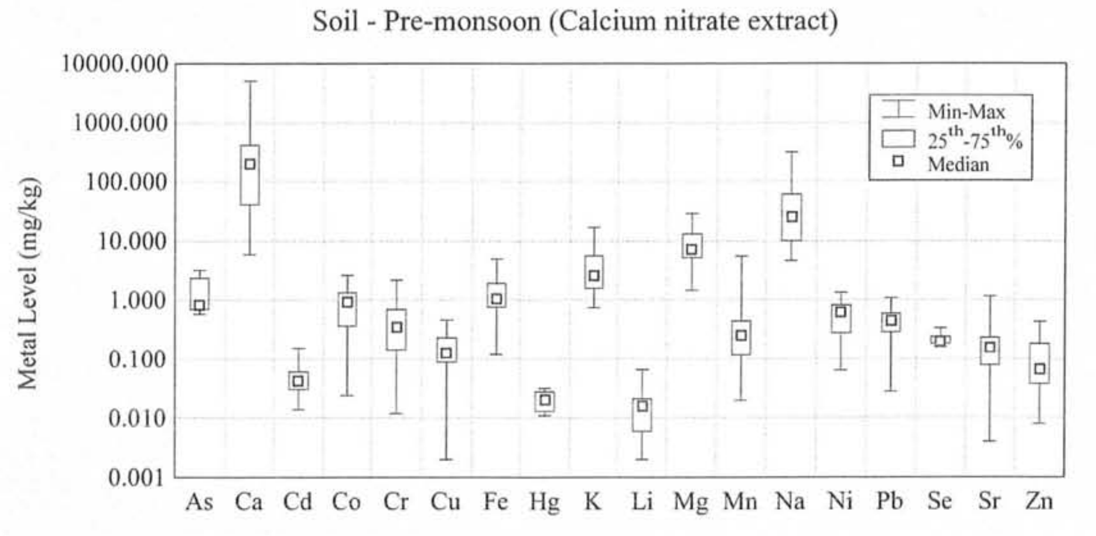

Figure 56. Quartile distribution of selected metal levels (mg/kg) in calcium nitrate extract of the soil during pre-monsoon

Table 77. Statistical distribution of selected metal levels (mg/kg) in calcium nitrate extract of the soil during monsoon (n = 100)

	Min	Max	Mean	Median	SD	SE	Skew	Kurt
As	0.331	2.195	0.939	0.625	0.588	0.093	0.747	-1.106
Ca	13.60	1893	229.7	135.7	346.6	54.80	3.808	15.75
Cd	0.008	0.102	0.039	0.034	0.022	0.003	1.032	1.089
Co	0.041	1.323	0.513	0.504	0.335	0.053	0.535	-0.432
Cr	0.073	1.126	0.399	0.349	0.271	0.043	1.187	1.117
Cu	0.025	0.275	0.105	0.085	0.065	0.010	0.872	0.022
Fe	0.450	7.340	2.188	1.897	1.239	0.196	2.002	6.842
Hg	0.012	0.029	0.020	0.020	0.005	0.001	0.255	-0.930
K	1.020	19.39	4.053	2.695	3.959	0.626	2.499	6.493
Li	0.003	0.070	0.022	0.018	0.016	0.003	1.424	1.927
Mg	1.986	16.30	7.248	6.568	3.519	0.556	1.055	0.467
Mn	0.041	2.786	0.367	0.152	0.637	0.101	2.901	7.503
Na	4.376	171.3	41.53	38.39	31.80	5.029	1.994	6.115
Ni	0.126	0.827	0.478	0.445	0.216	0.034	0.048	-1.276
Pb	0.064	0.860	0.391	0.361	0.167	0.026	0.443	0.491
Se	0.122	0.266	0.175	0.170	0.032	0.005	0.778	0.755
Sr	0.045	0.674	0.165	0.148	0.112	0.018	2.690	10.41
Zn	0.027	0.374	0.167	0.156	0.091	0.014	0.530	-0.366

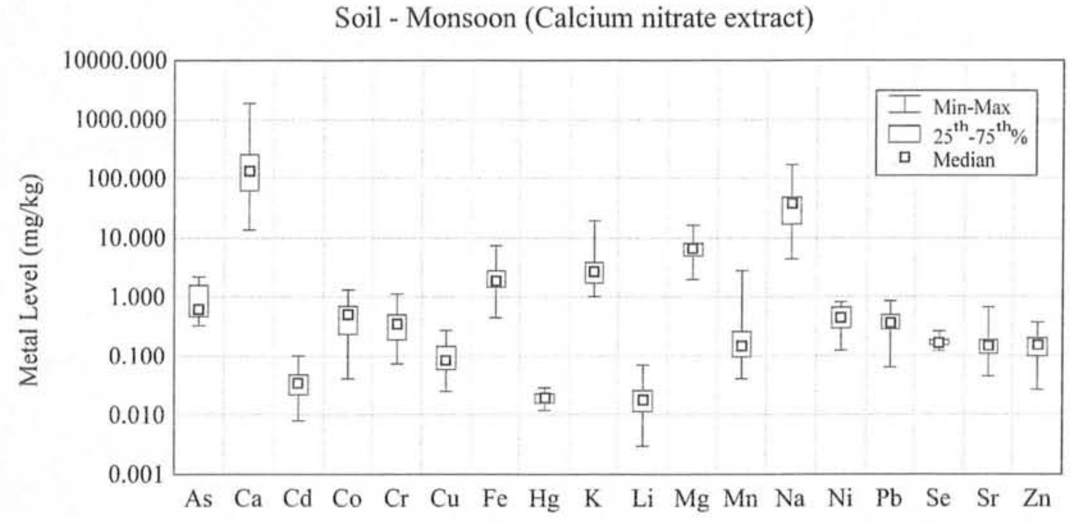

Figure 57. Quartile distribution of selected metal levels (mg/kg) in calcium nitrate extract of the soil during monsoon

Table 78. Statistical distribution of selected metal levels (mg/kg) in calcium nitrate extract of the soil during post-monsoon ($n = 100$)

	Min	Max	Mean	Median	SD	SE	Skew	Kurt
As	0.069	0.558	0.332	0.378	0.189	0.030	-0.336	-1.570
Ca	1.532	3402	199.2	37.75	633.5	100.2	4.492	20.09
Cd	0.002	0.058	0.023	0.019	0.018	0.003	0.422	-1.033
Co	0.004	0.228	0.083	0.073	0.052	0.008	0.709	0.121
Cr	0.088	1.010	0.305	0.208	0.241	0.038	1.546	1.202
Cu	0.002	0.112	0.040	0.031	0.029	0.005	0.818	-0.205
Fe	0.184	11.36	3.063	2.576	2.138	0.338	1.499	4.390
Hg	0.012	0.018	0.015	0.015	0.001	0.000	-0.025	-0.875
K	0.564	29.10	3.679	1.817	6.398	1.012	3.326	10.27
Li	0.002	0.122	0.027	0.012	0.033	0.005	1.701	2.038
Mg	1.360	28.99	5.711	4.320	5.445	0.861	3.330	11.98
Mn	0.004	0.114	0.064	0.064	0.025	0.004	-0.027	-0.594
Na	2.498	181.5	37.57	24.32	39.67	6.272	2.028	4.516
Ni	0.040	0.952	0.434	0.423	0.254	0.040	0.515	-0.687
Pb	0.016	1.238	0.309	0.292	0.228	0.036	1.754	5.874
Se	0.089	0.209	0.125	0.121	0.027	0.004	0.966	0.894
Sr	0.012	0.432	0.135	0.122	0.089	0.014	1.156	2.080
Zn	0.010	0.648	0.208	0.172	0.172	0.027	1.041	0.469

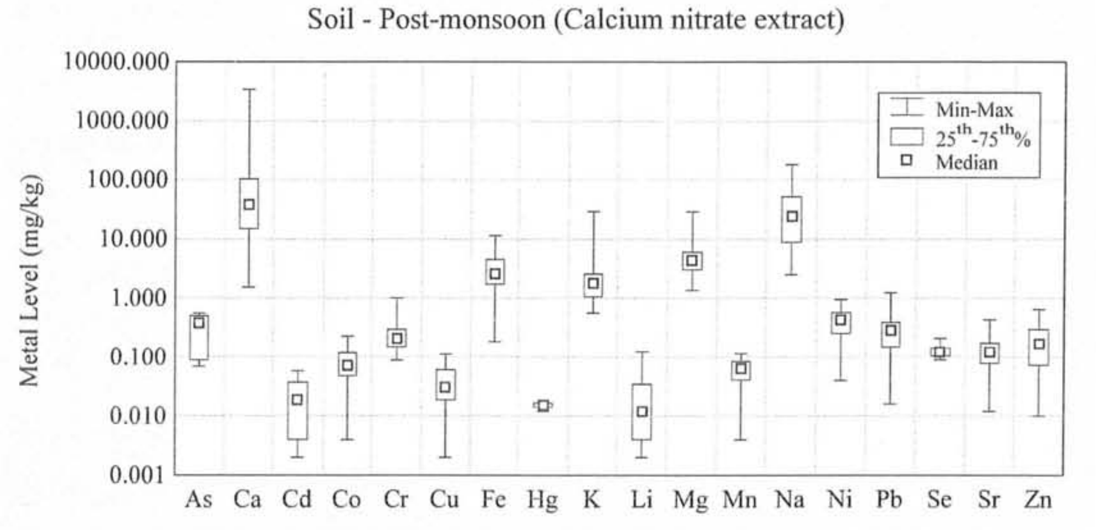

Figure 58. Quartile distribution of selected metal levels (mg/kg) in calcium nitrate extract of the soil during post-monsoon

Basic statistical parameters related to the distribution of selected metals in calcium nitrate extract of the soil samples during monsoon are given in Table 77. On the mean basis, Ca, Na, Mg, K, Fe and As were the major contributors with mean levels of 229.7, 41.53, 7.248, 4.053, 2.188 and 0.939 mg/kg, respectively, whereas Zn, Sr, Cu, Cd, Li and Hg were found in relatively smaller amount with mean levels of 0.167, 0.165, 0.105, 0.039, 0.022 and 0.020 mg/kg, respectively. Among the remaining metals, Co, Ni, Cr, Pb, Mn and Se were found at 0.513, 0.478, 0.399, 0.391, 0.367 and 0.175 mg/kg, respectively. Overall, selected metals concentrations revealed following increasing trend: Hg < Li < Cd < Cu < Sr < Zn < Se < Mn < Pb < Cr < Ni < Co < As < Fe < K < Mg < Na < Ca. Comparatively higher SD and SE values for Ca, Fe, K, Mg and Na exhibited their random distribution in the soil during monsoon season. Relatively higher asymmetry in the distribution of Ca, Cd, Cr, Fe, K, Li, Mg, Mn, Na and Sr was evidenced by rather large values of skewness and kurtosis. Box & Whisker plot showing the quartile distribution of selected metals in calcium nitrate extract of the soil during monsoon is shown in Figure 57. Most of the metals exhibited large variations in their quartile levels; however, more or less symmetrical and fairly narrow distribution was shown by Hg and Se in the soil samples during monsoon.

Statistical distribution of selected metals in calcium nitrate extract of the soil samples during post-monsoon is shown in Table 78. Highest mean levels (mg/kg) was noted for Ca (199.2), followed by, Na (37.57), Mg (5.711), K (3.679) and Fe (3.063), while relatively lower average concentrations were shown by Li (0.027), Cd (0.023) and Hg (0.015). Rest of the metal levels were ranging from 0.027 to 0.434 mg/kg. Overall, following increasing concentration order was noted for selected metals in the soil during post-monsoon: Hg < Cd < Li < Cu < Mn < Co < Se < Sr < Zn < Cr < Pb < As < Ni < Fe < K < Mg < Na < Ca. Generally, random distribution was observed for Ca, Fe, K, Mg and Na, as supported by relatively higher SD/SE values, whereas relatively asymmetric distribution was shown by Ca, Cr, Fe, K, Li, Mg, Na, Pb, Sr and Zn as revealed by higher skewness and kurtosis values. The quartile distribution of selected metals in calcium nitrate extract of the soil during post-monsoon is illustrated in Figure 58, which revealed that most of the metals showed relatively broad and asymmetrical distribution. However, Hg and Se exhibited very narrow distribution in the soil samples thus indicating their consistent contents.

Comparison of average metal levels in calcium nitrate extracts of the soil samples during pre-monsoon, monsoon and post-monsoon is depicted in Figure 59. Average concentrations of most of the metals were found to be relatively higher during pre-monsoon season, while considerably lower during post-monsoon season. Such variations in the metal levels might be attributed to the excessive anthropogenic activities (including agriculture, recreational and domestic/industrial activities, etc.) in the study area during pre-monsoon. More or less comparable mean levels in the soil samples were observed for K and Na during pre-monsoon, monsoon and post-monsoon, however, mean levels of Fe, Li and Zn were observed to be noticeably higher during post-monsoon season.

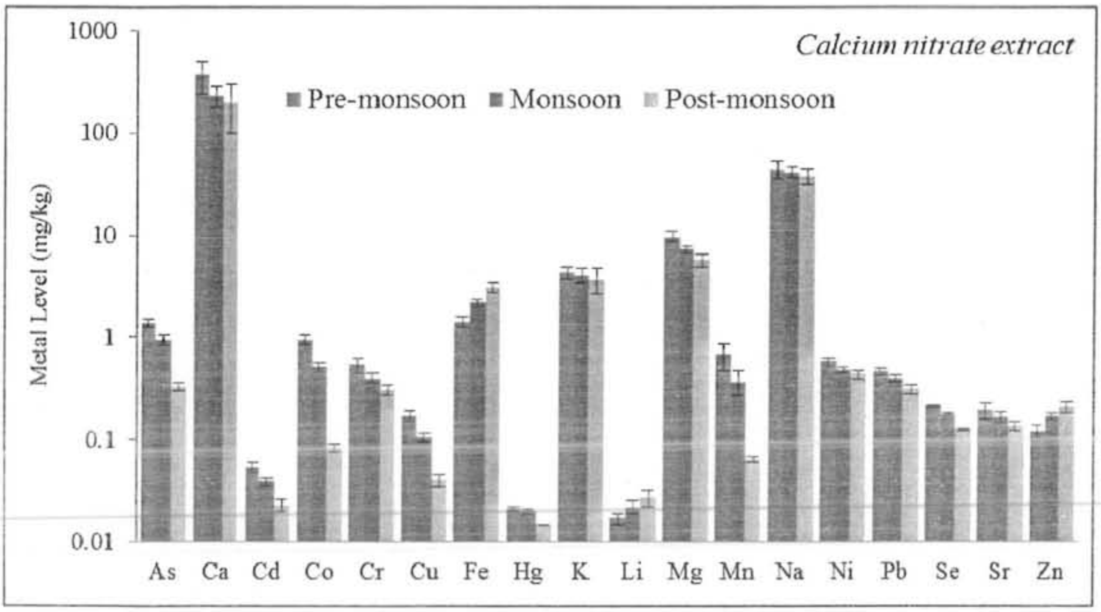

Figure 59. Comparison of average metal levels (mg/kg, ±SE) in calcium nitrate extracts of the soil during pre-monsoon, monsoon and post-monsoon

3.27 Distribution of Selected Metals in Acid Extract of Soil Samples

Basic statistical parameters related to the distribution of selected metals in acid extract of the soil samples during summer are given in Table 79. Most of the metals showed large variations as indicated by their lowest and highest levels. However, overwhelmingly higher mean concentration was recorded for Ca (40979 mg/kg), followed by, Fe (4038 mg/kg) and Mg (3408 mg/kg). The higher levels of Ca pointed out the fact that the soil samples in the study area are mostly calcite in nature which also revealed the general characteristics of lithosphere. Moderate mean levels were noted for K, Mn, Na, Zn, Sr, Co, Ni and Cr at their corresponding values of 854.4, 393.7, 186.9, 40.29, 38.56, 32.75, 29.12 and 21.23 mg/kg. Comparatively lower mean levels were found for Cd, Se and Hg as 1.337, 0.758 and 0.293 mg/kg in that order. Overall, average metal contents in acid extract of the soil exhibited following decreasing concentration order; Ca > Fe > Mg > K > Mn > Na > Zn > Sr > Co > Ni > Cr > Pb > As > Cu > Li > Cd > Se > Hg. Most of the metals showed random distribution as indicated by relatively higher SD and SE, except Cd, Hg and Se which exhibited rather lower dispersion. Among selected metals, Ca, Cu, Fe, Na, Pb and Zn revealed mostly asymmetrical distribution as evidenced by relatively higher skewness and kurtosis values. The quartile distribution of metals in acid extract of the soil during summer is presented in Figure 60. Most of the metals revealed narrow distribution; Fe exhibited narrowest distribution with overlapping of lower and upper quartile, however, Ca, Cd, Na, Ni and Pb exhibited relatively broad distribution between lower and upper quartile. In addition, mostly the metals showed asymmetric distribution in the soil samples during summer.

Table 79. Statistical distribution of selected metal levels (mg/kg) in acid extract of the soil during summer (*n* = 90)

	Min	Max	Mean	Median	SD	SE	Skew	Kurt
As	6.909	27.33	15.30	14.38	5.307	0.969	0.478	-0.480
Ca	3347	141332	40979	35305	25438	4644	2.468	8.143
Cd	0.049	2.465	1.337	1.324	0.632	0.115	-0.250	-0.569
Co	7.905	74.61	32.75	29.48	17.66	3.224	0.588	-0.293
Cr	7.708	40.33	21.23	20.37	7.513	1.372	0.360	0.258
Cu	6.238	29.37	14.76	14.12	4.641	0.847	1.212	3.258
Fe	3887	4308	4038	4027	105.4	19.24	1.922	4.662
Hg	0.128	0.494	0.293	0.281	0.099	0.018	0.386	-0.581
K	183.3	1653	854.4	772.1	401.1	73.23	0.375	-0.725
Li	2.426	18.88	10.39	10.97	3.676	0.671	-0.161	0.605
Mg	1850	3964	3408	3567	496.5	90.64	-1.747	2.829
Mn	263.8	562.2	393.7	394.1	69.99	12.78	0.349	0.202
Na	34.48	565.3	186.9	165.5	124.5	22.73	1.594	3.246
Ni	4.109	75.45	29.12	29.30	15.89	2.901	0.724	1.151
Pb	2.485	48.56	17.27	14.56	12.92	2.358	1.231	0.800
Se	0.468	1.222	0.758	0.738	0.199	0.036	0.507	-0.575
Sr	15.37	75.91	38.56	36.90	15.10	2.757	0.653	0.180
Zn	16.98	77.15	40.29	39.63	11.22	2.048	1.235	4.162

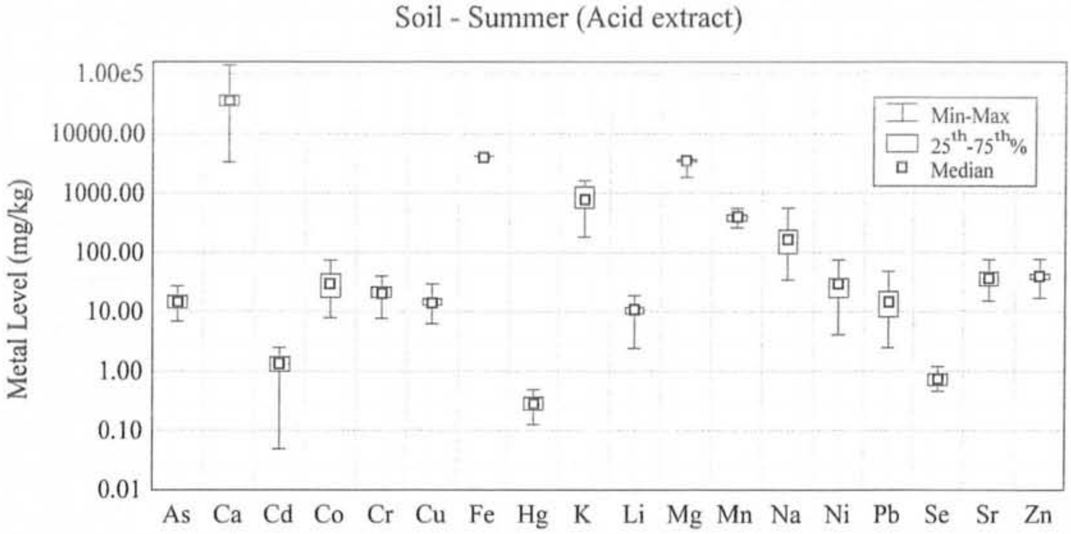

Figure 60. Quartile distribution of selected metal levels (mg/kg) in acid extract of the soil during summer

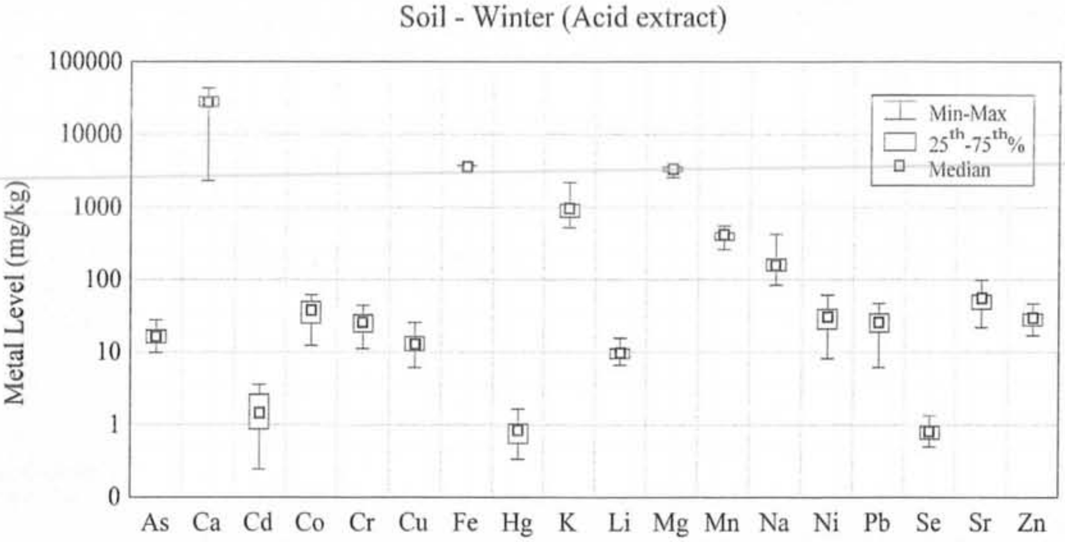

Figure 61. Quartile distribution of selected metal levels (mg/kg) in acid extract of the soil during winter

Various statistical distribution parameters for selected metals in acid extract of the soil samples during winter are shown in Table 80. Average levels of As, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Li, Mg, Mn, Na, Ni, Pb, Se, Sr and Zn in acid extract of the soil were measured as 16.97, 27874, 1.786, 38.11, 26.24, 13.62, 3673, 0.860, 1021, 10.02, 3347, 407.4, 182.4, 29.39, 26.02, 0.827, 54.13 and 29.58 mg/kg, respectively. Highest average concentration was once more shown by Ca, followed by, Fe, Mg and K while lowest values were shown by Cd, Se and Hg. Overall, mean metal levels in acid extract of the soil exhibited following decreasing concentration pattern: Ca > Fe > Mg > K > Mn > Na > Sr > Co > Zn > Ni > Pb > Cr > Cu > As > Li > Cd > Se > Hg. Most of the metals were found to be randomly distributed as exhibited by large SD and SE values, whereas, Na and K exhibited highest asymmetry in their distribution as shown by relatively higher skewness and kurtosis values. Box & Whisker plot showing quartile distribution of selected metals in acid extract of the soil during winter is depicted in Figure 61, which revealed relatively narrow and asymmetrical distribution pattern for most of the metals. However, Ca, Cd, Ni and Pb displayed relatively broad distribution among their lower and upper quartile, whereas, Fe exhibited narrowest distribution with overlapping of lower and upper quartile. Some of the metals (As and Se) demonstrated somewhat symmetric variations in the soil.

Table 80. Statistical distribution of selected metal levels (mg/kg) in acid extract of the soil during winter ($n = 90$)

	Min	Max	Mean	Median	SD	SE	Skew	Kurt
As	9.792	27.67	16.97	16.12	4.735	0.865	0.520	-0.503
Ca	2347	43467	27874	27404	9071	1656	-0.550	1.341
Cd	0.245	3.621	1.786	1.462	1.069	0.195	0.517	-0.999
Co	12.35	61.84	38.11	38.10	14.14	2.582	0.139	-1.091
Cr	11.15	44.28	26.24	25.35	8.974	1.638	0.437	-0.724
Cu	6.076	25.45	13.62	12.92	5.019	0.916	0.780	0.131
Fe	3517	3906	3673	3642	101.7	18.57	0.658	-0.406
Hg	0.336	1.662	0.860	0.837	0.368	0.067	0.607	-0.439
K	525.3	2219	1021	957.9	387.0	70.65	1.387	2.249
Li	6.582	15.59	10.02	9.568	2.304	0.421	0.837	0.191
Mg	2587	3774	3347	3392	313.7	57.27	-0.603	-0.248
Mn	262.1	554.6	407.4	417.7	64.72	11.82	-0.059	0.012
Na	84.02	427.7	182.4	158.3	80.35	14.67	1.484	2.207
Ni	8.127	61.61	29.39	30.54	12.69	2.317	0.263	0.081
Pb	6.250	46.86	26.02	25.88	11.67	2.131	-0.015	-0.840
Se	0.499	1.335	0.827	0.798	0.221	0.040	0.509	-0.557
Sr	21.82	98.78	54.13	55.24	18.95	3.460	0.530	-0.027
Zn	16.88	46.45	29.58	29.04	7.375	1.346	0.453	-0.398

Comparison of average metal levels in acid extract of the soil samples during two seasons (summer and winter) is shown in Figure 62. Most of the metals (Cd, Co, Cr, Hg, K, Pb and Sr) showed relatively higher concentrations in the soil during winter compared with summer season; these differences were statistically significant. Remaining metals exhibited almost comparable average concentrations during the two seasons.

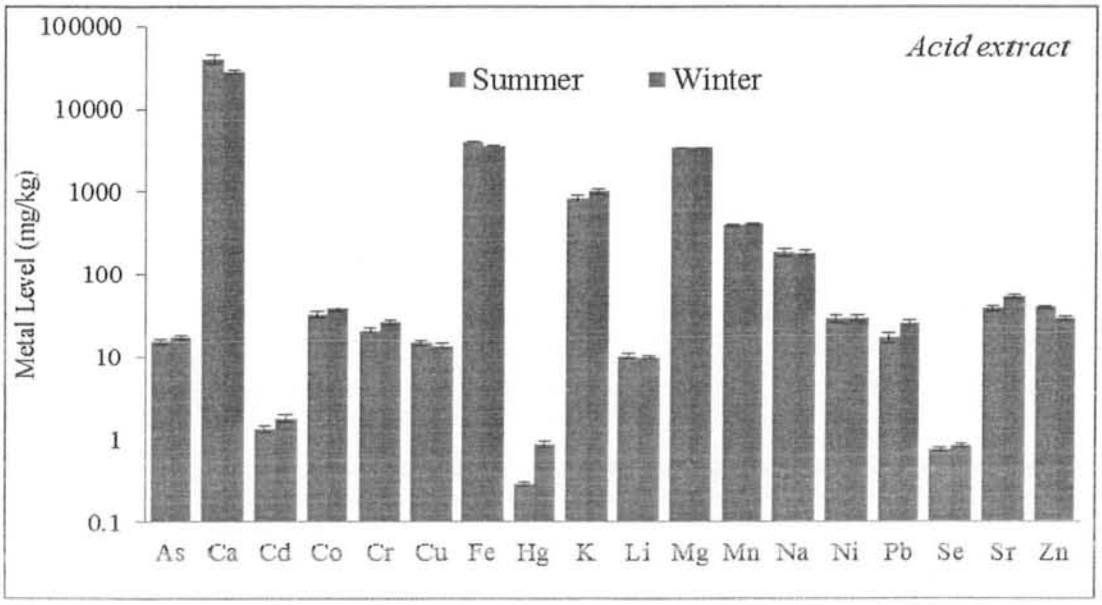

Figure 62. Comparison of average metal levels (mg/kg, ±SE) in acid extract of the soil during summer and winter

Basic statistical parameters related to distribution of selected metals in acid extract of the soil during pre-monsoon are given in Table 81. Average concentrations of As, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Li, Mg, Mn, Na, Ni, Pb, Se, Sr and Zn in acid extract of the soil samples during pre-monsoon season were measured as 28.13, 34471, 9.283, 49.04, 58.94, 31.83, 8765, 0.770, 1085, 13.63, 2904, 547.4, 231.0, 36.95, 87.40, 1.092, 65.92 and 73.65 mg/kg, respectively. Highest average concentration was shown by Ca, followed by, Fe, Mg and K, while lowest levels were observed for Cd, Se and Hg. Overall, mean metal levels in acid extract of the soil demonstrated following decreasing pattern; Ca > Fe > Mg > K > Mn > Na > Pb > Zn > Sr > Cr > Co > Ni > Cu > As > Li > Cd > Se > Hg. Majority of the metals exhibited random distribution as shown by relatively higher SD and SE values, except Hg and Se which exhibited fairly lower dispersion. Most of the metals showed relatively symmetrical dispersion as indicated by smaller skewness and kurtosis values.

Table 81. Statistical distribution of selected metal levels (mg/kg) in acid extract of the soil during pre-monsoon (*n* = 100)

	Min	Max	Mean	Median	SD	SE	Skew	Kurt
As	19.93	33.38	28.13	29.34	3.952	0.884	-0.567	-0.732
Ca	16245	53636	34471	35505	9767	2184	-0.063	-0.308
Cd	4.397	16.06	9.283	9.503	3.121	0.698	0.401	-0.462
Co	28.43	64.62	49.04	51.26	11.75	2.626	-0.302	-1.216
Cr	38.00	93.61	58.94	60.10	15.26	3.413	0.372	-0.497
Cu	19.92	48.66	31.83	31.84	6.144	1.374	0.649	2.264
Fe	6960	9487	8765	8807	569.0	127.2	-1.664	4.341
Hg	0.368	1.176	0.770	0.817	0.269	0.060	-0.020	-1.575
K	751.4	1512	1085	1034	219.4	49.07	0.462	-0.878
Li	6.573	24.98	13.63	12.74	5.307	1.187	0.892	0.335
Mg	1960	3972	2904	2782	634.6	141.9	0.322	-0.852
Mn	433.4	756.9	547.4	519.2	77.58	17.35	1.091	1.511
Na	128.7	432.5	231.0	211.7	88.48	19.79	1.116	0.724
Ni	22.92	54.35	36.95	37.54	8.185	1.830	0.206	-0.343
Pb	62.54	122.9	87.40	89.06	16.44	3.676	0.305	-0.215
Se	0.766	1.388	1.092	1.081	0.174	0.039	-0.188	-0.693
Sr	19.07	115.4	65.92	68.55	27.22	6.087	0.164	-0.754
Zn	60.89	109.0	73.65	70.52	12.30	2.751	2.076	4.107

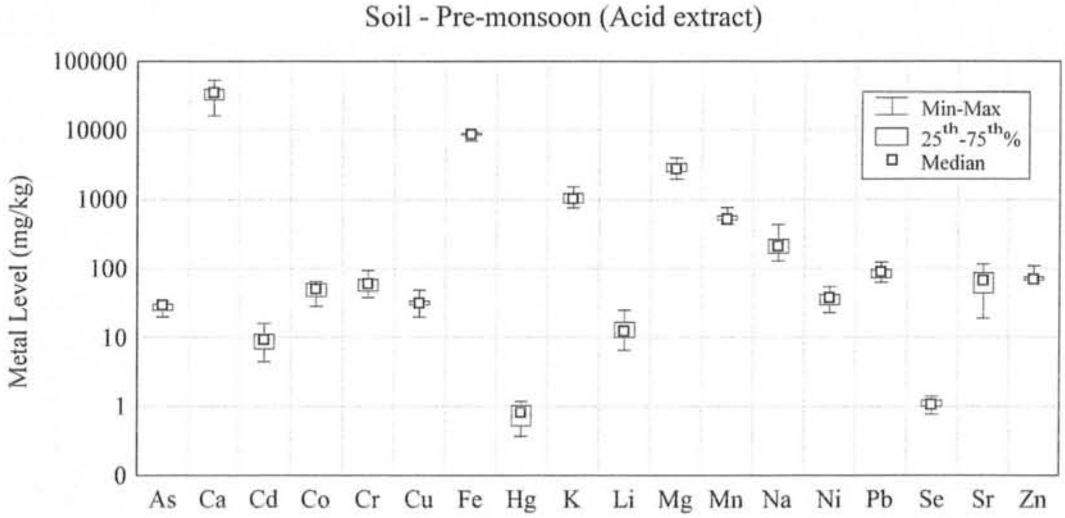

Figure 63. Quartile distribution of selected metal levels (mg/kg) in acid extract of the soil during pre-monsoon

Table 82. Statistical distribution of selected metal levels (mg/kg) in acid extract of the soil during monsoon ($n = 100$)

	Min	Max	Mean	Median	SD	SE	Skew	Kurt
As	15.24	24.56	20.55	21.17	2.824	0.632	-0.523	-0.657
Ca	21607	50254	36776	38376	8498	1900	-0.385	-0.796
Cd	4.880	12.964	8.189	8.127	2.250	0.503	0.539	-0.006
Co	30.76	64.41	45.31	44.14	9.479	2.120	0.165	-0.700
Cr	26.10	75.98	53.13	54.48	13.75	3.074	-0.222	-0.609
Cu	22.61	37.24	27.31	26.46	3.411	0.763	1.221	2.468
Fe	4489	8983	8005	8217	991.6	221.7	-2.583	8.199
Hg	0.335	1.184	0.618	0.533	0.253	0.056	1.270	0.630
K	532.0	1261	973.6	978.8	158.4	35.41	-0.833	2.086
Li	5.658	17.49	11.66	11.56	2.893	0.647	0.318	0.376
Mg	1964	3271	2790	2841	418.8	93.6	-0.789	-0.549
Mn	354.0	600.4	481.1	480.4	70.15	15.69	-0.019	-0.846
Na	160.5	413.7	238.5	225.6	70.29	15.72	1.377	1.942
Ni	19.63	44.94	34.81	34.71	6.627	1.482	-0.277	-0.169
Pb	60.93	88.46	72.12	70.28	8.578	1.918	0.306	-1.320
Se	0.768	1.254	1.022	1.055	0.139	0.031	-0.500	-0.530
Sr	25.23	97.56	62.38	64.91	18.70	4.182	0.015	-0.358
Zn	41.33	109.29	70.13	67.51	13.44	3.005	0.857	3.472

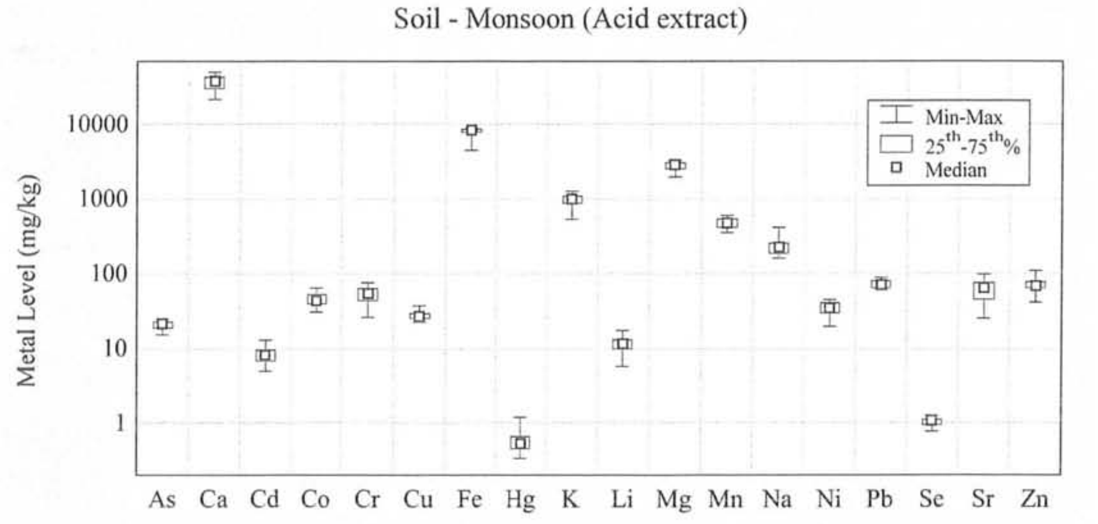

Figure 64. Quartile distribution of selected metal levels (mg/kg) in acid extract of the soil during monsoon

Table 83. Statistical distribution of selected metal levels (mg/kg) in acid extract of the soil during post-monsoon ($n = 100$)

	Min	Max	Mean	Median	SD	SE	Skew	Kurt
As	13.11	22.08	17.78	18.07	2.582	0.577	-0.321	-0.581
Ca	13170	61959	39395	36448	13365	2988	-0.163	-0.503
Cd	4.408	14.55	7.805	7.110	2.414	0.540	1.288	2.086
Co	29.97	62.44	44.07	45.06	8.39	1.876	0.075	-0.037
Cr	15.73	90.88	51.45	51.39	22.52	5.037	0.253	-0.913
Cu	19.82	35.49	26.09	25.25	4.455	0.996	0.645	-0.339
Fe	6281	9752	8503	8578	891.2	199.3	-0.951	0.869
Hg	0.201	0.518	0.365	0.380	0.084	0.019	-0.093	-0.527
K	645.1	1278	974.9	921.7	181.5	40.59	0.280	-0.806
Li	3.316	21.21	10.65	10.77	4.328	0.968	0.399	1.192
Mg	2018	3789	2937	2879	587.9	131.5	-0.011	-1.390
Mn	339.4	685.5	458.9	429.5	87.74	19.62	0.964	0.802
Na	109.9	525.6	250.5	220.3	106.2	23.75	1.178	0.996
Ni	17.69	57.15	34.93	34.68	10.40	2.325	0.189	-0.176
Pb	39.74	73.63	58.53	58.52	8.63	1.931	-0.384	0.620
Se	0.626	1.112	0.863	0.875	0.132	0.030	-0.122	-0.392
Sr	15.84	117.68	59.57	55.32	24.27	5.427	0.346	0.563
Zn	45.93	144.04	75.39	72.23	24.19	5.410	1.126	1.936

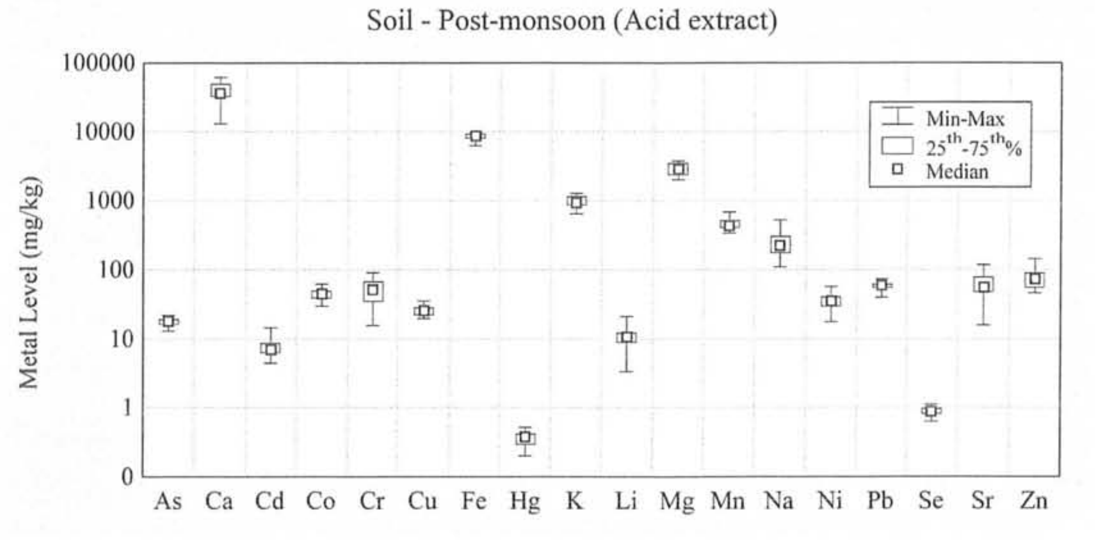

Figure 65. Quartile distribution of selected metal levels (mg/kg) in acid extract of the soil during post-monsoon

The corresponding quartile distribution of the metals in acid extract of the soil during pre-monsoon is shown in Figure 63. Most of the selected metals exhibited narrow distribution in the soil samples, nonetheless, Ca, Cd, Li, Na and Sr showed relatively broad dispersion than other metals. Lest variation in the measured levels of As, Fe, Mn and Zn were revealed by their small ranges as indicated by overlapping of their lower or upper quartile levels in the soil during pre-monsoon.

Statistical distribution parameters for selected metals in acid extract of the soil samples during monsoon are given in Table 82. Most of the metals showed large variations as indicated their lowest and highest levels. Predominantly higher mean concentration was found for Ca (36776 mg/kg), followed by, Fe (8005 mg/kg), Mg (2790 mg/kg) and K (973.6 mg/kg), while the lowest levels were observed for Cd (8.189 mg/kg), Se (1.022 mg/kg) and Hg (0.618 mg/kg). Among rest of the metals, mean levels of As, Co, Cr, Cu, Li, Mn, Na, Ni, Pb, Sr and Zn were noted as 20.55, 45.31, 53.13, 27.31, 11.66, 481.1, 238.5, 34.81, 72.12, 62.38 and 70.13 mg/kg, in that order. Overall, mean metal levels in acid extract of the soil exhibited following decreasing concentration pattern; Ca > Fe > Mg > K > Mn > Na > Pb > Zn > Sr > Cr > Co > Ni > Cu > As > Li > Cd > Se > Hg. Most of metals showed random distribution as indicated by relatively higher SD and SE, except Hg and Se which exhibited relatively lower dispersion. Similarly, most of the metals showed comparatively symmetrical distribution as shown by smaller skewness and kurtosis values, except Cu, Hg, Na and Zn which revealed rather asymmetrical distribution in the soil. Box and whisker plot related to the quartile distribution of selected metals in acid extract of the soil during monsoon is presented in Figure 64 which showed relatively narrow range but predominantly asymmetric distribution for most of the metal levels in the soil samples. Among the selected metals, As, Cu, Mg, Mn, Pb and Se displayed narrowest distribution in the soil as evidenced by overlapping of the lower or upper quartiles.

Basic statistical parameters for distribution of selected metals in acid extract of the soil samples during post-monsoon are given in Table 83. Mean levels in acid extract of the soil were measured at 17.78, 39395, 7.805, 44.07, 51.45, 26.09, 8503, 0.365, 974.9, 10.65, 2937, 458.9, 250.5, 34.93, 58.53, 0.863, 59.57 and 75.39 mg/kg for As, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Li, Mg, Mn, Na, Ni, Pb, Se, Sr and Zn, respectively. Highest average concentration was again shown by Ca, followed by, Fe, Mg and K, while lowest contributions were noted for Cd, Se and Hg. Overall, mean metal levels in acid extract of the soil exhibited following order: Ca > Fe > Mg > K > Mn > Na > Zn > Sr > Pb > Cr > Co > Ni > Cu > As > Li > Cd > Se > Hg. Most of the metals showed random distribution as shown by relatively higher SD and SE values, except Hg and Se which exhibited lower dispersion. Majority of the metals showed symmetrical distribution as revealed by skewness and kurtosis except Cd, Li, Na and Zn which revealed rather asymmetrical distribution in the soil samples. Figure 65 demonstrates the box and whisker plot, displaying the quartile distribution of selected metals in acid extract of the soil during post-monsoon. Most of the metals showed narrow range and relatively asymmetrical distribution. Very narrow distribution was observed for As, Fe and Pb as shown by overlapping of lower or upper quartiles, however, Ca, Cr, Li and Sr exhibited relatively broad distribution in the soil during post-monsoons season.

As a whole during three seasons, metal data showed the highest concentrations of Ca, Mg, K, Fe, Na, Mn and Zn, whereas the lowest concentrations were found for Cd, Se and Hg in the soil samples. Distribution of most of the metals was found to be non-Gaussian, as exhibited by large SD and SE values. Comparison of average metal levels in acid extract of the soil during three seasons (pre-monsoon, monsoon and post-monsoon) is shown in Figure 66. Most of the metals showed statistically insignificant differences in their average concentrations during the three seasons; nonetheless, some of the metals (As, Cd, Cr, Cu, Hg, Li, Pb and Se) showed relatively higher concentrations during pre-monsoon season which might be attributed to the excessive anthropogenic activities in the study area during pre-monsoon season.

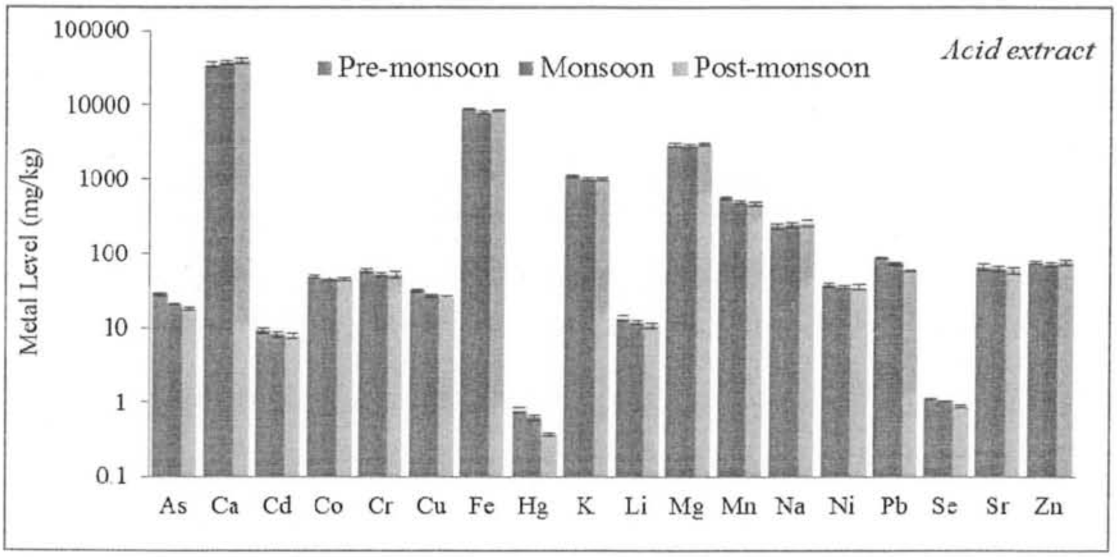

Figure 66. Comparison of average metal levels (mg/kg, ±SE) in acid extract of the soil during pre-monsoon, monsoon and post-monsoon

3.28 Comparison of Present Metal Levels in Soil with Worldwide Reported Levels and International Soil Quality Guidelines

Mean levels of selected metals in the soil samples during summer and winter around the water reservoir were compared with the reported levels from other regions around the world as shown in Table 84. The measured mean levels of As were found to be higher than the levels reported in soil of Changchun, China (Yang *et al.*, 2011), Chengdu, China (Shi, 2004), Napoli, Italy (Cicchella *et al.*, 2008a), Benevento, Italy (Cicchella *et al.*, 2008b), Ottawa, Canada (Rasmussen *et al.*, 2001), but the present levels were lower than the reported levels from Shenyang, China (Li *et al.*, 2013c). Similarly, mean levels of Ca were comparatively higher than those of Islamabad, Pakistan (Iqbal and Shah, 2011), Napoli, Italy while less than the levels reported from Benevento, Italy and Ottawa, Canada. Mean levels of Cd were higher than the reported concentrations from Changchun, China, Chengdu, China, Napoli, Italy, Benevento, Italy, Niger Delta, Nigeria (Olawoyin *et al.*, 2012), Shenyang, China, Amman, Jordan (Jiries, 2003), Ottawa, Canada, whereas the current levels were lower than those of Khanpur, Pakistan (Iqbal and Shah, 2015) and Islamabad, Pakistan. Likewise, mean levels of Co were higher than the reported levels from Islamabad, Pakistan, Khanpur, Pakistan, Napoli, Italy, Benevento, Italy and Ottawa, Canada. Average levels of Cr measured in the present study were found to be higher than those of Islamabad, Pakistan, Benevento, Italy, Niger Delta, Nigeria and Amman, Jordan, while the current levels were lower compared with those of Khanpur, Pakistan, Uttar Pradesh, India (Gowd *et al.*, 2010), Changchun, China, Chengdu, China, Napoli, Italy, Shenyang, China and Ottawa, Canada during both seasons. Measured mean levels of Cu, K, Na, Mn, Pb, Sr and Zn were found to be lower than most of the reported levels in the Table; average contents of Cu, K, Sr and Zn were only higher than the levels reported from Islamabad Pakistan; Pb levels were greater than the reported level from Khanpur, Pakistan; Mn levels were found to be elevated compared with the reported levels from Islamabad, Pakistan and Amman, Jordan. Mean concentrations of Ni and Li in the soil were noted to be higher than the levels reported from Amman, Jordan and Ottawa, Canada. In addition, measured mean levels of Fe were considerably higher than the reported levels from Niger Delta, Nigeria but lower than those of Khanpur, Pakistan, Napoli, Italy, Benevento, Italy, Amman, Jordan and Ottawa, Canada during both seasons. Similarly, mean levels of Hg measured in the present study were higher than the reported levels from Changchun, China, Chengdu, China, Napoli, Italy, Benevento, Italy, Shenyang, China and Ottawa, Canada during winter season while the existing levels were higher than those of Changchun, China, Benevento, Italy and Ottawa, Canada during summer. Present mean levels of Mg were noted to be higher than the levels reported from Islamabad, Pakistan, but lower than those of Napoli, Italy, Benevento, Italy and Ottawa, Canada. Moreover, mean levels of Se were found to be higher than the reported levels from Napoli, Italy, Benevento, Italy and Ottawa, Canada during both seasons.

Average metal concentrations in the soil samples during pre-monsoon, monsoon and post-monsoon seasons were also compared with the reported levels from national and international studies as shown in Table 85. Present mean levels of As were higher than the reported levels from Napoli, Italy (Cicchella *et al.,* 2008a), Caserta, Italy (Cicchella *et al.,* 2008b), Ottawa, Canada (Rasmussen *et al.,* 2001) and Tianjin, China (Zhao *et al.,* 2014). Similarly, mean levels of Ca and Co were higher than those of Himalaya Region, Pakistan (Shah *et al.,* 2012), Napoli, Italy, Caserta, Italy, Ottawa, Canada and Thiva, Greece (Kelepertzis, 2014). Mean levels of Cd in the present study were relatively higher than those of Himalaya Region, Pakistan, Napoli, Italy, Caserta, Italy, Ottawa, Canada, Ghaziabad, India (Chabukdhara and Nema, 2013), Tianjin, China, Beijing, China (Khan *et al.,* 2008) and Thiva, Greece but lower than the levels reported from Tehran, Iran (Saeedi *et al.,* 2012). Average levels of Cr were found to be higher than the reported levels from Himalaya Region, Pakistan, Karachi, Pakistan (Karim and Qureshi, 2014), Napoli, Italy, Caserta, Italy, Ottawa, Canada, Tehran, Iran and Tianjin, China, however, the measured levels were lower than those of Ghaziabad, India, Beijing, China and Thiva, Greece during all seasons. Moreover, Hg and Se levels were comparatively higher than those of Napoli, Italy, Caserta, Italy, Ottawa, Canada and Tianjin, China while Li levels were noted to be higher than those of Ottawa, Canada and Tehran, Iran. In addition, mean levels of Ni were higher than the reported levels from Napoli, Italy, Caserta, Italy, Ottawa, Canada, Tehran, Iran and Beijing, China while the present metal levels were lower than those of Ghaziabad, India, Tianjin, China and Thiva, Greece during all seasons. Measured mean levels of Pb were found to be higher than the levels reported from Himalaya Region, Pakistan, Karachi, Pakistan, Tianjin, China, Beijing, China and Thiva, Greece while lower than those of Napoli, Italy, Tehran, Iran and Ghaziabad, India. Mean contents of Cu, Fe, K, Mg, Mn, Na, Sr and Zn in the present study were mostly found to be lower than the reported levels given in Table 85.

Table 84. Average metal concentrations (mg/kg, dry weight) in the soil during summer and winter in comparison with the worldwide reported levels

	As	Ca	Cd	Co	Cr	Cu	Fe	Hg	K	Li	Mg	Mn	Na	Ni	Pb	Se	Sr	Zn	
Mangla Lake (Summer)	15.30	40979	1.337	32.75	21.23	14.76	4038	0.293	854.4	10.39	3408	393.7	186.9	29.12	17.27	0.76	38.56	40.29	Present study
Mangla Lake (Winter)	16.97	27874	1.786	38.11	26.24	13.62	3673	0.860	1021	10.02	3347	407.4	182.4	29.39	26.02	0.83	54.13	29.58	Present study
Islamabad, Pakistan (Summer)	-	27531	1.568	10.34	21.01	10.28	12784	-	737.9	10.87	2769	393.5	999.9	-	38.25	-	115.1	23.83	Iqbal & Shah, 2011
Islamabad, Pakistan (Winter)	-	23386	2.132	25.08	25.73	17.77	3958	-	1511	13.27	3206	453.6	254.6	-	27.35	-	53.30	45.03	Iqbal & Shah, 2011
Khanpur, Pakistan (Winter)	-	-	3.6	32	54	51	4863	-	-	-	-	435	-	-	57	-	468	98	Iqbal & Shah, 2015
Khanpur, Pakistan (Summer)	-	-	1.8	31	23	28	3802	-	-	-	-	490	-	-	19	-	225	62	Iqbal & Shah, 2015
Uttar Pradesh, India	-	-	-	-	2652.3	42.9	-	-	-	-	-	-	-	-	38.3	-	105.3	159.9	Gowd *et al.*, 2010
Changchun, China	12.5	-	0.132	-	66.0	29.4	-	0.118	-	-	-	-	-	-	35.4	-	-	90	Yang *et al.*, 2011
Chengdu, China	13.2	-	0.210	-	79.5	46.6	-	0.48	-	-	-	-	-	-	50.8	-	-	128.6	Shi, 2004
Napoli, Italy	13.4	26400	0.58	7.3	15.3	94	22000	0.31	15200	-	4700	683	5000	11.6	204	0.29	193	223	Cicchella *et al.*, 2008a
Benevento, Italy	8.3	47200	0.3	12.2	19.5	46	21100	0.059	6300	-	4500	1173	800	22.0	44	0.31	133	80.27	Cicchella *et al.*, 2008b
Niger Area, Nigeria	-	-	1.779	-	12.39	41.88	2038	-	-	-	-	211.1	-	42.54	915.8	-	-	63.37	Olawoyin *et al.*, 2012
Shenyang, China	22.69	-	1.1	-	67.9	92.45	-	0.39	-	-	-	635.9	-		116.8	-	-	234.8	Li *et al.*, 2013c
Amman, Jordan	-	-	1.1	-	18.3	249.6	5370.6	-	-	1.7	-	144.6	-	16.3	976	-	-	401	Jiries, 2003
Ottawa, Canada	1.3	96787	0.37	8.31	43.3	65.84	18948	0.029	14963	7.4	15780	431.5	18273	15.2	39.05	0.5	459	112.5	Rasmussen *et al.*, 2001

Table 85. Average metal concentrations (mg/kg, dry weight) in soil during pre-monsoon, monsoon and post-monsoon in comparison with the worldwide reported levels

	As	Ca	Cd	Co	Cr	Cu	Fe	Hg	K	Li	Mg	Mn	Na	Ni	Pb	Se	Sr	Zn	
Mangla Lake (Pre-monsoon)	28.1	34471	9.28	49.0	58.9	31.8	8765	0.77	1085	13.6	2904	547.4	231	36.95	87.4	1.09	65.9	73.65	Present Study
Mangla Lake (Monsoon)	20.6	36776	8.19	45.3	53.1	27.3	8005	0.62	973.6	11.7	2790	481.1	238.5	34.81	72.1	1.02	62.4	70.13	Present Study
Mangla Lake (Post-monsoon)	17.8	39395	7.81	44.1	51.5	26.1	8503	0.37	974.9	10.7	2937	458.9	250.5	34.93	58.5	0.86	59.6	75.39	Present Study
Himalaya Region, Pakistan	-	3520	1.90	3.49	32.6	18.1	1241	-	1489	19.6	906	343	92.3	-	47	-	-	35.5	Shah *et al.*, 2012
Karachi, Pakistan	-	-	-	-	9.6	33.3	908.4	-	-	-	-	-	-	-	42.1	-	-	99.5	Karim & Qureshi, 2014
Napoli, Italy	13.4	26400	0.58	7.3	15.3	94	22000	0.31	15200	-	4700	683	5000	11.6	204	0.29	193	223	Cicchella *et al.*, 2008a
Caserta, Italy	15.8	26500	0.7	9.4	14.7	36	27900	0.084	5900	-	4000	980	1000	12.8	68	0.35	108	116.4	Cicchella *et al.*, 2008b
Ottawa, Garden Soil Canada	3	26978	0.3	8.36	44.8	13.19	21481	0.107	18035	11.3	8937	525.3	22042	16.3	64.69	0.7	360	113.7	Rasmussen *et al.*, 2001
Tehran, Iran	-	-	10.7	-	33.5	225.3	47936	-	-	9.5	-	1214.5	-	34.8	257.4	-	-	873.2	Saeedi *et al.*, 2012
Ghaziabad, India	-	-	0.4	-	288	122	21433	-	-	-	-	386	-	147	147	-	-	187	Chabukdhara & Nema, 2013
Tianjin, China	11	-	0.18	-	51	33	-	0.43	-	-	-	-	-	39	45	-	-	148	Zhao *et al.*, 2014
Beijing, China	-	-	0.84	-	60.9	32.8	-	-	-	-	-		-	24.9	49.4	-	-	157	Khan *et al.*, 2008
Thiva, Greece	-	-	0.67	99	285	26	-	-	-	-	-	946	-	1777	30	-	-	78	Kelepertzis, 2014

Table 86. Average metal concentrations (mg/kg, dry weight) in the soil during summer, winter, pre-monsoon, monsoon and post-monsoon in comparison with the international guideline values

	As	Cd	Co	Cr	Cu	Hg	Ni	Pb	Se	Zn	
Mangla Lake (Summer)	15.3	1.34	32.8	21.2	14.8	0.29	29.1	17.3	0.76	40.3	Present study
Mangla Lake (Winter)	17.0	1.79	38.1	26.2	13.6	0.86	29.4	26.02	0.83	29.6	Present study
Mangla Lake (Pre-monsoon)	28.13	9.283	49.04	58.94	31.83	0.77	36.95	87.4	1.092	73.65	Present Study
Mangla Lake (Monsoon)	20.55	8.189	45.31	53.13	27.31	0.618	34.81	72.12	1.022	70.13	Present Study
Mangla Lake (Post-monsoon)	17.78	7.805	44.07	51.45	26.09	0.365	34.93	58.53	0.863	75.39	Present Study
California Human Health (SSLs)											
Residential	0.07	1.7	660	17	3000	18	1600	150	380	23000	Cal-EPA, 2005
Commercial/industrial	0.24	7.5	3200	37	38000	180	16000	3500	4800	100000	Cal-EPA, 2005
Dutch Soil Guidelines											
Background Concentration	29	0.8	9	100	36	0.3	35	85	0.7	140	VROM,2000
Target value	29	0.8	9	100	36	0.3	35	85	0.7	140	VROM,2000
Intervention value	55	12	240	380	190	10	210	530	100	720	VROM,2000
Canadian Soil Quality Guidelines											
Agricultural	12	1.4	-	64	63	6.6	50	70	1	200	CCME, 2007
Residential/parkland	12	10	-	64	63	6.6	50	140	1	200	CCME, 2007
Commercial	12	22	-	87	91	24	50	260	2.9	360	CCME, 2007
Industrial	12	22	-	87	91	50	50	600	2.9	360	CCME, 2007

Average levels of selected metals in the soil samples collected during summer, winter, pre-monsoon, monsoon and post-monsoon seasons were also compared with some international soil quality guidelines as shown in Table 86. Present mean concentrations of As exceeded the California human health residential & commercial/industrial limits and Canadian agricultural, residential/parkland, commercial, industrial soil quality guideline values. Similarly, mean levels of Cd were noted to be higher than the California human health residential & commercial/industrial limits, Dutch background concentration & target guideline values and Canadian agricultural guidelines value during all seasons. Likewise, average levels of Co, Hg and Se were found to be higher than the Dutch background concentration & target soil guideline values, while Cr levels were significantly higher than the California human health residential & commercial/industrial limits. Mean levels of Pb during pre-monsoon season were found to be higher than the Dutch background concentration and target soil guideline values. Average levels of Cu, Ni and Zn were safe and found to be within the California human health limits, Dutch and Canadian soil quality guidelines values. The guideline values/limits of the remaining metals (Ca, Fe, K, Li, Mg, Mn, and Na) were not listed in literature (California human health limits, Dutch & Canadian soil quality guidelines).

3.29 Distribution of Selected Metals in Sequentially Extracted Fractions of Soil Samples

Measurement of total metal contents is normally suitable as an indicator of metals contamination, however it provides little information about their bioavailability, mobility, toxicity and reactivity (Hooda 2010; Sundaray *et al.,* 2011). Fractionation of metals provides much valuable information regarding chemical nature or potential mobility and bioavailability in the environment (Yang *et al.,* 2009). Therefore, researchers are mostly interested in evaluating the associations of metals with different geochemical phases by sequential extraction methodologies (Rauret, 1998). In the present study, soil samples collected during summer and winter seasons were extracted employing *m*BCR sequential extraction procedure to determine the associations of metals with different geochemical phases in order to assess their bioavailability and toxicity.

3.29.1 Distribution of Selected Metals in Exchangeable Fraction of Soil

Statistical description of selected metal concentrations (mg/kg) in exchangeable fraction of the soil during summer is shown in Table 87. Average levels of As, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Li, Mg, Mn, Na, Ni, Pb, Se, Sr and Zn in exchangeable fraction of the soil during summer were measured as 0.381, 28235, 2.680, 11.00, 8.464, 4.086, 37.48, 0.008, 143.0, 0.495, 479.4, 88.08, 76.70, 13.57, 56.70, 0.350, 42.74 and 5.360 mg/kg, respectively. Highest average concentration was shown by Ca, followed by, Mg, K and Mn, whereas lowest contribution was shown by As, Se and Hg. Overall, average metal levels in exchangeable fraction of the soil during summer revealed following decreasing order; Ca > Mg > K > Mn > Na > Pb > Sr > Fe > Ni > Co > Cr > Zn > Cu > Cd > Li >As > Se > Hg. Most of the metals exhibited relatively large spread as shown by their minimum and maximum levels. Relatively higher dispersion was noted for Ca, Mg, Na, K, Mn, Sr and Fe as indicated by fairly higher values of SD and SE values. Appreciably higher skewness and kurtosis values for Cd, Li and Na showed their asymmetric variations in the soil samples.

Table 87. Statistical distribution of selected metal levels (mg/kg) in the exchangeable fraction of soil during summer ($n = 90$)

	Min	Max	Mean	Median	SD	SE	Skew	Kurt
As	0.228	0.529	0.381	0.364	0.088	0.020	0.013	-1.133
Ca	13533	45992	28235	28720	8796	1967	0.152	-0.225
Cd	1.250	6.650	2.680	1.997	1.372	0.307	1.385	2.200
Co	1.850	24.18	11.00	11.19	7.402	1.655	0.348	-1.170
Cr	0.950	14.84	8.464	7.875	4.270	0.955	-0.071	-1.010
Cu	1.896	6.088	4.086	4.119	1.238	0.277	-0.253	-0.754
Fe	16.04	67.22	37.48	35.44	13.70	3.063	0.597	-0.261
Hg	0.001	0.014	0.008	0.009	0.004	0.001	-0.385	-1.132
K	97.41	228.4	143.0	128.5	41.23	9.218	0.822	-0.418
Li	0.150	1.350	0.495	0.424	0.323	0.072	1.143	0.999
Mg	121.9	889.3	479.4	413.0	226.6	50.68	0.476	-0.758
Mn	39.62	129.0	88.08	90.19	29.12	6.512	-0.106	-1.160
Na	4.89	277.0	76.7	56.52	65.91	14.74	1.947	4.114
Ni	2.100	27.55	13.57	12.10	6.576	1.470	0.313	-0.453
Pb	42.35	76.55	56.70	55.82	9.901	2.214	0.411	-0.653
Se	0.236	0.448	0.350	0.359	0.056	0.013	-0.255	-0.615
Sr	5.384	81.9	42.74	45.31	20.29	4.537	-0.008	-0.644
Zn	2.395	10.23	5.360	4.766	2.229	0.498	0.658	-0.577

Table 88. Statistical distribution of selected metal levels (mg/kg) in the exchangeable fraction of soil during winter (*n* = 90)

	Min	Max	Mean	Median	SD	SE	Skew	Kurt
As	0.254	0.505	0.385	0.368	0.072	0.016	-0.012	-0.910
Ca	10860	56203	33590	31264	12249	2739	0.033	-0.585
Cd	0.599	4.441	2.118	2.297	1.031	0.231	0.406	-0.292
Co	1.399	28.69	12.21	10.96	7.474	1.671	0.511	-0.390
Cr	2.495	13.82	6.661	6.016	3.530	0.789	0.593	-0.729
Cu	0.599	4.192	2.233	2.345	0.892	0.200	0.270	0.563
Fe	11.69	78.14	32.38	31.18	15.32	3.426	1.242	3.094
Hg	0.004	0.012	0.007	0.007	0.002	0.001	0.553	-0.603
K	75.90	198.8	117.5	112.5	29.82	6.669	0.998	1.568
Li	0.100	1.748	0.721	0.549	0.467	0.104	1.037	0.241
Mg	200.9	968.4	563.1	519.9	250.7	56.07	0.235	-1.419
Mn	54.99	165.0	94.98	91.17	28.37	6.344	0.857	0.451
Na	20.58	242.7	100.2	75.27	70.58	15.78	0.778	-0.493
Ni	2.246	24.93	12.15	11.26	6.726	1.504	0.337	-0.650
Pb	18.51	49.05	32.83	32.21	8.592	1.921	0.253	-0.496
Se	0.168	0.531	0.350	0.348	0.102	0.023	0.038	-0.731
Sr	8.996	100.0	45.20	43.66	21.44	4.793	0.645	1.087
Zn	0.547	26.17	5.890	4.591	5.573	1.246	2.782	9.429

Distribution of selected metal concentrations (mg/kg) in exchangeable fraction of the soil during winter is shown in Table 88, in terms of basic statistical parameters. Mean levels of As, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Li, Mg, Mn, Na, Ni, Pb, Se, Sr and Zn in exchangeable fraction of the soil during winter were measured as 0.385, 33590, 2.118, 12.21, 6.661, 2.233, 32.38, 0.007, 117.5, 0.721, 563.1, 94.98, 100.2, 12.15, 32.83, 0.350, 45.20 and 5.890 mg/kg, respectively. Highest average concentration was shown by Ca, followed by, Mg, K, Na, Mn and Sr, while lowest levels were shown by Li, As, Se and Hg. Overall, average metal levels in exchangeable fraction during winter displayed following order; Ca > Mg > K > Na > Mn > Sr > Pb > Fe > Co > Ni > Cr > Zn > Cu > Cd > Li >As > Se > Hg. Among the metals, As, Cd, Cu, Hg, Li and Se showed somewhat normal distribution pattern as evidenced by very small values of SD and SE while higher dispersion was noted for Ca, Mg, Na, K, Mn, Sr and Fe. Moreover, large asymmetry in distribution of Zn, Fe and Li was evidenced by higher skewness and kurtosis values.

Table 89. Statistical distribution of selected metal levels (mg/kg) in the reducible fraction of soil during summer ($n = 90$)

	Min	Max	Mean	Median	SD	SE	Skew	Kurt
As	0.401	1.156	0.784	0.775	0.225	0.050	0.120	-1.089
Ca	1141	5633	3944	4176	1195	267.2	-1.019	0.623
Cd	0.150	2.250	1.299	1.298	0.584	0.131	-0.003	-0.411
Co	0.150	15.75	7.464	7.342	4.189	0.937	0.180	-0.325
Cr	0.697	16.22	7.823	7.896	3.993	0.893	0.246	-0.475
Cu	0.699	4.550	2.400	2.325	0.910	0.203	0.406	0.399
Fe	216.0	918.3	522.1	528.5	193.4	43.25	0.297	-0.741
Hg	0.010	0.083	0.033	0.026	0.023	0.005	1.348	0.629
K	35.68	122.6	71.63	69.18	23.14	5.175	0.796	0.202
Li	0.200	1.550	0.844	0.949	0.419	0.094	-0.031	-1.308
Mg	103.9	440.1	248.0	248.6	106.7	23.85	0.441	-1.054
Mn	58.63	424.6	212.6	209.1	99.72	22.30	0.277	0.181
Na	8.142	35.96	17.98	16.66	7.507	1.679	0.960	0.621
Ni	2.050	12.45	7.421	7.371	3.027	0.677	0.009	-0.485
Pb	3.450	37.55	17.72	18.67	8.499	1.900	0.227	0.285
Se	0.788	1.409	1.119	1.110	0.177	0.040	-0.217	-0.724
Sr	1.397	24.20	12.62	13.76	7.086	1.584	-0.103	-1.122
Zn	3.000	9.381	5.798	5.600	2.000	0.447	0.208	-1.206

3.29.2 Distribution of Selected Metals in Reducible Fraction of Soil

Basic statistical parameters for distribution of selected metal levels (mg/kg) in reducible fraction of the soil during summer are given in Table 89. Mean levels of As, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Li, Mg, Mn, Na, Ni, Pb, Se, Sr and Zn in reducible fraction of the soil during summer were determined as 0.784, 3944, 1.299, 7.464, 7.823, 2.400, 522.1, 0.033, 71.63, 0.844, 248.0, 212.6, 17.98, 7.421, 17.72, 1.119, 12.62 and 5.798 mg/kg, respectively. Highest average concentration was shown by Ca, followed by, Fe, Mg, Mn and K, while lowest levels were shown by Se, Li, As and Hg in the soil samples. Overall, average metal levels in reducible fraction of the soil during summer revealed following decreasing order: Ca > Fe > Mg > Mn > K > Na > Pb > Sr > Cr > Co > Ni > Zn > Cu > Cd > Se > Li > As > Hg. Most of the metals exhibited random distribution pattern as evidenced by fairly higher SD and SE values, however, some of the metals (As, Cd, Cu, Hg, Li and Se) exhibited normal distribution pattern. Fairly asymmetrical distribution was shown by Hg, followed by, K and Na as indicated by higher skewness and kurtosis values.

Table 90. Statistical distribution of selected metal levels (mg/kg) in the reducible fraction of soil during winter ($n = 90$)

	Min	Max	Mean	Median	SD	SE	Skew	Kurt
As	0.367	2.204	0.862	0.629	0.590	0.132	1.616	1.093
Ca	1591	5030	3520	3711	964.7	215.7	-0.425	-0.514
Cd	0.050	2.542	1.228	1.198	0.803	0.180	0.111	-1.123
Co	1.396	14.97	7.21	6.90	4.229	0.946	0.511	-0.776
Cr	1.748	13.92	6.996	7.039	3.858	0.863	0.276	-1.141
Cu	0.449	2.897	1.749	1.745	0.783	0.175	-0.096	-1.008
Fe	205.9	992.2	407.0	380.2	190.4	42.58	1.763	3.784
Hg	0.075	0.289	0.158	0.145	0.060	0.013	1.000	0.356
K	38.62	102.2	61.35	64.60	17.07	3.817	0.535	-0.009
Li	0.050	1.248	0.397	0.324	0.294	0.066	1.415	2.416
Mg	38.92	363.7	153.8	112.7	94.35	21.10	0.973	-0.031
Mn	34.72	370.0	149.3	128.8	90.50	20.24	0.896	0.308
Na	9.232	26.97	18.52	20.43	5.329	1.192	-0.310	-0.975
Ni	3.297	12.24	7.240	6.805	2.243	0.502	0.403	0.359
Pb	2.697	25.35	13.47	10.80	7.286	1.629	0.160	-1.613
Se	0.106	1.755	0.624	0.478	0.517	0.116	1.356	0.658
Sr	0.699	17.81	5.785	4.468	4.534	1.014	1.398	1.617
Zn	1.144	17.98	7.378	5.816	5.244	1.173	0.803	-0.532

Distribution of selected metals in terms of basic statistical parameters in reducible fraction of the soil during winter is shown in Table 90. Most of the metals exhibited large variation in their minimum and maximum levels. Mean levels of As, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Li, Mg, Mn, Na, Ni, Pb, Se, Sr and Zn in reducible fraction of the soil during winter were determined as 0.862, 3520, 1.228, 7.210, 6.996, 1.749, 407.0, 0.158, 61.35, 0.397, 153.8, 149.3, 18.52, 7.240, 13.47, 0.624, 5.785 and 7.378 mg/kg, respectively. Highest average concentration was shown by Ca, followed by, Fe, Mg, Mn, and K, while lowest levels were shown by As, Se, Li and Hg. Overall, average metal levels in reducible fraction of the soil during winter revealed following decreasing order: Ca > Fe > Mg > Mn > K > Na > Pb > Zn > Ni > Co > Cr > Sr > Cu > Cd > As > Se > Li > Hg. Most of the metals displayed random distribution pattern, however, distribution pattern for Ca, Fe, K, Mg and Mn was noted to be more dispersed as shown by their large SD and SE values. Large skewness and kurtosis values for As, Fe, Hg, Li, Se and Sr showed predominantly asymmetrical distribution of these metals in reducible fraction of the soil during winter season.

Table 91. Statistical distribution of selected metal levels (mg/kg) in the oxidiseable fraction of soil during summer (*n* = 90)

	Min	Max	Mean	Median	SD	SE	Skew	Kurt
As	0.555	1.852	1.021	0.916	0.378	0.085	1.086	0.342
Ca	45.51	251.7	94.98	87.76	44.45	9.939	2.405	7.962
Cd	0.249	1.800	1.032	1.024	0.462	0.103	-0.025	-1.108
Co	3.397	16.77	9.366	8.306	4.288	0.959	0.258	-1.390
Cr	4.096	18.98	11.69	11.93	4.451	0.995	-0.085	-1.011
Cu	1.250	5.145	3.382	3.495	1.164	0.260	-0.338	-0.900
Fe	45.95	391.3	195.7	178.5	112.5	25.15	0.187	-1.360
Hg	0.026	0.500	0.224	0.209	0.154	0.034	0.381	-1.028
K	20.26	150.9	80.72	83.10	37.90	8.475	0.199	-0.883
Li	1.050	3.750	2.512	2.448	0.734	0.164	-0.137	0.002
Mg	171.3	825.0	359.9	286.0	183.8	41.10	1.321	1.015
Mn	14.15	29.92	18.46	17.44	3.950	0.883	2.104	4.330
Na	13.49	67.50	41.05	41.73	14.53	3.249	-0.401	-0.294
Ni	1.697	6.786	4.750	4.820	1.272	0.284	-0.438	0.134
Pb	0.150	8.134	3.710	3.800	2.399	0.536	0.188	-0.814
Se	0.413	0.881	0.639	0.622	0.133	0.030	0.218	-0.800
Sr	1.400	9.422	5.164	4.920	2.222	0.497	0.396	-0.499
Zn	1.444	11.24	5.478	4.396	3.004	0.672	0.790	-0.404

3.29.3 Distribution of Selected Metals in Oxidiseable Fraction of Soil

Statistical distribution of selected metal levels (mg/kg) in oxidiseable fraction of the soil during summer is given in Table 91. An examination of the data revealed highest mean levels of Mg (359.9 mg/kg), followed by, Fe (195.7 mg/kg), Ca (94.98 mg/kg), K (80.72 mg/kg), Na (41.05 mg/kg) and Mn (18.46 mg/kg), while Cd (1.032 mg/kg), As (1.021 mg/kg), Se (0.639 mg/kg) and Hg (0.224 mg/kg) demonstrated relatively lower concentrations. The metals showed following decreasing order based on average concentration in oxidiseable fraction of the soil during summer: Mg > Fe > Ca > K > Na >

Mn > Cr > Co > Zn > Sr > Ni > Pb > Cu > Li > Cd > As > Se > Hg. Fairly lower SD and SE values for As, Cd, Hg, Li and Se indicated rather normal distribution pattern of these metals in soil. However, comparatively higher skewness and kurtosis values were noted for As, Ca, Mg and Mn which evidenced relatively asymmetrical distribution of these metals in the soil samples.

Table 92. Statistical distribution of selected metal levels (mg/kg) in the oxidiseable fraction of soil during winter ($n = 90$)

	Min	Max	Mean	Median	SD	SE	Skew	Kurt
As	0.396	2.709	1.397	1.163	0.743	0.166	0.407	-1.156
Ca	12.74	161.14	75.00	67.27	40.05	8.956	0.739	0.082
Cd	0.050	1.747	0.798	0.724	0.563	0.126	0.305	-1.391
Co	2.445	16.37	7.58	7.414	4.035	0.902	0.428	-0.747
Cr	0.549	15.42	8.709	9.331	4.505	1.007	-0.274	-0.845
Cu	0.398	5.838	2.709	2.498	1.720	0.385	0.373	-1.010
Fe	5.739	476.6	134.2	63.13	140.8	31.49	1.070	0.069
Hg	0.019	0.127	0.050	0.038	0.035	0.008	1.477	0.807
K	17.07	144.5	68.13	60.66	35.53	7.945	0.711	-0.285
Li	0.749	3.896	2.602	2.896	1.048	0.234	-0.720	-0.777
Mg	222.4	1118	503.4	522.0	223.1	49.88	1.099	1.847
Mn	10.08	27.76	16.47	16.03	4.442	0.993	0.779	0.643
Na	8.832	64.32	34.95	33.87	15.63	3.496	0.192	-0.279
Ni	2.894	7.393	5.166	5.237	1.480	0.331	-0.121	-1.312
Pb	0.500	9.690	4.379	3.817	2.570	0.575	0.404	-0.833
Se	0.360	1.257	0.700	0.636	0.269	0.060	0.855	-0.309
Sr	0.749	9.132	4.020	3.146	2.771	0.620	0.674	-0.974
Zn	0.499	16.28	4.827	4.616	3.629	0.811	2.009	4.944

Basic statistical distribution parameters for selected metals in oxidiseable fraction of the soil during winter are shown in Table 92. Highest mean level was noted for Mg (503.4 mg/kg), followed by, Fe (134.2 mg/kg), Ca (75.00 mg/kg), K (68.13 mg/kg), Na (34.95 mg/kg) and Mn (16.47 mg/kg), while As (1.397 mg/kg), Cd (0.798 mg/kg), Se (0.700 mg/kg) and Hg (0.050 mg/kg) demonstrated least concentrations. The metals exhibited following decreasing order based on average concentration in oxidiseable fraction of the soil during winter: Mg > Fe > Ca > K > Na > Mn > Cr > Co > Ni > Zn > Pb

> Sr > Cu > Li > As > Cd > Se > Hg. Most of the metals showed random dispersion as indicated by relatively higher SD and SE values, whereas, Ca, Fe, Hg, Mg, Mn and Zn showed asymmetrical distribution supported by their higher skewness and kurtosis values.

Table 93. Statistical distribution of selected metal levels (mg/kg) in the residual fraction of soil during summer ($n = 90$)

	Min	Max	Mean	Median	SD	SE	Skew	Kurt
As	4.197	13.63	8.235	7.909	2.848	0.637	0.510	-0.910
Ca	3.892	90.25	32.09	29.79	19.69	4.402	1.401	2.957
Cd	1.200	6.650	3.779	3.720	1.764	0.394	0.123	-1.204
Co	8.300	28.02	17.76	17.76	6.021	1.346	0.176	-0.997
Cr	10.65	40.77	27.95	28.24	7.471	1.671	-0.464	0.436
Cu	10.75	33.83	20.27	20.23	5.529	1.236	0.592	0.802
Fe	6266	8383	7591	7717	533.0	119.2	-0.601	0.271
Hg	0.024	0.080	0.050	0.048	0.017	0.004	0.351	-1.234
K	554.6	996.9	733.8	682.7	129.8	29.01	0.722	-0.467
Li	2.243	19.33	9.114	8.267	4.740	1.060	0.775	0.368
Mg	941.4	2223	1668	1708	346.1	77.40	-0.310	-0.591
Mn	140.2	330.4	201.5	186.5	51.59	11.53	1.315	1.032
Na	12.00	84.78	44.57	41.23	23.89	5.343	0.299	-1.233
Ni	1.497	15.73	8.852	9.191	3.888	0.869	-0.317	-0.438
Pb	0.550	9.600	4.835	4.250	2.580	0.577	0.084	-0.846
Se	0.124	0.366	0.206	0.185	0.070	0.016	1.332	0.894
Sr	0.200	7.850	2.136	1.424	1.958	0.438	1.728	2.782
Zn	41.45	80.77	53.33	50.95	10.79	2.412	1.582	2.234

3.29.4 Distribution of Selected Metals in Residual Fraction of Soil

Table 93 shows basic statistical distribution parameters for selected metal concentrations (mg/kg) in residual fraction of the soil during summer. Comparatively higher mean levels were noted for Fe (7591 mg/kg), Mg (1668 mg/kg), K (733.8 mg/kg), Mn (201.5 mg/kg), Zn (53.33 mg/kg), Na (44.57 mg/kg), and Ca (32.09 mg/kg), while lowest mean values were found for As (8.235 mg/kg), Pb (4.835 mg/kg), Cd (3.779 mg/kg), Sr (2.136 mg/kg), Se (0.206 mg/kg) and Hg (0.050 mg/kg). Average metal levels exhibited following order in the residual fraction of soil: Hg < Se < Sr < Cd < Pb < As < Ni < Li < Cu < Co < Cr < Ca < Na < Zn < Mn < K < Mg < Fe. Most of the metals showed large dispersion as revealed by SD and SE values, and relatively symmetrical distribution pattern as indicated by lower skewness and kurtosis values except Ca, Mn, Se, Sr and Zn.

Table 94. Statistical distribution of selected metal levels (mg/kg) in the residual fraction of soil during winter ($n = 90$)

	Min	Max	Mean	Median	SD	SE	Skew	Kurt
As	4.611	8.379	6.783	6.961	1.064	0.244	-0.448	-0.627
Ca	1.393	42.10	20.06	19.68	11.87	2.724	0.261	-0.830
Cd	1.299	6.431	3.209	3.194	1.215	0.279	0.983	1.546
Co	1.144	26.15	15.49	19.43	8.066	1.851	-0.496	-1.224
Cr	9.294	52.70	26.65	23.45	12.01	2.756	0.485	-0.512
Cu	11.59	22.95	18.04	18.76	3.393	0.778	-0.459	-0.767
Fe	5674	8686	7544	7691	745.4	171.0	-1.217	1.469
Hg	0.130	0.750	0.399	0.329	0.200	0.046	0.402	-1.181
K	437.5	969.8	683.2	645.9	146.6	33.63	0.506	-0.553
Li	0.547	16.62	6.655	6.044	3.595	0.825	1.050	2.643
Mg	991.3	2183	1581	1644	353.3	81.04	0.032	-1.087
Mn	101.0	270.2	179.5	174.7	53.94	12.37	0.223	-1.001
Na	18.26	83.43	38.74	35.89	14.69	3.371	1.461	3.885
Ni	1.397	21.73	7.910	8.259	5.134	1.178	1.016	1.399
Pb	0.399	9.640	4.626	5.245	2.649	0.608	0.121	-0.844
Se	0.019	0.263	0.156	0.178	0.079	0.018	-0.714	-0.605
Sr	0.149	5.739	1.487	1.397	1.169	0.268	2.791	10.32
Zn	34.83	105.6	54.05	52.95	16.879	3.872	1.584	3.841

Basic statistical parameters related to distribution of selected metal concentrations (mg/kg) in residual fraction of the soil during winter are given in Table 94. Comparatively higher mean levels were noted for Fe (7544 mg/kg), Mg (1581 mg/kg), K (683.2 mg/kg), Mn (179.5 mg/kg), Na (38.74 mg/kg), Zn (54.05 mg/kg) and Cr (26.65 mg/kg), while lowest mean levels were found for Li (6.655 mg/kg), Pb (4.626 mg/kg), Cd (3.209 mg/kg), Sr (1.487 mg/kg), Hg (0.399 mg/kg) and Se (0.156 mg/kg). The increasing trend in average metal levels exhibited following pattern: Se < Hg < Sr < Cd < Pb < Li < As < Ni < Co < Cu < Ca < Cr < Zn < Na < Mn < K < Mg < Fe. Most of metals showed large dispersion as indicated by higher SD and SE values except As, Cd, Hg and Se. Most of the metals showed predominantly symmetrical distribution pattern as shown by lower skewness and kurtosis values, except Cd, Li, Na, Ni, Sr and Zn which exhibited rather asymmetrical distribution in residual fraction of the soil during winter season.

3.29.5 Comparison of Selected Metal Levels in Various Sequentially Extracted Fractions of Soil

Mean metal levels in various sequentially extracted fractions of the soil during summer and winter were compared in order to assess their relative contributions and availability in the soil. Comparison of mean concentrations of the metals in each fraction of soil during summer and winter is shown in Figure 67. During summer, average levels of As in various fractions of soil were 0.381 mg/kg in exchangeable, 0.784 mg/kg in reducible, 1.021 mg/kg in oxidiseable and 8.235 mg/kg in the residual fraction. In comparison, during winter, the average metal levels were 0.385 mg/kg in exchangeable, 0.862 mg/kg in reducible, 1.397 mg/kg in oxidiseable and 6.783 mg/kg in residual fraction. Highest levels of As were observed in the residual fraction, followed by, oxidiseable fraction during both seasons. Relatively higher concentration of As was observed in the residual and oxidiseable fractions during winter compared with summer. Similarly, among different fractions of the soil during summer, mean levels of Ca were 28235 mg/kg in exchangeable, 3944 mg/kg in reducible, 94.98 mg/kg in oxidiseable and 32.09 mg/kg in residual fraction, while during winter mean levels were 33590 mg/kg in exchangeable, 3520 mg/kg in reducible, 75.00 mg/kg in oxidiseable and 20.06 mg/kg in residual fraction. Overall, highest Ca concentrations were found in exchangeable fractions, followed by, reducible, oxidiseable and residual fractions during both seasons. Hence, significant amounts of Ca were bioavailable during both seasons.

Comparison of mean levels of Cd in different fractions of soil during summer revealed that highest contribution was found in residual fraction (3.779 mg/kg), followed by exchangeable fraction (2.680 mg/kg), reducible fraction (1.299 mg/kg) and oxidiseable fraction (1.032 mg/kg). During winter, the statistical data for Cd showed its contributions of 2.118 mg/kg in exchangeable, 1.228 mg/kg in reducible, 0.798 mg/kg in oxidiseable and 3.209 mg/kg in residual fraction. Oxidiseable and reducible fractions of the soil showed lower Cd levels while residual and exchangeable fractions exhibited the elevated levels during both seasons. Average levels of Co in various fractions during summer were noted as 11.00 mg/kg in exchangeable, 7.464 mg/kg in reducible, 9.366 mg/kg in oxidiseable and 17.76 mg/kg in residual fraction. In comparison, the average metal levels during winter were 12.21 mg/kg in exchangeable, 7.210 mg/kg in reducible, 7.580 mg/kg in oxidiseable and 15.49 mg/kg in residual fraction. Overall Co showed following decreasing order during both season: residual > exchangeable > oxidiseable > reducible. Comparative data for mean levels of Cr in the soil showed its contribution at 8.464 mg/kg in exchangeable, 7.823 mg/kg in reducible, 11.69 mg/kg in oxidiseable and 27.95 mg/kg in residual fraction of the soil during summer. The counterpart data during winter exhibited the mean levels at 6.661 mg/kg in exchangeable, 6.996 mg/kg in reducible, 8.709 mg/kg in oxidiseable and 26.65 mg/kg in the residual fraction. On comparative basis, higher Cr levels were noted in residual fraction, followed by, oxidiseable, exchangeable and reducible fractions during both seasons.

Average levels of Cu extracted in various fractions of the soil during summer revealed highest contributions in the residual fraction at 20.27 mg/kg, followed by exchangeable fraction at 4.086 mg/kg, oxidiseable fraction at 3.382 mg/kg and reducible fraction at 2.400 mg/kg. However, during winter mean levels of Cu were noted at 2.233 mg/kg in exchangeable, 1.749 mg/kg in reducible, 2.709 mg/kg in oxidiseable and 18.04 mg/kg in residual fraction. Elevated concentration of Cu was found in the residual fraction, while lowest concentration was observed in the reducible fraction during both seasons. Overall, Cu showed following decreasing concentrations order during summer: residual fraction > exchangeable fraction > oxidiseable fraction > reducible fraction, while during winter the order was; residual fraction > oxidiseable fraction > exchangeable fraction > reducible. Average levels of Fe in soil during summer were observed at 37.48 mg/kg in exchangeable, 522.1 mg/kg in reducible, 195.7 mg/kg in oxidiseable and 7591 mg/kg in residual fraction. In comparison, during winter the average levels were noted as 32.38 mg/kg in exchangeable, 407.0 mg/kg in reducible, 134.2 mg/kg in oxidiseable and 7544 mg/kg in residual fraction. Comparatively higher Fe concentrations were observed in soil during summer than winter in first three fractions while comparable concentration was noted during winter and summer in the residual fraction. Overall, elevated Fe levels were found in the residual and reducible fractions during both seasons.

Average levels of Hg in soil during summer were found at 0.008 mg/kg in exchangeable, 0.033 mg/kg in reducible, 0.224 mg/kg in oxidiseable and 0.050 mg/kg in residual fraction. During winter, the average metal levels were noted as 0.007 mg/kg in exchangeable, 0.1150 mg/kg in reducible, 0.051 mg/kg in oxidiseable and 0.399 mg/kg in residual fraction. Highest mean level of Hg was observed in the oxidiseable fraction, followed by, residual and reducible fractions during summer, while the highest level was noted in the residual fraction, followed by, reducible and oxidiseable fractions during winter. However, almost comparable Hg levels were observed in the exchangeable fraction during both seasons. Mean levels of K were found at 143.0 mg/kg in exchangeable, 71.63 mg/kg in reducible, 80.72 mg/kg in oxidiseable and 733.8 mg/kg in residual fraction of soil during summer. During winter, mean levels were noted as 117.5 mg/kg in exchangeable, 61.35 mg/kg in reducible, 68.13 mg/kg in oxidiseable and 683.2 mg/kg in residual fraction. Hence, K was not abundantly bioavailable and exhibited following decreasing pattern during both seasons: residual > exchangeable > oxidiseable > reducible. Mean levels of Li in exchangeable, reducible, oxidiseable and residual fractions of soil were found at 0.495, 0.844, 2.512 and 9.114 mg/kg, respectively during summer, whereas during winter the metal levels were found at 0.721 mg/kg in exchangeable, 0.397 mg/kg in reducible, 2.602 mg/kg in oxidiseable and 6.655 mg/kg in residual fraction. Consequently, residual and oxidiseable fractions of soil exhibited higher Li levels while exchangeable and reducible fractions revealed lower levels during both seasons.

Average levels of Mg in various fractions of soil during summer were noted at 479.4 mg/kg in exchangeable, 248.0 mg/kg in reducible, 359.9 mg/kg in oxidiseable and 1668 mg/kg in residual fraction. In comparison, the average metal levels during winter were 563.1 mg/kg in exchangeable, 153.8 mg/kg in reducible, 503.4 mg/kg in oxidiseable and 1581 mg/kg in residual fraction. Overall, Mg showed following decreasing order during both seasons: residual > exchangeable > oxidiseable > reducible. Mean levels of Mn in soil during summer were recorded at 88.08 mg/kg in exchangeable, 212.6 mg/kg in reducible, 18.46 mg/kg in oxidiseable and 201.5 mg/kg in residual fraction. The counterpart data during winter exhibited the mean levels at 94.98 mg/kg in exchangeable, 149.3 mg/kg in reducible, 16.47 mg/kg in oxidiseable and 179.5 mg/kg in residual fraction. On comparative basis, higher Mn levels during summer were noted in reducible fraction, followed by, residual, exchangeable and oxidiseable fractions, whereas, it's elevated levels were found in residual fraction, followed by, reducible, exchangeable and oxidiseable fractions during winter.

Sodium contents extracted in various fractions of soil during summer revealed its mean levels as 76.70 mg/kg in exchangeable, 17.98 mg/kg in reducible, 41.05 mg/kg in oxidiseable and 44.57 mg/kg in residual fraction. However, during winter the metal levels were 100.2 mg/kg in exchangeable, 18.52 mg/kg in reducible, 34.95 mg/kg in oxidiseable and 38.74 mg/kg in residual fraction. Highest concentration was found in exchangeable fraction, while the lowest concentration was noted in reducible fraction during both seasons. Average levels of Ni extracted in various fractions of soil during summer were found at 13.57 mg/kg in exchangeable, 7.421 mg/kg in reducible, 4.750 mg/kg in oxidiseable and 8.852 mg/kg in residual fraction. During winter, mean concentrations of Ni were 12.15 mg/kg in exchangeable, 7.240 mg/kg in reducible, 5.166 mg/kg in oxidiseable and 7.910 mg/kg in residual fraction. Overall, comparatively higher concentration of Ni was observed in exchangeable and residual fractions during both seasons. Mean levels of Pb in the soil during summer were found at 56.70 mg/kg in exchangeable, 17.72 mg/kg in reducible, 3.710 mg/kg in oxidiseable and 4.835 mg/kg in residual fraction, whereas, during winter, the metal levels were 32.83 mg/kg in exchangeable, 13.47 mg/kg in reducible, 4.379 mg/kg in oxidiseable and 4.626 mg/kg in residual fraction. Highest Pb levels were found in exchangeable fraction, followed by, reducible fraction. It revealed relatively higher bioavailability of Pb, which may be associated with a number of ecological/health effects.

Average levels of Se in various fractions of soil during summer were noted as 0.350 mg/kg in exchangeable, 1.119 mg/kg in reducible, 0.639 mg/kg in oxidiseable and 0.206 mg/kg in residual fraction. In comparison, during winter, average metal levels were found at 0.350 mg/kg in exchangeable, 0.624 mg/kg in reducible, 0.700 mg/kg in oxidiseable and 0.156 mg/kg in residual fraction. Overall, elevated Se levels were found in oxidiseable and reducible fractions, followed by exchangeable and residual fractions during both seasons. Therefore, Se showed higher bioavailability and mobility in the soil samples. Average levels of Sr in the soil during summer were noted as 42.74 mg/kg in exchangeable, 12.62 mg/kg in reducible, 5.164 mg/kg in oxidiseable and 2.136 mg/kg in residual fraction. The counterpart data during winter exhibited following mean levels; 45.20 mg/kg in exchangeable, 5.785 mg/kg in reducible, 4.020 mg/kg in oxidiseable and 1.487 mg/kg in residual fraction. Overall, Sr showed following decreasing concentrations order: exchangeable fraction > reducible fraction > oxidiseable fraction > residual fraction. On comparative basis, higher Sr levels were noted in exchangeable and reducible fractions during both seasons; thus it also showed higher bioavailability and mobility in the soil during both seasons. The distribution pattern of Zn in various fractions of soil during summer and winter followed similar order: residual fraction > reducible fraction > oxidiseable fraction > exchangeable fraction. Comparatively higher concentration of Zn in the residual fraction indicated its low extractability, mobility and bioavailability in the soil samples during both seasons.

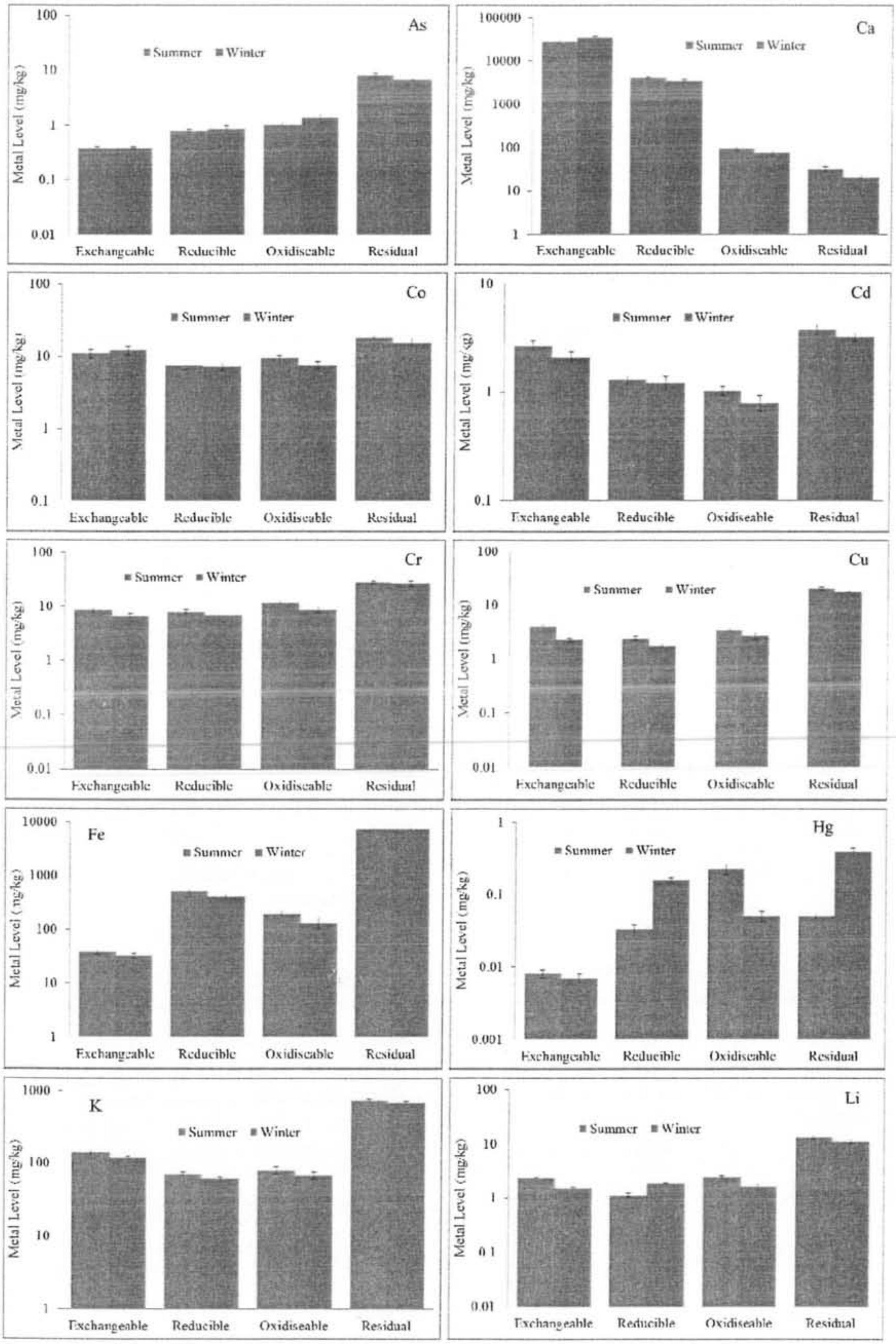

Figure 67. (Contd........)

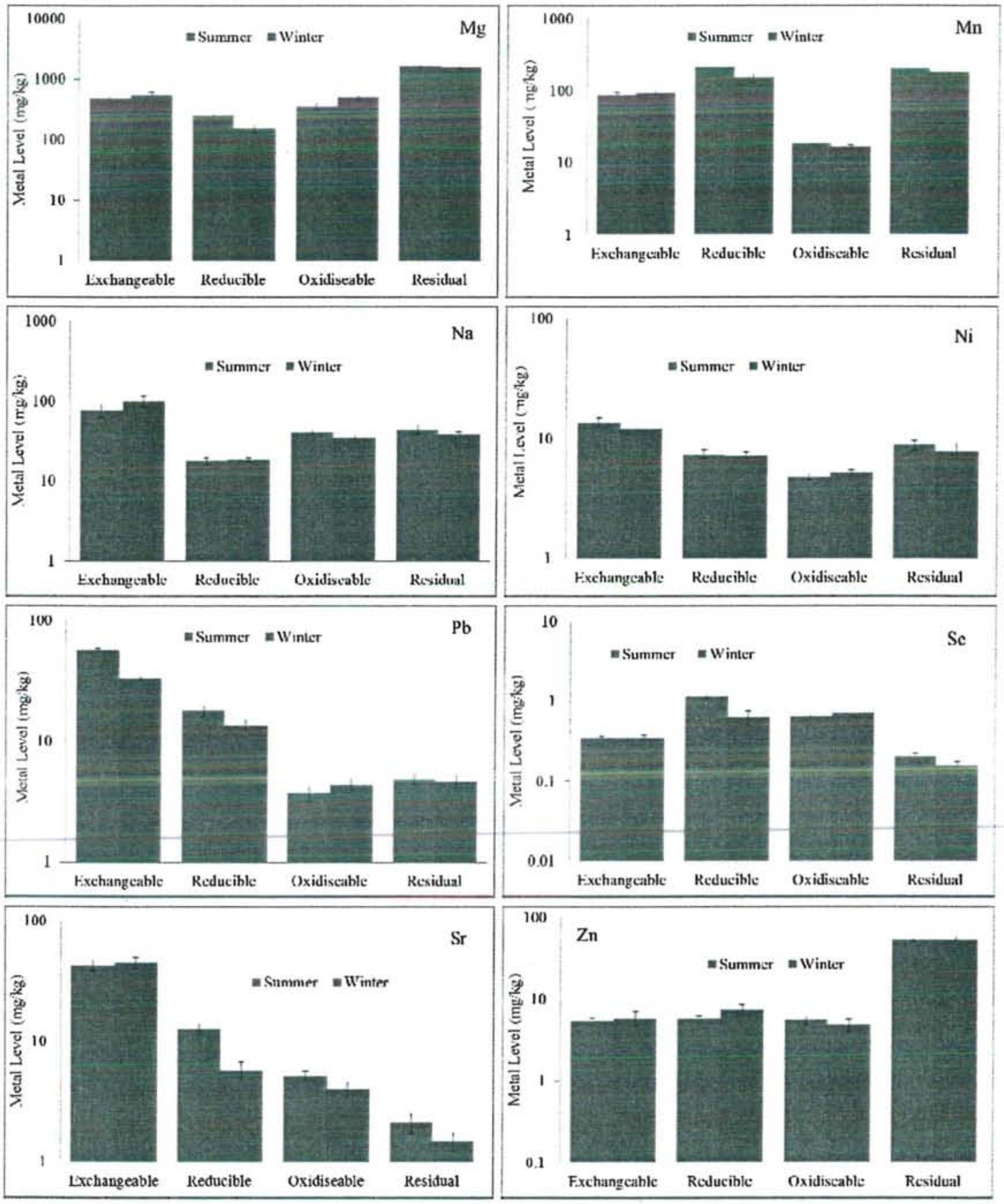

Figure 67. Comparison of selected metal levels (mg/kg) in various geochemical fractions of the soil during summer and winter

3.30 Spatial Distribution of Selected Metals in Soil Samples

Spatial variations in selected metal levels at ten sampling sites (as shown in Figure 52) during summer and winter are shown in Table 95. Most of the metals showed significant spatial variations ($p < 0.05$) among the sampling sites. During summer, highest levels of selected metals were observed as follow; As, Ca, Co, Hg, Li, Mn, Ni, Se and Sr at site S-2; Cd and Mg at site S-3; Cr, Na and Pb at site S-6; Cu, Fe and Zn at site S-1 and K at S-5 . However, during winter, highest concentrations of Cd, Cr and Sr were noted at site S-6; Ca, Co, Cu, Fe, Hg, Li, Mn, Na, Ni and Se at site S-2; Mg at site S-8; Zn at site S-3 and As, K and Pb at site S-10. Among the metals, Ca, Fe, Mg, K, and Mn were the most abundant metals, whereas Li, Cd, Se and Hg were the less abundant in surface soil during both seasons. Total concentrations of all selected metals in the soil exhibited highest average contributions at S-2 (4720 mg/kg), followed in order of abundance by, S-9 (3771 mg/kg), S-3 (3290 mg/kg), S-6 (2844 mg/kg), S-4 (2515 mg/kg), S-10 (2436 mg/kg), S-5 (2322 mg/kg), S-7 (2212 mg/kg), S-8 (2054 mg/kg) and S-1 (1660) during summer. On the other hand, during winter total concentrations of the metals exhibited highest average contents at S-2 (2617 mg/kg), followed in decreasing order of abundance by, S-9 (2327 mg/kg), S-5 (2190 mg/kg), S-4 (2126 mg/kg), S-1 (2120 mg/kg), S-3 (1916 mg/kg), S-6 (2061 mg/kg), S-10 (1831 mg/kg), S-8 (1821 mg/kg) and S-7 (1410 mg/kg).

Spatially, comparatively higher concentrations of the metals were found in the samples collected near Mirpur City (S-2), New City (S-3), Khaliqabad-Jari (S-4), and Dudial (S-9) while intermediate metal levels were observed in the samples collected from Chatterpari-Sadole (S-1), Islamghar (S-6) and Chakswari (S-7). However the soil samples collected from Kakra Town-Kalyal Bansi (S-5), Palak (S-8) and Siakh (S-10) exhibited considerably lower metal levels. Former areas are thickly populated typical urban localities around the lake, while in the latter areas are mostly remote and the population density is quite low in these locations. Consequently, higher metal levels in the soil samples may be ascribed to the excessive anthropogenic activities in the populated areas, whereas relatively lower metal contents were found in less-populated and remote areas. Besides the lithogenic contributions; atmospheric deposition, industrial effluents, untreated municipal wastes and agricultural activities were the major pollution sources of the metals in the study area (Saleem *et al.*, 2013 & 2014b).

Table 95. Average levels of selected metals (mg/kg) in the soil from various sites around Mangla Lake during summer and winter

	Code	Location	As	Ca	Cd	Co	Cr	Cu	Fe	Hg	K	Li	Mg	Mn	Na	Ni	Pb	Se	Sr	Zn
Summer	S-1	Chatterpari-Sadole	11.9	20410	1.33	27.0	26.6	21.8	4233	0.37	1012	11.0	3501	365	118	32.0	13.2	0.87	35.0	57.8
	S-2	Mirpur	20.6	76383	0.81	67.0	15.7	12.7	4106	0.44	805	15.8	2737	507	128	47.8	17.7	1.06	52.2	33.7
	S-3	New City	19.2	49748	1.74	47.6	26.8	16.6	4032	0.37	614	11.6	3862	428	260	40.6	19.9	0.86	49.4	42.1
	S-4	Khaliqabad-Jari	19.7	35446	1.07	24.9	23.5	14.6	4034	0.23	1296	9.05	3613	451	197	31.2	17.2	0.96	47.5	42.7
	S-5	Kakra Town-Kalyal	13.1	32343	1.14	23.9	15.5	15.2	4017	0.25	1330	11.5	3447	335	123	20.0	31.4	0.58	29.2	39.1
	S-6	Islamghar	18.5	43223	1.40	29.1	29.4	13.4	3960	0.19	312	7.41	2757	401	298	26.4	34.0	0.59	41.6	35.5
	S-7	Chakswari	14.8	31124	1.67	36.6	24.9	13.1	4009	0.28	692	11.1	3286	369	116	26.8	5.77	0.56	44.3	42.6
	S-8	Palak	9.8	27857	1.54	15.0	12.9	11.7	3983	0.20	758	4.04	3658	348	228	20.9	14.6	0.57	18.2	29.4
	S-9	Dadial	12.4	58525	1.18	45.0	19.2	15.3	4017	0.31	743	11.4	3719	388	257	27.5	10.1	0.85	39.9	43.9
	S-10	Siak-Chattroh	12.9	34731	1.49	11.4	17.9	13.2	3986	0.29	983	11.0	3498	344	145	17.9	8.87	0.67	28.3	36.1
Winter	S-1	Chatterpari-Sadole	12.5	29026	2.37	33.6	29.4	17.6	3732	0.69	1127	7.21	3443	447	131	14.4	36.3	0.58	60.8	33.6
	S-2	Mirpur	22.3	37582	1.51	56.7	29.1	18.2	3737	1.37	1223	12.0	3475	495	299	50.9	19.3	1.22	41.3	33.3
	S-3	New City	19.1	25581	0.79	31.9	28.4	16.6	3707	0.56	972	11.4	3234	450	261	31.7	21.9	0.99	77.5	34.2
	S-4	Khaliqabad-Jari	14.2	29442	2.52	32.8	29.1	15.6	3725	1.07	834	11.0	3472	410	138	31.1	24.6	0.63	46.7	31.4
	S-5	Kakra Town-Kalyal	14.5	30456	1.03	31.1	24.4	12.7	3681	0.90	1069	8.54	3512	381	115	21.9	26.0	0.76	45.0	27.1
	S-6	Islamghar	12.9	28893	2.86	50.4	34.3	9.76	3634	1.03	678	10.4	3049	412	146	28.8	24.9	1.03	79.8	30.4
	S-7	Chakswari	19.6	17082	2.06	50.5	32.4	8.45	3633	0.85	833	10.4	3006	390	163	32.7	25.3	0.89	56.1	25.8
	S-8	Palak	12.6	23738	0.53	35.9	16.8	11.3	3565	0.59	1212	8.92	3549	354	173	23.3	25.9	0.59	33.3	22.3
	S-9	Dadial	18.7	32962	2.45	37.8	21.3	12.9	3730	0.85	1027	10.4	3293	396	238	37.0	16.7	0.88	49.8	27.7
	S-10	Siak-Chattroh	23.3	23975	1.73	20.3	17.3	13.0	3585	0.69	1231	10.1	3438	339	161	22.1	39.3	0.69	51.1	29.8

3.31 Soil Texture and Particle Size Distribution

Soil texture is one of the most important characteristics, affecting many physical and chemical properties of the soil. A comprehensive approach to the textural characteristic of soil is to obtain a detailed particle size distribution by sieves and sedimentation of dispersed particles in a liquid, which provide more accurate description of the soil texture. In the present study, particle size distribution in the soil samples during summer and winter were studied in the range of 1 to > 2000 µm and then adding up various fractions to evaluate the prevailing texture of the samples. Particle size distribution for the soil samples during summer is shown in Table 96. Mean value of the particles in the range of 1-5 µm were 19.61%. According to USEPA classification, these particles belonged to the clay fraction of soil. Similarly, silt particles ranged from 5-75 µm and among these particles, highest mean percentage was noted for 30-75 µm (9.434%). Coarse particles were classified as fine sand; ranging from 75-400 µm with the highest mean percentage shown by particles in the range of 200-400 µm (15.44%). However, in case of medium sand; percentages of the particles ranged from 7.540 to 18.42% with the mean value of 12.96% (diameter of these particles were in the range of 400-2000 µm) while coarse sand (diameter >2000 µm) showed low contribution (1.593%). Ternary diagram showing the predominant texture of the soil samples collected during summer is shown in Figure 68. The soil samples exhibited high percentages of sand and low percentages of silt and clay. Consequently, the soil during summer mostly showed sandy loam texture (20 % clay, 25 % silt, 53 % sand).

During winter (Table 97), average percentage of fine particles/clay (1-5 µm) were 17.41%, while among the silt particles (5-75 µm), highest percentage (8.975%) was shown by 30-75 µm particles. Among the fine sand particles, considerable contribution was shown by the particles in range of 100-200 µm (12.71%), whereas relatively higher contribution was shown by the particles in range of 200-400 (32.73%). Medium sand (400-2000 µm) particles exhibited a mean value of 7.922% while coarse sand (> 2000 µm) showed average contribution of 0.456%. Ternary diagram for the soil samples during winter is shown in Figure 69. Most of the samples belonged to class 'sandy loam', which contained about 18% clay, 24% silt and 58% sand. The soil samples during summer and winter showed more or less similar texture and insignificant variations in the particle size distribution were observed. High percentage of sand in the soil indicated low bulk density, high porosity and low water holding capacity.

Table 96. Statistical distribution of various particle size fractions (%) in the soil during summer

	Min	Max	Mean	Median	SD	SE	Skew	Kurt
1-1.35 μm	5.976	17.63	10.72	10.25	2.816	0.630	0.689	0.467
1.35-5 μm	2.424	19.90	8.891	8.310	4.133	0.924	0.886	1.307
5-10 μm	4.077	11.67	6.056	5.245	2.178	0.487	1.509	1.722
10-20 μm	1.762	11.62	5.770	5.656	2.450	0.548	0.467	0.303
20-30 μm	0.675	5.805	2.697	2.346	1.376	0.308	0.974	0.542
30-75 μm	4.293	15.83	9.434	8.702	3.590	0.803	0.304	-0.827
75-100 μm	4.101	17.36	10.67	11.01	3.954	0.884	-0.034	-0.918
100-200 μm	6.498	18.55	12.31	12.06	3.550	0.794	0.247	-0.752
200-400 μm	9.493	24.36	15.44	14.91	3.982	0.890	0.592	-0.172
400-2000 μm	7.540	18.42	12.96	12.97	2.819	0.630	-0.060	-0.499
>2000 μm	0.438	4.761	1.593	1.164	1.228	0.275	1.788	2.199

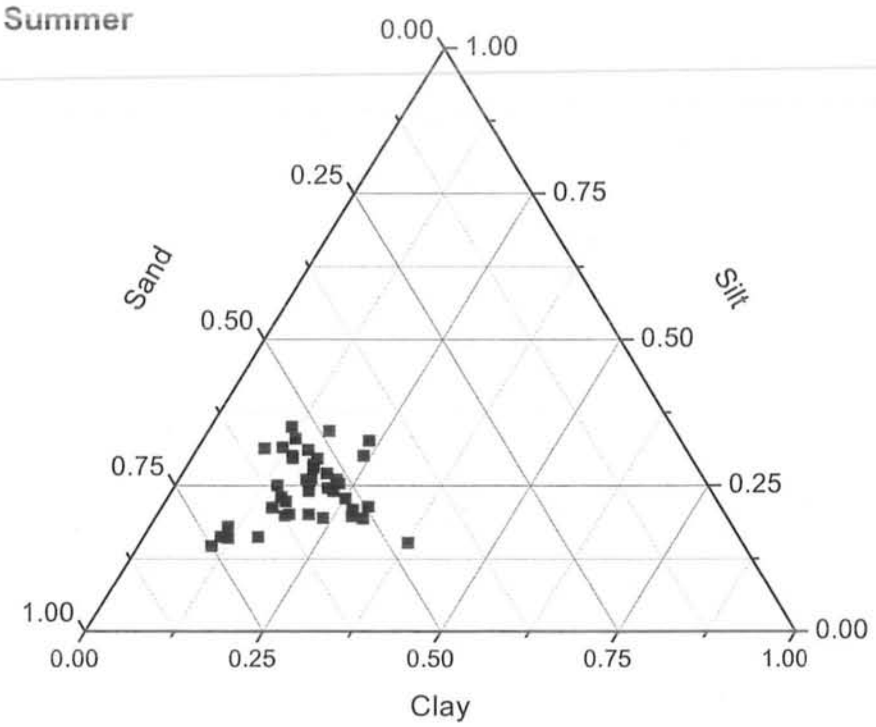

Figure 68. Ternary diagram showing the texture of the soil during summer

Table 97. Statistical distribution of various particle size fractions (%) in the soil during winter

	Min	Max	Mean	Median	SD	SE	Skew	Kurt
1-1.35 μm	4.315	25.81	11.75	10.24	5.852	1.309	1.191	0.869
1.35-5 μm	0.867	10.21	5.660	5.750	2.681	0.600	0.282	-0.701
5-10 μm	1.585	10.10	4.494	3.792	2.112	0.472	0.998	1.017
10-20 μm	1.320	12.60	6.840	7.019	2.899	0.648	-0.168	-0.096
20-30 μm	1.209	7.183	3.586	3.300	1.950	0.436	0.390	-1.196
30-75 μm	4.545	16.15	8.975	8.593	3.227	0.722	0.634	-0.165
75-100 μm	1.467	11.29	4.573	3.997	2.676	0.598	1.248	1.141
100-200 μm	4.783	23.00	12.71	11.66	5.519	1.234	0.445	-0.787
200-400 μm	13.99	57.73	32.73	33.10	12.76	2.853	0.305	-0.762
400-2000 μm	3.341	12.71	7.922	7.982	2.313	0.517	0.024	-0.120
>2000 μm	0.104	1.350	0.456	0.374	0.341	0.076	1.561	2.100

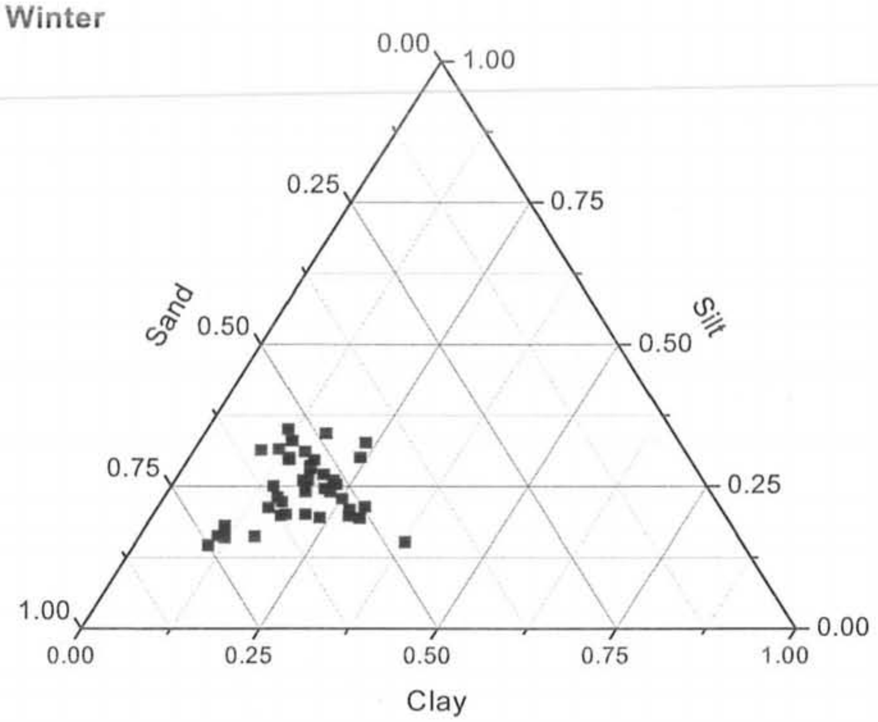

Figure 69. Ternary diagram showing the texture of the soil during winter

Table 98. Correlation coefficient (r)* matrix of physicochemical parameters in the soil during summer, winter, pre-monsoon, monsoon and post-monsoon

		T	pH	EC	TDS	TA	MC
Summer	pH	0.041					
	EC	0.090	-0.259				
	TDS	-0.045	-0.294	0.900			
	TA	0.082	0.914	-0.183	-0.226		
	MC	0.226	0.192	0.091	0.071	0.112	
	OM	0.119	-0.267	0.309	0.403	-0.275	-0.020
Winter	pH	0.227					
	EC	-0.526	-0.192				
	TDS	-0.526	-0.191	1.000			
	TA	0.046	0.650	-0.113	-0.114		
	MC	-0.307	0.102	-0.039	-0.040	0.115	
	OM	-0.410	0.187	-0.102	-0.102	0.277	0.189
Pre-monsoon	pH	0.191					
	EC	-0.437	-0.091				
	TDS	-0.437	-0.091	1.000			
	TA	-0.150	0.232	-0.052	-0.052		
	MC	-0.108	0.036	0.151	0.151	-0.169	
	OM	0.580	0.161	-0.251	-0.251	-0.236	0.125
Monsoon	pH	0.000					
	EC	-0.265	0.080				
	TDS	-0.265	0.079	1.000			
	TA	-0.339	0.234	0.008	0.008		
	MC	0.047	0.046	-0.024	-0.023	0.001	
	OM	0.446	-0.411	-0.044	-0.044	-0.277	0.103
Post-monsoon	pH	-0.385					
	EC	0.026	-0.175				
	TDS	0.026	-0.175	1.000			
	TA	-0.192	0.050	0.082	0.082		
	MC	0.010	-0.014	0.093	0.093	-0.093	
	OM	0.252	-0.371	-0.099	-0.099	-0.120	0.141

*r-values > 0.350 or < -0.350 are significantly correlated at $p < 0.05$

3.32 Correlation Study of Physicochemical Parameters and Selected Metals in Soil Samples

3.32.1 Correlation Study of Physicochemical Parameters in Soil Samples

The correlation coefficient matrix for physiochemical parameters in the soil during summer and winter is shown in Table 98. Among the physiochemical parameters, EC and TDS showed a direct strong relationship which is quite obvious. Likewise, pH and total alkalinity revealed a strong correlation during summer (r = 0.914) and winter (r = 0.650) and it is the established fact that higher pH is always associated with higher alkalinity. Other parameters showed weak or insignificant relationships with each other, however, during summer, TDS showed significant relationship with OM (r = 0.403) and during winter, T showed inverse relationship with EC (r = -0.526), TDS (r = -0.526) and OM (r = -0.410) in the soil samples.

The correlation coefficient matrix for physiochemical parameters in the soil during pre-monsoon, monsoon and post-monsoon is also shown in Table 98. Among the physiochemical parameters, apart from EC and TDS, OM revealed a positive correlation with T during pre-monsoon (r = 0.580) and monsoon (r = 0.446) seasons. In addition, T showed inverse correlation with EC & TDS (r = -0.437) and TA (r = -0.339) during pre-monsoon and monsoon seasons, respectively. Other parameters showed weak or insignificant relationships with each other in the soil samples during all seasons.

3.32.2 Correlation Study of Selected Metals in Calcium Nitrate Extract of Soil Samples

The correlation coefficient matrix pertaining to selected metal levels in calcium nitrate extract of the soil during summer is shown in Table 99. Several strong relationships were observed among the metals, such as, K-Ca (r = 0.768), Ca-Mg (r = 0.687), K-Mg (r = 0.642), Li-Mg (r = 0.548), Mn-Fe (r = 0.522), Cu-Zn (r = 0.541) and Li-Cu (r = 0.512). In addition, significant positive correlations were found between Cd-Li, Co-K, Co-Mg, Cu-Cr, Na-Fe, and Li-K. Some inverse correlations were also found between Mg-Fe (r = -0.460), Ca-Fe (r = -0.439) and Ca-Na (r = -0.369). Some of the metals, such as, As, Cd, Hg and Pb exhibited unique behaviour; they were not significantly correlated with any other metal, thus exhibiting their independent variations in the soil samples.

The correlation coefficient matrix for selected metal levels in calcium nitrate extract of the soil during winter is also shown in Table 99. Among the selected metals, Ca was found to be strongly correlated with Mg ($r = 0.715$) and Sr ($r = 0.619$); Mg revealed strong relationships with Sr ($r = 0.691$) and K ($r = 0.503$); and Se showed strong association with Fe ($r = 0.514$). Significant interrelationships were also found between As-Cr, As-Cu, Ca-Cu, Cr-Cu, Sr-K, Cr-Li, Ni-Fe, and Pb-Mg. Among all the metals, Ca, K, Sr and Mg showed similar and strong mutual correlations, thus pointing towards their common origin and mutual variations in the soil samples.

The correlation coefficient matrix for selected metals in calcium nitrate extract of the soil during pre-monsoon is shown in Table 100. Strong positive correlation was observed between Mn and K ($r = 0.677$), followed by K-Mg ($r = 0.622$) and Ca-Mg ($r = 0.591$). Among the selected metals, significant correlations were noted between Mg-Mn, Na-Li, Co-Cr, Co-K, Co-Mg, Co-Ni and Cd-Li, whereas, significant inverse relationship were noted between Hg-K ($r = -0.365$).

The data on metal-to-metal correlation in calcium nitrate extract of the soil during monsoon are given in Table 101, wherein the significant r-values are shown at $p < 0.05$. Strong positive correlations were observed between Ca-Sr ($r = 0.690$), Ca-Mg ($r = 0.669$), Co-Zn ($r = 0.602$) and Co-Ni ($r = 0.586$). In addition, many significant correlations were found between Ca-Cr, Cr-Co, K-Co, Mg-K, Li-K, Ni-K, Ni-Li, Li-Se, Mg-Sr, Pb-Sr, Zn-Mn, Zn-Ni and Mn-Mg, which may be attributed to their mutual variations in the soil. Conversely, significant negative correlations were observed between Cr-Cd, Cd-Co, Cd-K, K-Na and Se-Cd, thus indicating their opposing distribution in the soil samples during monsoon.

The correlation coefficient matrix for selected metal levels in calcium nitrate extract of the soil during post-monsoon is shown in Table 102. Strong positive correlations were observed between Ca-Mg ($r = 0.911$), Cr-Cu ($r = 0.775$), Cd-Cu ($r = 0.673$), As-Se ($r = 0.567$) and Ni-Li ($r = 0.528$). In addition, some significant positive correlations were found between As-Hg, Cd-Cr, Co-Fe, Co-Mn, Na-Co, Na-Fe, Ni-Mn, Hg-Se, Ca-Pb and Zn-Ni in the soil samples. On the contrary, significant negative correlations were observed between Cd-Li, Cr-Li, Cu-Li, Ni-Mg and Co-Zn, thus manifesting inverse association of these metals in calcium nitrate extract of the soil samples during post-monsoon season. Consequently, the correlation study revealed significantly diverse association among the selected metal contents in the soil during summer, winter, pre-monsoon, monsoon and post-monsoon seasons.

Table 99. Correlation coefficient (r)* matrix for selected metal levels in calcium nitrate extract of the soil during summer (below the diagonal) and winter (above the diagonal)

	As	Ca	Cd	Co	Cr	Cu	Fe	Hg	K	Li	Mg	Mn	Na	Ni	Pb	Se	Sr	Zn
As	1	0.250	-0.115	-0.039	0.481	0.388	-0.064	-0.231	-0.127	0.107	0.023	0.013	0.246	-0.340	-0.118	-0.312	0.065	-0.120
Ca	-0.233	1	-0.103	-0.034	0.029	0.402	0.221	-0.149	0.267	-0.241	0.715	0.034	0.231	0.204	0.212	0.116	0.619	0.029
Cd	-0.089	0.246	1	0.011	-0.222	-0.052	-0.261	-0.003	0.191	-0.168	0.030	0.247	0.079	-0.302	0.240	0.274	0.044	0.122
Co	0.168	0.350	0.296	1	-0.112	-0.202	-0.007	-0.024	-0.012	-0.276	-0.076	-0.023	0.089	-0.019	-0.353	0.145	-0.144	0.435
Cr	-0.150	-0.306	0.161	-0.198	1	0.488	-0.067	-0.083	-0.141	0.364	-0.133	-0.099	0.315	-0.170	0.027	-0.274	0.017	-0.403
Cu	-0.064	-0.003	0.143	-0.228	0.363	1	0.238	0.034	-0.128	0.012	0.057	-0.040	0.244	0.123	0.074	-0.109	0.097	-0.208
Fe	0.318	-0.439	-0.036	-0.077	0.273	0.087	1	0.035	0.059	-0.021	0.289	0.296	0.013	0.394	-0.010	0.514	-0.087	0.126
Hg	-0.110	0.178	0.321	0.102	-0.175	-0.223	-0.059	1	0.224	-0.102	-0.023	-0.008	-0.130	0.256	-0.117	-0.164	-0.251	0.153
K	-0.090	0.768	0.168	0.402	-0.082	0.102	-0.066	0.066	1	0.192	0.503	-0.250	-0.133	0.129	0.212	0.109	0.469	0.016
Li	-0.027	0.232	0.356	0.203	0.283	0.512	-0.200	-0.315	0.356	1	0.129	-0.100	0.294	-0.146	0.152	-0.300	0.104	-0.322
Mg	-0.190	0.687	0.219	0.413	-0.104	-0.025	-0.460	-0.121	0.642	0.548	1	0.294	0.293	0.009	0.426	0.129	0.691	0.056
Mn	0.199	-0.151	-0.141	0.192	0.155	0.064	0.522	-0.257	0.095	-0.084	-0.178	1	0.268	-0.215	0.059	0.141	0.125	0.157
Na	0.265	-0.369	-0.169	-0.073	0.128	0.049	0.396	-0.170	0.017	0.042	-0.144	0.225	1	-0.427	0.040	-0.170	0.246	0.164
Ni	0.036	-0.082	0.005	-0.238	0.054	0.114	-0.108	0.012	-0.195	-0.173	-0.271	0.303	-0.226	1	0.062	0.339	-0.173	0.216
Pb	-0.150	0.233	-0.154	0.194	-0.210	-0.063	0.003	0.143	0.134	-0.232	-0.126	0.172	-0.237	-0.042	1	0.195	0.298	0.071
Se	0.148	0.093	-0.132	0.235	-0.287	-0.334	0.143	0.145	0.155	-0.225	0.092	0.027	-0.077	-0.221	0.062	1	-0.144	0.360
Sr	-0.090	0.108	0.183	0.140	-0.130	0.162	0.025	0.112	0.150	-0.045	0.070	0.003	0.285	-0.419	0.013	0.392	1	-0.144
Zn	-0.220	0.201	-0.041	-0.182	-0.074	0.541	-0.138	0.067	0.157	0.220	0.044	0.270	-0.014	0.397	-0.004	-0.174	0.142	1

*r-values > 0.350 or < -0.350 are significantly correlated at $p < 0.05$

Table 100. Correlation coefficient (r)* matrix for selected metal levels in calcium nitrate extract of the soil during pre-monsoon

	As	Ca	Cd	Co	Cr	Cu	Fe	Hg	K	Li	Mg	Mn	Na	Ni	Pb	Se	Sr	Zn
As	1																	
Ca	-0.166	1																
Cd	0.053	-0.130	1															
Co	-0.082	0.284	-0.326	1														
Cr	-0.083	0.259	-0.310	0.368	1													
Cu	0.147	-0.077	-0.220	0.016	0.061	1												
Fe	-0.008	-0.088	-0.139	0.158	-0.075	0.333	1											
Hg	0.324	-0.141	0.085	0.009	-0.226	0.206	0.076	1										
K	-0.118	0.094	-0.284	0.406	0.119	0.169	0.205	-0.365	1									
Li	-0.093	-0.066	0.382	-0.234	-0.228	0.030	-0.268	0.156	-0.251	1								
Mg	-0.022	0.591	-0.318	0.418	0.155	0.329	0.238	-0.182	0.622	-0.129	1							
Mn	-0.026	0.109	-0.196	0.306	-0.037	0.063	0.201	-0.075	0.677	-0.253	0.476	1						
Na	0.004	0.073	-0.021	-0.184	-0.065	0.112	-0.130	0.127	-0.292	0.451	-0.049	-0.176	1					
Ni	0.010	-0.180	0.245	0.352	0.166	0.048	-0.116	0.037	0.132	0.319	-0.021	-0.055	-0.215	1				
Pb	0.318	-0.005	-0.182	0.240	0.202	0.029	-0.200	0.103	0.012	-0.197	0.071	0.141	-0.146	0.064	1			
Se	0.244	0.106	-0.083	-0.070	-0.132	0.343	0.078	-0.031	-0.024	0.209	0.167	-0.204	0.159	-0.030	-0.144	1		
Sr	-0.081	-0.152	0.105	-0.124	0.180	-0.088	-0.087	-0.221	-0.218	0.075	-0.267	-0.166	-0.061	0.127	0.086	-0.063	1	
Zn	0.166	-0.181	0.334	-0.033	-0.105	-0.018	-0.150	0.107	-0.211	0.123	-0.225	0.066	-0.053	0.073	0.107	-0.297	0.081	1

*r-values > 0.350 or < -0.350 are significantly correlated at $p < 0.05$

Table 101. Correlation coefficient (r)* matrix for selected metal levels in calcium nitrate extract of the soil during monsoon

	As	Ca	Cd	Co	Cr	Cu	Fe	Hg	K	Li	Mg	Mn	Na	Ni	Pb	Se	Sr	Zn
As	1																	
Ca	0.080	1																
Cd	0.032	-0.149	1															
Co	-0.144	0.156	-0.356	1														
Cr	0.063	0.352	-0.330	0.353	1													
Cu	-0.095	-0.160	-0.183	-0.014	0.110	1												
Fe	-0.156	-0.214	-0.026	0.182	-0.007	0.152	1											
Hg	0.288	-0.099	-0.050	0.023	0.295	0.051	-0.068	1										
K	-0.137	0.294	-0.330	0.380	0.198	-0.044	-0.009	-0.255	1									
Li	0.131	0.017	-0.176	0.247	0.009	0.072	-0.089	-0.017	0.345	1								
Mg	-0.206	0.669	-0.325	0.310	0.224	0.139	-0.057	-0.175	0.406	0.177	1							
Mn	-0.210	0.112	-0.258	0.295	-0.113	-0.005	0.055	-0.341	0.294	0.258	0.350	1						
Na	0.001	-0.099	0.201	-0.162	-0.021	0.164	0.306	-0.067	-0.392	-0.028	-0.162	-0.250	1					
Ni	0.014	0.041	0.029	0.586	0.243	-0.028	0.055	0.077	0.342	0.414	0.073	0.223	-0.283	1				
Pb	-0.120	0.314	-0.049	0.187	0.030	-0.062	-0.215	-0.238	-0.004	-0.243	0.209	0.077	-0.119	0.137	1			
Se	0.076	-0.212	-0.369	0.063	0.152	0.208	-0.022	-0.064	0.107	0.397	-0.099	-0.060	0.071	0.112	-0.026	1		
Sr	0.028	0.690	0.119	-0.083	0.154	-0.118	-0.159	-0.136	-0.055	-0.212	0.485	-0.093	0.218	-0.070	0.418	-0.301	1	
Zn	-0.232	-0.009	-0.053	0.602	0.007	0.027	0.084	-0.175	0.176	0.216	0.096	0.390	-0.147	0.366	0.023	-0.052	-0.232	1

*r-values > 0.350 or < -0.350 are significantly correlated at $p < 0.05$

Table 102. Correlation coefficient (r)* matrix for selected metal levels in calcium nitrate extract of the soil during post-monsoon

	As	Ca	Cd	Co	Cr	Cu	Fe	Hg	K	Li	Mg	Mn	Na	Ni	Pb	Se	Sr	Zn
As	1																	
Ca	0.189	1																
Cd	-0.016	-0.030	1															
Co	-0.193	0.224	0.260	1														
Cr	0.141	-0.069	0.486	-0.037	1													
Cu	0.055	-0.220	0.673	0.087	0.775	1												
Fe	-0.119	-0.227	0.241	0.389	0.021	0.136	1											
Hg	0.484	0.215	0.154	0.106	0.125	0.055	0.134	1										
K	0.000	0.313	-0.307	0.010	-0.197	-0.302	-0.008	-0.060	1									
Li	0.082	-0.032	-0.480	-0.289	-0.353	-0.350	-0.136	-0.240	0.324	1								
Mg	0.099	0.911	0.021	0.209	-0.031	-0.182	-0.319	0.126	0.281	-0.122	1							
Mn	-0.006	-0.035	-0.103	0.383	-0.066	-0.055	0.307	-0.030	0.067	0.324	-0.136	1						
Na	-0.006	0.250	0.254	0.356	-0.116	0.013	0.401	0.280	-0.162	-0.053	0.261	-0.122	1					
Ni	0.070	-0.305	-0.150	-0.203	-0.220	-0.250	0.083	-0.148	0.125	0.528	-0.376	0.445	-0.241	1				
Pb	-0.044	0.386	0.212	0.062	0.112	-0.006	-0.191	-0.007	-0.060	-0.199	0.347	-0.160	0.340	-0.162	1			
Se	0.567	0.131	-0.146	0.207	0.218	0.099	0.053	0.476	-0.015	-0.162	-0.005	0.281	-0.177	-0.024	-0.077	1		
Sr	-0.209	-0.115	0.113	-0.033	0.242	0.100	0.302	-0.160	-0.149	-0.134	-0.200	-0.092	0.024	0.087	0.153	-0.015	1	
Zn	-0.064	-0.181	0.004	-0.451	0.229	0.091	0.025	-0.179	0.125	0.149	-0.166	0.183	-0.271	0.489	0.004	-0.266	0.084	1

*r-values > 0.350 or < -0.350 are significantly correlated at $p < 0.05$

Table 103. Correlation coefficient (r)* matrix for selected metal levels in acid extract of the soil during summer (below the diagonal) and winter (above the diagonal)

	As	Ca	Cd	Co	Cr	Cu	Fe	Hg	K	Li	Mg	Mn	Na	Ni	Pb	Se	Sr	Zn
As	1	-0.030	-0.003	-0.200	0.170	0.607	0.563	0.474	0.271	0.586	0.399	0.424	0.331	-0.330	-0.167	0.750	0.024	0.456
Ca	0.154	1	-0.004	0.119	0.233	-0.135	-0.040	-0.096	0.015	0.068	0.349	-0.141	0.293	-0.025	0.001	0.028	0.024	-0.074
Cd	-0.170	-0.059	1	0.169	0.292	0.145	0.313	-0.047	0.117	0.297	0.291	0.183	0.085	0.103	-0.279	-0.123	-0.161	0.262
Co	0.521	-0.052	-0.060	1	0.234	0.055	-0.027	-0.284	-0.027	0.031	0.149	-0.008	0.057	0.385	0.336	-0.318	-0.032	0.291
Cr	-0.267	-0.199	0.251	-0.444	1	0.466	0.642	-0.115	0.277	0.504	0.617	0.531	0.295	-0.361	-0.294	-0.010	-0.251	0.602
Cu	0.105	0.048	0.214	-0.086	0.641	1	0.846	0.354	0.343	0.553	0.606	0.500	0.324	-0.105	-0.192	0.476	-0.079	0.834
Fe	0.346	-0.066	-0.016	0.006	0.480	0.843	1	0.200	0.442	0.683	0.780	0.590	0.241	-0.277	-0.346	0.322	-0.278	0.820
Hg	0.543	0.219	-0.124	0.254	-0.152	0.344	0.567	1	0.251	0.281	0.007	0.286	0.388	-0.076	0.002	0.690	-0.005	0.071
K	-0.086	-0.233	0.116	0.118	0.238	0.575	0.376	0.087	1	0.696	0.446	0.343	0.379	-0.280	-0.137	0.207	-0.324	0.439
Li	-0.364	-0.239	0.182	-0.255	0.517	0.598	0.340	-0.181	0.842	1	0.668	0.411	0.454	-0.239	-0.216	0.365	-0.284	0.606
Mg	-0.237	0.041	0.127	-0.411	0.523	0.560	0.247	-0.241	0.634	0.826	1	0.414	0.134	-0.200	-0.329	0.214	-0.116	0.726
Mn	-0.167	-0.085	-0.261	-0.249	0.269	0.192	0.289	0.034	-0.150	0.088	0.024	1	0.272	-0.344	-0.321	0.298	-0.110	0.606
Na	-0.222	0.169	0.139	-0.443	0.223	0.313	0.264	0.206	0.253	0.402	0.309	0.285	1	-0.151	0.271	0.301	-0.233	0.241
Ni	-0.129	-0.104	-0.206	0.204	-0.375	-0.390	-0.410	-0.041	0.147	0.036	-0.020	-0.163	-0.177	1	0.411	-0.250	0.150	-0.009
Pb	0.043	-0.076	-0.067	0.246	0.008	0.101	-0.111	-0.053	0.106	0.060	0.054	0.066	-0.154	-0.114	1	-0.016	0.051	-0.202
Se	0.777	0.167	-0.127	0.585	-0.396	-0.002	0.321	0.460	-0.125	-0.405	-0.451	-0.099	-0.108	-0.172	-0.132	1	0.103	0.181
Sr	0.346	0.089	-0.081	0.554	-0.120	0.112	0.095	0.227	0.327	0.055	0.058	-0.347	-0.313	0.207	0.170	0.185	1	-0.065
Zn	0.088	-0.012	0.095	-0.198	0.618	0.895	0.789	0.332	0.535	0.631	0.648	0.168	0.352	-0.250	0.016	-0.058	0.065	1

*r-values > 0.350 or < -0.350 are significantly correlated at $p < 0.05$

Table 104. Correlation coefficient (r)* matrix for selected metal levels in acid extract of the soil during pre-monsoon

	As	Ca	Cd	Co	Cr	Cu	Fe	Hg	K	Li	Mg	Mn	Na	Ni	Pb	Se	Sr	Zn
As	1																	
Ca	-0.091	1																
Cd	-0.167	0.229	1															
Co	0.347	0.422	-0.035	1														
Cr	0.128	0.047	0.603	-0.034	1													
Cu	-0.152	0.205	0.119	-0.219	0.272	1												
Fe	-0.237	-0.294	-0.239	-0.491	0.276	0.366	1											
Hg	0.094	-0.023	0.224	-0.346	0.192	0.158	-0.017	1										
K	-0.181	-0.030	-0.045	0.002	0.181	0.292	0.167	-0.111	1									
Li	-0.071	0.022	0.163	0.001	-0.012	0.249	-0.128	0.167	0.137	1								
Mg	-0.318	0.415	0.046	-0.115	0.205	0.738	0.204	0.226	0.652	0.220	1							
Mn	0.318	-0.246	-0.255	0.033	0.092	0.092	0.311	-0.049	-0.425	-0.448	-0.368	1						
Na	-0.340	0.132	-0.052	-0.240	-0.057	0.400	0.199	0.143	-0.097	0.423	0.225	0.020	1					
Ni	-0.402	0.072	0.447	-0.373	0.352	0.250	0.271	-0.125	-0.110	0.061	0.050	0.046	0.325	1				
Pb	0.064	0.109	0.417	-0.256	0.083	0.274	-0.345	0.141	0.005	0.014	0.136	-0.176	-0.001	0.338	1			
Se	0.407	0.076	-0.470	-0.102	-0.113	0.233	0.258	0.213	-0.242	-0.009	0.049	0.403	0.093	-0.251	-0.162	1		
Sr	-0.333	0.692	0.533	0.165	0.413	0.323	-0.133	0.113	0.348	0.325	0.640	-0.593	0.171	0.253	0.127	-0.300	1	
Zn	0.218	-0.170	-0.219	-0.110	0.079	0.379	0.322	0.077	0.290	0.343	0.291	0.203	0.064	-0.058	-0.022	0.420	-0.153	1

*r-values > 0.350 or < -0.350 are significantly correlated at $p < 0.05$

Table 105. Correlation coefficient (r)* matrix for selected metal levels in acid extract of the soil during monsoon

	As	Ca	Cd	Co	Cr	Cu	Fe	Hg	K	Li	Mg	Mn	Na	Ni	Pb	Se	Sr	Zn
As	1																	
Ca	-0.100	1																
Cd	-0.672	0.106	1															
Co	0.253	-0.053	-0.127	1														
Cr	-0.589	0.142	0.690	-0.240	1													
Cu	0.008	0.252	0.015	-0.011	0.208	1												
Fe	0.238	-0.220	-0.250	-0.064	0.100	0.482	1											
Hg	0.403	0.188	0.222	0.169	0.168	0.100	0.049	1										
K	0.121	-0.326	0.022	0.124	0.203	0.294	0.633	0.068	1									
Li	-0.159	-0.243	0.261	0.408	0.164	-0.104	-0.343	-0.053	0.102	1								
Mg	-0.070	0.379	0.117	-0.196	0.363	0.594	0.589	0.092	0.519	-0.263	1							
Mn	0.150	0.028	-0.102	-0.034	0.070	0.456	0.639	0.249	0.245	-0.328	0.337	1						
Na	-0.678	0.304	0.216	-0.102	0.135	0.129	-0.393	-0.466	-0.449	-0.003	-0.087	-0.186	1					
Ni	-0.129	0.173	0.153	-0.169	0.186	0.197	0.022	0.034	-0.340	-0.361	0.168	-0.078	0.097	1				
Pb	-0.343	0.274	0.465	-0.297	0.214	-0.002	-0.394	0.009	-0.451	-0.032	-0.112	-0.134	0.235	0.161	1			
Se	0.702	-0.048	-0.495	0.023	-0.439	-0.127	0.088	0.026	0.132	-0.049	0.077	-0.162	-0.632	-0.159	-0.199	1		
Sr	-0.508	0.662	0.487	-0.094	0.579	0.079	-0.390	-0.001	-0.108	0.249	0.292	-0.358	0.401	0.119	0.236	-0.278	1	
Zn	0.153	0.086	0.078	0.122	0.195	0.351	0.613	0.437	0.337	-0.286	0.434	0.347	-0.210	0.134	-0.012	-0.166	-0.071	1

*r-values > 0.350 or < -0.350 are significantly correlated at $p < 0.05$

Table 106. Correlation coefficient (r)* matrix for selected metal levels in acid extract of the soil during post-monsoon

	As	Ca	Cd	Co	Cr	Cu	Fe	Hg	K	Li	Mg	Mn	Na	Ni	Pb	Se	Sr	Zn
As	1																	
Ca	0.108	1																
Cd	-0.481	-0.092	1															
Co	-0.047	-0.011	-0.193	1														
Cr	-0.662	-0.005	0.627	-0.280	1													
Cu	-0.593	0.002	0.294	0.014	0.485	1												
Fe	-0.614	0.080	0.136	-0.094	0.356	0.409	1											
Hg	0.074	0.022	0.055	0.203	0.058	0.039	-0.195	1										
K	0.090	-0.040	-0.143	0.462	-0.015	-0.002	0.260	0.166	1									
Li	-0.195	0.390	-0.017	0.053	0.440	-0.020	0.034	0.086	0.335	1								
Mg	-0.027	0.523	0.159	0.063	0.280	0.222	0.424	0.041	0.447	0.241	1							
Mn	-0.671	-0.192	0.177	-0.452	0.463	0.286	0.523	-0.399	-0.241	0.181	-0.238	1						
Na	-0.762	0.120	0.467	-0.040	0.526	0.492	0.593	-0.368	0.036	0.187	0.359	0.508	1					
Ni	0.069	-0.121	-0.258	0.225	-0.311	-0.042	0.292	-0.017	0.314	-0.153	0.359	-0.115	0.033	1				
Pb	-0.471	0.268	0.246	0.018	0.517	0.634	0.084	-0.057	-0.307	0.047	0.088	0.198	0.386	-0.442	1			
Se	0.588	-0.244	-0.680	0.343	-0.771	-0.458	-0.366	0.220	0.064	-0.432	-0.356	-0.404	-0.688	0.161	-0.410	1		
Sr	0.037	0.821	0.098	0.191	0.282	0.112	0.001	0.042	0.199	0.551	0.594	-0.308	0.180	-0.288	0.430	-0.375	1	
Zn	-0.309	-0.141	0.128	-0.123	0.558	0.204	0.543	-0.250	0.280	0.123	0.376	0.226	0.418	0.048	0.197	-0.413	0.120	1

*r-values > 0.350 or < -0.350 are significantly correlated at $p < 0.05$

3.32.3 Correlation Study of Selected Metals in Acid Extract of Soil Samples

The correlation coefficient matrix for selected metal levels in acid extract of the soil during summer is shown in Table 103. A number of significant relationships were observed among the metals; As was positively associated with Se (r = 0.777), Hg (r = 0.543) and Co (r = 0.521) while inversely related to Li (r = -0.364). Similarly, Cr was strongly correlated with Cu (r = 0.641), Zn (r = 0.618), Mg (r = 0.523), Li (r = 0.517), Fe (r = 0.480) but inversely associated with Se (r = -0.396) and Ni (r = -0.375). Cobalt exhibited strong positive relationships with Se (r = 0.585), and Sr (r = 0.554) while negatively correlated with Cr (r = -0.444), Na (r = -0.443) and Mg (r = -0.411). Copper also exhibited strong correlation with Zn (r = 0.895), Fe (r = 0.843), Li (r = 0.598), K (r = 0.575) and Mg (r = 0.560) but inversely correlated with Ni (r = -0.390). Likewise, Fe also showed significant correlations with Zn (r = 0.789), Hg (r = 0.567) and K (r = 0.376) while inversely correlated with Ni (r = -0.410). Among rest of the metals, Hg exhibited positive relationship with Se (r = 0.460); K revealed positive relationship with Li (r = 0.842), Mg (r = 0.634) and Zn (r = 0.535); Li was significantly associated with Mg (r = 0.826), Zn (r = 0.631) and Na (r = 0.402); Mg was strongly associated with Zn (r = 0.648) but inversely correlated with Se (r = -0.451). These mutual associations displayed common variations and shared origin of the metals in soil samples.

The correlation coefficient matrix for selected metal levels in acid extract of the soil during winter is also shown in Table 103. Numerous significant correlations were observed among the metals; As was found to be positively associated with Se (r = 0.750), Cu (r = 0.607), Li (r = 0.586), Fe (r = 0.563), Hg (r = 0.474), Zn (r = 0.456), Mn (r = 0.424) and Mg (r = 0.399); Co was significantly correlated with Ni (r = 0.385); Cr showed positive relationships with Fe (r = 0.642), Mg (r = 0.617), Zn (r = 0.602), Mn (r = 0.531), Li (r = 0.504) and Cu (r = 0.466); Cu was strongly associated with Fe (r = 0.846), Zn (r = 0.834), Mg (r = 0.606), Li (r = 0.553), Mn (r = 0.500), Se (r = 0.476) and Hg (r = 0.354); Fe exhibited positive associations with Zn (r = 0.820), Mg (r = 0.780), Li (r = 0.683), Mn (r = 0.590) and K (r = 0.442). Among rest of the metals, Hg showed positive relationships with Se (r = 0.690) and Na (r = 0.388); K exhibited significant relationships with Li (r = 0.696), Mg (r = 0.446), Zn (r = 0.439) and Na (r = 0.379); Li exhibited significant associations with Mg (r = 0.668), Zn (r = 0.606), Na (r = 0.454), Mn (r = 0.411) and Se (r = 0.365); Mg showed positive correlations with Zn (r = 0.726) and Mn (r = 0.414); Mn exhibited positive relationship with Zn (r = 0.606); and Ni was significantly associated with Pb (r = 0.411). The correlation study thus revealed complicated relationships for the metal levels in acid-extract of the soil, where number of metals exhibited similar or opposite associations which may be associated with their origin/source in the soil.

The metal-to-metal correlation data pertaining to acid extract of the soil during pre-monsoon is shown in Table 104. Strong positive relationships were observed between Mg-Cu ($r = 0.738$), Ca-Sr ($r = 0.692$), Mg-K ($r = 0.652$), Mg-Sr ($r = 0.640$), Cd-Cr ($r = 0.603$) and Sr-Cd ($r = 0.533$). In addition, numbers of significant correlations were observed between As-Se, Ca-Co, Ca-Mg, Cd-Ni, Cd-Pb, Cr-Sr, Cu-Fe, Cu-Na, Li-Na, Se-Mn, Se-Zn, Cr-Ni and Zn-Cu in the soil samples. However, some significantly inverse relationships were found between As-Ni, Cd-Se, Co-Fe, Co-Ni, K-Mn, Li-Mn, Mg-Mn and Sr-Mn, thus indicating their opposing variations in the metal levels during pre-monsoon season.

The correlation coefficient matrix pertaining to selected metal levels in acid extract of the soil during monsoon is shown in Table 105. Significantly positive relationships were observed among the metals; As was strongly associated with Se ($r = 0.702$), and Hg ($r = 0.403$) but inversely correlated with Na ($r = -0.678$), Cd ($r = -0.672$), Cr ($r = -0.589$) and Sr ($r = -0.508$). Similarly, Ca was positively correlated with Sr ($r = 0.662$) and Mg (r =0.379); Co exhibited significant associations with Li ($r = 0.408$); Cr revealed positive associations with Sr ($r = 0.579$) and Mg ($r = 0.363$); Cu showed significantly positive correlations with Mg ($r = 0.594$), Fe ($r = 0.482$) and Mn ($r = 0.456$). In addition, strong positive correlations were observed for Fe with Mn ($r = 0.639$), K ($r = 0.633$), Zn ($r = 0.613$) and Mg ($r = 0.589$) whereas it was inversely correlated with Sr ($r = -0.390$), Pb ($r = -0.394$) and Na ($r = -0.393$). Likewise, significantly positive relationships were noted between K-Mg ($r = 0.519$), Hg-Zn ($r = 0.437$), Mg-Zn ($r = 0.434$) and Na-Sr ($r = 0.401$) while negative associations were found between Na-Se ($r = -0.632$), Hg-Na ($r = -0.466$), K-Pb ($r = -0.451$), K-Na ($r = -0.449$), Li-Ni ($r = -0.361$) and Mn-Sr ($r = -0.358$) in the soil samples during monsoon season.

The correlation coefficient matrix for selected metal contents in acid extract of the soil during post-monsoon is shown in Table 106. Significant relationships were observed among the metals; As exhibited significant negative associations with Na ($r = -0.762$), Cr ($r = -0.662$), Mn ($r = -0.671$), Fe ($r = -0.614$), Cu ($r = -0.593$), Cd ($r = -0.481$), Pb ($r = -0.471$) and positive associations with Se ($r = 0.588$). Similarly, Ca showed positive relationships with Sr ($r = 0.821$), Mg ($r = 0.523$) and Li ($r = 0.390$); Cd displayed strong correlations with Cr ($r = 0.627$) and Na ($r = 0.467$); Co revealed significant correlations with K (*r* = 0.462) and Mn (*r* = -0.452). Likewise, Cr exhibited strong association with Zn (*r* = 0.558), Na (*r* = 0.526), Pb (*r* = 0.517), Cu (*r* = 0.485), Mn (*r* = 0.463) and Li (*r* = 0.440) while it was negatively correlated with Se (*r* = -0.771). Cu contents in the soil showed significantly positive relationships with Pb (*r* = 0.634), Na (*r* = 0.492) and Fe (*r* = 0.409) but negatively associated with Se (*r* = -0.458). In the same way, Fe was significantly associated with Na (*r* = 0.593), Zn (*r* = 0.543), Mn (*r* = 0.523) and Mg (*r* = 0.424) but negative associated with Se (*r* = -0.366). Mercury showed inverse correlation with Mn (*r* = -0.399) and Na (*r* = -0.368). In addition, Mg was significantly associated with Sr (*r* = 0.594), Zn (*r* = 0.376), Na (*r* = 0.359) and Ni (*r* = 0.359). Moreover, significant positive relationships were also observed between Li-Sr (*r* = 0.551), Mn-Na (*r* = 0.508), K-Mg (*r* = 0.447), Pb-Sr (*r* = 0.430), Na-Zn (*r* = 0.418) and Na-Pb (*r* = 0.386), whereas significant negative associations were found between Na-Se (*r* = -0.688), Ni-Pb (*r* = -0.442), Li-Se (*r* = -0.432), Pb-Se (*r* = -0.410), Se-Zn (*r* = -0.413), Mn-Se (*r* = -0.404) and Se-Sr (*r* = -0.375). The correlation study thus showed some communal variations in metal contents of the soil, the sources of which would be explored in next section by multivariate methods.

3.33 Multivariate Analysis of Selected Metals in Soil Samples

Source identification and apportionment of selected metals in the soil was carried out by principle component analysis (PCA) and cluster analysis (CA) which were commonly employed in order to understand the complex nature of the relationships among the metal contents in soil. The PC loadings extracted by varimax normalized rotation of the data-set for selected metals in acid-extract of the soil during summer are shown in Table 107, whereas the corresponding CA of selected metals using Ward's method is shown in the form of dendrogram in Figure 70. Six PCs with eigenvalue > 1 were extracted for selected metals during summer, yielding more than 81% of cumulative variance of the data. PC 1 showed highest loadings for Ca, Cu, Fe, K, Li, Mg and Zn; PC 2 displayed highest loadings for As, Hg and Se; PC 3 indicated highest loadings for Cr along with significant contributions of Ni; PC 4 revealed higher contributions of Co and Pb; PC 5 exhibited highest loadings for Cd and last PC showed the contribution of Mn, Na and Sr. In case of CA, first cluster was composed of Ca-Cu-Zn-Fe-K-Li-Mg; second cluster was consisted of Sr-Mn-Na which revealed that these metals were mostly contributed by the lithogenic sources. Similarly, third cluster showed also shared contributions of Co-Cr-Pb-

Ni and fourth cluster exhibited the associations of As-Se-Hg-Cd. These two clusters of the metals were believed to be associated with the anthropogenic activities, particularly industrial, municipal sewage, atmospheric deposition, fuel combustion, recreational and agricultural activities around the water reservoir.

Table 107. Principal component analysis of selected metal levels in the soil during summer

	PC 1	PC 2	PC 3	PC 4	PC 5	PC 6
Eigenvalue	5.124	3.439	2.271	1.365	1.312	1.083
Total Variance (%)	28.47	19.11	12.62	7.582	7.287	6.016
Cumulative Eigenvalue	5.124	8.564	10.83	12.20	13.51	14.59
Cumulative Variance (%)	28.47	47.58	60.19	67.78	75.06	81.08
As	-0.081	0.848	0.050	-0.184	-0.045	0.082
Ca	0.936	0.136	0.037	0.029	-0.052	-0.092
Cd	0.127	-0.160	0.388	0.179	0.725	-0.098
Co	-0.147	0.221	-0.294	0.783	-0.214	-0.213
Cr	0.273	-0.288	0.663	0.042	0.063	-0.182
Cu	0.839	0.229	0.119	-0.019	0.043	0.044
Fe	0.734	0.149	0.291	0.161	0.230	-0.217
Hg	0.175	0.770	-0.010	0.164	0.179	0.207
K	0.849	0.020	-0.306	-0.082	-0.173	-0.157
Li	0.885	-0.330	-0.093	0.042	-0.038	-0.130
Mg	0.808	-0.388	-0.006	-0.033	-0.061	0.183
Mn	-0.111	-0.099	0.267	0.113	0.071	0.811
Na	0.326	-0.111	0.109	0.294	0.199	0.700
Ni	-0.046	-0.113	0.874	0.038	0.006	-0.108
Pb	0.067	-0.115	0.139	0.831	0.169	0.053
Se	-0.221	0.866	0.043	0.041	-0.056	0.003
Sr	0.240	0.183	-0.266	0.078	-0.285	0.598
Zn	0.859	0.174	0.289	0.078	0.118	0.042

The PC loadings for selected metals in the soil during winter are shown in Table 108, while the corresponding CA is shown in Figure 71. Five PCs with eigenvalue greater than one were extracted, yielding more than 74% of cumulative variance of the data. PC 1 showed highest loadings for Ca, Cu, Fe, Mg, Mn and Zn; PC 2 for K, Li, Na and Sr; PC 3 for Co, Cr and Ni; PC 4 for Cd and Pb while the last PC exhibited the contribution of As, Hg and Se. Similarly, CA showed shared clusters of As-Se-Hg; Cd-Pb; Co-Ni-Cr. These metals were believed to be associated with the anthropogenic activities, while the clusters consisting of Sr-K-Li-Na; Ca-Mn; and Cu-Fe-Zn-Mg were mostly associated with natural contributions. Overall, PCA results were in good agreement with the CA findings.

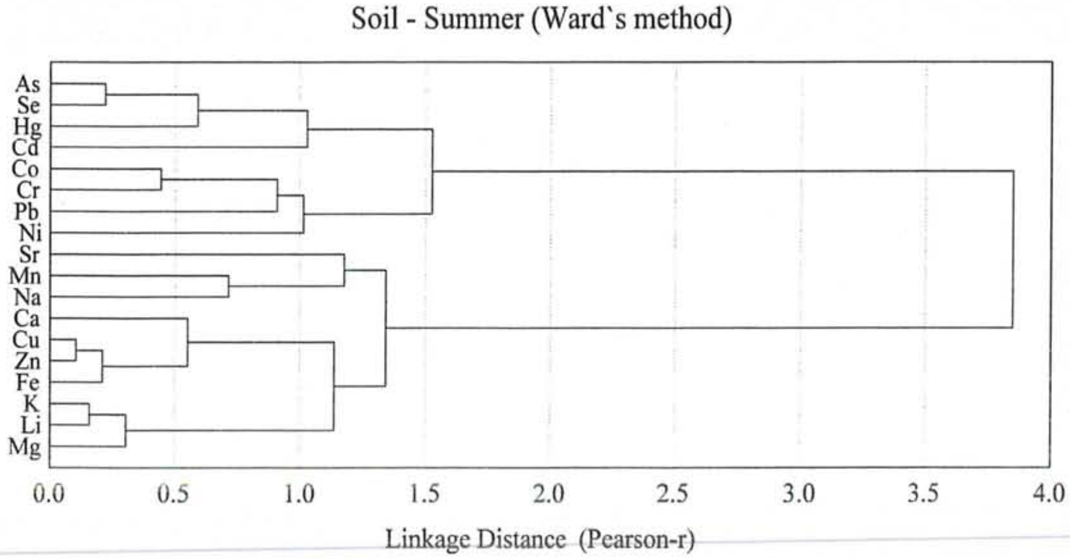

Figure 70. Cluster analysis of selected metal levels in the soil during summer

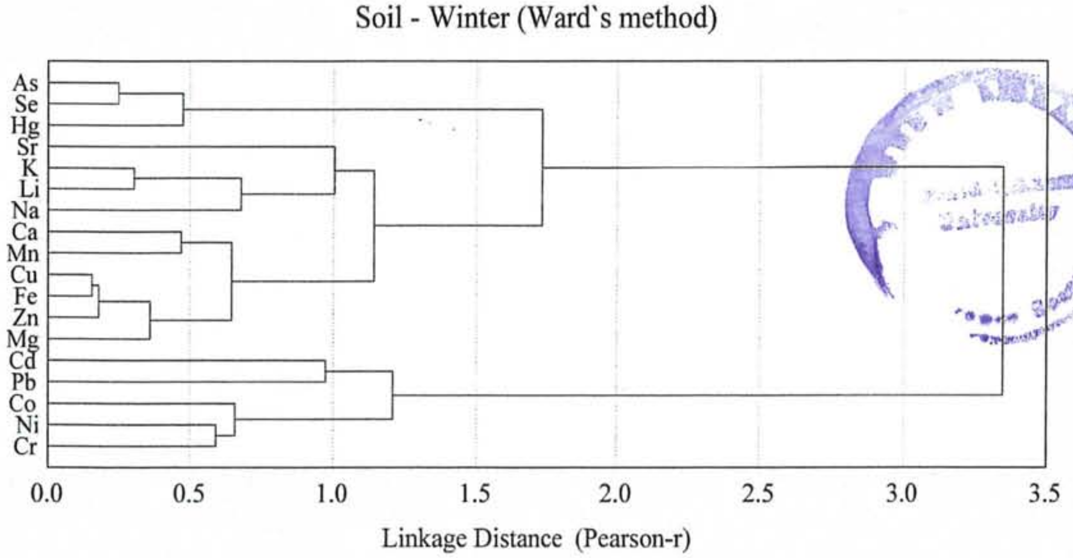

Figure 71. Cluster analysis of selected metal levels in the soil during winter

Table 108. Principal component analysis of selected metal levels in the soil during winter

	PC 1	PC 2	PC 3	PC 4	PC 5
Eigenvalue	6.247	2.500	1.775	1.513	1.248
Total Variance (%)	34.71	13.89	9.858	8.404	6.931
Cumulative Eigenvalue	6.247	8.747	10.52	12.03	13.28
Cumulative Variance (%)	34.71	48.59	58.45	66.86	73.79
As	0.157	0.129	-0.176	-0.012	0.727
Ca	0.942	-0.006	0.009	-0.011	-0.049
Cd	0.029	-0.191	0.211	0.621	-0.120
Co	0.274	-0.163	0.703	0.117	0.149
Cr	-0.156	-0.195	0.713	0.247	0.323
Cu	0.804	0.220	0.068	0.092	-0.122
Fe	0.883	0.195	-0.165	0.187	-0.041
Hg	0.019	-0.149	-0.019	0.176	0.809
K	0.372	0.633	-0.104	0.041	0.210
Li	0.170	0.745	-0.270	0.133	0.201
Mg	0.830	0.021	-0.113	0.044	0.260
Mn	0.626	0.224	-0.225	0.167	-0.137
Na	0.132	0.652	0.240	0.579	0.174
Ni	-0.106	-0.161	0.767	-0.235	-0.182
Pb	-0.077	0.175	0.104	0.757	0.090
Se	0.173	0.059	-0.141	-0.056	0.885
Sr	-0.073	0.799	0.084	0.098	0.177
Zn	0.935	0.106	0.160	0.048	-0.058

The PC loadings for selected metals in the soil during pre-monsoon are shown in Table 109, where eight significant PCs were extracted, cumulatively explaining more than 89% of the variance of data. The corresponding CA in the form of dendrogram is shown in Figure 72. PC 1 with maximum cumulative variance of the data (22%) showed elevated loadings of Ca and Sr which is in very good agreement with the CA, which also showed shared cluster of Ca-Sr. PC 2 showed higher loadings of Cu, K and Mg, while PC 3 revealed higher loading of Fe. PC 4 showed higher loadings of As and Co; PC 5 revealed higher loading of Cr and Ni; PC 6 showed higher loadings of Cd, Mn, Se and Zn. PC 7 revealed higher loading of Li and Na; while PC 8 showed the contributions of Hg and Pb at 5.896% of the variance. The metals in PC 1, PC 2, PC 3 and PC 7 were believed to be associated with the lithogenic sources while the metals in PC 4, PC 5, PC 6 and PC 8 were mainly derived from anthropogenic activities. CA showed shared clusters of As-Co; Cd-Mn-Se-Zn; Hg-Pb; Ni-Cr and Ca-Sr; Cu-Mg-K; Fe-Li-Na. Overall, the PCA and CA results were in good agreement with each other.

Table 109. Principal component analysis of selected metal levels in the soil during pre-monsoon

	PC 1	PC 2	PC 3	PC 4	PC 5	PC 6	PC 7	PC 8
Eigenvalue	3.976	2.905	2.194	1.806	1.565	1.452	1.102	1.061
Total Variance (%)	22.09	16.14	12.19	10.03	8.692	8.069	6.120	5.896
Cumulative Eigenvalue	3.976	6.881	9.075	10.88	12.45	13.90	15.00	16.06
Cumulative Variance (%)	22.09	38.23	50.42	60.45	69.14	77.21	83.33	89.23
As	-0.083	-0.202	0.089	0.748	0.131	0.269	0.112	0.043
Ca	0.952	0.068	0.035	0.008	-0.019	0.000	0.079	-0.025
Cd	0.185	-0.098	0.133	0.155	0.103	0.757	0.236	-0.174
Co	0.213	-0.117	0.013	0.685	0.088	-0.104	-0.223	0.156
Cr	0.030	0.167	-0.059	-0.011	0.938	0.108	-0.062	0.096
Cu	0.236	0.724	0.176	0.194	0.153	0.179	0.252	0.079
Fe	-0.248	0.299	0.618	0.185	-0.188	0.201	0.337	0.015
Hg	0.002	-0.007	0.143	-0.025	0.113	0.081	0.064	0.933
K	-0.085	0.908	0.048	-0.085	0.049	-0.196	-0.058	-0.135
Li	0.034	0.129	0.033	0.053	0.007	-0.078	0.957	0.090
Mg	0.200	0.835	0.038	0.231	0.081	0.084	0.069	0.203
Mn	-0.195	-0.388	0.104	0.042	-0.325	0.718	-0.105	-0.163
Na	0.209	-0.100	-0.107	-0.043	0.292	0.181	0.807	0.086
Ni	-0.010	-0.120	0.206	0.034	0.781	-0.037	0.312	-0.236
Pb	0.028	0.056	0.112	0.041	-0.016	-0.056	0.081	0.967
Se	0.077	-0.042	-0.267	-0.080	0.011	0.800	-0.110	0.288
Sr	0.777	0.288	0.293	0.140	0.197	-0.348	0.007	0.098
Zn	-0.288	0.189	0.028	-0.101	0.208	0.691	0.028	-0.061

The PC loadings for selected metals in the soil during monsoon are shown in Table 110, while the counterpart CA is shown in Figure 73, in the form of dendrogram. Six PCs with eigenvalue greater than one were extracted for selected metals, yielding more than

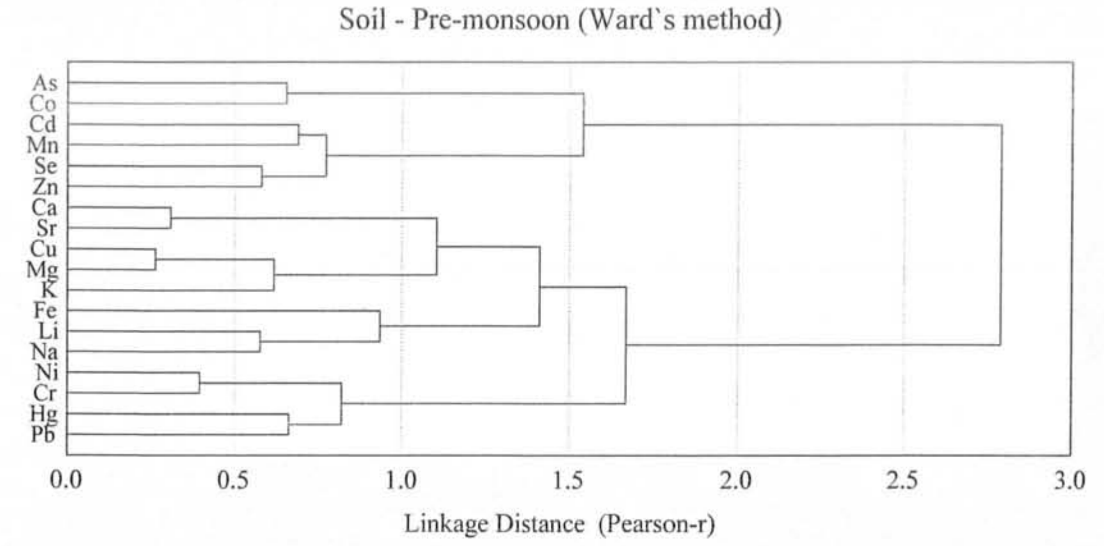

Figure 72. Cluster analysis of selected metal levels in the soil during pre-monsoon

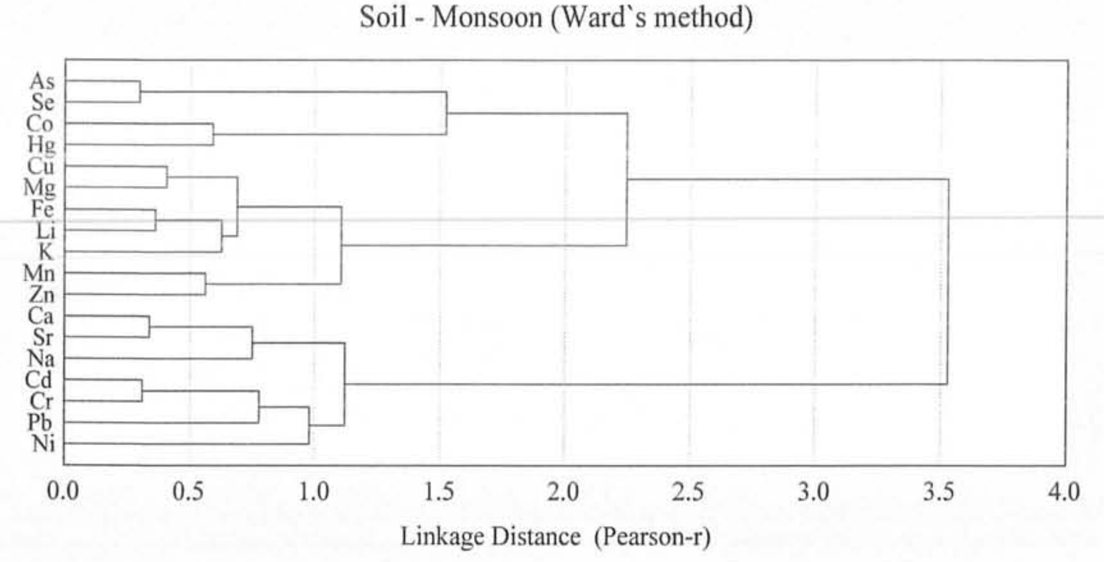

Figure 73. Cluster analysis of selected metal levels in the soil during monsoon

The PC loadings for selected metals in the soil during post-monsoon are shown in Table 111, while the CA is shown in Figure 74. Total six significant PCs with eigenvalue greater than one were extracted, yielding more than 82% of cumulative variance of the data. PC 1 showed highest loadings for Cu, Mn, Na and Zn; PC 2 exhibited highest loadings for Ca, Li, Mg and Sr; PC 3 indicated elevated loadings for As, Cd, K and Pb; PC 4 indicated the highest loadings for Co and Ni; PC 5 exhibited highest loadings for Cr and Fe while PC 6 revealed higher contributions of Hg and Se. Similarly, first cluster showed shared contributions of Hg-Se, while second cluster showed mutual associations of Co-Ni-Fe-Cr; these metals were mainly associated with fuel combustion, industrial emissions and atmospheric deposition. Metals constituting third cluster (Ca-Sr-Mg-Li) and fifth cluster (Cu-Mn-Na-Zn) were mostly derived from natural sources while fourth cluster (Cd-K-As-Pb) might be contributed by anthropogenic activities, particularly agricultural activities and atmospheric deposition. Overall, PCA results are a good agreement with the CA findings for selected metals in the soil samples.

Table 111. Principal component analysis of selected metal levels in the soil during post-monsoon

	PC 1	PC 2	PC 3	PC 4	PC 5	PC 6
Eigenvalue	5.523	2.967	2.339	1.532	1.297	1.126
Total Variance (%)	30.69	16.48	12.99	8.512	7.203	6.257
Cumulative Eigenvalue	5.523	8.490	10.83	12.36	13.66	14.78
Cumulative Variance (%)	30.69	47.17	60.16	68.67	75.87	82.13
As	0.212	-0.094	0.839	0.168	-0.233	-0.252
Ca	-0.003	0.923	-0.061	-0.105	0.087	-0.058
Cd	0.122	-0.041	0.800	0.169	-0.089	-0.049
Co	0.259	0.055	0.207	0.650	0.137	-0.316
Cr	0.188	0.043	0.015	-0.006	0.721	0.298
Cu	0.826	0.062	0.079	0.077	-0.135	0.158
Fe	0.072	-0.024	0.267	-0.168	0.636	0.133
Hg	-0.056	-0.059	-0.078	0.086	0.070	0.806
K	-0.075	0.041	0.776	0.270	0.142	-0.172
Li	0.007	0.892	0.011	-0.002	0.229	0.109
Mg	0.075	0.861	0.248	0.111	-0.024	0.250
Mn	0.776	-0.174	-0.054	0.215	0.289	0.210
Na	0.666	0.123	0.211	-0.252	0.108	0.296
Ni	-0.122	-0.122	-0.010	0.753	-0.250	-0.250
Pb	-0.008	0.199	0.751	-0.269	-0.055	0.118
Se	-0.197	-0.268	-0.087	0.230	-0.237	0.708
Sr	0.124	0.911	-0.030	0.155	0.204	0.082
Zn	0.602	-0.002	0.195	-0.209	0.211	0.164

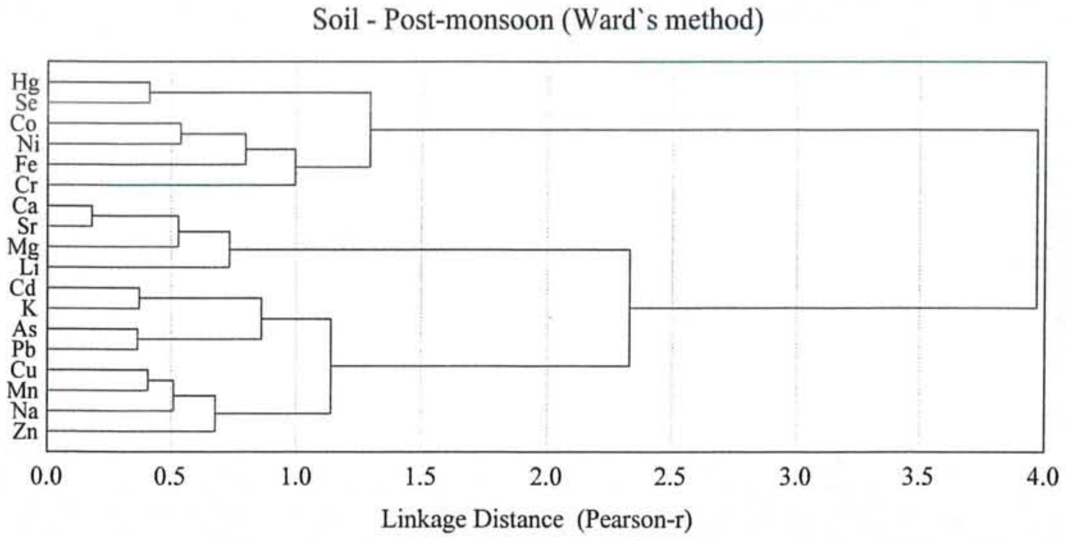

Figure 74. Cluster analysis of selected metal levels in the soil during post-monsoon

3.34 Pollution Assessment of Selected Metals in Soil Samples

Assessment of metal pollution in the soil was carried out using enrichment factor (*EF*), geo-accumulation index (I_{geo}), contamination factor (*Cf*), degree of contamination (C_{deg}) and pollution load index (*PLI*) as reported earlier.

3.34.1 Enrichment Factor (*EF*) of Selected Metals in Soil Samples

Comparison of metal levels in the examined soil with the background reference levels is generally used to measure the metal's enrichment in soil samples and it helps in the assessment of anthropogenic impact relative to the background or pre-industrial levels. The fundamental concept is to produce numerical results comparing the measured metal levels with the background levels, such as, the average continental crust abundances. Enrichment factor (*EF*) estimates the anthropogenic impact on soil, using a normalization element in order to alleviate the variations produced by heterogeneity of the soil. Mean *EF* values of selected metals in soil during summer and winter are shown in Figure 75, which revealed following decreasing order: Se > Cd > As > Hg > Co > Pb > Ca > Zn > Li > Mn > Ni > Cu > Cr > Mg > Sr > K > Na during summer and Se > Cd > Hg > As > Pb > Co > Ca > Li > Mn > Zn > Ni > Cr > Cu > Sr > Mg > K > Na during winter. Among these metals, Se, As, Cd and Hg showed extremely severe enrichment, while K, Mg, Na and Sr showed minor enrichment during summer and winter. However, Pb showed very severe enrichment during winter and severe enrichment during summer, while Co and Ca exhibited severe enrichment during both seasons. Moreover, Cr, Cu, Li, Mn, Ni and Zn showed minor to moderately severe enrichment during summer and winter. Overall, most of the metals showed relatively higher enrichment during winter thus manifesting more anthropogenic impact during winter than summer.

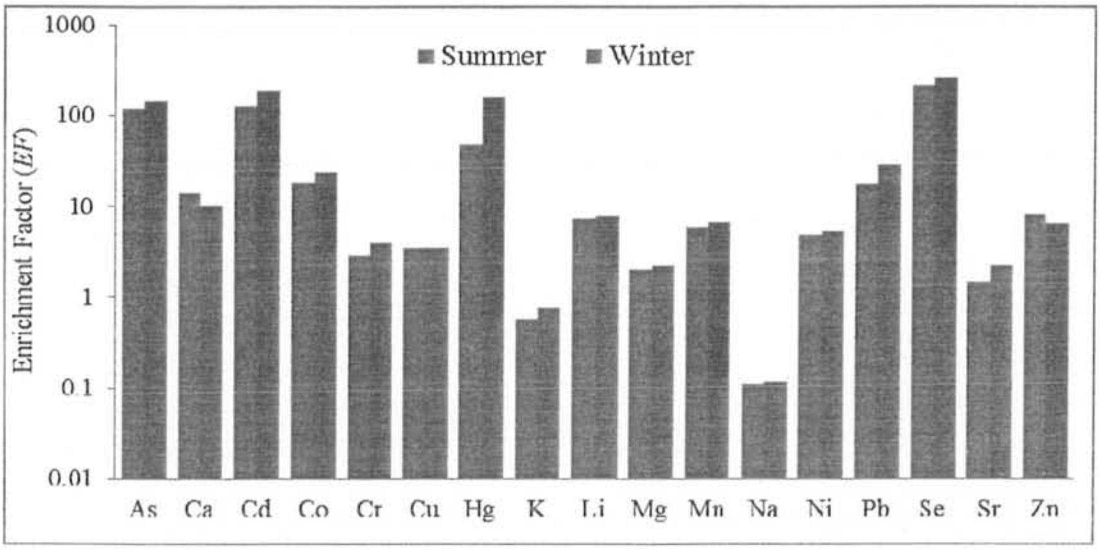

Figure 75. Average enrichment factors (*EF*) of selected metals in the soil during summer and winter

Similarly, *EF* was also assessed in the soil samples during pre-monsoon, monsoon and post-monsoon seasons. Average *EF* of selected metals in acid extract of the soil during pre-monsoon, monsoon and post-monsoon are shown in Figure 76. Mean *EF* of the metals during three seasons showed following decreasing trend: Cd > Se > As > Hg > Pb > Co > Zn > Ca > Li > Cr > Mn > Cu > Ni > Sr > Mg > K > Na. Among the metals, Se, Cd, As, Hg, Pb and Co was highly enriched in the soil, while K, Mg and Na displayed no enrichment in the soil. However, Se, Cd, and As exhibited extremely severe enrichment while Hg exhibited extremely severe enrichment during pre-monsoon and monsoon but very severe enrichment during post-monsoon. Pb showed very severe enrichment while Co exhibited severe enrichment during three seasons while rest of metals revealed minor to moderately severe enrichment in the soil samples. On average basis, *EF* showed that most of the metals exhibited highest contamination during pre-monsoon which may be ascribed to higher anthropogenic activities in the study area during pre-monsoon. As, Cd, Cr, Cu, Hg K, Li, Mn and Pb showed highest *EF* values during pre-monsoon season, while Ca and Zn exhibited higher enrichment during post-monsoon. Overall, the soil samples were highly enriched by Cd, Se, As, Hg, Pb and Co which might be associated with municipal/domestic wastes, fuel combustion, agriculture practices, atmospheric deposition and automobile exhausts which are responsible for elevated metal levels in the soil.

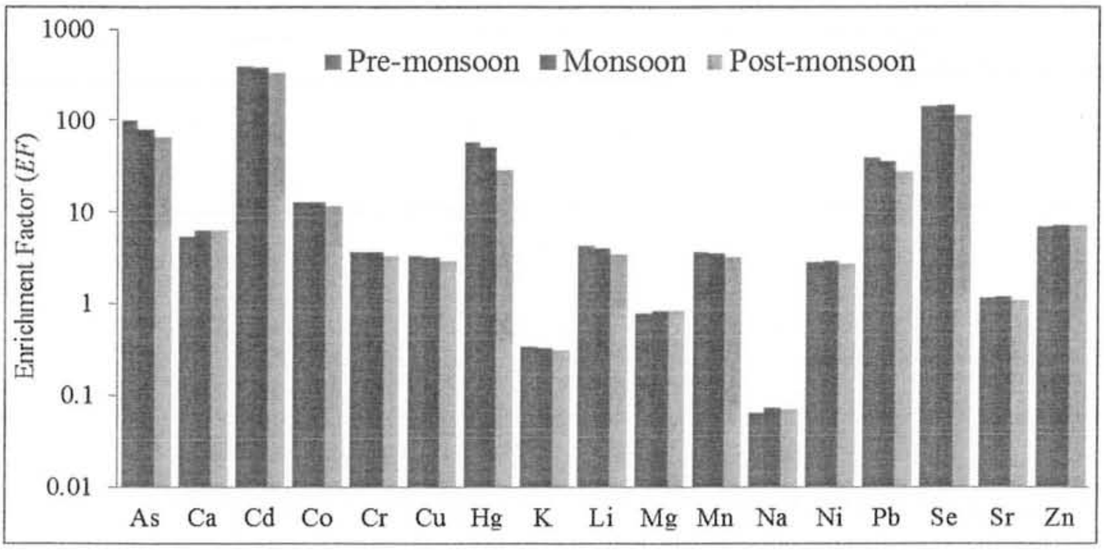

Figure 76. Average enrichment factors (*EF*) of selected metals in the soil during pre-monsoon, monsoon and post-monsoon

3.34.2 Geo-accumulation Index (I_{geo}) of Selected Metals in Soil Samples

Geo-accumulation index (I_{geo}) is not readily comparable to the other indices of metal pollution due to the nature of its calculation, which involves a log function and a background multiplication of 1.5. Average I_{geo} values of the metals in the soil during summer and winter seasons are shown in Figure 77, which revealed that most of the metals show no sign of contamination during both seasons. However, As, Cd, Hg, Pb and Se showed significant accumulation in the soil samples; Se exhibited 'heavy contamination'; As and Cd exhibited 'moderate to heavy contamination'; Hg revealed 'moderate contamination' during summer and 'moderate to heavy contamination' during winter, while Pb and Co revealed 'no contamination to moderate contamination' during winter season.

Figure 78 demonstrated I_{geo} of selected metals in acid extract of the soil during pre-monsoon, monsoon and post-monsoon seasons. Among the metals, Cd exhibited 'extreme contamination' during pre-monsoon, monsoon and post-monsoon; Se in all seasons and As during pre-monsoon showed 'heavy contamination'. Similarly, 'moderate to heavy contamination' was shown by As (monsoon & post-monsoon), Hg (pre-monsoon

& monsoon) and Pb (pre-monsoon); while Pb revealed 'moderate contamination' during monsoon and post-monsoon seasons. Likewise, Hg showed 'moderate contamination' during post-monsoon, while Co exhibited 'un-contamination to moderate contamination' during three seasons. Comparatively higher I_{geo} was shown by Cd, Se, As, Hg, Pb and Co during pre-monsoon than monsoon and post-monsoon seasons. This indicated that the soil was highly polluted by the metals during pre-monsoon.

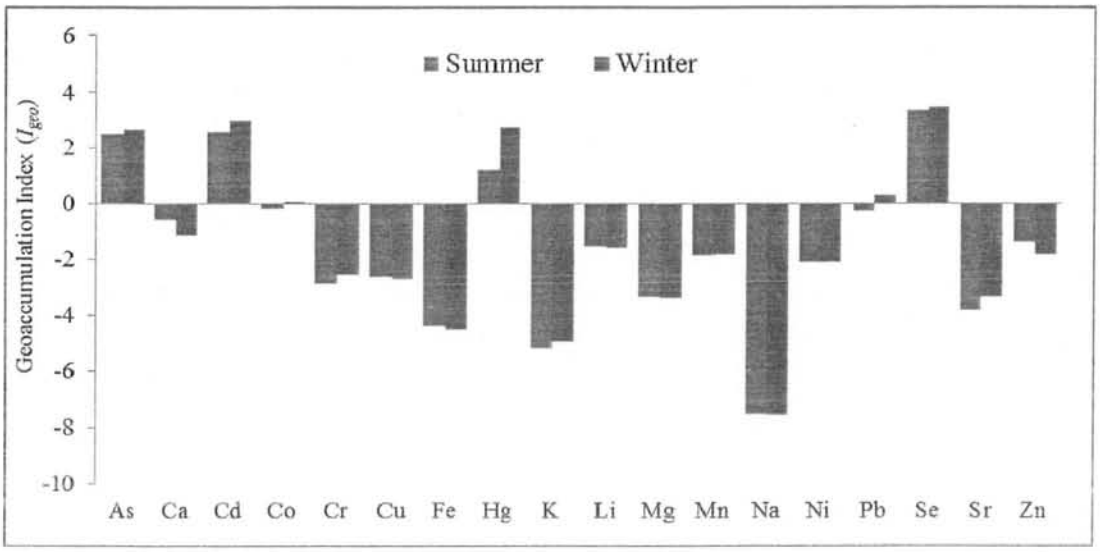

Figure 77. Average geo-accumulation indices (I_{geo}) for selected metals in the soil during summer and winter

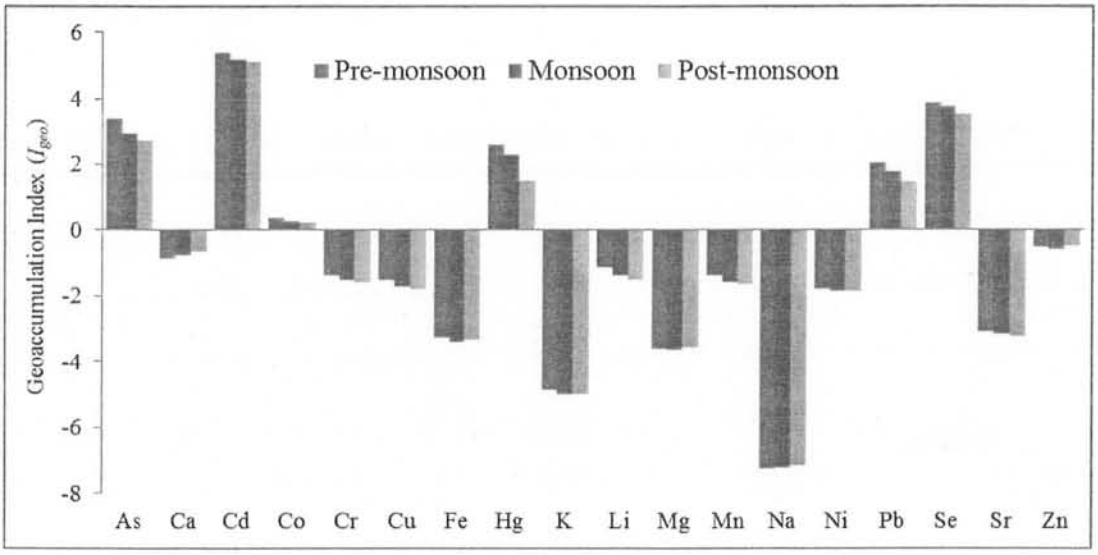

Figure 78. Average geo-accumulation indices (I_{geo}) for selected metals in the soil during pre-monsoon, monsoon and post-monsoon

3.34.3 Contamination Factor (*C_f*), Degree of Contamination (*C_{deg}*) and Pollution Load Index (*PLI*) of Selected Metals in Soil Samples

The soil contamination was also evaluated by C_f, C_{deg} and *PLI*: in former case, average metal concentrations measured in the soil are compared with the reference values in background soil, while C_{deg} referred to the sum of individual C_f. It was used as an investigative tool for determining the degree of pollution in the soil. A fundamental feature of the C_{deg} is that it facilitates the assessment of total degree of contamination based on the available contaminant measurements. In addition, *PLI* is widely used to assess the metal contamination and pollution in the soil. Average values of C_f for selected metals in acid extract of the soil during summer and winter are shown in Figure 79. Mean C_f values for Ca, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, Sr and Zn were < 1, demonstrating their 'low contamination' in the soil during summer and winter. However, Co and Pb showed 'moderate contamination' during both seasons and on the average basis, As, Cd, Se and Hg revealed 'very high contamination' during summer and winter except Hg which showed 'considerable contamination' during summer.

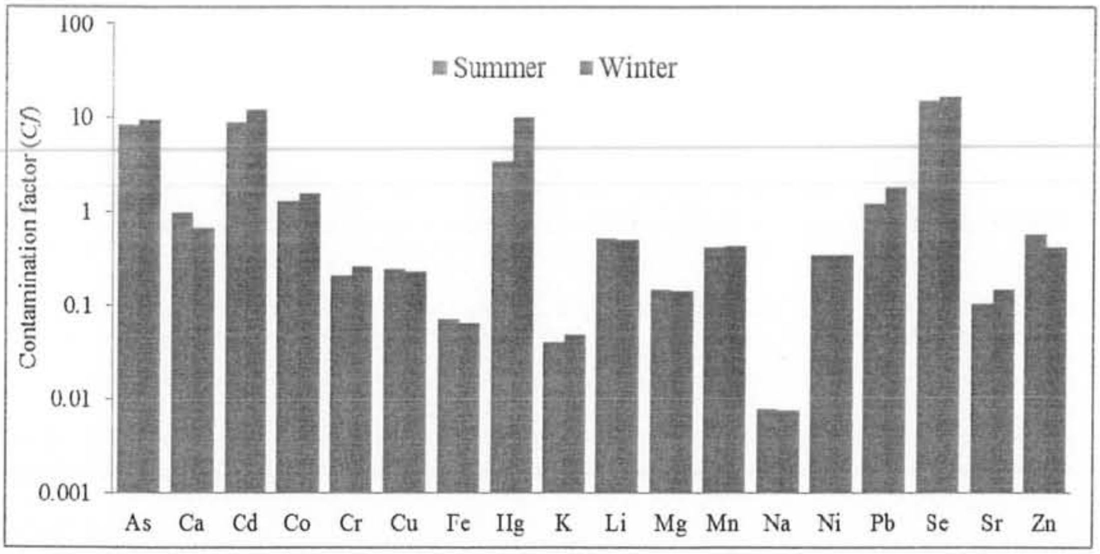

Figure 79. Average contamination factors (C_f) of selected metals in the soil during summer and winter

Additionally, C_{deg} was also calculated to evaluate the overall contamination status (Figure 80); mean values of C_{deg} during summer and winter were 42.23 and 54.65, respectively, showing 'very high degree of contamination' in the soil during both seasons. According to *PLI* values, the soil samples were found to be 'un-polluted' by the metals during both seasons as *PLI* was less than 1. The calculated *PLI* values were 0.51 and 0.56

during summer and winter, respectively. Potential ecological risk factor (E_i) of selected metals in acid-extract of the soil during summer and winter are shown in Figure 80. The results revealed that Cr, Cu, Pb and Zn caused 'low risk'; As showed 'considerable risk' during both seasons. Similarly, Hg showed 'considerable risk' during summer and 'very great risk' during winter while Cd exhibited 'great risk' during summer and 'very great risk' during winter season. Overall, the cumulative potential risk index (*RI*) showed 'very high risk' for the soil during both seasons. However, relatively higher pollution and risk was observed during winter than summer. The classification related to E_i and *RI* was suggested by Hakanson (1980).

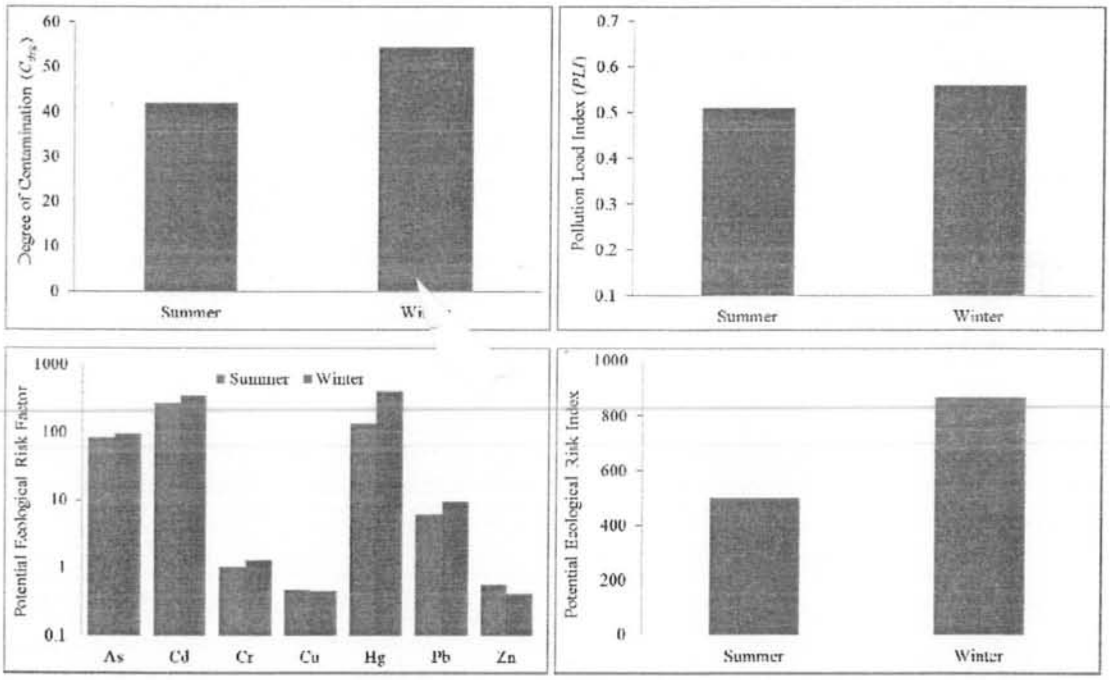

Figure 80. Average degree of contamination (C_{deg}), pollution load index (*PLI*), potential ecological risk factor (E_i) and potential ecological risk index (*RI*) for selected metals in the soil during summer and winter

Average C_f values of selected metals in acid extract of the soil during pre-monsoon, monsoon and post-monsoon are shown in Figure 81. Mean contamination factors for Ca, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni and Sr were < 1, manifesting 'low contamination' of these metals during pre-monsoon, monsoon and post-monsoon. On average basis, Co and Zn showed 'moderate contamination' while As, Cd and Hg revealed 'very high contamination' during pre-monsoon, monsoon and post-monsoon seasons.

Mercury showed 'very high contamination' during pre-monsoon and monsoon while 'considerable contamination' during post-monsoon. Moreover, Pb exhibited 'considerable contamination' during monsoon and post-monsoon whereas 'very high contamination' was noted during pre-monsoon. Comparatively higher contamination was observed during pre-monsoon than other seasons.

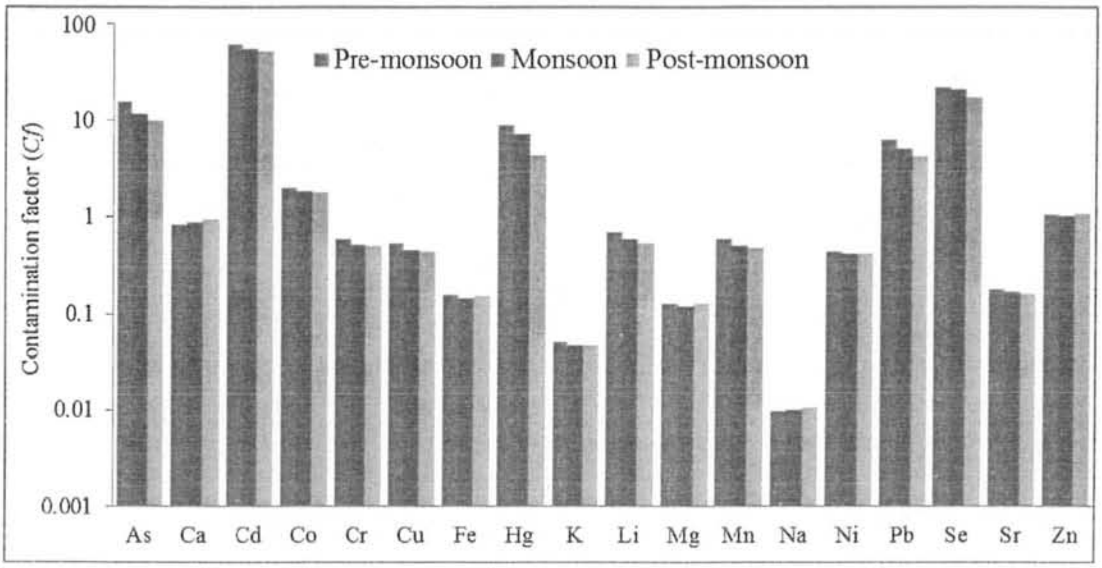

Figure 81. Average contamination factors (C_f) of selected metals in the soil during pre-monsoon, monsoon and post-monsoon

As a whole, C_{deg} (Figure 82) revealed very high degree of contamination in the soil samples during pre-monsoon (C_{deg} = 121.8), monsoon (C_{deg} = 105.5) and post-monsoon (C_{deg} = 94.30). According to the *PLI* values, the soil samples were 'non-polluted' with respect to the metals in all seasons as *PLI* was observes less than 1 (Figure 82). Outcomes of the C_{deg} assessment and PLI are different because degree of contamination (C_{deg}), a cumulative index, is computed as numeric sum of individual 'C_f' of each sample while PLI is a comparative index to determine the degree of metals pollution, computed as the nth root of n C_{fn} multiplied together. Potential ecological risk factor (E_i) values for selected metals during pre-monsoon, monsoon and post-monsoon are shown in Figure 82. The results demonstrated that Cr, Cu, Pb and Zn caused 'low risk'; As showed 'considerable risk' and Cd exhibited 'very great risk' during pre-monsoon, monsoon and post-monsoon seasons. Mercury revealed 'great risk' during monsoon and post-monsoon while 'very great risk' during pre-monsoon. Generally, the metals showed highest E_i during pre-monsoon. Overall, the cumulative potential ecological risk index (*RI*) showed 'very high risk' for the soil during three seasons, revealing relatively higher pollution during pre-monsoon season.

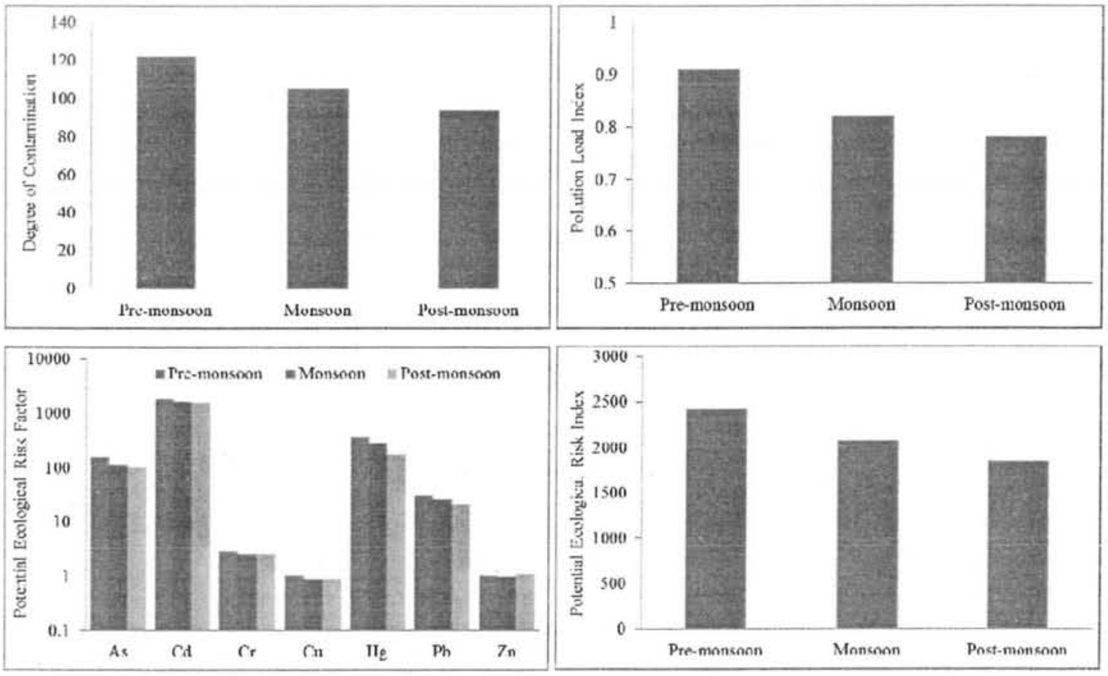

Figure 82. Average degree of contamination (*C_{deg}*), pollution load index (*PLI*), potential ecological risk factor (*E_i*) and potential ecological risk index (*RI*) for selected metals in the soil during pre-monsoon, monsoon and post-monsoon

3.35 Health Risk Assessment for Selected Metals in Soil Samples

Descriptive summary for health risk assessment of selected metals through oral and dermal exposure of soil during summer and winter is given in Table 112, whereas the detail of other input values for exposure assessment of the metals are shown in Appendix-K. During summer, average values of Exp_{ing} for selected metals showed following order: Ca > Fe > Mg > K > Mn > Na > Zn > Sr > Co > Ni > Cr > Pb > As > Cu > Li > Cd > Se > Hg. However, during winter, average values of Exp_{ing} for selected metals showed the following pattern: Ca > Fe > Mg > K > Mn > Na > Sr > Co > Zn > Ni > Cr > Pb > As > Cu > Li > Cd > Hg > Se. The results revealed dominant contributions by Ca, Fe, Mg and K, whereas minor contributions were noted for Cd, Se and Hg through oral exposure during both seasons. Hazard quotients (HQ_{ing} and HQ_{derm}) were used to calculate the non-carcinogenic health risks; $HQ_{ing/derm} > 1$ showed the probability of adverse health effects. Average values of HQ_{ing} for selected metals during summer showed following decreasing order: Co > As > Ca > Mn > Cr > Fe > Li > Pb > Ni > Cd > Hg > Mg > Cu > Se > Zn > Sr

> K > Na. HQ_{derm} for selected metals during summer also showed similar trend as shown by HQ_{ing} with only difference that HQ_{derm} value of As was higher than that of Co. Moreover, average levels of HQ_{ing} for selected metals during winter showed following trend: Co > As > Ca > Mn > Cr > Pb > Fe > Li > Hg > Cd > Ni > Mg > Cu > Se > Zn > Sr > K > Na. The non-carcinogenic risk results exhibited the dominant contributions for As, Co, Ca, Mn, Li, Pb, Cr, Hg, Cd, Fe and Ni while minor contributions were shown by Zn, K and Na during both seasons. Average values of HQ_{ing} and HQ_{derm} were observed to be lower than safety limit unity, indicating that the selected metals were not associated with any adverse non-carcinogenic health risks via ingestion or dermal exposure during both seasons.

Table 112. Description of health risk assessment for selected metals in acid-extract of the soil during summer and winter

	RfD/RDA	Summer		Winter		Summer		Winter	
	(mg/kg/day)	Exp_{ing}	Exp_{derm}	Exp_{ing}	Exp_{derm}	HQ_{ing}	HQ_{derm}	HQ_{ing}	HQ_{derm}
As	3.0E-04	2.4E-05	2.5E-06	2.7E-05	2.8E-06	8.0E-02	8.4E-03	8.8E-02	9.3E-03
Ca	[illegible]E+00	6.4E-02	2.2E-04	4.4E-02	1.5E-04	6.4E-02	2.2E-04	4.4E-02	1.5E-04
Cd	1.0E-03	2.1E-06	7.3E-09	2.8E-06	9.8E-09	2.1E-03	7.3E-06	2.8E-03	9.8E-06
Co	3.0E-04	5.1E-05	1.8E-07	6.0E-05	2.1E-07	1.7E-01	6.0E-04	2.0E-01	6.9E-04
Cr	3.0E-03	3.3E-05	1.2E-07	4.1E-05	1.4E-07	1.1E-02	3.9E-05	1.4E-02	4.8E-05
Cu	4.0E-02	2.3E-05	8.1E-08	2.1E-05	7.4E-08	5.8E-04	2.0E-06	5.3E-04	1.9E-06
Fe	7.0E-01	6.3E-03	2.2E-05	5.7E-03	2.0E-05	9.0E-03	3.2E-05	8.2E-03	2.9E-05
Hg	3.0E-04	4.6E-07	1.6E-09	1.3E-06	4.7E-09	1.5E-03	5.3E-06	4.5E-03	1.6E-05
K	7.8E+01	1.3E-03	4.7E-06	1.6E-03	5.6E-06	1.7E-05	6.0E-08	2.0E-05	7.2E-08
Li	2.0E-03	1.6E-05	5.7E-08	1.6E-05	5.5E-08	8.1E-03	2.8E-05	7.8E-03	2.7E-05
Mg	5.8E+00	5.3E-03	1.9E-05	5.2E-03	1.8E-05	9.1E-04	3.2E-06	9.0E-04	3.1E-06
Mn	2.4E-02	6.1E-04	2.2E-06	6.4E-04	2.2E-06	2.6E-02	9.0E-05	2.7E-02	9.3E-05
Na	5.5E+01	2.9E-04	1.0E-06	2.8E-04	1.0E-06	5.3E-06	1.9E-08	5.2E-06	1.8E-08
Ni	2.0E-02	4.5E-05	1.6E-07	4.6E-05	1.6E-07	2.3E-03	8.0E-06	2.3E-03	8.0E-06
Pb	4.0E-03	2.7E-05	9.4E-08	4.1E-05	1.4E-07	6.7E-03	2.4E-05	1.0E-02	3.6E-05
Se	5.0E-03	1.2E-06	4.1E-09	1.3E-06	4.5E-09	2.4E-04	8.3E-07	2.6E-04	9.0E-07
Sr	6.0E-01	6.0E-05	2.1E-07	8.5E-05	3.0E-07	1.0E-04	3.5E-07	1.4E-04	4.9E-07
Zn	3.0E-01	6.3E-05	2.2E-07	4.6E-05	1.6E-07	2.1E-04	7.3E-07	1.5E-04	5.4E-07
					HI	3.8E-01	9.4E-03	4.1E-01	1.0E-02

Hazard index (HI_{ing} and HI_{derm}) were also estimated to evaluate the overall non-carcinogenic risk caused by the metals via ingestion route and dermal route. The HI_{ing} and HI_{derm} during summer were noted to be 3.8E-01 and 9.4E-03, while mean values during winter were; 4.1E-01 and 1.0E-02, respectively. Consequently, *HI* results revealed that metals could not pose any adverse health effect to local population during both seasons.

Health risk assessment was also evaluated for selected metals in the soil during pre-monsoon, monsoon and post-monsoon as shown in Table 113. Average values of Exp_{ing} for selected metals during pre-monsoon and monsoon exhibited following trend: Ca > Fe > Mg > K > Mn > Na > Pb > Zn > Sr > Cr > Co > Ni > Cu > As > Li > Cd > Se > Hg, while during post-monsoon, mean values of Exp_{ing} for selected metals showed following order: Ca > Fe > Mg > K > Mn > Na > Zn > Sr > Pb > Cr > Co > Ni > Cu > As > Li > Cd > Se > Hg. Hazard quotients (HQ_{ing} and HQ_{derm}) were also calculated during pre-monsoon, monsoon and post-monsoon seasons. Average values of HQ_{ing} and HQ_{derm} for selected metals during pre-monsoon showed following trend: Co > As > Ca > Mn > Pb > Cr > Fe > Cd > Li > Hg > Ni > Cu > Mg > Zn > Se > Sr > K > Na and As > Co > Ca > Mn > Cr > Pb > Fe > Li > Hg > Cd > Ni > Mg > Cu > Se > Zn > Sr > K > Na, respectively. In addition, mean values of HQ_{ing} and HQ_{derm} for selected metals during monsoon showed following trend: Co > As > Ca > Mn > Pb > Cr > Fe > Cd > Li > Hg > Ni > Cu > Mg > Zn > Se > Sr > K > Na and As > Co > Ca > Mn > Pb > Cr > Fe > Cd > Li > Hg > Ni > Cu > Mg > Zn > Se > Sr > K > Na, respectively. Average calculated values of HQ_{ing} and HQ_{derm} for selected metals during post-monsoon exhibited following trend: Co > As > Ca > Mn > Cr > Pb > Fe > Cd > Li > Ni > Hg > Cu > Mg > Zn > Se > Sr > K > Na and As > Co > Ca > Mn > Cr > Pb > Fe > Cd > Li > Ni > Hg > Cu > Mg > Zn > Se > Sr > K > Na, respectively. The non-carcinogenic risk results revealed dominant contributions for As, Co, Ca, Mn, Cr, Li, Pb, Fe and Cd while minor contributions were noted for Sr, K and Na during pre-monsoon, monsoon and post-monsoon seasons. Nevertheless, HQ_{ing} and HQ_{derm} values were noted to be less than unity, thus manifesting no health hazard. Overall, non-carcinogenic risk associated with selected metals via ingestion route and dermal route was computed in terms of HI_{ing} and HI_{derm}, which were noted at 6.1E-01 and 1.0E-02; 5.4E-01 and 1.3E-02; 5.1E-01 and 1.1E-02 during pre-monsoon, monsoon and post-monsoon seasons, respectively. The *HQ* and *HI* results showed that metal contents in the soil of the study area could not pose any adverse health effect to the local population during all seasons.

Table 113. Description of health risk assessment for selected metals in acid-extract of the soil during pre-monsoon, monsoon and post-monsoon

	RfD/RDA (mg/kg/day)	Pre-monsoon				Monsoon				Post-monsoon			
		Exp_{ing}	Exp_{derm}	HQ_{ing}	HQ_{derm}	Exp_{ing}	Exp_{derm}	HQ_{ing}	HQ_{derm}	Exp_{ing}	Exp_{derm}	HQ_{ing}	HQ_{derm}
As	3.0E-04	4.4E-05	2.8E-06	1.5E-01	9.3E-03	3.2E-05	3.4E-06	1.1E-01	1.1E-02	2.8E-05	2.9E-06	9.3E-02	9.7E-03
Ca	1.0E+00	5.4E-02	1.5E-04	5.4E-02	1.5E-04	5.7E-02	2.0E-04	5.7E-02	2.0E-04	6.2E-02	2.2E-04	6.2E-02	2.2E-04
Cd	1.0E-03	1.4E-05	9.8E-09	1.4E-02	9.8E-06	1.3E-05	4.5E-08	1.3E-02	4.5E-05	1.2E-05	4.3E-08	1.2E-02	4.3E-05
Co	3.0E-04	7.7E-05	2.1E-07	2.6E-01	6.9E-04	7.1E-05	2.5E-07	2.4E-01	8.3E-04	6.9E-05	2.4E-07	2.3E-01	8.0E-04
Cr	3.0E-03	9.2E-05	1.4E-07	3.1E-02	4.8E-05	8.3E-05	2.9E-07	2.8E-02	9.7E-05	8.0E-05	2.8E-07	2.7E-02	9.4E-05
Cu	4.0E-02	5.0E-05	7.4E-08	1.2E-03	1.9E-06	4.3E-05	1.5E-07	1.1E-03	3.7E-06	4.1E-05	1.4E-07	1.0E-03	3.6E-06
Fe	7.0E-01	1.4E-02	2.0E-05	2.0E-02	2.9E-05	1.3E-02	4.4E-05	1.8E-02	6.3E-05	1.3E-02	4.6E-05	1.9E-02	6.6E-05
Hg	3.0E-04	1.2E-06	4.7E-09	4.0E-03	1.6E-05	9.7E-07	3.4E-09	3.2E-03	1.1E-05	5.7E-07	2.0E-09	1.9E-03	6.7E-06
K	7.8E+01	1.7E-03	5.6E-06	2.2E-05	7.2E-08	1.5E-03	5.3E-06	1.9E-05	6.8E-08	1.5E-03	5.3E-06	2.0E-05	6.8E-08
Li	2.0E-03	2.1E-05	5.5E-08	1.1E-02	2.7E-05	1.8E-05	6.4E-08	9.1E-03	3.2E-05	1.7E-05	5.8E-08	8.3E-03	2.9E-05
Mg	5.8E+00	4.5E-03	1.8E-05	7.8E-04	3.1E-06	4.4E-03	1.5E-05	7.5E-04	2.6E-06	4.6E-03	1.6E-05	7.9E-04	2.8E-06
Mn	2.4E-02	8.5E-04	2.2E-06	3.6E-02	9.3E-05	7.5E-04	2.6E-06	3.1E-02	1.1E-04	7.2E-04	2.5E-06	3.0E-02	1.0E-04
Na	5.5E+01	3.6E-04	1.0E-06	6.6E-06	1.8E-08	3.7E-04	1.3E-06	6.8E-06	2.4E-08	3.9E-04	1.4E-06	7.1E-06	2.5E-08
Ni	2.0E-02	5.8E-05	1.6E-07	2.9E-03	8.0E-06	5.4E-05	1.9E-07	2.7E-03	9.5E-06	5.5E-05	1.9E-07	2.7E-03	9.5E-06
Pb	4.0E-03	1.4E-04	1.4E-07	3.4E-02	3.6E-05	1.1E-04	3.9E-07	2.8E-02	9.9E-05	9.1E-05	3.2E-07	2.3E-02	8.0E-05
Se	5.0E-03	1.7E-06	4.5E-09	3.4E-04	9.0E-07	1.6E-06	5.6E-09	3.2E-04	1.1E-06	1.3E-06	4.7E-09	2.7E-04	9.4E-07
Sr	6.0E-01	1.0E-04	3.0E-07	1.7E-04	4.9E-07	9.7E-05	3.4E-07	1.6E-04	5.7E-07	9.3E-05	3.3E-07	1.6E-04	5.4E-07
Zn	3.0E-01	1.2E-04	1.6E-07	3.8E-04	5.4E-07	1.1E-04	3.8E-07	3.7E-04	1.3E-06	1.2E-04	4.1E-07	3.9E-04	1.4E-06
			HI	6.1E-01	1.0E-02			5.4E-01	1.3E-02			5.1E-01	1.1E-02

Section-IV: FISH

3.36 Sampling Progress

Five fish species locally named as (English and *Latin* names in bracket) Gulfam (Common carp, *Cyprinus carpio),* Thaila (Indian carp, *Catla catla),* Silver (Silver carp, *Hypophthalmichthys molitrix),* Mulli (Wallago catfish, *Wallago attu)* and Singhari (Indus catfish, *Sperata sarwari)* were collected in the present study from Mangla Lake during 2011 and 2012. These were the most common fish species in the lake and they were most frequently consumed in the study area. Each year, 30 samples of every fish species were collected; thus a total of 300 fish samples were collected during 2011 and 2012 (150 samples each year). The samples were collected as per standard procedure and their biometric data were recorded immediately.

3.37 Biometric Data for Selected Fish Species

The biometric data (length – L, weight – W, coefficient of condition – K) for the five fish species (*Cyprinus carpio, Catla catla, Hypophthalmichthys molitrix, Wallago attu* and *Sperata sarwari*) collected in the present study from Mangla Lake are given in Table 114. The coefficient of condition is used to assess the fish plumpness or robustness and it was calculated from the weight and length of fish. It is related to the environmental conditions, giving indication about the growth, nutritional condition and energy levels of the fish. Higher K value represents that fish are more healthy and plump (Choongo *et al.,* 2005; Akoto *et al.,* 2014). The measured average values of K for *Cyprinus carpio, Catla catla, Hypophthalmichthys molitrix, Wallago attu* and *Sperata sarwari* were 1.335, 1.440, 1.228, 0.517 and 0.481, respectively. The result revealed the fish plumpness or robustness in following decreasing order: *Catla catla* > *Cyprinus carpio* > *Hypophthalmichthys molitrix* > *Wallago attu* > *Sperata sarwari*. Therefore, the data indicated that *Catla catla* was most healthy fish and *Sperata sarwari* were least in the water reservoir. However, to ensure fish excellent sensorial and nutritional qualities and their shelf life the determination of the water contents is extremely important. Water strongly affects their microbiological and chemical stability, physical properties and technological processes (processing, storage and distribution), and is also used to determine their nutritional composition (da Silva *et al.,* 2008). Moisture content (MC, %) were also calculated in various tissues of the fish samples and the data showed that *Cyprinus carpio, Wallago attu*, and *Sperata sarwari* showed highest moisture contents in their muscles while *Catla catla* and *Hypophthalmichthys molitrix* exhibited relatively higher MC in their gill tissues. In addition, the scales exhibited lowest moisture contents in all fish species.

Table 114. Statistical summary of biometric analysis for selected fish species included in the present study

Fish Specie (English/Local Name)		W (g)	L (mm)	CF (K)	Moisture Contents (%)		
					Muscles	Gills	Scales
Cyprinus carpio	Min	612	319.5	0.889	52.69	55.97	43.35
(Common carp /	Max	1357	525.8	1.913	83.57	78.35	63.22
Gulfam)	Mean	878	408.9	1.335	69.76	67.02	52.81
Catla catla (Indian carp / Thaila)	Min	711	338.3	1.138	45.30	57.78	47.68
	Max	1302	485.4	1.836	74.08	71.02	62.66
	Mean	925	401.6	1.440	59.42	65.20	55.64
Hypophthalmichthys	Min	927	386.3	0.989	25.39	64.52	49.09
molitrix	Max	1418	520.1	1.608	37.08	88.27	71.62
(Silver carp / Silver)	Mean	1170	458.6	1.228	32.43	76.82	59.76
Wallago attu	Min	239	331.5	0.384	65.30	58.89	-
(Wallago catfish /	Max	740	565.4	0.665	81.35	70.62	-
Mulli)	Mean	451	441.6	0.517	73.63	65.01	-
Sperata sarwari	Min	243	342.9	0.372	68.49	65.76	-
(Indus catfish /	Max	1313	661.4	0.617	83.38	86.31	-
Singhari)	Mean	635	494.0	0.481	76.67	77.03	-

Cyprinus carpio is an omnivorous fish. It is mud- filter feeds on phytoplankton, zooplankton and other small insects. It collects food from bottom mud by taking mud into the mouth, filtering out digestible particles and rejecting the rest. Its spawning period extends from February to April. *Catla catla* is surface-feeder. Adult usually feeds on phytoplankton, zooplankton, small insects and crustacean. During fingerling stage, it feeds mostly on crustaceans and algae. Its spawning period extends from April to late July. *Hypophthalmichthys molitrix* is an herbivorous fish. The adult has distinct preference for vegetable food such as plankton, leaves of tree, and crustaceans. Its spawning period extends from April to late July. Silver carp has elongated and moderately compressed body. Scales on the body are of moderate size. The colour of the body is silvery and fins are slightly blackish. *Wallago attu* is a freshwater river and Lake Fish found in Indus Plains and adjoining hilly areas in Pakistan. Skin is scaleless. Color of body is silvery or sometimes olive. It is extremely carnivorous and feeds on all types of aquatic animals as well as on dead bodies. As such, it is also called "Freshwater Shark. It breeds during July and August. *Sperata sarwari* is a common giant catfish of freshwater rivers, lakes, channels and reservoirs. It feeds on different aquatic animals including crustaceans, molluscs, frogs and small fishes. It breeds during May, June & July and attains a length of more than one meter. This fish is very much liked for its flesh (with nominal intramuscular bones), taste and sport (FWF, 2016).

3.38 Distribution of Selected Metals in Selected Fish Species

3.38.1 Distribution of Selected Metals in *Cyprinus carpio*

Statistical summary related to the distribution of selected metal concentrations (µg/g) in the muscles of *Cyprinus carpio* is shown in Table 115. On the average basis, measured levels of As, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Li, Mg, Mn, Na, Ni, Pb, Se, Sr and Zn in the muscles were found at 0.644, 659.9, 0.796, 2.946, 5.249, 0.907, 29.13, 0.391, 2217, 0.120, 56.81, 3.982, 1323, 6.607, 4.779, 5.696, 0.985 and 58.89 µg/g, respectively. Among the selected metals, comparatively higher concentrations were noted for K, Na, Ca, Zn and Mg, while Sr, Cu, Cd, As, Hg and Li were found at lower levels in the muscles of *Cyprinus carpio*. Overall, average metal levels in the muscles exhibited following decreasing order: K > Na > Ca > Zn > Mg > Fe > Ni > Se > Cr > Pb > Mn > Co > Sr > Cu > Cd > As > Hg > Li. Some of the metals (Cu, Sr and Hg) showed almost equivalent mean and median levels. Most of the metals showed non-Gaussian distribution pattern as exhibited by relatively higher SD and SE values, however, Ca, K, Na and Zn showed highest dispersion as evidenced by very higher SD and SE values. Similarly, most of the metals demonstrated lower skewness and kurtosis values, showing more or less symmetrical distribution, while Ca, Fe, Na, Ni and Zn revealed relatively asymmetrical distribution in the muscles of *Cyprinus carpio*.

Table 115. Statistical distribution of selected metal levels (μg/g, wet weight) in the muscles of *Cyprinus carpio*

	Min	Max	Mean	Median	SD	SE	Skew	Kurt
As	0.093	1.176	0.644	0.712	0.340	0.088	-0.410	-0.713
Ca	364.5	1454	659.9	500.7	339.3	87.60	1.464	1.105
Cd	0.329	1.644	0.796	0.588	0.423	0.109	0.774	-0.753
Co	0.834	4.704	2.946	3.140	1.151	0.297	-0.779	-0.113
Cr	0.141	8.321	5.249	6.003	2.899	0.749	-1.010	-0.241
Cu	0.540	1.308	0.907	0.909	0.206	0.053	0.091	-0.256
Fe	14.91	53.75	29.13	26.56	10.65	2.750	1.074	0.897
Hg	0.123	0.754	0.391	0.360	0.187	0.048	0.357	-0.517
K	1693	2734	2217	2291	316.2	81.65	0.093	-0.957
Li	0.042	0.261	0.120	0.093	0.068	0.018	0.831	-0.447
Mg	40.83	74.29	56.81	55.24	10.13	2.617	0.188	-0.701
Mn	1.314	8.782	3.982	3.372	2.269	0.586	0.871	-0.102
Na	634.4	3094	1323	1028	748.4	193.2	1.579	1.387
Ni	3.159	15.43	6.607	5.171	3.762	0.971	1.519	1.222
Pb	1.729	8.331	4.779	5.604	2.378	0.614	-0.062	-1.696
Se	1.842	12.56	5.696	5.220	3.165	0.817	0.926	0.259
Sr	0.390	1.883	0.985	0.988	0.472	0.122	0.330	-0.962
Zn	26.95	136.05	58.89	47.54	33.10	8.548	1.454	1.133

Basic statistical distribution parameters for selected metal levels (μg/g) in the gills of *Cyprinus carpio* are shown in Table 116. Most of the metals showed large spread in their concentrations. On the average basis, highest level was noted for Ca (8055 μg/g), followed by, Na (3364 μg/g), Zn (774.6 μg/g), K (737.6 μg/g) and Fe (144.9 μg/g), while Se (4.275 μg/g), Cu (2.248 μg/g), Cd (1.972 μg/g), Li (0.724 μg/g), As (0.279 μg/g) and Hg (0.098 μg/g) revealed comparatively lower concentrations. Overall, the metals exhibited following decreasing order based on mean concentration in the gills samples: Ca > Na > Zn > K > Fe > Mn > Mg > Ni > Pb > Sr > Co > Cr > Se > Cu > Cd > Li > As > Hg. Some of the metals (As, K and Hg) showed almost comparable mean and median levels. Among the selected metals, Ca, K, Na, Zn and Fe showed noticeably higher non-Gaussian distribution pattern as shown by very high SD and SE values while remaining metals showed relatively small dispersion in their distribution. Similarly, most of the metals showed fairly symmetrical distribution as indicated by lower skewness and kurtosis values except Mg and Ni, which showed moderately unsymmetrical distribution supported by higher values of skewness and kurtosis.

Table 116. Statistical distribution of selected metal levels (μg/g, wet weight) in the gills of *Cyprinus carpio*

	Min	Max	Mean	Median	SD	SE	Skew	Kurt
As	0.079	0.564	0.279	0.277	0.147	0.038	0.465	-0.402
Ca	6038	9954	8055	7813	1141	294.5	-0.002	-0.733
Cd	0.349	3.535	1.972	2.502	1.301	0.336	-0.316	-1.978
Co	4.639	19.687	10.83	8.830	5.453	1.408	0.453	-1.579
Cr	2.630	19.702	9.180	9.328	5.544	1.432	0.492	-0.771
Cu	0.292	4.419	2.248	1.849	1.389	0.359	0.074	-1.247
Fe	106.3	191.9	144.9	146.3	23.84	6.155	0.298	-0.375
Hg	0.064	0.155	0.098	0.088	0.027	0.007	0.733	-0.063
K	428.2	1120	737.6	737.9	187.4	48.38	0.375	-0.013
Li	0.036	1.259	0.724	0.924	0.461	0.119	-0.491	-1.529
Mg	4.192	50.77	19.38	15.54	14.48	3.739	1.290	0.688
Mn	18.57	48.47	34.71	36.70	9.146	2.361	-0.171	-0.766
Na	2097	4628	3364	3499	796.4	205.6	0.089	-1.114
Ni	6.628	50.14	18.68	13.81	14.43	3.727	1.384	0.667
Pb	7.308	28.19	16.95	18.35	6.681	1.725	0.051	-1.283
Se	1.788	8.013	4.275	3.824	1.808	0.467	0.701	0.048
Sr	7.260	23.65	15.89	16.78	5.025	1.297	-0.293	-0.892
Zn	282.2	1097	774.6	828.5	261.1	67.43	-0.902	-0.290

Table 117 shows the statistical distribution parameters for concentrations (μg/g) of selected metals in the scales of *Cyprinus carpio*. Dominant mean levels were shown by Ca (8802 μg/g), followed by, Na (754.8 μg/g), K (172.0 μg/g), Zn (114.5 μg/g), Mg (60.32 μg/g) and Fe (56.37 μg/g), while comparatively lower mean levels were shown by Cu (1.437 μg/g), followed by, Cd (1.386 μg/g), Li (0.861 μg/g), As (0.188 μg/g) and Hg (0.013 μg/g). On the average basis, metal levels exhibited following decreasing order: Ca > Na > K > Zn > Mg > Fe > Mn > Sr > Ni > Pb > Co > Cr > Se > Cu > Cd > Li > As > Hg. Significantly random distribution pattern was shown by As, Cd, Cr, Cu, Co, Hg, Mn, Li, Ni, Se, Sr and Pb as evidenced by higher SD and SE values, whereas, Ca, Fe, K, Na, Zn and Mg showed highest dispersion among the metals as revealed by elevated SD and

SE values. Most of the metals showed fairly symmetrical distribution as exhibited by relatively lower skewness and kurtosis values.

Table 117. Statistical distribution of selected metal levels (µg/g, wet weight) in the scales of *Cyprinus carpio*

	Min	Max	Mean	Median	SD	SE	Skew	Kurt
As	0.052	0.293	0.188	0.226	0.086	0.022	-0.443	-1.324
Ca	6388	11919	8802	8276	1619	418.0	0.389	-0.696
Cd	0.520	3.296	1.386	1.118	0.858	0.222	1.418	0.922
Co	4.999	10.185	7.546	7.665	1.441	0.372	0.066	-0.580
Cr	3.176	7.225	4.352	4.055	1.198	0.309	1.500	1.559
Cu	0.259	3.260	1.437	1.537	1.006	0.260	0.384	-1.043
Fe	35.69	77.58	56.37	55.86	14.00	3.616	-0.065	-1.425
Hg	0.006	0.022	0.013	0.011	0.005	0.001	0.496	-1.142
K	92.71	307.5	172.0	153.0	65.60	16.94	0.864	-0.310
Li	0.555	1.169	0.861	0.893	0.165	0.043	-0.020	-0.326
Mg	20.51	80.26	60.32	65.87	20.30	5.241	-1.189	0.129
Mn	14.51	25.33	19.79	19.57	3.083	0.796	0.131	-0.606
Na	466.5	1108	754.8	740.4	194.7	50.26	0.191	-1.006
Ni	4.163	23.06	12.86	14.62	6.276	1.620	-0.003	-1.412
Pb	6.116	19.24	11.26	10.62	3.781	0.976	0.804	0.014
Se	0.985	10.55	3.979	3.111	2.994	0.773	1.389	0.844
Sr	10.55	22.15	15.32	14.83	3.102	0.801	0.719	0.387
Zn	92.29	141.9	114.5	112.2	14.79	3.818	0.118	-0.633

3.38.2 Distribution of Selected Metals in *Catla catla*

Basic statistical data for the distribution of selected metal levels (µg/g) in the muscles of *Catla catla* are shown in Table 118. On the average basis, the measured levels of As, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Li, Mg, Mn, Na, Ni, Pb, Se, Sr and Zn in the muscles were found at 0.487, 1316, 0.320, 0.685, 0.704, 1.669, 19.80, 0.361, 1768, 0.187, 60.68, 5.790, 1309, 0.409, 5.150, 2.590, 4.280 and 35.59 µg/g, respectively. Among the selected metals, K, Na, Ca, Mg and Zn were the dominant contributors, while As, Ni, Cd, Hg and Li were the minor contributors in the muscle of *Catla catla*. Average metal levels in the muscles revealed following decreasing order: K > Na >Ca > Mg > Zn > Fe > Mn > Pb > Sr > Se > Cu > Cr > Co > As > Ni > Hg > Cd > Li. Most of the metals showed more or less random distribution pattern in their concentration as indicated by fairly higher SD and SE values, while Ca, K, Na, Mg and Zn showed predominantly non-Gaussian distribution supported by very high SD and SE values. Similarly most of the metals showed lower skewness and kurtosis values, manifesting their symmetrical distribution, while As, Fe and Li exhibited comparatively unsymmetrical distribution as indicated by rather high skewness values in the muscles of *Catla catla.*

Table 118. Statistical distribution of selected metal levels (µg/g, wet weight) in the muscles of *Catla catla*

	Min	Max	Mean	Median	SD	SE	Skew	Kurt
As	0.271	0.936	0.487	0.423	0.218	0.056	1.216	0.256
Ca	1057	1627	1316	1289	182.1	47.02	0.398	-1.007
Cd	0.099	0.492	0.320	0.336	0.135	0.035	-0.470	-0.978
Co	0.245	1.356	0.685	0.479	0.425	0.110	0.488	-1.707
Cr	0.183	1.218	0.704	0.720	0.320	0.083	-0.280	-0.389
Cu	1.296	2.140	1.669	1.644	0.242	0.062	0.487	-0.462
Fe	16.14	26.15	19.80	19.23	2.828	0.730	1.107	0.823
Hg	0.248	0.477	0.361	0.372	0.075	0.019	-0.099	-1.461
K	1385	2053	1768	1783	184.5	47.63	-0.443	-0.363
Li	0.072	0.407	0.187	0.157	0.107	0.028	1.277	0.536
Mg	45.31	69.87	60.68	62.33	7.201	1.859	-0.726	-0.195
Mn	4.079	8.893	5.790	5.620	1.522	0.393	0.930	-0.092
Na	1143	1481	1309	1331	102.3	26.43	-0.116	-0.772
Ni	0.016	0.924	0.409	0.247	0.391	0.101	0.356	-1.956
Pb	1.984	7.837	5.150	5.432	1.772	0.457	-0.641	-0.108
Se	1.768	3.747	2.590	2.585	0.612	0.158	0.526	-0.728
Sr	3.033	5.168	4.280	4.302	0.676	0.175	-0.419	-1.039
Zn	26.90	45.05	35.59	35.26	5.032	1.299	0.185	-0.442

Basic statistical distribution parameters for selected metal levels (µg/g) in the gills of *Catla catla* are shown in Table 119, which revealed highest mean level for Ca (8334 µg/g), followed by, Na (1892 µg/g), Zn (453.4 µg/g), K (316.1 µg/g) and Fe (79.76 µg/g) whereas Co (2.774 µg/g), Cd (1.191 µg/g), Li (0.807 µg/g), As (0.498 µg/g) and Hg (0.074 µg/g) exhibited relatively lower concentrations. Overall, the metals showed following decreasing order based on average levels in the gills samples: Ca > Na > Zn > K > Fe > Mn > Mg > Sr > Pb > Ni > Cr > Cu > Se > Co > Cd > Li > As > Hg. Some of the metals (Se, Sr and Hg) showed comparable mean and median levels thus indicating their normal distribution in the gills. Most of the metals showed relatively non-Gaussian distribution; however, significantly higher SD and SE values were noted for Ca, K, Na, Zn and Fe thereby showing predominantly random distribution pattern in their concentrations. Most of the metals showed relatively lower skewness and kurtosis values, thus manifesting fairly symmetrical distribution in the gills.

Table 119. Statistical distribution of selected metal levels (μg/g, wet weight) in the gills of *Catla catla*

	Min	Max	Mean	Median	SD	SE	Skew	Kurt
As	0.228	0.862	0.498	0.519	0.227	0.059	0.187	-1.506
Ca	6958	9316	8334	8445	689.7	178.1	-0.306	-0.675
Cd	0.896	1.815	1.191	1.075	0.290	0.075	1.250	0.484
Co	0.827	3.648	2.774	3.120	1.006	0.260	-1.381	0.397
Cr	1.738	6.442	3.910	3.715	1.427	0.369	0.202	-0.492
Cu	2.573	4.333	3.463	3.426	0.531	0.137	0.127	-0.967
Fe	54.38	104.1	79.76	79.15	14.96	3.863	-0.142	-1.022
Hg	0.048	0.107	0.074	0.075	0.018	0.005	0.263	-0.928
K	147.6	438.5	316.1	334.5	92.66	23.93	-0.764	-0.518
Li	0.305	1.308	0.807	0.761	0.324	0.084	-0.086	-0.982
Mg	52.20	72.73	60.18	60.71	5.778	1.492	0.594	0.365
Mn	53.69	82.26	67.02	65.70	8.521	2.200	0.155	-0.807
Na	1653	2116	1892	1918	144.1	37.20	-0.171	-0.875
Ni	0.419	12.007	5.379	3.120	4.331	1.118	0.389	-1.677
Pb	6.769	11.989	9.575	9.726	1.475	0.381	-0.322	-0.489
Se	2.294	3.358	2.873	2.878	0.303	0.078	-0.194	-0.662
Sr	25.22	36.37	30.06	29.72	3.055	0.789	0.440	0.002
Zn	360.1	542.4	453.4	460.9	49.83	12.87	-0.050	-0.467

Table 120. Statistical distribution of selected metal levels (µg/g, wet weight) in the scales of *Catla catla*

	Min	Max	Mean	Median	SD	SE	Skew	Kurt
As	0.096	0.211	0.154	0.152	0.040	0.010	0.108	-1.529
Ca	7068	11845	10145	10387	1459	376.6	-0.900	-0.077
Cd	0.706	1.872	1.208	1.080	0.383	0.099	0.450	-1.234
Co	1.048	3.100	2.016	2.072	0.628	0.162	0.085	-0.772
Cr	1.637	4.029	2.794	3.106	0.881	0.228	-0.122	-1.772
Cu	1.530	3.026	2.124	2.058	0.457	0.118	0.644	-0.417
Fe	24.02	57.10	35.91	34.08	9.832	2.539	1.262	0.710
Hg	0.002	0.011	0.007	0.008	0.003	0.001	-0.604	-0.976
K	154.1	262.0	221.5	225.2	32.18	8.308	-0.858	-0.123
Li	0.461	1.268	0.740	0.669	0.248	0.064	1.314	0.674
Mg	62.92	81.16	72.00	72.07	5.417	1.399	-0.147	-0.837
Mn	29.18	49.98	40.83	42.33	6.413	1.656	-0.240	-0.918
Na	691.5	1015	864.8	871.0	87.73	22.65	-0.189	-0.407
Ni	0.295	4.780	2.406	2.634	1.437	0.371	0.014	-0.702
Pb	4.172	11.32	8.342	9.582	2.733	0.706	-0.430	-1.737
Se	0.924	1.920	1.374	1.353	0.307	0.079	0.203	-1.006
Sr	17.86	32.85	25.22	24.90	4.154	1.073	0.074	-0.353
Zn	63.04	110.9	94.24	95.09	15.08	3.894	-0.923	-0.142

Statistical parameters related to the distribution of selected metal levels (µg/g) in the scales of *Catla catla* from Mangla Lake are shown in Table 120. Average concentrations of As, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Li, Mg, Mn, Na, Ni, Pb, Se, Sr and Zn in the scales were measured at 0.154, 10145, 1.208, 2.016, 2.794, 2.124, 35.91, 0.007, 221.5, 0.740, 72.00, 40.83, 864.8, 2.406, 8.342, 1.374, 25.22 and 94.24 µg/g, respectively. Among the selected metals, Ca, Na, K, Zn and Mg were the dominant contributors, while Cd, Li, As and Hg were the minor components in the scales of *Catla catla*. Overall, following decreasing order was found on the basis of mean metal levels in the scales: Ca > Na > K > Zn > Mg > Mn > Fe > Sr > Pb > Cr > Ni > Cu > Co > Se > Cd > Li > As > Hg. Most of the metals showed relatively non-Gaussian distribution in their concentrations as shown by fairly higher SD and SE values; nevertheless, highest dispersion and predominantly random distribution was noted for Ca, K, Na and Zn. Similarly, most of metals revealed somewhat lower skewness and kurtosis values, demonstrating their symmetrical distribution, while Fe and Li revealed the moderately unsymmetrical distribution pattern in the scales of *Catla catla*.

3.38.3 Distribution of Selected Metals in *Hypophthalmichthys molitrix*

Basic statistical data related to the distribution of selected metal levels (μg/g) in the muscles of *Hypophthalmichthys molitrix* is shown in Table 121. Minimum-maximum levels along with the mean contents (in brackets) of As, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Li, Mg, Mn, Na, Ni, Pb, Se, Sr and Zn in the muscles were found as: 0.999-2.357 (1.719); 734.8-3104 (1633); 0.332-0.933 (0.515); 0.319-1.378 (0.769); 0.445-1.164 (0.822); 0.910-2.455 (1.603); 12.31-26.79 (18.24); 0.135-0.282 (0.217); 1320-1998 (1643); 0.033-0.190 (0.111); 47.62-73.08 (61.85) 2.199-8.532 (4.794); 851.8-1484 (1127); 0.519-5.954 (2.595); 3.202-8.250 (5.592); 1.808-3.097 (2.403); 1.123-6.412 (3.557) and 15.68-27.94 (21.62) μg/g, respectively. Among the selected metals K, Na, Ca, Mg and Zn were the dominant components, while Cr, Co, Cd, Hg and Li were found at rather lower levels in the muscle of *Hypophthalmichthys molitrix*. Overall, mean metal levels in the muscles showed following decreasing order: K > Ca > Na > Mg > Zn > Fe > Pb > Mn > Sr > Ni > Se > As > Cu > Cr > Co > Cd > Hg > Li. About half of the metals exhibited relatively non-Gaussian distribution pattern in their concentrations as shown by reasonably higher SD and SE values, however, highest dispersion was shown by Ca, K, and Na. Similarly, most of the metals showed lower skewness and kurtosis values, thereby demonstrating symmetrical distribution, while Cd showed relatively asymmetrical distribution in the muscles of *H. molitrix*.

Statistical distribution parameters for selected metal levels (μg/g) in the gills of *Hypophthalmichthys molitrix* are shown in Table 122. Average concentrations of As, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Li, Mg, Mn, Na, Ni, Pb, Se, Sr and Zn in the muscles were noted as 0.527, 10061, 1.771, 3.987, 6.185, 4.012, 247.1, 0.052, 602.6, 0.836, 47.43, 75.67, 2074, 9.617, 13.99, 2.201, 36.55 and 186.7 μg/g, respectively. Overall, based on mean metal concentrations in the gills, following decreasing pattern was observed: Ca > Na > K > Fe > Zn > Mn > Mg > Sr > Pb > Ni > Cr > Cu > Co > Se > Cd > Li > As > Hg. Most of the selected metals showed quite non-Gaussian distribution, however, Ca, K, Na, Fe and Zn revealed very high dispersion and randomness in their concentrations as exhibited by relatively higher SD and SE values. In addition, most of the metals showed somewhat symmetrical distribution as evidenced by lower skewness and kurtosis values except Co and K which showed rather asymmetrical distribution in the gills.

Table 121. Statistical distribution of selected metal levels (µg/g, wet weight) in the muscles of *Hypophthalmichthys molitrix*

	Min	Max	Mean	Median	SD	SE	Skew	Kurt
As	0.999	2.357	1.719	1.831	0.450	0.116	-0.301	-1.430
Ca	734.8	3104	1633	1620	785.9	202.9	0.660	-0.588
Cd	0.332	0.933	0.515	0.449	0.197	0.051	1.363	0.619
Co	0.319	1.378	0.769	0.791	0.344	0.089	0.350	-0.897
Cr	0.445	1.164	0.822	0.884	0.240	0.062	-0.294	-1.441
Cu	0.910	2.455	1.603	1.466	0.536	0.139	0.323	-1.555
Fe	12.31	26.79	18.24	17.82	4.365	1.127	0.632	-0.411
Hg	0.135	0.282	0.217	0.226	0.045	0.012	-0.444	-0.851
K	1320	1998	1643	1655	183.8	47.45	0.206	-0.281
Li	0.033	0.190	0.111	0.131	0.059	0.015	-0.187	-1.786
Mg	47.62	73.08	61.85	62.17	8.698	2.246	-0.212	-1.339
Mn	2.199	8.532	4.794	4.458	1.971	0.509	0.654	-0.376
Na	851.8	1484	1127	1106	180.5	46.61	0.541	-0.372
Ni	0.519	5.954	2.595	2.517	1.812	0.468	0.704	-0.524
Pb	3.202	8.250	5.592	4.931	1.798	0.464	0.316	-1.627
Se	1.808	3.097	2.403	2.368	0.406	0.105	0.285	-1.137
Sr	1.123	6.412	3.557	3.407	1.663	0.429	0.173	-0.679
Zn	15.68	27.94	21.62	21.52	3.576	0.923	0.101	-0.818

Distribution of selected metal concentrations in the scales of *Hypophthalmichthys molitrix* is shown in Table 123 in terms of basic statistical parameters. Mean levels of As, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Li, Mg, Mn, Na, Ni, Pb, Se, Sr and Zn in scales were found at 0.272, 10091, 1.962, 2.637, 4.296, 3.670, 240.5, 0.019, 380.9, 0.713, 32.17, 58.00, 527.1, 8.585, 11.77, 1.983, 23.11 and 172.6 µg/g, respectively. Among the selected metals, Ca, Na, K, Zn and Fe were the dominant contributors, while Cd, Li, As and Hg showed least contributions in the scales of *H. molitrix*. On comparative basis, following decreasing order was noted for mean metal levels in the scales: Ca > Na > K > Fe > Zn > Mn > Mg > Sr > Pb > Ni > Cr > Cu > Co > Se > Cd > Li > As > Hg. Some of the metals (As, Sr, Se and Hg) showed comparable mean and median concentrations in the scales. Most of the metals demonstrated non-Gaussian distribution in their concentrations as exhibited by relatively higher SD and SE values. However, Ca, K, Na and Fe showed highest dispersion and randomness. Similarly, most of the metals revealed rather lower skewness and kurtosis values, thus showing relatively symmetrical distribution, while Cr and Cd showed comparatively asymmetrical distribution pattern in the scales as indicated by higher magnitude of the symmetry parameters.

Table 122. Statistical distribution of selected metal levels (μg/g, wet weight) in the gills of *Hypophthalmichthys molitrix*

	Min	Max	Mean	Median	SD	SE	Skew	Kurt
As	0.323	0.756	0.527	0.469	0.148	0.038	0.306	-1.521
Ca	8160	12289	10061	10070	1127	291.0	0.301	-0.224
Cd	1.081	3.164	1.771	1.496	0.706	0.182	0.991	-0.328
Co	2.779	5.943	3.987	3.820	0.917	0.237	1.076	0.487
Cr	4.777	7.867	6.185	5.943	0.907	0.234	0.233	-0.732
Cu	2.437	6.061	4.012	3.899	1.165	0.301	0.381	-1.112
Fe	97.28	456.9	247.1	227.9	125.3	32.35	0.386	-1.345
Hg	0.025	0.085	0.052	0.049	0.022	0.006	0.234	-1.667
K	470.7	868.0	602.6	563.6	121.5	31.37	1.222	0.565
Li	0.167	1.436	0.836	0.915	0.406	0.105	-0.469	-0.568
Mg	29.17	60.71	47.43	49.95	9.732	2.513	-0.596	-0.600
Mn	46.03	101.2	75.67	80.02	17.85	4.608	-0.319	-1.291
Na	1353	2885	2074	2055	438.9	113.3	0.215	-0.426
Ni	0.235	17.49	9.617	11.60	5.882	1.519	-0.563	-0.921
Pb	1.460	27.07	13.99	11.83	8.709	2.249	-0.019	-1.178
Se	1.560	2.883	2.201	2.114	0.421	0.109	0.235	-1.235
Sr	28.33	44.59	36.55	36.65	4.483	1.158	0.030	-0.479
Zn	138.1	247.4	186.7	178.3	36.36	9.387	0.370	-1.325

Table 123. Statistical distribution of selected metal levels (μg/g, wet weight) in the scales of *Hypophthalmichthys molitrix*

	Min	Max	Mean	Median	SD	SE	Skew	Kurt
As	0.188	0.376	0.272	0.264	0.057	0.015	0.408	-0.856
Ca	8856	11544	10091	10284	786.3	203.0	-0.025	-0.609
Cd	1.095	3.796	1.962	1.668	0.862	0.223	1.432	0.775
Co	1.508	4.500	2.637	2.542	0.966	0.249	0.728	-0.441
Cr	3.333	6.256	4.296	3.957	0.890	0.230	1.289	0.713
Cu	2.948	4.498	3.670	3.608	0.436	0.112	0.240	-0.472
Fe	71.28	333.9	240.5	270.6	88.62	22.88	-1.275	0.284
Hg	0.015	0.025	0.019	0.019	0.003	0.001	0.731	-0.087
K	206.5	583.1	380.9	374.4	129.7	33.48	0.173	-1.535
Li	0.251	1.137	0.713	0.820	0.304	0.078	-0.333	-1.389
Mg	16.93	44.34	32.17	33.94	8.365	2.160	-0.604	-0.455
Mn	43.19	72.69	58.00	58.39	8.637	2.230	0.038	-0.867
Na	381.3	784.4	527.1	472.2	128.1	33.07	0.909	-0.372
Ni	0.582	19.06	8.585	9.726	6.283	1.622	0.214	-1.077
Pb	0.582	23.71	11.77	9.581	8.887	2.295	0.145	-1.734
Se	1.552	2.340	1.983	2.006	0.223	0.058	-0.230	-0.624
Sr	16.72	28.49	23.11	23.98	4.330	1.118	-0.257	-1.658
Zn	138.3	202.2	172.6	174.0	17.28	4.461	-0.201	-0.393

3.38.4 Distribution of Selected Metals in *Wallago attu*

Basic statistical summary for the distribution of selected metal concentrations (μg/g) in the muscles of *Wallago attu* is shown in Table 124. On the average basis, measured levels of As, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Li, Mg, Mn, Na, Ni, Pb, Se, Sr and Zn in the muscles were found at 0.153, 921.5, 0.406, 0.756, 0.870, 0.794, 16.83, 0.425, 1702, 0.283, 51.91, 3.172, 1133, 2.689, 4.872, 1.031, 1.406 and 41.48 μg/g, respectively. Among the selected metals, K, Na, Ca, Mg and Zn exhibited dominant levels, while Hg, Cd, Li, and As were the minor contributors in the muscle of *Wallago attu*. Overall, mean metal levels in the muscles showed following decreasing order: K > Na > Ca > Mg > Zn > Fe > Pb > Mn > Ni > Sr > Se > Cr > Cu > Co > Hg > Cd > Li > As. Mean and median concentrations of Li, Co and As in the muscle were almost comparable, thus indicating their normal distribution. Most of the metals showed relatively Gaussian distribution in their concentrations as shown by fairly lower SD and SE values, while Ca, K, Na, Zn, Fe and Zn showed moderately non-Gaussian distribution as shown by relatively higher SD and SE values. Similarly, most of the metals exhibited lower skewness and kurtosis values, demonstrating nearly symmetrical distribution, while Hg and Se displayed rather asymmetrical distribution in the muscles of *Wallago attu*.

Table 124. Statistical distribution of selected metal levels (μg/g, wet weight) in the muscles of *Wallago attu*

	Min	Max	Mean	Median	SD	SE	Skew	Kurt
As	0.095	0.211	0.153	0.144	0.040	0.010	0.197	-1.439
Ca	87.46	2399	921.5	546.6	806.0	208.1	0.812	-0.739
Cd	0.100	0.726	0.406	0.340	0.241	0.062	0.183	-1.750
Co	0.512	1.162	0.756	0.711	0.200	0.052	0.881	-0.081
Cr	0.333	1.515	0.870	0.945	0.403	0.104	0.045	-1.364
Cu	0.546	1.191	0.794	0.655	0.240	0.062	0.559	-1.595
Fe	7.025	32.06	16.83	11.04	9.505	2.454	0.532	-1.691
Hg	0.174	0.952	0.425	0.353	0.259	0.067	1.247	0.308
K	1224	2285	1702	1689	303.8	78.45	0.432	-0.466
Li	0.231	0.362	0.283	0.278	0.036	0.009	0.787	0.357
Mg	35.66	63.57	51.91	54.46	9.461	2.443	-0.348	-1.347
Mn	0.883	6.247	3.172	3.350	1.865	0.482	0.242	-1.300
Na	508.2	1996	1133	1051	501.8	129.6	0.423	-1.197
Ni	0.408	5.410	2.689	2.570	1.578	0.407	0.183	-0.519
Pb	3.813	5.814	4.872	4.804	0.581	0.150	-0.143	-0.823
Se	0.379	2.360	1.031	0.851	0.643	0.166	1.340	0.588
Sr	0.395	2.283	1.406	1.857	0.769	0.199	-0.356	-1.960
Zn	8.928	69.00	41.48	40.41	20.82	5.376	-0.317	-1.099

Basic statistical distribution parameters for selected metal levels in the gills of *Wallago attu* are given in Table 125. Among the selected metals, highest mean level was noted for Ca (14972 μg/g), followed by considerably higher concentrations of Na (2553 μg/g), K (1065 μg/g), Fe (229.0 μg/g) and Zn (170.3 μg/g), while Cd (2.121 μg/g), Se (1.769 μg/g), Li (1.685 μg/g), As (0.628 μg/g) and Hg (0.252 μg/g) exhibited comparatively lower concentrations. Overall, the metals exhibited following decreasing trend based on average concentration in the gills samples: Ca > Na > K > Fe > Zn > Mn > Pb > Ni > Sr > Mg > Cr > Co > Cu > Cd > Se > Li > As > Hg. Some of the metals (Pb, Sr and Hg) displayed almost similar mean and median levels thus demonstrating their normal distribution. Most of the metals showed random distribution in their concentrations as shown by relatively higher SD and SE values, whereas Ca, Na, K and Fe showed highest dispersion and randomness as shown by very high SD and SE values. Most of the selected metals revealed fairly symmetrical distribution as revealed by relatively lower skewness and kurtosis values, except Co and Fe, which showed somewhat asymmetrical distribution supported by higher values of skewness and kurtosis.

Table 125. Statistical distribution of selected metal levels (μg/g, wet weight) in the gills of *Wallago attu*

	Min	Max	Mean	Median	SD	SE	Skew	Kurt
As	0.287	1.049	0.628	0.582	0.271	0.070	0.260	-1.597
Ca	12598	17021	14972	14856	1296	334.6	-0.085	-0.648
Cd	1.303	3.332	2.121	1.814	0.668	0.172	0.619	-1.073
Co	3.719	7.944	5.065	4.619	1.322	0.341	1.354	0.712
Cr	4.070	8.594	5.966	5.761	1.354	0.350	0.555	-0.466
Cu	0.539	4.692	3.330	3.870	1.479	0.382	-1.349	0.374
Fe	121.0	483.1	229.0	194.3	122.2	31.54	1.359	0.508
Hg	0.113	0.452	0.252	0.239	0.108	0.028	0.601	-0.577
K	672.6	1401	1065	1085	221.7	57.24	-0.282	-0.824
Li	1.186	2.342	1.685	1.637	0.360	0.093	0.445	-0.966
Mg	4.601	29.12	11.45	12.55	11.60	2.995	-0.006	-1.274
Mn	30.13	82.24	49.84	44.49	16.27	4.201	0.908	-0.217
Na	2130	3058	2553	2593	251.9	65.03	0.291	-0.135
Ni	1.026	42.33	23.45	31.69	15.65	4.040	-0.433	-1.664
Pb	8.192	43.20	24.74	24.69	10.58	2.731	0.049	-0.255
Se	0.914	2.470	1.769	1.866	0.478	0.124	-0.551	-0.575
Sr	12.93	19.10	15.82	15.60	1.882	0.486	0.292	-0.798
Zn	104.8	202.3	170.3	175.8	31.61	8.162	-1.127	0.119

3.38.5 Distribution of Selected Metals in *Sperata sarwari*

Basic statistical data for the distribution of selected metal levels (μg/g) in the muscles of *Sperata sarwari* are shown in Table 126. Most of the metals showed significant variations in their concentrations; highest levels were noted for K ranging from 1718 to 2299 μg/g with a mean value of 2057 μg/g. Similarly, Na levels varied from 1005 to 1552 μg/g with mean contribution of 1301 μg/g. In addition, considerably higher levels were found for Ca, Mg, Fe and Zn with mean contents of 292.1, 48.89, 34.58 and 20.70 μg/g, and the corresponding ranges of 74.58 to 786.0 μg/g, 40.03 to 61.90 μg/g, 19.69 to 45.01 μg/g and 15.05 to 27.90 μg/g. However, comparatively lower concentrations were noted for Cu (0.939 μg/g), Cd (0.504 μg/g), Sr (0.406 μg/g), As (0.166 μg/g) and Li (0.149 μg/g) in the muscle of *Sperata sarwari*. Overall, mean metal levels in the muscles exhibited following decreasing order: K > Na > Ca > Mg > Fe > Zn > Pb > Ni > Se > Mn > Cr > Co > Hg > Cu > Cd > Sr > As > Li. About half of the metals showed more or less Gaussian distribution pattern in their concentrations as evidenced by relatively lower SD and SE values, nonetheless, Ca, K, and Na exhibited very large dispersion and non-Gaussian distribution. Similarly, most of the metals showed comparatively lower skewness and kurtosis values, thus demonstrating fairly symmetrical distribution; however, Ca, Cd and Sr showed relatively asymmetrical distribution.

Table 126. Statistical distribution of selected metal levels (μg/g, wet weight) in the muscles of *Sperata sarwari*

	Min	Max	Mean	Median	SD	SE	Skew	Kurt
As	0.116	0.232	0.166	0.157	0.033	0.009	0.605	-0.181
Ca	74.58	786.0	292.1	241.7	241.6	62.37	1.349	0.491
Cd	0.274	0.947	0.504	0.477	0.221	0.057	1.026	-0.003
Co	0.161	3.005	1.315	1.523	1.009	0.260	0.294	-1.199
Cr	1.760	3.838	2.781	2.844	0.622	0.161	-0.009	-0.866
Cu	0.644	1.152	0.939	0.959	0.148	0.038	-0.617	-0.329
Fe	19.69	45.01	34.58	36.87	8.369	2.161	-0.508	-0.884
Hg	0.730	1.721	1.186	1.245	0.323	0.083	0.124	-1.324
K	1718	2299	2057	2087	169.2	43.69	-0.321	-0.682
Li	0.042	0.336	0.149	0.152	0.102	0.026	0.641	-0.731
Mg	40.03	61.90	48.89	48.29	5.986	1.546	0.779	0.428
Mn	1.449	4.303	3.114	3.536	0.968	0.250	-0.600	-1.001
Na	1005	1552	1301	1303	165.3	42.67	-0.135	-0.943
Ni	1.361	7.511	4.160	3.398	2.245	0.580	0.281	-1.672
Pb	4.782	8.569	6.276	5.977	1.124	0.290	0.779	-0.231
Se	2.738	5.263	4.138	4.319	0.779	0.201	-0.357	-0.936
Sr	0.129	1.058	0.406	0.286	0.316	0.082	1.408	0.566
Zn	15.05	27.90	20.70	19.64	4.108	1.061	0.422	-1.174

Basic statistical parameters for the distribution of selected metal levels (μg/g) in the gills of *Sperata sarwari* are shown in Table 127. Average levels of As, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Li, Mg, Mn, Na, Ni, Pb, Se, Sr and Zn in the gills were noted as 0.461, 11881, 1.977, 7.358, 6.137, 2.270, 113.7, 0.308, 699.3, 0.900, 17.87, 24.03, 1833, 14.70, 18.53, 3.024, 12.47 and 97.15 μg/g, respectively. Overall, the metals showed following decreasing trend based on the mean levels in the gills: Ca > Na > K > Fe > Zn > Mn > Pb > Mg > Ni > Sr > Co > Cr > Se > Cu > Cd > Li > As > Hg. Some of the metals (As, Mn and Hg) showed almost comparable mean and median levels, thereby indicating least variations in these metal levels. However, most of the metals showed relatively non-Gaussian distribution; Ca, K, Na, Fe and Zn showed highest dispersion in their concentrations as shown by very high SD and SE values. The skewness and kurtosis values revealed somewhat symmetrical distribution for most of the metals, except Cd and Zn which exhibited rather asymmetrical distribution in the gills samples.

Table 127. Statistical distribution of selected metal levels (μg/g, wet weight) in the gills of *Sperata sarwari*

	Min	Max	Mean	Median	SD	SE	Skew	Kurt
As	0.190	0.810	0.461	0.461	0.232	0.060	0.154	-1.701
Ca	9126	14637	11881	11833	1581	408.3	0.085	-0.728
Cd	1.086	4.011	1.977	1.641	0.954	0.246	1.497	0.837
Co	4.282	10.84	7.358	7.313	1.945	0.502	0.182	-0.582
Cr	3.311	9.697	6.137	5.125	2.374	0.613	0.391	-1.749
Cu	1.511	3.314	2.270	2.065	0.624	0.161	0.448	-1.467
Fe	49.15	204.5	113.7	114.5	50.12	12.94	0.484	-0.770
Hg	0.170	0.448	0.308	0.318	0.092	0.024	-0.032	-1.378
K	315.5	982.2	699.3	697.8	222.5	57.45	-0.489	-0.784
Li	0.619	1.254	0.900	0.822	0.215	0.056	0.414	-1.455
Mg	5.760	37.10	17.87	17.46	9.975	2.576	0.813	-0.155
Mn	13.05	35.15	24.03	23.97	6.504	1.679	-0.124	-0.446
Na	1389	2283	1833	1788	258.8	66.83	0.013	-0.830
Ni	1.517	26.54	14.70	15.14	8.272	2.136	-0.403	-0.776
Pb	11.25	30.04	18.53	17.76	6.337	1.636	0.550	-1.005
Se	2.193	4.188	3.024	2.918	0.572	0.148	0.715	-0.091
Sr	8.044	16.31	12.47	13.00	2.513	0.649	-0.279	-0.915
Zn	75.78	146.3	97.15	88.41	21.96	5.669	1.462	1.026

3.39 Comparison of Metal Levels in Various Tissues of Selected Fish Species

Trace metals in aquatic environment can be accumulated in the fish tissues even at very low concentrations; therefore, the measurement of metal contents can reflect the exposure effects. Various tissues have different accumulating capacities for the metals, which may be due to the diverse metabolic roles and functions of organs (Ashraf, 2005). In addition, metal's concentrations in different fish species might be a result of different ecological needs, metabolisms, age, size/length of the fish, habitats and feeding patterns (Allen-Gil and Martynov 1995). Comparison of average metal levels in the muscles, gills and scales of *Cyprinus carpio* during 2011 and 2012 are shown in Figure 83. The result revealed that different metals showed dissimilar accumulation in various organs. Among the selected metals, Cd, Co, Cu, Fe, Mn, Pb, Sr and Zn exhibited relatively higher concentrations in the gills during 2011 and showed following decreasing order in various tissues: gills > scales > muscles, whereas As, K, Hg and Se showed following pattern; muscles > gills > scales. Additionally, Cr and Na displayed highest concentrations in the gills but lowest concentrations in the scales. Nevertheless, mean levels of Li and Ca exhibited following order: scales > gills > muscles. Besides, Mg exhibited higher concentration in the muscles and lower in the gills during 2011. Similarly, comparison of mean metal concentrations in the muscles, gills and scales of *Cyprinus carpio* during 2012 showed that Ca, Cd, Co, Cr, Cu, Fe, Li, Mg, Mn, Ni, Pb, Sr and Zn were found at comparatively higher levels in the gills and showed following decreasing order in various tissues: gills > scales > muscles. However, As, K, Hg and Se showed relatively higher contents in the muscles and these metals exhibited following pattern: muscles > gills > scales. In addition, Na revealed highest concentrations in the gills and lowest concentrations in the scales during 2012.

Comparison of average metal levels in the muscles, gills and scales of *Catla catla* during 2011 and 2012 are shown in Figure 84. An examination of the data revealed that mean levels of Co, Cr, Cu, Fe, Li, Mn, Ni, Pb, Sr and Zn were comparatively higher in the gills and showed following decreasing order in different tissues: gills > scales > muscles. However, average concentrations of K and Hg showed following pattern: muscles > gills > scales. In addition, As, Se and Na revealed highest concentrations in the gills but lowest in the scales, while mean levels of Cd and Ca exhibited following order: scales > gills > muscles. Similarly, comparison of mean metal levels in the muscles, gills and scales of

Catla catla during 2012 revealed that Ca, Cd, Co, Cr, Cu, Fe, Hg, Li, Mg, Mn, Na, Ni, Pb, Sr and Zn were found at relatively higher mean concentrations in the gills and showed following decreasing order in different tissues: gills > scales > muscles. However, As and K showed highest contributions in the muscles, followed by gills and scales. Besides, Se displayed highest concentrations in the gills but lowest in the scales.

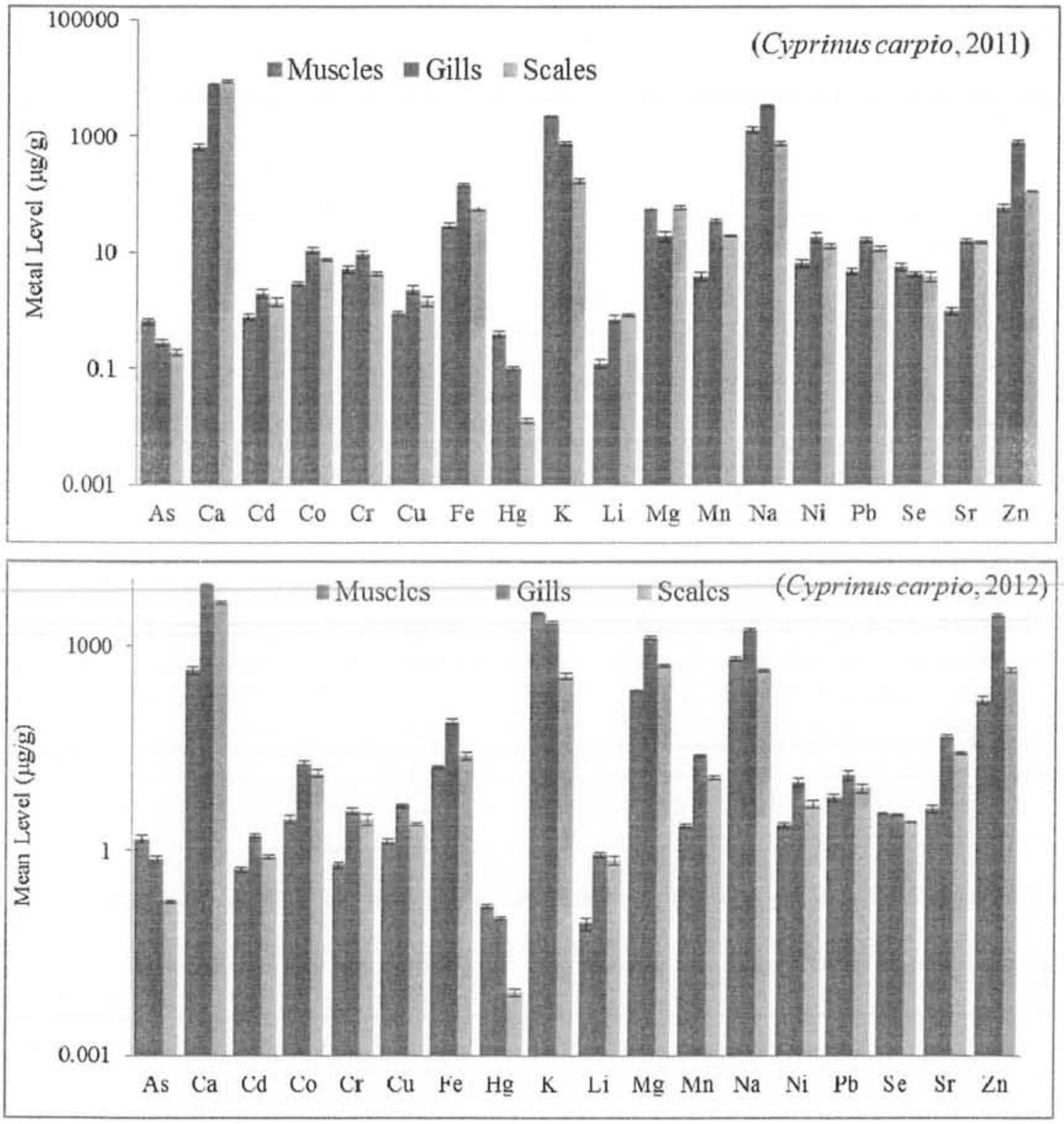

Figure 83. Comparison of average metal levels (µg/g) in the muscles, gills and scales of *Cyprinus carpio* during 2011 and 2012

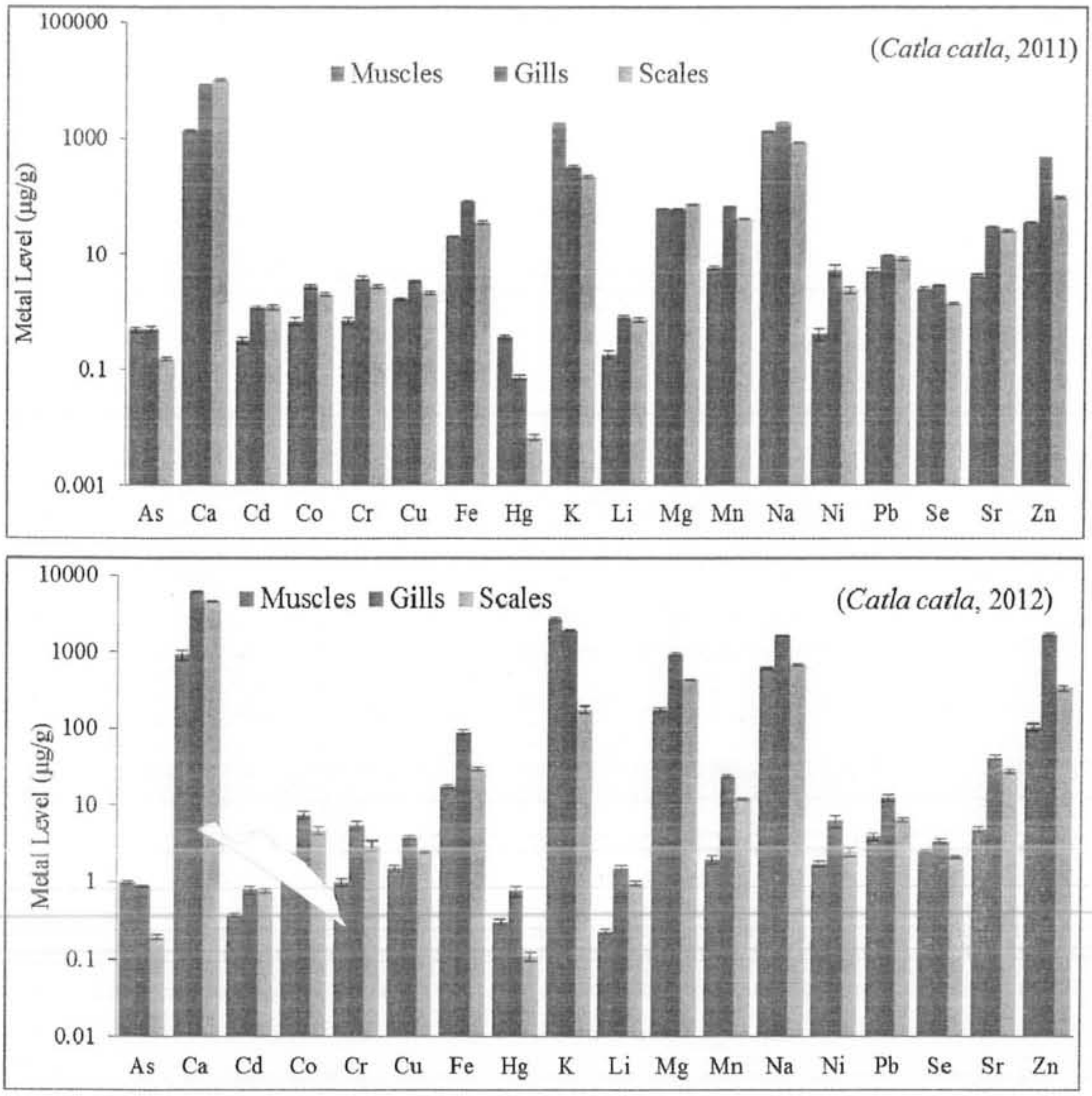

Figure 84. Comparison of average metal levels (µg/g) in the muscles, gills and scales of *Catla catla* during 2011 and 2012

Average metal levels in the muscles, gills and scales of *Hypophthalmichthys molitrix* during 2011 and 2012 were also compared as shown in Figure 85. The result demonstrated relatively higher concentrations of Co, Cr, Cu, Li, Mn, Ni, Pb, Sr and Zn in the gills, followed by scales and muscles. Nevertheless, mean concentrations of As, Hg, K, Mg and Se exhibited comparatively higher contributions in the muscles, followed by gills and lowest in the scales. Lowest average concentrations of Ca, Cd and Fe were found in the muscles and comparable levels were noted in the gills and scales. In addition, Na showed highest concentration in the gills but lowest in the scales. Comparison of metal levels in the muscles, gills and scales of *Hypophthalmichthys molitrix* during 2012 exhibited that As, Cu, Fe, Mn, Se, Sr and Zn were found at higher concentrations in the gills and showed the following decreasing trend in different tissues: gills > scales > muscles, while mean levels of Ca, Cd, Co, Cr and Ni showed following decreasing order in different tissues: scales > gills > muscles. However, among the selected metals, Cr, Li, Mg and Pb exhibited lowest concentrations in the muscles and comparable levels in the gills and scales. Moreover, Na showed highest contribution in the gills but lowest in the scales, whereas Hg and K showed highest levels in the muscles, followed by, gills and scales.

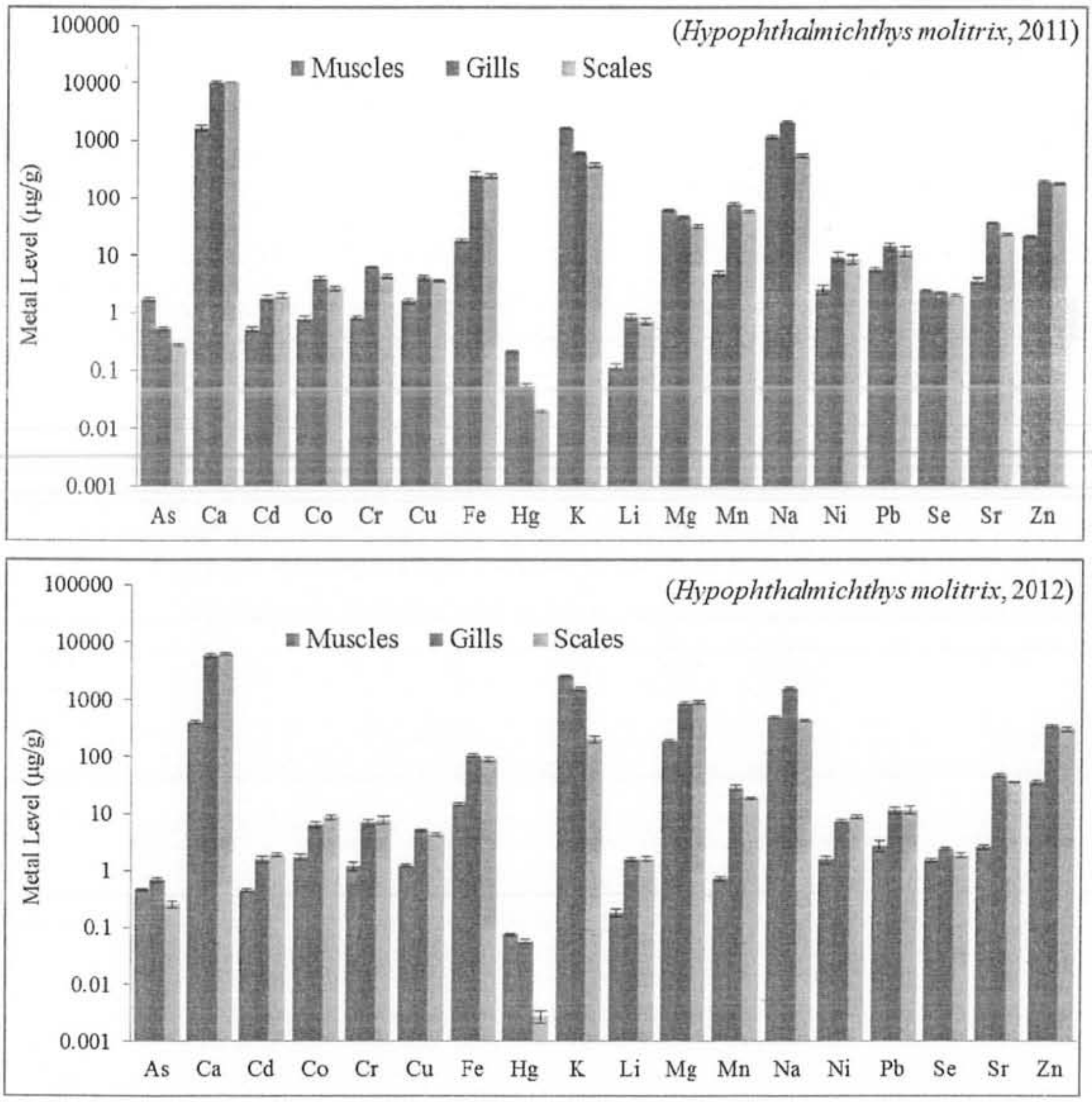

Figure 85. Comparison of average metal levels (µg/g) in the muscles, gills and scales of *Hypophthalmichthys molitrix* during 2011 and 2012

Comparison of mean metal levels in the muscles and gills of *Wallago attu* during 2011 and 2012 is shown in Figure 86. The result showed that mean levels of As, Ca, Cd, Co, Cr, Cu, Fe, Li, Mn, Na, Ni, Pb, Se, Sr and Zn in the gills were higher than the muscles, while average levels of Mg, Hg and K were considerably higher in the muscles compared with the gills during 2011. Similarly, comparison of mean metal levels in the muscles and gills of *Wallago attu* during 2012 revealed that Ca, Cd, Co, Cr, Cu, Fe, Li, Mg, Mn, Na, Ni, Pb, Sr and Zn exhibited relatively higher concentrations in the gills, while average concentrations of Hg, Se and K were noticeably higher in the muscles compared with the gills. Arsenic indicated comparable mean levels in the muscles and gills during 2012.

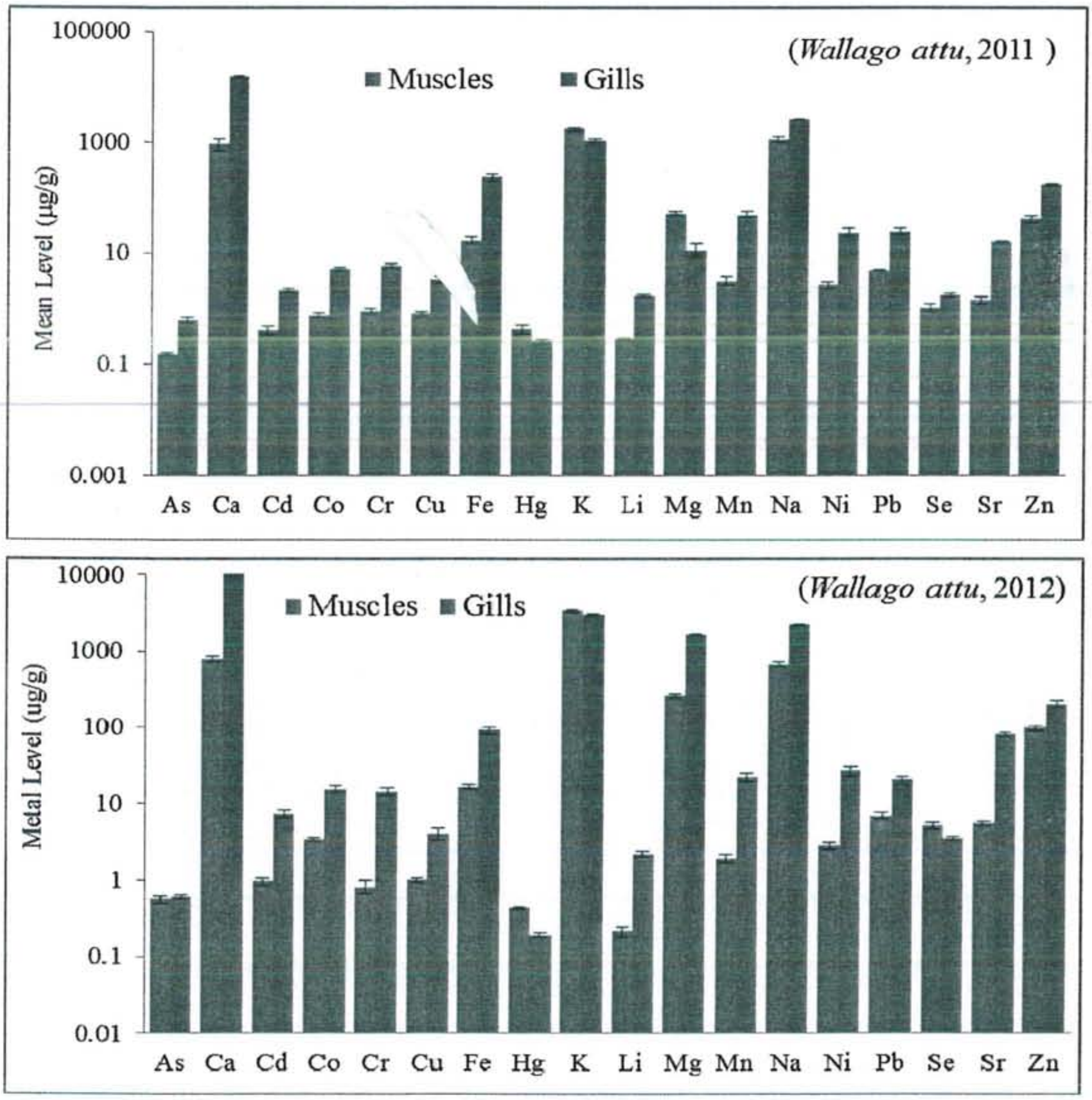

Figure 86. Comparison of average metal levels (µg/g) in the muscles and gills of *Wallago attu* during 2011 and 2012

Comparison of mean metal levels in the muscles and gills of *Sperata sarwari* during 2011 and 2012 is shown in Figure 87. Comparative evaluation of the average metal contents revealed that As, Ca, Cd, Co, Cr, Cu, Fe, Li, Mn, Na, Ni, Pb, Sr and Zn were considerably higher in the gills than the muscles, however, mean concentrations of Mg, Hg, Se and K revealed relatively higher levels in the muscles than gills during 2011. Mean metal levels were also compared in the muscles and gills of *Sperata sarwari* during 2012 and the results showed that most of the metal levels were significantly higher in the gills except Hg, Se and K, which showed comparatively higher concentration in the muscles than gills.

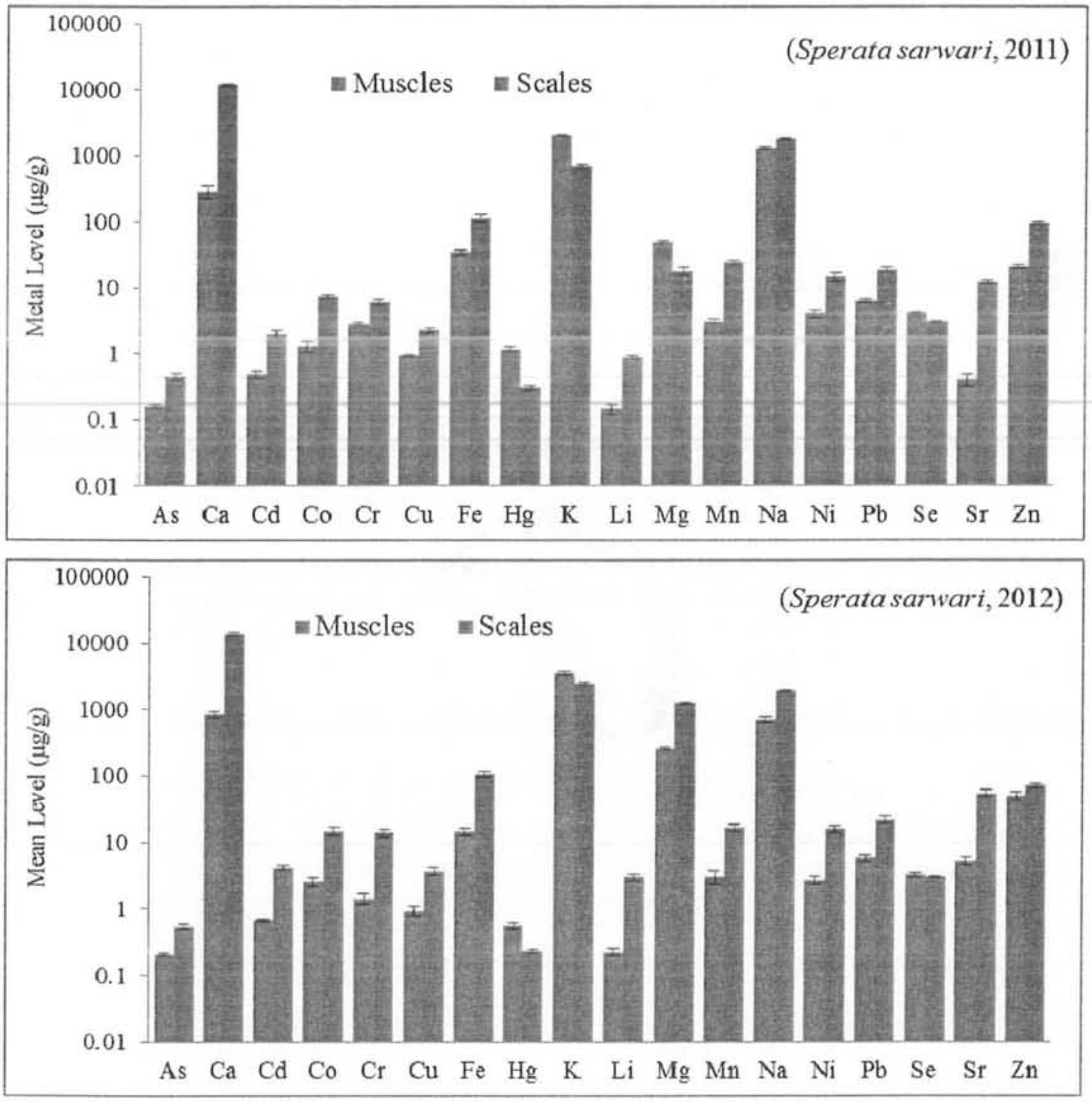

Figure 87. Comparison of average metal levels (µg/g) in the muscles and gills of *Sperata sarwari* during 2011 and 2012

In general, the gills showed elevated metal levels than other tissues of all fish species. The gills are considered as more metal accumulator than muscles because greater amounts of the metals are accumulated in these tissues which could be due to metal complexation with mucus (Demirak *et al.,* 2006). Most commonly, metal ion exchange from water is also carried out through gills and rapid diffusion of trace metals take place due to large surface areas of the gills. Therefore, the metal contents accrued in the gills were mainly concentrated from water (Qadir and Malik, 2011; Gorur *et al.,* 2012; El-Moselhy *et al.,* 2014).

Comparison of the metal concentrations in various tissues of two or more different species is very difficult because of diverse feeding habits, variations in the aquatic environment regarding the type and level of water pollution, growth rates of the species, types of tissue analysed and other related factors (Papagiannis *et al.,* 2004; Demirak *et al.,* 2006). Overall, most of the essential metals (Ca, K, Fe, Mg, Na and Zn) were dominant in the muscles of all species, while Li, Hg and As were the least constituents. However, Pb, Mn, Ni, Co and Cr showed moderate levels in the muscles. On the basis of total metal contents, *Catla catla* exhibited the highest levels, while *Sperata sarwari* showed the least contents.

3.40 Comparison of Present Metal Levels in Fish Muscles with Worldwide Reported Levels

Average levels of selected metals in the investigated fish samples collected from Mangla Lake were compared with the reported levels from other lakes around the world. Mean levels of selected metals in the edible part/muscles of *C. carpio, C. catla* and *H. molitrix* determined in the present investigation were compared with other reported levels for comparative assessment as shown in Table 128. The measured levels of As were higher than the reported levels from Nansi Lake (Zhu *et al.,* 2015), Chascomus Lake (Schenone *et al.,* 2014) and HLJ, China (Qin *et al.,* 2015). Present mean levels of Ca, K and Na were higher than those reported from Karacaoren Dam (Kalyoncu *et al.,* 2012), which exhibited relatively higher levels for Mg. Average concentrations of Cd in the muscles of the *C. carpio, C. catla* and *H. molitrix* were higher than the reported levels from Umiam Lake (Nongbri and Syiem, 2012), Damsa Dam (Mert *et al.,* 2014), Nansi Lake, Chascomus Lake, HLJ, China, Titicaca (Monroy *et al.,* 2014), Taihu Lake (Hao *et al.,* 2013), Lake Kasumigaura (Alam *et al.,* 2002) but the present levels were lower than the reported levels from Rawal Lake (Iqbal and Shah, 2014a) and Karacaoren Dam. Mean levels of Co in the present study were higher than the reported concentrations from Damsa Dam, Chascomus Lake, HLJ, China, Titicaca, Lake Kasumigaura, while the current levels were lower than those reported from Rawal Lake and Karacaoren Dam. Similarly, average levels of Cr and Cu were found to higher than those of Umiam Lake, Damsa Dam, HLJ, China, Titicaca, Taihu lake and Lake Kasumigaura, nonetheless, the metal levels were lower than the levels reported from Karacaoren Dam and Nansi Lake in the fish species. Average levels of Li were comparatively higher than the reported concentrations from Chascomus Lake and HLJ, China. Likewise, average levels of Hg were noted to be higher than the levels reported from HLJ, China, and Taihu Lake, whereas average levels of Sr were found to be lower than those of Karacaoren Dam and Chascomus Lake. Moreover, mean levels of Fe, Mn, Ni, Pb, Se and Zn in the muscles of *C. carpio, C. catla* and *H. molitrix* were noted to be higher than most of the reported levels given in Table 128, thus demonstrating significant accumulation in the water reservoir.

Table 129 shows the comparison of mean levels of selected metals in the muscles (edible part) of *W. attu* and *S. sarwari* with other reported levels worldwide. The measured concentrations of As, Ni and Pb in these species were higher than the reported levels from LN, China (Qin *et al.,* 2015), Isikli Dam & Karacaoren Dam (Kalyoncu *et al.,* 2012), Damsa Dam (Mert at al. 2014), Nansi Lake (Zhu *et al.,* 2015), Chascomus Lake (Schenone *et al.,* 2014), Titicaca (Monroy *et al.,* 2014) and Taihu lake (Hao *et al.,* 2013). Present mean levels of Ca, K and Na were comparatively higher than those of Isikli Dam and Karacaoren Dam, while Mg levels were lower than the reported levels from Isikli Dam and Karacaoren Dam. Similarly, mean levels of Cd, Co and Cr in the muscles of the *W. attu* and *S. sarwari* were higher than the levels reported from LN, China, Damsa Dam, Nansi Lake, Chascomus Lake, Titicaca and Taihu Lake but found to be lower than the reported levels from Isikli Dam and Karacaoren Dam. Current mean levels of Li and Sr were considerably higher than the reported concentration from Chascomus Lake and LN, China but lower than the reported levels from Isikli and Karacaoren Dam. The measured levels of Cu and Se were higher than the reported levels from LN, China, Damsa Dam and Chascomus Lake, however, Cu levels were found to be lower than the reported levels from Isikli Dam, Karacaoren Dam, Nansi Lake and Titicaca. Average levels of Hg were noted to be higher than the reported levels from LN, China and Taihu Lake but found to be lower levels than those reported from Titicaca.

Table 128. Average metal levels (µg/g, wet weight) in the muscles of selected fish species in comparison with the worldwide reported levels

	As	Ca	Cd	Co	Cr	Cu	Fe	Hg	K	Li	Mg	Mn	Na	Ni	Pb	Se	Sr	Zn	Reference
Mangla Lake[a]	0.644	659.9	0.796	2.946	5.249	0.907	29.13	0.391	2217	[illegible]	56.81	3.982	1323	6.607	4.779	5.696	0.985	58.89	Present study
Mangla Lake[b]	0.487	1316	0.320	0.685	0.704	1.669	19.80	0.361	[illegible]	[illegible]	60.68	5.790	1309	0.409	5.150	2.590	4.280	35.59	Present study
Mangla Lake[c]	1.719	1633	0.515	0.769	0.822	1.603	18.24	0.217	[illegible]	0.111	61.85	4.794	1127	2.595	5.592	2.403	3.557	21.62	Present study
Umiam Lake	-	-	0.009		0.01	0.015	0.58	-	-			0.009	-	0.018	0.005	1.585	-	1.16	Nongbri & Syiem, 2012
Karacaoren Dam	-	132.4	2.27	2.8	13.48	1.6	12.33	-	295	23.19	202.2	9.94	467	1.57	2.41	-	10.77	24.27	Kalyoncu *et al.*, 2012
Damsa Dam	-	-	0.1304	0.2198	0.3578	0.1094	6.48	-	-	-	-	0.101	-	0.91	0.7	0.066	-	7.046	Mert *at al.*, 2014
Nansi Lake	0.08	-	0.28			4.35	31.62	-	-	-	-	2.86	-	1.81	0.34	-	-	11.54	Zhu *et al.*, 2015
Rawal Lake	-	-	0.745	4.917	2.399	1.293	9.835	-	-	-	-	0.487	-	-	8.796	-	-	24.3	Iqbal and Shah, 2014
Chascomus Lake	0.27	-	<0.01	0.058	2.23	1.35	52.1	-	-	0.046	-	1.58	-	1.04	1.3	2.28	22.9	20.8	Schenone *et al.*, 2014
HLJ, China	0.09	-	0.014	-	0.173	0.241	7.12	0.01	-	0.013	-	0.1	-	0.165	0.181	0.23	1.15	6.62	Qin *et al.*, 2015
Titicaca	-	-	0.006	0.01		1.26	12.31	0.76	-	-	-		-	-	0.02	-	-	30.6	Monroy *et al.*, 2014
Taihu lake	0.166	-	0.011		0.4		15.9	0.073	-	-	-	1.95	-	-	0.047	-	-	24.4	Hao *et al.*, 2013
Lake Kasumigaura	0.095	-	0.009	0.005	0.067	0.249	2.729	-	-	-	-	0.307	-	0.041	0.031	0.3	-	5.433	Alam *et al.*, 2002

[a]*C. carpio;* [b]*C. catla;* [c]*H. molitrix*

Table 129. Average metal levels (µg/g, wet weight) in the muscles of selected fish species in comparison with worldwide reported levels

	As	Ca	Cd	Co	Cr	Cu	Fe	Hg	K	Li	Mg	Mn	Na	Ni	Pb	Se	Sr	Zn	Reference
ManglaLake[a]	0.153	921.5	0.406	0.756	0.870	0.794	16.83	0.425	1702	0.283	51.91	3.172	1133	2.689	4.872	1.031	1.406	41.48	Present study
ManglaLake[b]	0.166	292.1	0.504	1.315	2.781	0.939	34.58	1.186	2057	0.149	48.89	3.114	1301	4.160	6.276	4.138	0.406	20.70	Present study
LN, China	0.114		0.013	BDL	0.164	0.435	6.99	0.021	-	0.015	-	0.26	-	0.158	0.326	0.33	1.79	10.1	Qin et al. 2015
Isikli Dam		146	2.1	2.37	32.08	0.91	2.62	-	38.27	21.51	154.4	9.29	224.2	1.65	1.24	-	10.87	2.64	Kalyoncu *et al.*, 2012
Karacaoren Dam		132.4	2.27	2.8	13.48	1.6	12.33	-	295	23.19	202.2	9.94	467	1.57	2.41	-	10.77	24.27	Kalyoncu *et al.*, 2012
Damsa Dam		-	0.1766	0.1264	0.548	0.1934	74.66	-	-	-	-	4.85	-	0.876	0.939	0.142	-	430.6	Mert *at al.*, 2014
Nansi Lake	0.07	-	0.12	-	-	1.47	19.56	-	-	-	-	2.81	-	2.65	0.65	-	-	12.61	Zhu *et al.*, 2015
Nansi Lake	0.08	-	0.21	-	-	1.58	25.31	-	-	-	-	3.55	-	1.63	0.28	-	-	25.49	Zhu *et al.*, 2015
Chascomus Lake	0.13	-	<0.01	0.022	1.75	0.95	25.5	-	-	0.024	-	0.84	-	0.84	0.37	1.78	2	23.1	Schenone *et al.*, 2014
Titicaca		-	0.007	0.03	-	1.3	23.68	0.74	-	-	-		-	-	0.02	-	-	38.45	Monroy *et al.*, 2014
Taihu lake	0.12	-	0.034	-	0.518	-	16.4	0.071	-	-	-	6.92	-	-	0.127	-	-	71.2	Hao *et al.*, 2013
Taihu lake	0.112	-	0.024	-	0.358	-	27	0.071	-	-	-	2.241	-	-	0.044	-	-	34.5	Hao *et al.*, 2013

[a]*W. attu;* [b]*S. sarwari*

Mean levels of Zn in the muscles of the *W. attu* and *S. sarwari* were found to be higher than the reported levels from LN, China, Isikli Dam, Karacaoren Dam, Nansi Lake, Chascomus Lake and Taihu Lake; nevertheless, the measured levels were considerably lower than those of Damsa Dam and Taihu Lake. In addition, Fe and Mn levels in the muscles of *W. attu* and *S. sarwari* were noted to be lower than most of the reported levels from different Lakes/dams as shown in Table 129. Overall, most of the metals showed relatively higher concentration in the muscles of fish species collected from Mangla Lake compared with the other studies worldwide, thus showing considerable accumulation of the metals which may pose a serious threat to the local population and fish consumers.

3.41 Correlation Study of Selected Metals in the Muscles of Fish Species

Spearman correlation coefficients (r) for selected metal levels in the muscles (edible portion) of selected fish species were computed to investigate their inter-relationships and mutual variations. The correlation coefficient matrix for selected metal levels in the muscles of *Cyprinus carpio* is shown in Table 130. Very strong positive correlations were observed between Ni-Ca, Zn-Ca, Ni-Na, Zn-Fe, Mn-Ca, Zn-Na, Fe-Ca, Zn-Mn, Na-Ca, Cd-Ca, Mn-Cd, Zn-Cd, Zn-Ni, Fe-Cd, Sr-Cd, Na-Mn, Fe-Na, Mn-Fe, Ni-Mn, Fe-Sr, Sr-Ca, Ni-Fe, Zn-Sr, Mg-Cu, Na-Cd, and Se-Cu. Similarly, significantly strong correlations were noted between Co-As, Cr-Ca, Cr-Cd, Fe-Co, K-Cr, Li-Co, Li-Cr, Li-Cu, Mg-K, Mg-Li, Mn-Cr, Na-Cr, Na-K, Ni-Cd, Ni-K, Pb-As, Pb-Co, Pb-Cu, Pb-Li, Se-Cr, Se-Li, Se-Mg, Se-Pb, Sr-Co, Co-Cd, Sr-Na, Sr-Ni and Zn-Cr. Moreover, a number of significant interrelationships between different metals were also observed while some strong inverse correlations were found between Hg-As, Ni-Cu, Pb-Ni, Sr-Cu and Sr-Se in the muscles of *C. carpio*. These strong and significant correlations showed mutual variations of these metals which may share common sources in the water reservoir, while the inverse relationships displayed their opposing variations in the fish muscles.

Correlation coefficient matrix for selected metal levels in the muscles of *Catla catla* is shown in Table 131, wherein the significant r-values are specified at $p < 0.05$. Very strong positive correlations were observed between Cu-Fe, As-Se, Mn-Zn, Hg-Sr, Mg-Zn, K-Pb, Ca-Hg, Cd-Mn, Ca-Zn, Li-Mn, As-Fe, K-Na, Ni-Se and As-Ni. Similarly, significantly strong correlations were also noted between Cd-As, Cd-Ca, Cu-As, K-Cd, K-Co, K-Hg, Li-Co, Mg-Ca, Mn-Ca, Mn-Mg, Na-Cd, Na-Cu, Na-Fe, Na-Mn, Pb-Cd, Pb-Co, Pb-Hg, Se-Cd, Se-Fe, Se-K, Sr-Ca, Sr-Co, Sr-K, Sr-Pb, Zn-Cd, Zn-Li and Zn-Na.

Moreover, a number of significant interrelationships between the metals were also observed while some significant and strong inverse correlations were found between As-Cr, Cr-Se and Co-Ni. In addition, considerable inverse correlations were also found between Cr-Cd, Cr-Fe, Cu-Hg, Li-Ni, Cr-Pb and Sr-Cu in the muscles of *C. catla*.

Correlation coefficient matrix for selected metals in the muscles of *Hypophthalmichthys molitrix* is shown in Table 132. Very strong positive correlations were observed between Sr-Mn, Zn-Sr, Mn-Ca, Li-Hg, Zn-Mn, Fe-Cr, Zn-Mg, Mn-Cd, Ca-Zn, Sr-Ca, Cr-Mg, Pb-Na, Pb-Fe, Na-Cu, Sr-Cd, Zn-K, Cr-Pb, Zn-Na, Cd-K, Na-Mn, Co-Mg, Mn-K, Sr-K, Ca-Cd, Na-Cd, Zn-Cr, Mg-Ca, Pb-Zn, Pb-Ca, Fe-Mg, Mn-Pb, Sr-Mg, Sr-Na, Zn-Cd, Sr-Pb, Ca-Cr, Cu-Cd, Cu-K, Cu-Hg, Mn-Mg and Ni-Fe. Similarly, significantly strong correlations ($r > 0.500$) were also noted between Ca-Co, Co-Cr, Co-Fe, Ca-Fe, Ca-K, K-Mg, Li-Cu, Mg-K, Fe-Mn, Mn-Cr, Mn-Cu, Na-Cr, Na-Fe, Na-K, Na-Mg, Ni-Cr, Pb-Cd, K-Pb, Pb-Mg, Co-Se, Mg-Se, Co-Sr, Cr-Sr, Cu-Sr, Fe-Sr, Co-Zn, Cu-Zn and Fe-Zn. Several other significant relationships were also observed among the metals. On the other hand, some significant and strong inverse correlations were found between As-Pb, As-Ca, As-Mn, As-Sr and As-Na. In addition, significant inverse correlations were noted between As-Cr, As-Zn, As-Fe, As-Cd, and Ni-Li in the muscles of *H. molitrix*.

Correlation coefficient matrix for selected metals in the muscles of *Wallago attu* is shown in Table 133. Very strong positive correlations were observed between Na-Mn, Na-Fe, Sr-Cr, Mn-Cr, Na-K, Fe-Cd, Mn-Fe, Cu-Cd, Mn-K, Na-Cd, K-Fe, Na-Cr, Sr-Mg, Mn-Cd, Sr-Mn, Cr-Ca, Mn-Mg, Zn-Fe, Cr-Cd, Zn-K, Zn-Na, Mg-Cr, Zn-Cu, Na-Mg, Na-Cu, Mg-K, Sr-Na, Zn-Mn, K-Cr, K-Cu, Fe-Cr, Mn-Ca, Sr-Cd, K-Cd, Zn-Mg, Mg-Cd, Fe-Co, Sr-Ca, Mn-Cu, Zn-Cd, Se-Li, Na- Ca, Mg-Fe, Ni-Li, K-Co and Na-Co. Similarly, significantly strong correlations were noted between Ca-Cd, Ca-Co, Co-Cd, Cu-Co, Cu-Cr, Fe-Ca, Cr-Co, Hg-As, K-As, K-Ca, Mg-Ca, Mn-Co, Ni-Cu, Ni-Fe, Ni-Cd, Ni-Cr, Ni-Mg, Ni-Mn, Ni-Na, Pb-As, Pb-Hg, Pb-K, Se-Cd, Se-Cu, Se-Mg, Se-Ni, Sr-Cu, Sr-Fe, Sr-K, Sr-Ni, Zn-As, Zn-Cr, Zn-Pb, Zn-Se and Zn Sr. Moreover, a number of significant inverse correlations between the metals were observed in the muscle samples.

Correlation coefficient matrix for selected metals in the muscles of *Sperata sarwari* is shown in Table 134, wherein the significant r-values are specified at $p < 0.05$. Very strong positive correlations were observed between Se-Cu, Hg-As, Mn-Fe, Pb-Sr, Zn-As, Zn-Hg, Zn-Mn, Li-Sr, Mn-Cu, Na-Fe, Ni-Cd, Pb-Li, Zn-Cr, Fe-Cu, Mn-Cr, Mg-Ca, Ca-As, As-Cu, Sr-Co and Fe-Cd. Similarly, considerably strong correlations were noted between Cu-Cd, Fe-Cd, Fe-Cr, Hg-Ca, Hg-Cu, Mg-As, Mg-Cu, Mg-Hg, Mg-K, Mn-As, Mn-Cd, Mn-Hg, Na-Cd, Na-Cu, Na-Mn, Ni-Cu, Ni-Mg, Pb-Co, Se-As, Cd-Se, Se-Fe, Se-Hg, Se-K, Se-Mg, Se-Mn, Se-Ni, Zn-Se, Zn-Mg, Zn-Fe, Zn-Cu and Zn-Ca. Moreover, some significant and strong inverse correlations were found between Sr-Fe, Co-Se, Cu-Co, Co-Cd, Sr-Mn, Co-Mn and Co-Ni. In addition, significant inverse correlation were found between Co-As, Co-Fe, Li-Fe, Pb-Li, Co-Zn, Sr-Cu, Pb-Fe, Li-Mn, Li-Na, Mn-Pb, Pb-Na, Sr-Cd and Sr-Se in muscles. Strong positive correlations indicated common sources of the metals while inverse relationships showed their opposing variations in the fish muscles.

Table 130. Correlation coefficient (r)* matrix for selected metals in the muscles of *Cyprinus carpio* from Mangla Lake

	As	Ca	Cd	Co	Cr	Cu	Fe	Hg	K	Li	Mg	Mn	Na	Ni	Pb	Se	Sr	Zn
As	1																	
Ca	0.137	1																
Cd	0.177	0.935	1															
Co	0.657	0.460	0.671	1														
Cr	-0.252	0.519	0.501	0.300	1													
Cu	0.156	-0.465	-0.390	0.169	0.222	1												
Fe	0.438	0.949	0.904	0.629	0.401	-0.338	1											
Hg	-0.540	0.145	0.350	0.126	0.227	0.006	-0.018	1										
K	0.035	0.454	0.329	0.160	0.525	0.414	0.463	0.162	1									
Li	-0.082	0.053	0.272	0.555	0.706	0.562	0.036	0.444	0.202	1								
Mg	-0.323	-0.189	-0.143	-0.023	0.413	0.781	-0.228	0.492	0.667	0.549	1							
Mn	0.013	0.961	0.926	0.484	0.724	-0.334	0.876	0.229	0.470	0.290	-0.049	1						
Na	0.107	0.946	0.771	0.244	0.515	-0.447	0.889	-0.085	0.521	-0.112	-0.202	0.895	1					
Ni	-0.051	0.914	0.721	0.085	0.450	-0.516	0.813	0.017	0.527	-0.210	-0.163	0.850	0.977	1				
Pb	0.572	-0.324	-0.111	0.642	0.091	0.745	-0.102	-0.106	-0.003	0.634	0.290	-0.226	-0.438	-0.600	1			
Se	0.005	-0.177	-0.220	0.092	0.644	0.756	-0.145	-0.246	0.382	0.617	0.544	0.027	-0.063	-0.171	0.528	1		
Sr	0.331	0.820	0.896	0.615	0.078	-0.505	0.849	0.319	0.210	-0.045	-0.288	0.701	0.639	0.623	-0.174	-0.565	1	
Zn	0.233	0.990	0.906	0.485	0.520	-0.436	0.967	0.011	0.444	0.037	-0.240	0.948	0.960	0.905	-0.267	-0.110	0.782	1

*r-values > 0.350 or < -0.350 are significantly correlated at $p < 0.05$

Table 131. Correlation coefficient (r)* matrix for selected metals in the muscles of *Catla catla* from Mangla Lake

	As	Ca	Cd	Co	Cr	Cu	Fe	Hg	K	Li	Mg	Mn	Na	Ni	Pb	Se	Sr	Zn
As	1																	
Ca	0.068	1																
Cd	0.652	0.543	1															
Co	-0.321	0.026	0.251	1														
Cr	-0.808	0.151	-0.655	-0.143	1													
Cu	0.563	-0.372	0.054	-0.179	-0.314	1												
Fe	0.798	-0.155	0.386	-0.148	-0.560	0.933	1											
Hg	-0.169	0.842	0.390	0.342	0.085	-0.632	-0.434	1										
K	0.313	0.462	0.614	0.603	-0.453	0.133	0.334	0.593	1									
Li	-0.131	0.294	0.517	0.640	0.023	-0.039	0.031	0.171	0.300	1								
Mg	0.277	0.678	0.303	-0.482	0.283	0.207	0.287	0.194	0.030	0.162	1							
Mn	0.297	0.652	0.831	0.264	-0.173	-0.004	0.219	0.358	0.399	0.811	0.558	1						
Na	0.487	0.355	0.550	0.297	-0.321	0.623	0.738	0.174	0.785	0.375	0.417	0.515	1					
Ni	0.768	0.213	0.286	-0.760	-0.419	0.236	0.416	-0.018	-0.022	-0.584	0.430	-0.023	0.089	1				
Pb	0.136	0.362	0.534	0.677	-0.505	-0.289	-0.063	0.702	0.854	0.179	-0.332	0.215	0.356	-0.093	1			
Se	0.899	0.113	0.525	-0.228	-0.795	0.447	0.677	0.059	0.509	-0.368	0.119	0.053	0.495	0.773	0.392	1		
Sr	-0.507	0.720	0.140	0.527	0.399	-0.582	-0.519	0.892	0.516	0.356	0.148	0.311	0.188	-0.407	0.553	-0.299	1	
Zn	0.286	0.821	0.671	-0.056	0.062	0.026	0.217	0.424	0.311	0.565	0.855	0.897	0.526	0.203	0.034	0.094	0.362	1

*r-values > 0.350 or < -0.350 are significantly correlated at $p < 0.05$

Table 132. Correlation coefficient (*r*)* matrix for selected metals in the muscles of *Hypophthalmichthys molitrix* from Mangla Lake

	As	Ca	Cd	Co	Cr	Cu	Fe	Hg	K	Li	Mg	Mn	Na	Ni	Pb	Se	Sr	Zn
As	1																	
Ca	-0.833	1																
Cd	-0.705	0.821	1															
Co	-0.284	0.581	0.123	1														
Cr	-0.698	0.762	0.356	0.727	1													
Cu	-0.181	0.449	0.762	0.112	-0.084	1												
Fe	-0.639	0.584	0.285	0.518	0.932	-0.158	1											
Hg	0.178	0.196	0.289	0.474	0.003	0.759	-0.063	1										
K	-0.419	0.676	0.838	0.264	0.424	0.760	0.438	0.565	1									
Li	0.281	0.090	0.201	0.388	-0.209	0.747	-0.338	0.947	0.362	1								
Mg	-0.520	0.801	0.476	0.832	0.903	0.244	0.790	0.383	0.659	0.173	1							
Mn	-0.809	0.942	0.911	0.478	0.667	0.637	0.571	0.370	0.830	0.224	0.754	1						
Na	-0.759	0.873	0.805	0.275	0.720	0.308	0.664	-0.041	0.741	-0.219	0.714	0.833	1					
Ni	-0.261	0.013	-0.312	0.147	0.602	-0.746	0.754	-0.546	-0.175	-0.741	0.294	-0.076	0.218	1				
Pb	-0.865	0.790	0.638	0.316	0.853	0.076	0.881	-0.157	0.595	-0.386	0.714	0.779	0.899	0.526	1			
Se	0.249	-0.056	-0.423	0.675	0.463	-0.272	0.487	0.364	0.027	0.198	0.535	-0.075	-0.126	0.471	0.042	1		
Sr	-0.788	0.908	0.858	0.533	0.690	0.626	0.614	0.435	0.823	0.271	0.779	0.989	0.774	-0.036	0.767	0.029	1	
Zn	-0.683	0.907	0.771	0.638	0.802	0.518	0.720	0.430	0.856	0.223	0.919	0.942	0.840	0.099	0.800	0.228	0.949	1

**r*-values > 0.350 or < -0.350 are significantly correlated at $p < 0.05$

Table 133. Correlation coefficient (*r*)* matrix for selected metals in the muscles of *Wallago attu* from Mangla Lake

	As	Ca	Cd	Co	Cr	Cu	Fe	Hg	K	Li	Mg	Mn	Na	Ni	Pb	Se	Sr	Zn
As	1																	
Ca	0.310	1																
Cd	0.102	0.635	1															
Co	0.333	0.667	0.731	1														
Cr	0.203	0.895	0.884	0.661	1													
Cu	0.252	0.384	0.924	0.715	0.683	1												
Fe	0.404	0.627	0.942	0.799	0.822	0.945	1											
Hg	0.700	-0.446	-0.344	-0.251	-0.437	-0.033	-0.065	1										
K	0.632	0.705	0.816	0.753	0.826	0.825	0.922	0.079	1									
Li	-0.339	-0.266	0.386	-0.034	0.137	0.487	0.219	-0.099	0.159	1								
Mg	0.323	0.641	0.805	0.414	0.872	0.718	0.769	-0.109	0.847	0.431	1							
Mn	0.393	0.822	0.911	0.692	0.960	0.797	0.927	-0.198	0.923	0.125	0.891	1						
Na	0.448	0.770	0.923	0.750	0.920	0.858	0.967	-0.118	0.955	0.148	0.865	0.989	1					
Ni	-0.425	0.222	0.749	0.186	0.600	0.645	0.519	-0.497	0.355	0.769	0.673	0.539	0.508	1				
Pb	0.743	-0.087	0.185	0.403	0.003	0.498	0.431	0.711	0.559	0.199	0.236	0.215	0.335	-0.174	1			
Se	-0.012	-0.206	0.534	-0.018	0.237	0.682	0.492	0.226	0.365	0.778	0.556	0.366	0.402	0.721	0.330	1		
Sr	0.086	0.798	0.818	0.426	0.958	0.595	0.705	-0.443	0.718	0.258	0.915	0.896	0.831	0.709	-0.128	0.348	1	
Zn	0.562	0.401	0.780	0.485	0.658	0.867	0.891	0.293	0.877	0.304	0.812	0.831	0.873	0.467	0.561	0.702	0.626	1

**r*-values > 0.350 or < -0.350 are significantly correlated at $p < 0.05$

Table 134. Correlation coefficient (*r*)* matrix for selected metals in the muscles of *Sperata sarwari* from Mangla Lake

	As	Ca	Cd	Co	Cr	Cu	Fe	Hg	K	Li	Mg	Mn	Na	Ni	Pb	Se	Sr	Zn
As	1																	
Ca	0.771	1																
Cd	0.050	-0.129	1															
Co	-0.511	-0.265	-0.772	1														
Cr	0.446	0.360	0.462	-0.377	1													
Cu	0.763	0.319	0.596	-0.824	0.431	1												
Fe	0.463	-0.006	0.732	-0.742	0.710	0.807	1											
Hg	0.958	0.691	-0.090	-0.387	0.493	0.652	0.469	1										
K	0.375	0.222	0.011	-0.001	-0.186	0.422	-0.042	0.191	1									
Li	-0.306	0.270	-0.065	0.333	-0.149	-0.446	-0.611	-0.466	0.242	1								
Mg	0.714	0.781	0.340	-0.449	0.486	0.614	0.291	0.527	0.581	0.349	1							
Mn	0.714	0.331	0.555	-0.753	0.784	0.833	0.930	0.731	-0.047	-0.576	0.458	1						
Na	0.163	-0.430	0.570	-0.384	0.396	0.626	0.824	0.187	0.187	-0.632	0.012	0.612	1					
Ni	0.256	0.355	0.823	-0.750	0.387	0.547	0.427	0.030	0.196	0.339	0.697	0.412	0.106	1				
Pb	-0.043	0.402	-0.480	0.615	-0.152	-0.428	-0.683	-0.126	0.461	0.820	0.372	-0.555	-0.588	-0.063	1			
Se	0.706	0.315	0.566	-0.830	0.208	0.964	0.655	0.546	0.514	-0.340	0.608	0.674	0.499	0.590	-0.371	1		
Sr	-0.365	0.182	-0.540	0.754	-0.280	-0.724	-0.837	-0.401	0.165	0.851	0.060	-0.758	-0.716	-0.190	0.928	-0.657	1	
Zn	0.880	0.710	0.266	-0.530	0.816	0.702	0.655	0.878	0.118	-0.260	0.718	0.867	0.276	0.376	-0.100	0.550	-0.369	1

**r*-values > 0.350 or < -0.350 are significantly correlated at $p < 0.05$

3.42 Multivariate Analyses of Selected Metals in the Fish Species

Trace metals in the sediments and fish may threaten the existence and survival of aquatic biota and human health; therefore, it is considered imperative to investigate and regulate the pollution sources. One of the most important aspects of the present study was the identification and apportionment of sources of metal pollutants in the aquatic system. For this purpose, PCA and CA were employed to assess the possible pollution sources in the fish species. The PC loadings of selected metals in the fish samples are shown in Table 135, where five PCs were extracted with eigenvalues greater than one, together explaining more than 81% of cumulative variance of the data. The dendrogram of CA related to the metal levels in fish samples is shown in Figure 88, which exhibited four significant clusters of the metals. In case of PCA, first PC showed highest loadings for Cu, Fe, K, Mg, Na and Zn; PC 2 exhibited highest loadings for Ca, Mn and Sr; PC 3 revealed highest loadings for Co, Cr and Se; PC 4 demonstrated highest loadings for Cd, Li and Ni, while last PC exhibited highest loadings for As, Hg and Pb.

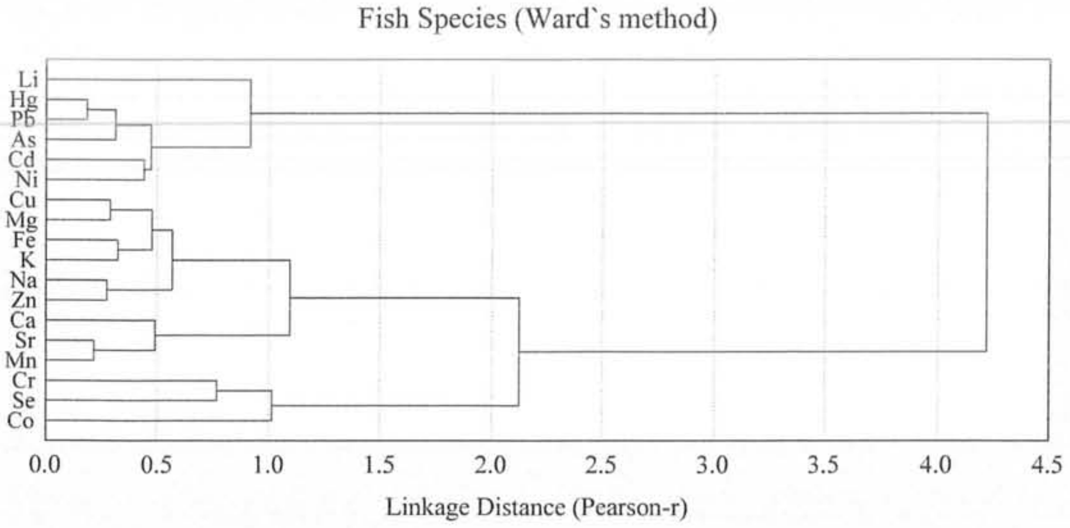

Figure 88. Cluster analysis of selected metal levels in the muscles of fish species

Similarly, in CA, first cluster was composed of Hg–Pb–As–Cd–Ni–Li which showed that these metals were mostly contributed by the anthropogenic activities including industrial emissions, municipal waste, urban runoffs, atmospheric deposition, fuel combustion and agricultural runoffs. Likewise, second cluster was consisted of Cu–Mg–Fe–K–Na–Zn while third cluster was comprised of Ca–Sr–Mn. The metals in these two clusters were mainly contributed by natural inputs/lithogenic sources. Last cluster contained Cr–Se–Co, which were mostly contributed by mixed sources (anthropogenic as well as lithogenic contributions). Overall, CA results were in very good agreement with PCA findings and both multivariate methods revealed significant contamination in the water reservoir.

Table 135. Principle component analysis of selected metal levels in the muscles of fish species

	PC 1	PC 2	PC 3	PC 4	PC 5
Eigenvalue	5.714	4.337	1.776	1.584	1.323
Total Variance (%)	31.74	24.10	9.869	8.799	7.347
Cumulative Eigenvalue (%)	5.714	10.05	11.83	13.41	14.73
Cumulative Variance (%)	31.74	55.84	65.71	74.51	81.86
As	-0.146	0.272	0.080	-0.202	0.689
Ca	0.176	0.843	-0.203	-0.034	-0.220
Cd	0.056	0.152	0.321	0.806	-0.007
Co	0.254	-0.186	0.736	-0.127	-0.182
Cr	0.259	-0.225	0.792	0.062	0.146
Cu	0.836	-0.201	-0.059	0.226	0.008
Fe	0.877	-0.141	0.283	0.235	0.162
Hg	0.002	-0.323	0.108	0.003	0.872
K	0.825	0.052	-0.045	0.327	0.366
Li	-0.083	0.038	-0.032	0.898	-0.072
Mg	0.769	0.065	0.248	0.002	-0.106
Mn	0.314	0.805	-0.047	-0.071	0.062
Na	0.866	0.290	-0.041	0.028	0.231
Ni	0.177	-0.293	0.293	0.769	-0.010
Pb	-0.239	0.298	0.162	-0.241	0.630
Se	0.141	-0.062	0.837	0.257	0.158
Sr	-0.081	0.893	-0.242	-0.065	-0.195
Zn	0.871	0.060	0.146	-0.224	-0.191

Generally, the metals build-up in sediments at much higher levels than those in water, whereas the metal contents in fish tissues were intermediate between the sediment and water. Most of the metals might be transferred through the food chain via following route: sediment/water–biota–human. In present study, most of the metals showed relatively higher levels in the sediment, followed by fish and least levels were observed in the water e.g., Cd levels were observed in water, sediment and *Cyprinus carpio* muscles as 0.033 mg/L, 1.328 mg/kg and 0.796 µg/g respectively. Similar results supported the above hypothesis that the sediment was the major sink for metal pollutants than water and might play an important role in the metals' uptake by fish (Gao, 2001; Yi *et al.,* 2011). Therefore, control of the pollution sources in the aquatic system must be ensured for protection of the aquatic biota and human health.

3.43 Potential Health Risk Assessment for Selected Metals in Fish Species

3.43.1 Potential Health Risk Assessment for *Cyprinus carpio*

Fish is an essential part of human diet as it provides proteins, certain minerals, and vitamins. Therefore, it was vital to evaluate the health risks associated with the consumption of the fish species. As reported in literature, carcinogenic and non-carcinogenic health risks can be associated with fish consumption mainly due to the environmental contaminants, which may be bioaccumulated and biomagnified in the fish tissues. Generally, fish consumption is the main source of human exposure to the pollutants (Zhao *et al.,* 2012b; Iqbal and Shah, 2014a). *Cyprinus carpio* is sediment dwelling and omnivorous in nature. In the present study, provisional tolerable weekly intake (PTWI) (mg/week/70 kg, body weight), provisional tolerable daily intake (PTDI) (mg/day/70 kg, body weight), estimated weekly intake (EWI) (mg/week/70 kg, body weight) and estimated daily intake (EDI) (mg/day/70 kg, body weight) of selected metals in the muscles of *Cyprinus carpio* from Mangla Lake were computed as given in Table 136. The EWI and EDI values for As, Cd, Cr, Hg, Ni and Pb were noted to be higher than the recommended PTWI and PTDI values, while rest of the metals were well below the recommended PTWI and PTDI levels. Since, As, Pb, Cd, Cr, Ni and Hg levels in the fish muscles were relatively higher, so careful attention should be paid to the fish consumption from Mangla Lake, Pakistan.

Similarly, average metal levels (Table 115) in the *Cyprinus carpio* muscle tissues were compared with the tolerable and permissible levels (Appendix N) to evaluate the potential health risks for humans. In the present study, the muscles showed significantly elevated concentrations of K, Na, Mg and Ca, which are considered essential for various physiological functions (Barrento *et al.,* 2008). Similarly average levels of Cd, Mn, Fe, Zn, Se and Pb were observed to be higher than the international permissible limits in the muscles (USEPA, 1983; MAFF, 2000; WHO, 1996; FAO, 1983; EC Regulation, 2006; Ministry of Health and Social Care and Republic of Croatia, 2005; Australia New Zealand Food Authority, 1998; Machova *et al.*, 1991). However, mean concentrations of As were less than the MAC for Croatia (2.0 mg/kg, Ministry of Health and Social Care and Republic of Croatia, 2005). Likewise, average levels of Hg were lower than the international permissible limits in the muscles (Appendix N).

Table 136. Description of health risk assessment for selected metals in the muscles of *Cyprinus carpio* from Mangle Lake

	PTWI	*PTDI*	*EWI*	*EDI*	*RfD/RDA (μg/g/day)*	Exp_{ing}	*MOE*	HQ_{ing}	*TCR*
As	1.05	0.15	2.059	0.294	0.0003	0.002	14.01	7.351	3.31E-03
Ca	6953	993.3	2545	363.6	13.33	2.260	0.390	0.170	-
Cd	0.49	0.07	2.877	0.411	0.001	0.003	5.872	2.728	1.64E-03
Co	29.4	4.2	8.232	1.176	0.06	0.010	0.280	0.168	-
Cr	1.47	0.21	14.56	2.080	0.003	0.018	9.906	5.993	8.99E-03
Cu	245	35	2.290	0.327	0.04	0.003	0.117	0.078	-
Fe	392	56	94.06	13.44	0.7	0.100	0.274	0.143	-
Hg	0.35	0.05	1.320	0.189	0.0003	0.001	8.981	4.464	-
K	38381	5483	4785	683.6	78	7.592	0.125	0.097	-
Li	9.8	1.4	0.456	0.065	0.002	0.000	0.466	0.205	-
Mg	2858	408.3	130.0	18.57	5.83	0.195	0.046	0.033	-
Mn	68.6	9.8	15.37	2.196	0.14	0.014	0.224	0.097	-
Na	26950	3850	5414	773.4	55	4.530	0.201	0.082	-
Ni	2.45	0.35	27.00	3.857	0.02	0.023	2.755	1.131	3.85E-02
Pb	1.75	0.25	14.58	2.083	0.004	0.016	7.438	4.091	1.39E-04
Se	196	28	21.99	3.141	0.005	0.020	8.974	3.902	-
Sr	294	42	3.295	0.471	0.6	0.003	0.011	0.006	-
Zn	490	70	238.1	34.01	0.3	0.202	1.620	0.672	-
				HI				31.41	

Potential non-carcinogenic health risk was evaluated in terms of MOE, HQ and HI as shown in Table 136, whereas the related parameters used for calculation of health risk assessment are provided in Appendix L. Generally, MOE > 1 indicated chronic non-carcinogenic health effects to human for fish consumption. The MOE values for As, Cd, Cr, Hg, Ni, Pb, Se and Zn were significantly higher than safe limit, however, remaining metals revealed the safe levels. Higher MOE values for As, Pb, Hg, Cd, Ni, and Cr in the muscles specified a higher dose exposure than the safe daily dose for chronic non-carcinogenic effects to humans (Watanabe *et al.,* 2003; Costa and Hartz, 2009). The dominant average levels of Exp_{ing} were observed for K (7.592), Na (4.530), Ca (2.260), Zn (0.202), Mg (0.195) and Fe (0.100) while least values were noted for Li (0.001), Hg (0.001), As (0.002), Cd = Cu = Sr (0.003). The health protection standard for non-carcinogenic lifetime risks for HQ_{ing} and HI_{ing} is 1 (unity) (USEPA, 2006). The measured HQ_{ing} values for As, Cr, Ni, Pb, Cd, Se and Hg were much higher than unity, which revealed that contaminated fish consumption may cause non-carcinogenic risks to the consumers. The HI_{ing} value was noted as 31.41 manifesting lifetime non-carcinogenic health risks to the consumers. The carcinogenic risk for As, Cd, Cr, Ni and Pb related with fish consumption by humans was also evaluated. Comparatively higher value of target cancer risk (TCR) were noted for As (3.31E-03), Cd (1.64E-03), Cr (8.99E-03), Ni (3.85E-02) and Pb (1.39E-04) than the acceptable risk limit of cancer (1×10^{-6}) (USEPA, 2006), which revealed that the populations consuming *Cyprinus carpio* from Mangla Lake on continuous basis were exposed to As, Cd, Cr, Ni and Pb contamination with a lifetime carcinogenic risk.

3.43.2 Potential Health Risk Assessment for *Catla catla*

Carcinogenic and non-carcinogenic risks associated with the consumption of *Catla catla* were also evaluated. The statistical summary related to the health risk assessment for selected metals in the muscles of *Catla catla* from Mangla Lake is shown in Table 137. Average values of EWI and EDI for As, Cd, Cr, Hg and Pb were noted to be higher than the recommended PTWI and PTDI values, while the remaining metals were within the recommended limits. Average metal levels (Table 118) in the muscles *Catla catla* showed significantly elevated contributions of essential metals (K, Na, Mg Ca and Zn). Similarly, mean levels of Pb was observed to be higher than the international permissible limits (USEPA, 1983; MAFF, 2000; WHO, 1996; FAO, 1983; EC Regulation, 2006; Ministry of Health and Social Care and Republic of Croatia, 2005; Machova *et al.,* 1991), while mean levels of Cd was higher than most of the recommended levels (MAFF, EC Regulation, 2006; Ministry of Health and Social Care and Republic of Croatia, Machova *et al.,* 1991). On the other hand, mean concentrations of Hg and As were lower than the international permissible limits. The MOE values for As, Cd, Cr, Hg, Pb, and Se were significantly higher than safe limit, while the remaining metals revealed the safe levels. Relatively higher average levels of Exp_{ing} were observed for K (6.055), Ca (4.506), Na (4.483), Mg (0.208), Zn (0.122), and Fe (0.068) while least values were noted for As = Co = Cr (0.002) and Cd = Hg = Li = Ni (0.001). The measured HQ_{ing} values for As, Cd, Hg, Pb, and Se were higher than unity, which revealed that consumption of contaminated *Catla catla* may cause non-carcinogenic risks. The HI_{ing} value was noted as 19.54, thus exhibiting lifetime non-carcinogenic health risks to the local population.

Table 137. Description of health risk assessment for selected metals in the muscles of *Catla catla* from Mangle Lake

	PTWI	*PTDI*	*EWI*	*EDI*	*RfD/RDA (µg/g/day)*	Exp_{ing}	*MOE*	HQ_{ing}	*TCR*
As	1.05	0.15	1.637	0.234	0.0003	0.002	11.14	5.560	2.50E-03
Ca	6953	993.3	2847	406.7	13.33	4.506	0.436	0.338	-
Cd	0.49	0.07	0.861	0.123	0.001	0.001	1.758	1.096	6.57E-04
Co	29.4	4.2	2.373	0.339	0.06	0.002	0.081	0.039	-
Cr	1.47	0.21	2.132	0.305	0.003	0.002	1.450	0.803	1.21E-03
Cu	245	35	3.745	0.535	0.04	0.006	0.191	0.143	-
Fe	392	56	45.77	6.538	0.7	0.068	0.133	0.097	-
Hg	0.35	0.05	0.834	0.119	0.0003	0.001	5.675	4.122	-
K	38381	5483	3593	513.3	78	6.055	0.094	0.078	-
Li	9.8	1.4	0.713	0.102	0.002	0.001	0.727	0.319	-
Mg	2858	408.3	122.3	17.47	5.83	0.208	0.043	0.036	-
Mn	68.6	9.8	15.56	2.223	0.14	0.020	0.227	0.142	-
Na	26950	3850	2592	370.3	55	4.483	0.096	0.082	-
Ni	2.45	0.35	1.618	0.231	0.02	0.001	0.165	0.070	2.38E-03
Pb	1.75	0.25	13.71	1.959	0.004	0.018	6.997	4.409	1.50E-04
Se	196	28	6.557	0.937	0.005	0.009	2.676	1.774	-
Sr	294	42	9.043	1.292	0.6	0.015	0.031	0.024	-
Zn	490	70	78.84	11.26	0.3	0.122	0.536	0.406	-
				HI				31.41	

The carcinogenic risk for As, Cd, Cr, Ni and Pb related with fish consumption was also evaluated. Significantly higher values of target cancer risk (TCR) for As (2.50E-03), Cd (6.57E-04), Cr (1.21E-03), Ni (2.38E-03) and Pb (1.50E-04) than the acceptable risk limit (1×10^{-6}) (USEPA, 2006) exhibited that the consumption of *Catla catla* from Mangla Lake on continuous basis was associated with lifetime carcinogenic risk.

3.43.3 Potential Health Risk Assessment for *Hypophthalmichthys molitrix*

Statistical summary of carcinogenic and non-carcinogenic risks associated with the metal levels in the muscles of *Hypophthalmichthys molitrix* is shown in Table 138. In this case, mean values of EWI and EDI for As, Cd, Cr, Hg, Ni and Pb were observed to be higher than the recommended PTWI and PTDI values while rest of the metals were found to be within the recommended levels. The muscle samples of *H. molitrix* showed significantly elevated concentrations of essential metals (K, Na, Mg, and Ca), while mean level of Pb was also observed to be higher than the international permissible limits (USEPA, 1983; MAFF, 2000; WHO, 1996; FAO, 1983; EC Regulation, 2006; Ministry of Health and Social Care and Republic of Croatia, 2005; Machova *et al.,* 1991). Similarly mean contents of Cd were higher than most of the permissible levels (MAFF/FAO, EC Regulation, 2006; Ministry of Health and Social Care and Republic of Croatia, 2005; Machova *et al.*, 1991), while mean level of Hg was lower than the international permissible limits. Average level of Se was higher than recommended level of Australia & New Zealand Food Authority.

Moreover, potential non-carcinogenic health risk was assessed by computing MOE, HQ and HI (Table 138). The MOE values for As, Cd, Cr, Hg, Pb, Ni and Se were significantly higher than the safe limit unity, while the remaining metals revealed MOE values less than unity during the study period. Nevertheless, comparatively higher average levels of Exp_{ing} were observed for K (5.626), Ca (5.592), Na (3.861), Mg (0.212), Zn (0.074) and Fe (0.062) while least values of Exp_{ing} were noted for Cr = Co (0.003), Cd (0.002), Hg (0.001) and Li (0.000). The measured HQ_{ing} values for As, Cd, Hg, Pb and Se were higher than unity, which revealed that consumption of contaminated fish specie (*H. molitrix*) with As, Cd, Cr, Hg, Pb and Se may cause non-carcinogenic risks. The HI_{ing} value was found at 33.12, hence revealing lifetime non-carcinogenic health risks to the consumers. The carcinogenic risk for As, Cd, Cr, Ni and Pb levels in the fish muscles were also determined. Relatively higher value of target cancer risk (TCR) for As (8.83E-03), Cd (1.06E-03), Cr (1.41E-03), Ni (1.51E-02) and Pb (1.63E-04) than the acceptable cancer risk limit (1×10^{-6}) (USEPA, 2006) showed that the consumption of *Hypophthalmichthys molitrix* from Mangla Lake was associated with lifetime carcinogenic risk.

Table 138. Description of health risk assessment for selected metals in the muscles of *Hypophthalmichthys molitrix* from Mangle Lake

	PTWI	*PTDI*	*EWI*	*EDI*	*RfD/RDA* *(µg/g/day)*	Exp_{ing}	*MOE*	HQ_{ing}	*TCR*
As	1.05	0.15	4.125	0.589	0.0003	0.006	28.06	19.62	8.83E-03
Ca	6953	993.3	5432	776.0	13.33	5.592	0.832	0.419	-
Cd	0.49	0.07	1.632	0.233	0.001	0.002	3.331	1.763	1.06E-03
Co	29.4	4.2	2.411	0.344	0.06	0.003	0.082	0.044	-
Cr	1.47	0.21	2.037	0.291	0.003	0.003	1.386	0.938	1.41E-03
Cu	245	35	4.296	0.614	0.04	0.005	0.219	0.137	-
Fe	392	56	46.88	6.697	0.7	0.062	0.137	0.089	-
Hg	0.35	0.05	0.494	0.071	0.0003	0.001	3.363	2.472	-
K	38381	5483	3497	499.6	78	5.626	0.091	0.072	-
Li	9.8	1.4	0.333	0.048	0.002	0.000	0.340	0.190	-
Mg	2858	408.3	127.9	18.27	5.83	0.212	0.045	0.036	-
Mn	68.6	9.8	14.93	2.133	0.14	0.016	0.218	0.117	-
Na	26950	3850	2597	371.0	55	3.861	0.096	0.070	-
Ni	2.45	0.35	10.42	1.489	0.02	0.009	1.063	0.444	1.51E-02
Pb	1.75	0.25	14.44	2.062	0.004	0.019	7.366	4.787	1.63E-04
Se	196	28	5.420	0.774	0.005	0.008	2.212	1.646	-
Sr	294	42	11.22	1.603	0.6	0.012	0.038	0.020	-
Zn	490	70	48.90	6.986	0.3	0.074	0.333	0.247	-
				HI				33.12	

3.43.4 Potential Public Health Risk Assessment for *Wallago attu*

Summarized results for health risk assessment related to the metal levels in the muscles of *Wallago attu* are shown in Table 139. Average values of EWI and EDI for Cd, Cr, Hg, Ni and Pb were noted to be higher than the recommended PTWI and PTDI values, while the remaining metals were within the recommended PTWI and PTDI levels. The metal contents in the muscles showed significantly elevated concentrations of K, Na, Mg Ca and Zn. Similarly, mean levels of Pb and Cd were observed to be higher than most of the international permissible limits (USEPA, 1983; MAFF, 2000; WHO, 1996; FAO, 1983; EC Regulation, 2006; Ministry of Health and Social Care and Republic of Croatia, 2005; Machova *et al.*, 1991), while average levels of Se were higher than the Australia & New Zealand Food Authority (1998). Mean levels of Mn and Fe were found to be higher than the WHO (1996) limits, while Zn level was higher than the FAO (1983) limit. However, mean concentrations of Hg and As were lower than the international permissible limits in the muscles.

Table 139. Description of health risk assessment for selected metals in the muscles of *Wallago attu* from Mangle Lake

	PTWI	*PTDI*	*EWI*	*EDI*	*RfD/RDA* (*μg/g/day*)	Exp_{ing}	*MOE*	HQ_{ing}	*TCR*
As	1.05	0.15	0.369	0.053	0.0003	0.001	2.513	1.749	7.87E-04
Ca	6953	993.3	4198	599.7	13.33	3.156	0.643	0.237	-
Cd	0.49	0.07	1.271	0.182	0.001	0.001	2.594	1.390	8.34E-04
Co	29.4	4.2	2.034	0.291	0.06	0.003	0.069	0.043	-
Cr	1.47	0.21	2.651	0.379	0.003	0.003	1.804	0.993	1.49E-03
Cu	245	35	2.085	0.298	0.04	0.003	0.106	0.068	-
Fe	392	56	56.10	8.014	0.7	0.058	0.164	0.082	-
Hg	0.35	0.05	1.665	0.238	0.0003	0.001	11.33	4.849	-
K	38381	5483	3999	571.3	78	5.828	0.105	0.075	-
Li	9.8	1.4	0.633	0.090	0.002	0.001	0.646	0.485	-
Mg	2858	408.3	111.3	15.89	5.83	0.178	0.039	0.030	-
Mn	68.6	9.8	10.93	1.562	0.14	0.011	0.159	0.078	-
Na	26950	3850	3494	499.1	55	3.879	0.130	0.071	-
Ni	2.45	0.35	9.467	1.352	0.02	0.009	0.966	0.460	1.57E-02
Pb	1.75	0.25	10.17	1.453	0.004	0.017	5.191	4.171	1.42E-04
Se	196	28	4.130	0.590	0.005	0.004	1.686	0.706	-
Sr	294	42	3.995	0.571	0.6	0.005	0.014	0.008	-
Zn	490	70	120.8	17.25	0.3	0.142	0.821	0.473	-
				HI				15.97	

Potential non-carcinogenic health risk was also evaluated in terms of MOE, HQ and HI (Table 139). The MOE values for As, Cd, Cr, Hg, Pb, and Se were significantly higher than the safe limit (1), while the remaining metals revealed MOE levels lower than unity. Similarly, dominant average levels of Exp_{ing} were observed for K (5.828), Na (3.879), Ca (3.156), Zn (0.142), Mg (0.178) and Fe (0.058) while least values of Exp_{ing} were noted for Li = Hg = Cd = As (0.001), Co = Cr = Cu (0.003). The measured HQ_{ing} values for As, Cd, Hg and Pb were higher than unity while Cr was near to unity. The health protection standard for HQ_{ing} and HI_{ing} is 1 (unity) (USEPA, 2006), therefore, HQ_{ing} result revealed that the fish muscles were contaminated with As, Cd, Cr, Hg and Pb which may cause non-carcinogenic risks. The HI_{ing} value was found at 15.97, which revealed lifetime non-carcinogenic health risks to the consumers. In case of carcinogenic risk, significantly higher values of target cancer risk (*TCR*) were observed for As (7.87E-04), Cd (8.34E-04), Cr (1.49E-03), Ni (1.57E-02) and Pb (1.42E-04) than the acceptable cancer risk limit (1×10^{-6}) (USEPA, 2006); consequently the consumption of *Wallago attu* from Mangla Lake was associated with lifetime carcinogenic risk.

3.43.5 Potential Public Health Risk Assessment for *Sperata sarwari*

Carcinogenic and non-carcinogenic risks associated with the consumption *Sperata sarwari* were assessed as shown in Table 140. Average values of EWI and EDI for Cd, Cr, Hg, Ni and Pb were observed to be higher than the recommended PTWI and PTDI values; therefore, careful consideration should be given to the fish consumption. Moreover, significantly elevated concentrations of essential metals (K, Na, Mg, Ca and Fe) in the muscles were observed, while mean levels of Pb and Cd were also higher than most of the international permissible limits (USEPA, 1983; MAFF, 2000; WHO, 1996; FAO, 1983; EC Regulation, 2006; Ministry of Health and Social Care and Republic of Croatia, 2005; Machova *et al.,* 1991). Similarly, Mn and Fe levels were higher than WHO/FAO limits. Mean level of Hg was higher than some international permissible limits (FAO 1983; EC Regulation, 2006; Ministry of Health and Social Care and Republic of Croatia, 2005; Machova *et al.,* 1991), whereas mean concentration of As was lower than the international permissible limits. On the other hand, MOE values for As, Cd, Cr, Hg, Ni, Pb, and Se were significantly higher than safe limit, while the remaining metals were within the safe limit. Elevated values of MOE for As, Cd, Cr, Hg, Pb, Se, Ni and Zn in the muscles revealed higher exposure which may result in chronic non-carcinogenic effects (Watanabe *et al.,* 2003; Costa and Hartz, 2009). In case of Exp_{ing}, dominant average levels were found for K (7.044), Na (4.456), Ca (1.000), Mg (0.167) and Fe (0.118), while least values were noted for Cu (0.003), Cd (0.002) and As = Li = Sr (0.001). The measured HQ_{ing} values for As, Cd, Cr, Hg, Pb, and Se were higher than unity, which revealed that consumption of contaminated fish with As, Cd, Cr, Hg, Pb and Se may cause non-carcinogenic risks. The HI_{ing} value was noted at 30.42, this demonstrating lifetime non-carcinogenic health risks. The carcinogenic risk for As, Cd, Cr, Ni and Pb related to the fish consumption was also determined. The calculated target cancer risks (TCR) for As (8.50E-04), Cd (1.04E-03), Cr

(4.76E-03), Ni (2.42E-02) and Pb (1.83E-04) were considerably higher than the acceptable risk limit (1×10^{-6}) (USEPA, 2006), which showed that the consumers were exposed to these metals with a significant probability of lifetime carcinogenic risk.

Table 140. Description of health risk assessment for selected metals in the muscles of *Sperata sarwari* from Mangle Lake

	PTWI	*PTDI*	*EWI*	*EDI*	*RfD/RDA (μg/g/day)*	Exp_{ing}	*MOE*	HQ_{ing}	*TCR*
As	1.05	0.15	0.406	0.058	0.0003	0.001	2.763	1.890	8.50E-04
Ca	6953	993.3	1375	196.5	13.33	1.000	0.211	0.075	-
Cd	0.49	0.07	1.657	0.237	0.001	0.002	3.382	1.727	1.04-E03
Co	29.4	4.2	5.258	0.751	0.06	0.005	0.179	0.075	-
Cr	1.47	0.21	6.716	0.959	0.003	0.010	4.569	3.174	4.76E-03
Cu	245	35	2.015	0.288	0.04	0.003	0.103	0.080	-
Fe	392	56	78.76	11.25	0.7	0.118	0.230	0.169	-
Hg	0.35	0.05	3.012	0.430	0.0003	0.004	20.49	13.54	-
K	38381	5483	4024	574.9	78	7.044	0.105	0.090	-
Li	9.8	1.4	0.588	0.084	0.002	0.001	0.600	0.256	-
Mg	2858	408.3	108.3	15.48	5.83	0.167	0.038	0.029	-
Mn	68.6	9.8	7.530	1.076	0.14	0.011	0.110	0.076	-
Na	26950	3850	2716	388.1	55	4.456	0.101	0.081	-
Ni	2.45	0.35	13.14	1.878	0.02	0.014	1.341	0.712	2.42E-02
Pb	1.75	0.25	15.00	2.142	0.004	0.021	7.651	5.374	1.83E-04
Se	196	28	9.210	1.316	0.005	0.014	3.759	2.834	-
Sr	294	42	1.851	0.264	0.6	0.001	0.006	0.002	-
Zn	490	70	48.83	6.976	0.3	0.071	0.332	0.236	-
				HI				30.42	

3.44 Salient Findings of the Present Study

Based on the deliberations in the foregoing sections, following major findings emerged from the present study:

Most of the water samples exhibited slightly basic pH during summer, winter, pre-monsoon and monsoon while it was slightly acidic during post-monsoon. Overall, the pH values in the water samples were within acceptable limits. Electrical conductivity and total dissolved solids in the water samples mostly showed random distribution but their average levels were within the water quality guidelines. Aquatic ecosystem in the water reservoir was under stress due to low DO contents in the water during summer, winter and pre-monsoon. Dominant contributions were found for Ca, Mg, Na and K in the water samples, while As, Li, Se and Mn showed relatively lower contributions. Overall, on the average basis, metal levels showed following decreasing order during summer: Ca > Mg > Na > K > Pb > Co > Sr > Fe > Ni > Cr > Cd > Zn > Cu > Mn >As > Li >Se while during winter the order was: Ca > Na > Mg > K > Pb > Sr > Co > Fe > Ni > Cr > Zn > Cd > Cu > Mn > Li > As > Se. Mean levels of As, Cd, Co, Cr, Ni and Pb in the water samples were higher than the national/international water quality guidelines. Average levels of most of the metals were relatively higher during pre-monsoon compared with the monsoon and post-monsoon seasons. Metal contents exhibited significant spatial variability and elevated metals levels were observed at the sites near highly urbanized areas around the Lake. Principle components analysis (PCA) and cluster analysis (CA) indicated major anthropogenic contribution of As, Cd, Co, Cr, Ni and Pb in the water samples from Mangla Lake during all seasons.

Average contents of total alkalinity (TA) in the water samples during pre-monsoon and monsoon were higher than the permissible limits. Water samples were found to be moderately hard during summer and pre-monsoon; soft during monsoon and post-monsoon seasons. Average levels of Cl^- in the water samples were within the permissible limits, indicating that the water was suitable for drinking/irrigation purpose. Most of the water samples were found to be unsuitable for irrigation with respect to bicarbonate and RSBC levels, however, mean values of SAR, KR, PS, MAR and Mg/Ca showed that the water was suitable and safe for irrigation. Permeability index also indicated suitability of the water for irrigation. On the mean basis of IWQ index, most of the water samples exhibited high to medium suitability for irrigation purpose. Mostly, water samples demonstrated medium degree of pollution by the metals. Heavy metals pollution in the water samples highlighted Cd, Cr, Ni and Pb as major potential contributors towards the metal contamination in the water reservoir. HQ_{ing} and HI values for As, Cd, Co, Cr, Ni and Pb were higher than safe limit (unity) in the water samples indicating significant non-carcinogenic risks.

In the case of sediments, considerable variations were observed for EC and TDS. The sediments were mostly associated with very high concentrations of soluble ions in the sediments. In calcium nitrate extract of the sediment, Ca, K, Mg, Na and Sr exhibited highest concentrations, while Hg, Li and Zn showed lowest concentrations. In calcium nitrate extracts of the sediment samples, average levels of Cd, Cr, Cu, Fe, Na, Ni, Sr and Mn were relatively higher during winter, while mean levels of As, Co, K, Pb, Li and Se were higher during summer. In acid-extract of the sediment samples, Ca, Fe, K, Mg, Mn and Na revealed fairly higher concentrations while lowest levels were noted for As, Cd, Hg, Li and Se. Most of the metals in acid-extract of the sediments showed relatively higher contributions during winter season which indicated the enrichment of metal pollutants in the sediments during winter. Most of the selected metals in sediment samples showed random distribution, large dispersion and predominantly asymmetrical variations. Average metal levels in the sediments in the present study were found to be higher than most of the reported levels around the world. In *m*BCR sequential extraction, Ca, K, Mg and Na showed comparatively higher concentrations in the exchangeable fraction, while Cd, Li, Se and Hg exhibited rather lower concentrations in the reducible fraction of sediments. Similarly, Ca, Fe, K and Mg showed higher concentrations in the oxidiseable fraction, whereas Ca, Fe and K revealed higher concentrations in the residual fraction of sediments.

Spatial variability of the metal contents in the sediments was also evaluated which showed significantly higher concentrations at sampling sites located near highly urbanized and semi-urban areas. Among the metals, Se, Sr, Cd, Pb, Ni and Co were highly mobile and bioavailable in the sediments. Numerous strong and significantly diverse correlations were observed among the metals which revealed common variations/origin of the metals in sediments. Particle size analysis showed predominant sandy loam texture of the sediments in the study area. PCA and CA evidenced anthropogenic contributions of As, Cd, Co, Cr, Hg, Ni, Pb, Se and Zn in the sediments, predominantly contributed by urban/rural waste, agriculture run-offs, industrial activities and fuel combustion. Enrichment factor showed that As, Ca, Cd, Co, Hg, Pb, Se and Zn were highly enriched in the sediments while rest of metals showed moderate or no enrichment. Geo-accumulation index indicated that As, Cd, Hg, Pb, Se and Zn were highly accumulated in the sediment samples. Contamination factor revealed that As, Ca, Cd, Co, Hg, Pb, Se and Zn showed moderate to very high contamination, while degree of contamination indicated very high degree of contamination in the sediments. The potential ecological risk factor revealed that Cr, Cu, Pb and Zn caused low risk; As, Cd and Hg showed considerable to very great risk in the sediments. Cumulative potential ecological risk index demonstrated very high risk for the metals in sediments. Sediment quality guidelines indicated that As, Cd, Hg, Ni and Pb levels were likely to result in frequently occurring harmful effects on sediment-dwelling biota. Average values of HQ_{ing}, HQ_{derm} and HI in the sediments were observed to be lower than unity, indicating that the metals would not pose any adverse non-carcinogenic health risks to the organism via ingestion or dermal exposure.

Soil samples mostly showed slightly acidic pH during summer and winter. Large variations in EC and TDS of the soil pointed out very high concentration of soluble ions in the soil. In calcium nitrate extract of the soil, Ca, Fe, K, Mg and Na exhibited highest concentrations, while Cd, Cu, Hg and Li showed relatively lower contributions. Average concentration of As, Cd, Cr, Cu, Fe, Li, Mn, Na, Se and Zn were relatively higher during winter than summer in calcium nitrate extract of the soil. Most of the metal levels were comparatively higher during pre-monsoon than monsoon and post-monsoon seasons. Quartile distribution showed that most of the metals exhibited broad and asymmetrical distribution in the soil. Acid-extract of the soil samples revealed fairly higher concentrations for Ca, Fe, K, Mg, Mn, Na and Zn while lowest levels were noted for Cd, Hg, Li and Se. Significantly higher concentrations of Cd, Co, Cr, Hg, K, Pb and Sr were found during winter than summer season. Most of the metals showed almost comparable average concentrations in acid extract of the soil during monsoon and post-monsoon, while As, Cd, Cr, Cu, Hg, Li, Pb and Se showed relatively higher contributions during pre-monsoon. Quartile distribution of selected metals in acid extract of soil showed narrow and largely asymmetrical distribution during all seasons. Mean levels of Cu, K, Na, Mn, Pb, Sr and Zn in the soil were found to be lower than most of the reported levels around the world. In sequential extraction study, Ca, Mg and K showed highest levels in the exchangeable fraction; Ca, Fe and Mg exhibited highest contents in the reducible fraction; Mg, Fe and Ca showed highest concentrations in the oxidiseable fraction; and Fe, Mg and K revealed highest contributions in the residual fraction of soil. Present average levels of As, Cd, Cr, Hg, Ni and Se in the soil were higher than the international soil quality guidelines. Relatively higher concentrations of the most of the metals were observed in thickly populated areas and lower concentration were noted in less population density areas. Particle size analysis exhibited high percentage of sand and low percentages of silt and clay, indicating predominant sandy loam texture of the soil in the study area. Numerous strong and significantly diverse relationships were observed among the metals which revealed common variations/origin of the metals in soil. PCA and CA evidenced anthropogenic contributions of As, Cd, Cr, Co, Hg, Ni, Pb and Se in the soil samples.

Enrichment factor and geo-accumulation index revealed that among selected metals, As, Cd, Co, Hg, Pb and Se were highly enriched and accumulated in the soil samples during all seasons. Contamination factor disclosed that As, Cd, Co, Hg, Pb and Se showed moderate to very high contamination, while degree of contamination indicated very high degree of contamination in the soil samples. *PLI* result showed that the soil samples were most polluted during pre-monsoon and least polluted during post-monsoon season. Potential ecological risk factor demonstrated that Cr, Cu, Pb and Zn caused low risk; As, Cd and Hg showed considerable to very great risk in the soil. Cumulative potential ecological risk index showed very high risk for the metal contents in soil. Average values of HQ_{ing}, HQ_{derm} and *HI* were lower than safety limit unity, thus indicating that the metals would not cause any adverse non-carcinogenic health risks via ingestion or dermal exposure.

Among the fish species, coefficient of condition (K) showed the *Catla catla* and *Cyprinus carpio* were more healthy. Generally, fish species exhibited higher concentrations of Ca, Fe, K, Mg, Na and Zn while lowest concentrations were observed for As, Cd, Hg and Li in the tissues. Highest concentrations of most of the metals were found in the gills of fish species. PCA and CA evidenced anthropogenic contributions of As, Cd, Co, Cr, Hg, Ni and Pb in the fish muscles. Relatively higher concentrations of As, Cd, Co, Cr, Hg, Ni, Pb, Se and Zn were found in the muscles of fish species collected from Mangla Lake compared with the reported levels from other regions of the world. A number of strong and significant correlations were noted among various metals in the muscles of fish species thus manifesting their common variations/origin. Generally, fish species exhibited higher concentrations of As, Cd, Hg, Pb, Se and Zn in the muscles than the international permissible limits. *EWI* and *EDI* values of As, Cd, Cr, Hg, Ni and Pb were noted to be higher than the recommended *PTWI* and *PTDI* values, respectively. Higher *MOE* values for As, Cd, Cr, Hg, Ni, Pb and Se in the muscles indicated higher exposure which may result in chronic non-carcinogenic effects to consumers. HQ_{ing} results revealed that the fish consumption may cause non-carcinogenic risks associated with the elevated levels of As, Cd, Cr, Hg, Ni, Pb, Se and Zn. Target cancer risk revealed that the consumption of fish from Mangla Lake was associated with lifetime carcinogenic risk with respect to As, Cd, Cr, Ni and Pb levels in the fish muscles, particularly when consumption exceeds 700 g/week.

3.45 Recommendations

The focus of the present study was to assess the pollution status of one of the largest freshwater reservoir in Pakistan. This study formed a strong basis for the future environmental pollution abatement plan. The experimental results showed that the chief criteria pollutants in the reservoir, especially trace metals existed at elevated levels than most of the guidelines. This situation calls for a well structured and well organized pollution control programme. In the light of present findings, following impotant possible recommendations may be considered to control the existing pollution scenario.

- Monitor and assess the water quality of the reservoir on regular basis.
- Prevent contamination of the water from point and non-point sources by controlling the point runoffs and should also reduced the non-point runoffs.
- Should not dump domestic/industrial wastes into the water reservoir directly. Wastes should be treated properly to make them environmentally safe before dumpimg. Appropriate policies should be made to stop the discharge of industrial effuluents in the reservoir without treatment.
- Should not be permitted to throw wastes into the water reservoir at picnic points around the reservoir
- Prevent indiscriminate use of fertilizer and pesticide in agricultural practices to avoid the contamination caused by the agricultural runoffs
- Make awareness in people related to causes and effects of pollution by means of seminar, meetings etc
- Practice four R's (refuse, reuse, reduce, recycle) for the resources.
- Use biodegradable products instead of non-biodegradable products

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Appendix-A

Optimum analytical conditions for the analysis of selected metals on FAAS

(Shimadzu AA-670, Japan)

Metal	Wavelength (nm)	HC lamp current (mA)	Slit width (nm)	Fuel-gas flow rate (L/min.)	1% Absorption concentration (ppm)
Ca	422.7	6.0	0.5	2.0	0.08
Cd	228.8	4.0	0.3	1.8	0.02
Co	240.7	6.0	0.2	2.2	0.20
Cr	357.9	5.0	0.5	2.6	0.09
Cu	324.8	3.0	0.5	1.8	0.09
Fe	248.3	8.0	0.2	2.0	0.10
K	766.5	5.0	0.5	1.9	0.04
Li	670.7	4.0	0.5	1.6	0.05
Mg	285.2	4.0	0.5	1.6	0.007
Mn	279.5	5.0	0.4	1.9	0.05
Na	589.0	6.0	0.5	1.6	0.02
Ni	232.0	4.0	0.15	1.7	0.10
Pb	217.0	7.0	0.3	1.8	0.20
Sr	460.7	4.0	0.5	1.6	0.10
Zn	213.9	4.0	0.5	2.0	0.02

Appendix-B

Analytical conditions maintained on ICP-MS (Agilent 7500ce, UK) for the analysis of selected metals

Parameter	Description/Value
Plasma gas flow rate	15.0 L/min
Auxiliary gas flow rate	0.9 L/min
Carrier gas flow rate	0.8 L/min
RF power	1500 W
Nebulizer gas flow	0.50 L/min
Make up gas flow	0.25 L/min
Nebulizer	Mira Mist
Spray chamber	Quartz, Double pass
Spray chamber Temperature	15 °C
Sampling depth	7.1 mm
Sample uptake rate	0.4 mL/min
Sampler/Skimmer Cone	Nickel
Detector mode	Auto
Point/mass	3
Analysis time/mass	0.30 sec
Number of replicates	4
Total analysis time/sample	135

Certified versus estimated concentrations of selected metals in standard reference material of water (NIST SRM 1643d) and fish (NIST SRM 1946) (n= 3)

Metal	SRM 1643d (mg/L)			SRM 1946 (µg/g)		
	Certified	Measured	Recovery (%)	Certified	Measured	Recovery (%)
As	0.05602 ± 0.00073	0.054 ± 0.0008	96	0.277 ± 0.010	0.266 ± 0.016	96
Ca	31.04 ± 0.50	30.26 ± 0.71	97	59.1 ± 1.5	56.4 ± 1.3	95
Cd	0.00647 ± 0.00037	0.006 ± 0.00030	93	0.00208 ± 0.0026	0.002 ± 0.0031	96
Co	0.025 ± 0.00059	0.023 ± 0.00041	92	-	-	-
Cr	0.01853 ± 0.0002	0.019 ± 0.0003	103	-	-	-
Cu	0.0205 ± 0.0038	0.019 ± 0.0026	93	0.476 ± 0.060	0.466 ± 0.048	98
Fe	0.0912 ± 0.0039	0.092 ± 0.0043	101	4 ± 0.32	3.89 ± 0.39	97
Hg	-	-	-	0.433 ± 0.009	0.411 ± 0.007	95
K	2.356 ± 0.035	2.385 ± 0.029	101	3330 ± 180	3292 ± 202	99
Li	0.0165 ± 0.00055	0.016 ± 0.00061	97	-	-	-
Mg	7.989 ± 0.035	7.816 ± 0.039	98	226 ± 18	216.4 ± 22	96
Mn	0.03766 ± 0.00083	0.038 ± 0.00071	101	0.07 ± 0	0.068 ± 0	97
Na	22.07 ± 0.64	21.77 ± 0.70	99	458 ± 25	439 ± 19	96
Ni	0.0581 ± 0.0027	0.061 ± 0.0031	105	-	-	-
Pb	0.01815 ± 0.00064	0.019 ± 0.00081	105	0.7 ± 0	0.67 ± 0	96
Se	0.01143 ± 0.00017	0.012 ± 0.00011	105	0.491 ± 0.043	0.477 ± 0.049	97
Sr	0.2948 ± 0.0034	0.286 ± 0.0042	97	-	-	-
Zn	0.07248 ± 0.00065	0.071 ± 0.00074	98	3.10 ± 0.18	3.15 ± 0.22	102

Appendix-D

Certified versus estimated concentrations (mg/kg) of selected metals in standard reference material for sediment and soil

Metal	SRM 2709 (Sediment)			SRM 2711 (Soil)			BCR-701 (Sediment/Soil)								
							Fraction 1			Fraction 2			Fraction 3		
	C	M	R	C	M	R	C	M	R	C	M	R	C	M	R
As	17.7	17.1	97	105	101	96	-	-	-		-	-	-	-	-
Ca	18900	18700	99	28800	27985	97	-	-	-	-	-	-	-	-	-
Cd	0.38	0.35	92	41.7	40.98	98	7.34	7.21	98	3.77	3.85	102	0.27	0.28	104
Co	13.4	12.98	97	10	9.6	96	-	-	-	-	-	-		-	-
Cr	130	140.1	108	47	47.56	101	2.26	2.23	99	45.7	43.8	96	143	140	98
Cu	34.6	35.69	103	114	114.9	101	49.3	47.9	97	124	118	95	55.2	54.9	99
Fe	35000	34800	99	28900	27800	96	-	-	-	-	-	-	-	-	-
Hg	1.4	1.33	95	6.25	6.01	96	-	-	-	-	-	-	-	-	-
K	20300	20085	99	24500	24100	98	-	-	-	-	-	-	-	-	-
Li	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Mg	15100	14900	99	10500	10265	98	-	-	-	-	-	-	-	-	-
Mn	538	552.2	103	638	655	103	-	-	-	-	-	-	-	-	-
Na	11600	11365	98	11400	11134	98	-	-	-	-	-	-	-	-	-
Ni	88	85	97	20.6	21.1	102	15.4	15.1	98	26.6	25.7	97	15.3	14.9	97
Pb	18.9	19.71	104	1162	1180	102	3.18	3.2	101	126	119	94	9.3	8.8	95
Se	1.57	1.49	95	1.52	1.59	105	-	-	-	-	-	-	-	-	-
Sr	231	225	97	245.3	239.1	97	-	-	-	-	-	-	-	-	-
Zn	106	109.5	103	350.4	341.1	97	205	199	97	114	109	96	45.7	44.9	98

C: Certified value; M: Measured value; R: Recovery (%)

Appendix-E

Classification for irrigation water quality (*IWQ*) index parameters

<table>
<tr><th>Hazard</th><th>Weight</th><th colspan="6">Parameters</th><th>Range</th><th>Rating</th><th>Suitability</th></tr>
<tr><td>Salinity hazard</td><td>5</td><td colspan="6">Electrical Conductivity (μS/cm)</td><td>$EC < 700$</td><td>3</td><td>High</td></tr>
<tr><td></td><td></td><td colspan="6"></td><td>$700 \leq EC \leq 3000$</td><td>2</td><td>Medium</td></tr>
<tr><td></td><td></td><td colspan="6"></td><td>$EC > 3000$</td><td>1</td><td>Low</td></tr>
<tr><td>Infiltration and Permeability hazard</td><td>4</td><td></td><td colspan="5">SAR</td><td></td><td></td><td></td></tr>
<tr><td></td><td></td><td></td><td>< 3</td><td>3-6</td><td>6-12</td><td>12-20</td><td>> 20</td><td></td><td></td><td></td></tr>
<tr><td></td><td></td><td></td><td>> 700</td><td>> 1200</td><td>> 1900</td><td>> 2900</td><td>> 5000</td><td></td><td>3</td><td>High</td></tr>
<tr><td></td><td></td><td>EC</td><td>700-200</td><td>1200-300</td><td>1900-500</td><td>2900-1300</td><td>5000-2900</td><td></td><td>2</td><td>Medium</td></tr>
<tr><td></td><td></td><td></td><td>< 200</td><td>< 300</td><td>< 500</td><td>< 1300</td><td>< 2900</td><td></td><td>1</td><td>Low</td></tr>
<tr><td>Specific ion toxicity</td><td>3</td><td colspan="6">Sodium adsorption ration (SAR)</td><td>$SAR < 3.0$</td><td>3</td><td>High</td></tr>
<tr><td></td><td></td><td colspan="6"></td><td>$3.0 \leq SAR \leq 9.0$</td><td>2</td><td>Medium</td></tr>
<tr><td></td><td></td><td colspan="6"></td><td>$SAR > 9.0$</td><td>1</td><td>Low</td></tr>
<tr><td></td><td></td><td colspan="6">Chloride (mg/L)</td><td>$Cl^- < 140$</td><td>3</td><td>High</td></tr>
<tr><td></td><td></td><td colspan="6"></td><td>$140 \leq Cl^- \leq 350$</td><td>2</td><td>Medium</td></tr>
<tr><td></td><td></td><td colspan="6"></td><td>$Cl^- > 350$</td><td>1</td><td>Low</td></tr>
<tr><td>Trace element toxicity</td><td>2</td><td colspan="6">See Appendix-F</td><td></td><td></td><td></td></tr>
<tr><td>Miscellaneous effects to sensitive crops</td><td>1</td><td colspan="6">Bicarbonate (mg/L)</td><td>$HCO_3^- < 90$</td><td>3</td><td>High</td></tr>
<tr><td></td><td></td><td colspan="6"></td><td>$90 \leq HCO_3^- \leq 500$</td><td>2</td><td>Medium</td></tr>
<tr><td></td><td></td><td colspan="6"></td><td>$HCO_3^- > 500$</td><td>1</td><td>Low</td></tr>
<tr><td></td><td></td><td colspan="6">Nitrate</td><td>$NO_3^- < 5.0$</td><td>3</td><td>High</td></tr>
<tr><td></td><td></td><td colspan="6"></td><td>$5.0 \leq NO_3^- \leq 30.0$</td><td>2</td><td>Medium</td></tr>
<tr><td></td><td></td><td colspan="6"></td><td>$NO_3^- > 30.0$</td><td>1</td><td>Low</td></tr>
<tr><td></td><td></td><td colspan="6">pH</td><td>$7.0 \leq pH \leq 8.0$</td><td>3</td><td>High</td></tr>
<tr><td></td><td></td><td colspan="6"></td><td>$6.5 \leq pH < 7.0$ and $8.0 < pH \leq 8.5$</td><td>2</td><td>Medium</td></tr>
<tr><td></td><td></td><td colspan="6"></td><td>$pH < 6.5$ or $pH > 8.5$</td><td>1</td><td>Low</td></tr>
</table>

Simsek C, Gunduz O, 2007. IWQ Index: A GIS-Integrated Technique to Assess Irrigation Water Quality. Environmental Monitoring and Assessment, 128, 277–300.

Appendix-F

Classification of trace metal toxicity for IWQ index in water

Metal	Range	Rating	Suitability
	$\mathrm{As} < 0.1$	3	High
As	$0.1 \leq \mathrm{As} \leq 2.0$	2	Medium
	$\mathrm{As} > 2.0$	1	Low
	$\mathrm{Cd} < 0.01$	3	High
Cd	$0.01 \leq \mathrm{Cd} \leq 0.05$	2	Medium
	$\mathrm{Cd} > 0.05$	1	Low
	$\mathrm{Co} < 0.05$	3	High
Co	$0.05 \leq \mathrm{Co} \leq 5.0$	2	Medium
	$\mathrm{Co} > 5.0$	1	Low
	$\mathrm{Cr} < 0.1$	3	High
Cr	$0.1 \leq \mathrm{Cr} \leq 1.0$	2	Medium
	$\mathrm{Cr} > 1.0$	1	Low
	$\mathrm{Cu} < 0.2$	3	High
Cu	$0.2 \leq \mathrm{Cu} \leq 5.0$	2	Medium
	$\mathrm{Cu} > 5.0$	1	Low
	$\mathrm{Fe} < 5.0$	3	High
Fe	$5.0 \leq \mathrm{Fe} \leq 20.0$	2	Medium
	$\mathrm{Fe} > 20.0$	1	Low
	$\mathrm{Li} < 2.5$	3	High
Li	$2.5 \leq \mathrm{Li} \leq 5.0$	2	Medium
	$\mathrm{Li} > 5.0$	1	Low
	$\mathrm{Mn} < 0.2$	3	High
Mn	$0.2 \leq \mathrm{Mn} \leq 10.0$	2	Medium
	$\mathrm{Mn} > 10.0$	1	Low
	$\mathrm{Ni} < 0.2$	3	High
Ni	$0.2 \leq \mathrm{Ni} \leq 2.0$	2	Medium
	$\mathrm{Ni} > 2.0$	1	Low
	$\mathrm{Pb} < 5.0$	3	High
Pb	$5.0 \leq \mathrm{Pb} \leq 10.0$	2	Medium
	$\mathrm{Pb} > 10.0$	1	Low
	$\mathrm{Se} < 0.01$	3	High
Se	$0.01 \leq \mathrm{Se} \leq 0.02$	2	Medium
	$\mathrm{Se} > 0.02$	1	Low
	$\mathrm{Zn} < 2.0$	3	High
Zn	$2.0 \leq \mathrm{Zn} \leq 10.0$	2	Medium
	$\mathrm{Zn} > 10.0$	1	Low

Simsek C, Gunduz O, 2007. IWQ Index: A GIS-Integrated Technique to Assess Irrigation Water Quality. Environmental Monitoring and Assessment, 128, 277–300.

Appendix-G

Description of classification for physicochemical parameters in water

Parameter	Classification	Range	Reference
TH (mg $CaCO_3$/L)	Soft	< 75	WHO, 2008
	Moderately hard	75-150	
	Hard	150-300	
	Very hard	> 300	
EC (µS/cm)	Excellent	< 250	Wilcox, 1955
	Good	250-750	
	Permissible	750-2250	
	Doubtful	2250-5000	
	Unsuitable	> 5000	
PS (%)	Excellent	0-20	Wilcox, 1955
	Good	20-40	
	Permissible	40-60	
	Doubtful	60-80	
	Unsuitable	> 80	
SAR	Excellent	< 10	Richard, 1954
	Good	10-18	
	Doubtful	18-26	
	Unsuitable	>26	
pH	No problem	6.5-8.4	Ayers and Westcot, 1994
	Moderate	5.1-6.4 & 8.5-9.5	
	Severe	0.0-5.0 & > 9.5	
Cl^- (meq/L)	No problem	< 4	Ayers and Westcot, 1994
	Moderate	4-10	
	Severe	> 10	
Mg/Ca	Safe	< 1.5	Kumar *et al.,* 2007
	Moderate	1.5-3.0	
	Unsafe	> 3.0	
IWQ index	Low	< 22	Simsek and Gunduz, 2007.
	Medium	22-37	
	High	> 37	

WHO, 2008. Guidelines for drinking-water quality, Recommendations incorporating 1st and 2nd addenda, Volume 1, 3rd edition, World Health Organization, Geneva.

Wilcox LV, 1955. Classification and use of irrigation waters, USDA Circular No. 969.

Richards LA, 1954. Diagnosis and improvement of saline and alkali soils, USDA Handbook no. 60, Washington.

Ayers RS, Westcot DW, 1994. Water quality for agriculture, FAO Irrigation and Drainage, Paper 29, Rev. 1, pp. 1–130.

Kumar M, Kumari K, Ramanathan AL, Saxena R, 2007. A comparative evaluation of groundwater suitability for irrigation and drinking purposes in two intensively cultivated districts of Punjab, India. Environmental Geology, 53, 553–574.

Description of individual contamination factor (*ICF*)[a], Global contamination factor (*GCF*)[a], Risk assessment code(*RAC*)[b], Heavy metal evaluation index (*HEI*)[c] and Degree of contamination (C_d)[c].

Value	Soil/Sediments quality	Value	Water quality
ICF < 1	Low contamination	HEI < 150	Low pollution
1 < ICF < 3	Moderate contamination	HEI = 150-300	Medium pollution
3 < ICF < 6	Considerable contamination	HEI > 300	High pollution
ICF > 6	High contamination		
GCF < 6	Low contamination	C_d < 150	Low pollution
6 < GCF < 12	Moderate contamination	C_d = 150-300	Medium pollution
12 < GCF < 24	Considerable contamination	C_d> 300	High pollution
GCF > 24	High contamination		
RAC < 1%	No risk		
RAC = 1-10%	Low risk		
RAC = 11-30%	Medium risk		
RAC = 31-50%	High risk		
RAC > 50%	Very high risk		

[a] Zhao S, Feng C, Yang Y, Niu J, Shen Z, 2012. Risk assessment of sedimentary metals in the Yangtze Estuary: new evidence of the relationships between two typical index methods. Journal of Hazardous Materials, 241–242, 164–172.

[b] Perin G, Craboledda L, Lucchese M, Cirillo R, Dotta L, *et al.,* 1985. Heavy metal speciation in the sediments Northern Adriatic Sea, a new approach for environmental toxicity determination. In Heavy Metals in the Environment; CEP Consultants: Edinburgh, Scotland, 2, 454–456.

[c] Bhuiyan MAH, Islam MA, Dampare SB, Parvez L, Suzuki S, 2010. Evaluation of hazardous metal pollution in irrigation and drinking water systems in the vicinity of a coal mine area of northwestern Bangladesh. Journal of Hazardous Materials, 179, 1065–1077.

Appendix-I

Description of geoaccumulation index [a](I_{geo}), enrichment factor [b](EF), contamination factor [c](C_f), degree of contamination [c](C_{deg}), potential ecological risk factor [c](E_i) and potential ecological risk index [c](RI) in soil/sediments

Value	Soil/Sediments quality	Value	Soil/Sediments quality
$I_{geo} \le 0$	practically uncontaminated	$EF < 1$	no enrichment,
$0 < I_{geo} < 1$	uncontaminated to moderately contaminated	$EF < 3$	minor enrichment
$1 < I_{geo} < 2$	moderately contaminated	$EF = 3– 5$	moderate enrichment
$2 < I_{geo} < 3$	moderately to heavily contaminated	$EF = 5 – 10$	moderately severe enrichment
$3 < I_{geo} < 4$	heavily contaminated	$EF = 10– 25$	severe enrichment
$4 < I_{geo} < 5$	heavily to extremely contaminated	$EF = 25\text{-}50$	very severely enrichment
$5 < I_{geo}$	extremely contaminated	$EF > 50$	extremely severe enrichment
$C_f < 1$	low contamination factor indicating low contamination	$C_{deg} < 8$	low degree of contamination
$1 \le C_f < 3$	moderate contamination factor	$8 \le C_{deg} < 16$	moderate degree of contamination
$3 \le C_f < 6$	considerable contamination factor	$16 \le C_{deg} < 32$	considerable degree of contamination
$6 \le C_f$	very high contamination factor	$32 \le C_{deg}$	very high degree of contamination
$E_i < 40$	low risk	$RI < 65$	low risk
$40 \le E_i < 80$	moderate risk	$65 \le RI < 130$	moderate risk
$80 \le E_i < 160$	considerable risk	$130 \le RI < 260$	considerable risk
$160 \le E_i < 320$	great risk	$RI \ge 260$	very high risk
$E_i \ge 320$	very great risk		

[a] Muller G, 1969. Index of geoaccumulation in sediments of the Rhine River, Journal of Geology, 2, 108–118.

[b] Birch G, 2003. A scheme for assessing human impacts on coastal aquatic environments using sediments, In: Woodcoffe CD, Furness RA (Eds.), Coastal GIS, Wollongong University Papers in Center for Maritime Policy, 14, Australia.

[c] Hakanson L, 1980. An ecological risk index for aquatic pollution control: A sedimentological approach. Water Research, 14, 975–1001.

Description of input parameters for exposure assessment of selected metals in water through ingestion pathway and dermal absorption

Parameter	Unit	Value	Reference
Ingestion Rate (IR)	L	2.2 for adults and 1.8 for children	Wu *et al.*, 2009
Exposure Frequency (EF)	Days/Year	350	Wu *et al.*, 2009
Exposure Duration (ED),	Years	70 for adults and 6 for children	Wu *et al.*, 2009
Body Weight (BW)	kg	70 for adults and 15 for children	USEPA, 2004
Average Time (AT)	Days	25550 for adults and 2190 for children	Wu *et al.*, 2009; USEPA, 2004
Exposure Time (ET)	hours/day	0.58 for adults and 1 for children	USEPA, 2004
Conversion Factor (CF)	L/cm^3	0.001	USEPA, 2004
Skin-Surafce Area (SA)	cm^2	18000 for adults and 6600 for children	USEPA, 2004
Permeability Coefficient (Kp)	cm/hour	0.001 (As, Cd, Cu, Fe, Li, Mn, Se & Sr) 0.002 (Cr) 0.0004 (Co, Ni & Pb) 0.0006 (Zn)	USEPA, 2004

Wu B, Zhao DY, Jia HY, Zhang Y, Zhang XX, *et al.*, 2009. Preliminary risk assessment of trace metal pollution in surface water from Yangtze River in Nanjing Section, China. Bulletin of Environmental Contamination and Toxicology, 82, 405–409.

USEPA, 2004. Risk Assessment Guidance for Superfund, Volume 1, Human Health Evaluation Manual (Part E, Supplemental Guidance for Dermal Risk Assessment), Report EPA/540/R/99/005, U.S. Environmental Protection Agency, Washington, DC.

Description of input parameters for health risk assessment of selected metals in soil/sediments

Parameter	Value	Unit	Reference
Exposure Frequency (EF)	350	days	USEPA, 1989 & 2004; Rovira *et al.*, 2011
Exposure Duration (ED)	30	year	USEPA, 1989 & 2004; Rovira *et al.*, 2011
Ingestion Rate (IR)	114	mg/day	Rovira *et al.*, 2011
Body Weight (BW)	70	kg	USEPA, 1989 & 2004
Sediments/Soil Adherence Factor (AF)	0.07	mg/cm^2	USEPA, 1989 & 2004
Dermal Absorption Factor (ABS)	0.001 & 0.03 (As)	unit less	De Miguel *et al.*, 2007; USDoE, 2005
Exposed Skin Area (SA)	5700	cm^2	USEPA, 2004
Averaging Time (AT)	10950	days	USEPA, 1989 & 2004
Conversion Factor (CF)	10^{-6}	kg/mg	USEPA, 1989 & 2004

De Miguel E, Iribarren I, Chacon E, Ordonez A, Charlesworth S, 2007. Risk-based evaluation of the exposure of children to trace elements in playgrounds in Madrid (Spain). Chemosphere, 66, 505–513.

Rovira J, Mari M, Schuhmacher M, Nadal M, Domingo JL, 2011. Monitoring environmental pollutants in the vicinity of a cement plant: A temporal study. Archives of Environmental Contamination and Toxicology, 60, 372–384.

USDoE (US Department of Energy), 2005. RAIS: Risk Assessment Information System. Available from: <http://risk.lsd.ornl.gov/rap_hp.shtml>.

USEPA, 1989. Risk Assessment Guidance for Superfund, Volume 1, Human Health Evaluation Manual (Part A), Report EPA/540/1-89/002, U.S. Environmental Protection Agency, Washington, DC, USA.

USEPA, 2004. Risk Assessment Guidance for Superfund, Volume 1, Human Health Evaluation Manual (Part E, Supplemental Guidance for Dermal Risk Assessment), Report EPA/540/R/99/005, U.S. Environmental Protection Agency, Washington, DC, USA.

Input parameters of health risk assessment for selected metals in the muscles of fish

Parameter	Unit	Value	Reference
Ingestion Rate (IR)	kg	0.250	Shah *et al.,* 2009
Exposure Frequency (EF)	days/year	350	Lin, 2009; Vieira *et al.,* 2011
Exposure Duration (ED), non-carcinogenic assessment	years	30	Lin, 2009; USEPA, 2004
Exposure Duration (ED), carcinogenic assessment	years	70	Lin, 2009; USEPA, 2004
Body Weight (BW)	kg	70	Lin, 2009; USEPA, 2004
Averaging Time (AT), non-carcinogenic assessment	days	10950	Lin, 2009; USEPA, 2004
Averaging Time (AT), carcinogenic assessment	days	25550	Lin, 2009; USEPA, 2004

Lin MC, 2009. Risk assessment on mixture toxicity of arsenic, zinc and copper intake from consumption of milkfish, Chanos chanos (Forsskal), Cultured using contaminated groundwater in Southwest Taiwan. Bulletin of Environmental Contamination and Toxicology, 83, 125–129.

Shah AQ, Kazi TG, Arain MB, Baig JA, Afridi HI, *et al.,* 2009. Hazardous impact of arsenic on tissues of same fish species collected from two ecosystems. Journal of Hazardous Materials, 167, 511–515.

USEPA, 2004. Risk Assessment Guidance for Superfund, Volume 1, Human Health Evaluation Manual (Part E, Supplemental Guidance for Dermal Risk Assessment), Report EPA/540/R/99/005, U.S. Environmental Protection Agency, Washington, DC, USA.

Vieira C, Morais S, Ramos S, Delerue-Matos C, Oliveira MBPP, 2011. Mercury, cadmium, lead and arsenic levels in three pelagic fish species from the Atlantic Ocean: intra- and inter-specific variability and human health risks for consumption. Food and Chemical Toxicology, 49, 923-932.

International and national water quality guidelines for the selected metals in water

Parameters	WHO	USEPA	Pak-EPA
As (mg/L)	0.01	0.01	0.05
Ca (mg/L)	100	-	200
Cd (mg/L)	0.003	0.005	0.01
Co (mg/L)	0.04	-	-
Cr (mg/L)	0.05	0.1	0.05
Cu (mg/L)	2.0	1.3	2.0
Fe (mg/L)	0.3	0.3	-
Hg (mg/L)	0.006	0.002	0.001
K (mg/L)	12	-	-
Li (mg/L)	-	-	-
Mg (mg/L)	50	-	-
Mn (mg/L)	0.1	0.05	0.5
Na (mg/L)	200	-	-
Ni (mg/L)	0.07	0.7	0.02
Pb (mg/L)	0.01	0.015	0.05
Se (mg/L)	0.04	0.05	0.01
Sr (mg/L)	-	-	-
Zn (mg/L)	3.0	5.0	5.0
pH	6.5-8.5	6.5-8.5	6.5-8.5
TA as $CaCO_3$ (mg/L)	200	-	-
EC (μS/cm)	1500	-	-
TDS (mg/L)	1200	500	1000
SO_4^{-2}	-	250	-
F^{-1}	1.5	4	1.5
NO_3^{-1}	50	10	50
TH as $CaCO_3$ (mg/L)	500	-	500
Cl^- (mg/L)	250	250	250
Reference	WHO, 2011	US-EPA, 2012	Pak-EPA, 2008

USEPA, 2012. 2012 Edition of the Drinking Water Standards and Health Advisories, EPA 822-S-12-001, Office of Water, US Environmental Protection Agency, Washington, DC.

Pak-EPA, 2008. National Standards for Drinking Water Quality, Pakistan Environmental Protection Agency (Pak-EPA), Ministry of Environment, Government of Pakistan, Islamabad.

WHO, 2011. Guidelines for drinking-water quality, 4th edition, World Health Organization, Geneva, Switzerland.

Appendix-N

Tolerable and permissible levels of selected metals in the muscles of fish

	[a]Health Criteria (µg/g, ww)	[b]MAFF (µg/g, ww)	[c]WHO/[d]FAO (µg/g, ww)	Maximun level [e](EC) (µg/g, ww)	MAC [f](Croatia) (µg/g, ww)	MAC [f](other countries) (µg/g, ww)
Fe	-	-	2[c]	-	-	-
As	-	-	-	-	2.0	1.0
Cu	120	20	30[c,d]	-	-	-
Hg	-	-	0.5[d]	0.5	0.5	0.5
Mn	-	-	1[c], (0.5)[d]	-	-	-
Zn	480	50	30[d]	-	-	-
Se	-	-	-	-	-	1.0[g]
Cr	8.0	-	-	-	-	-
Cd	-	0.2	0.5[d]	0.1	0.1	0.2
Pb	4.0	2.0	2.0[c], (0.5)[d]	0.3	1.0	0.7

[a] USEPA, 1983. Methods for chemical analysis of water and waste, EPA Report 600/4-79-020, Office of water, Unites States Environmental Protection Agency, Cincinnati, Ohio, USA.

[b] MAFF, 2000. Monitoring and surveillance of non-radioactive contaminants in the aquatic environment and activities regulating the disposal of wastes at sea, 1997, Aquatic environment monitoring report number 52, Ministry of Agriculture, Fisheries and Food (MAFF), Lowestoft, UK.

[c] WHO, 1996. Health criteria other supporting information, In: Guidelines for Drinking Water Quality, 2nd ed., World Health Organization, Geneva, Switzerland, pp. 31-388.

[d] FAO, 1983. Compilation of legal limits for hazardous substances in fish and fishery products, FAO Fishery Circular No. 464, 5-10, Food and Agriculture Organization of the United Nations, Rome.

[e] Vieira C, Morais S, Ramos S, Delerue-Matos C, Oliveira MBPP, 2011. Mercury, cadmium, lead and arsenic levels in three pelagic fish species from the Atlantic Ocean: Intra- and inter-specific variability and human health risks for consumption. Food and Chemical Toxicology, 49, 923–932. (European Commission 2006, Regulation (EC) No 1881/2006 of 19 December 2006. setting maximum levels for certain contaminants in foodstuffs, Brussels.

[f] Has-Schon E, Bogut I, Vukovic R, Galovic D, Bogut A, Horvatic J, 2015. Distribution and age-related bioaccumulation of lead (Pb), mercury (Hg), cadmium (Cd), and arsenic (As) in tissues of common carp (Cyprinus carpio) and European catfish (Sylurus glanis) from the Busko Blato reservoir (Bosnia and Herzegovina). Chemosphere, 135, 289–296. (Ministry of Health and Social Care, Republic of Croatia, 2005. By-law on Toxins, Metals, Metalloids and Other Harmful Substances in Food. Narodne Novine No. 16, pp. 5–11 & Machova J, Svobodova Z, Hrjtmanek M, Hrbkova M, 1991. Control of hygienic quality of fish from the point of view of foreign substances content. In: Vykusová, B. (Ed.), Diagnostic, Prevention and Therapy of Fish Diseases and Intoxications. Manual, Vodnany, Czech Republic, pp. 325–445)

[g] Ghani SAA, 2015. Trace metals in seawater, sediments and some fish species from Marsa Matrouh Beaches in north-western Mediterranean coast, Egypt. Egyptian Journal of Aquatic Research, 41, 145–154. (Australian Bureau of Statistics, 1998. National Nutrition Survey: Nutrient Intakes and Physical Measurements, Australia 1995, Catalogue No. 4805.0. Aus Info, Canberra).