

**Assessment of Water Quality with respect to the
Physicochemical Parameters and Trace Metals
Contamination from Tarbela Dam, Pakistan**



By

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***Assessment of Water Quality with respect to the
Physicochemical Parameters and Trace Metals
Contamination from Tarbela Dam, Pakistan***

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In the name of Allah, the Most Merciful, the Most Kind

DEDICATION

*Every challenging work needs self-efforts as well as guidance of elders
especially those who are very close to our hearts*

Father and Mother,

*Whose affection, love, encouragement and prays of day and night make me
able to get such success and honour,*

Along with all hardworking and respected Teachers

And above all to the Almighty Allah!

DECLARATION

This is to certify that this dissertation entitled “*Assessment of Water Quality with respect to the Physicochemical Parameters and Trace Metals Contamination from Tarbela Dam, Pakistan*” by *Mohammad Muneeb Saddiqui* is accepted in its present form by the Department of Chemistry, Quaid-i-Azam University, Islamabad, Pakistan as satisfying the dissertation requirements for the degree of *Master in Philosophy* in *Analytical/Inorganic Chemistry*.

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ABSTRACT

Present study is based on the investigation of physicochemical parameters and trace metal concentrations in the surface water of Tarbela Dam, Pakistan in order to study their distribution, correlation, source apportionment and health risk assessment. The concentrations of trace metals in water samples were determined by flame atomic absorption spectrophotometry whereas physicochemical parameters were estimated as per standard methodology. The data were subjected to various statistical analyses to find the plausible correlations among the metals and various physicochemical parameters. Source apportionment of the metal data in the water samples was also carried out using principle component analysis and cluster analysis. Among the physicochemical parameters, pH of the water samples was found close to neutrality and strong associations were observed among most of the physicochemical parameters. Among the metals, higher concentration was observed for Ca, K, Mg and Na while least concentration was noted for Li. The selected metals showed following decreasing order; $Mg > Ca > Na > K > Pb > Co > Fe > Mn > Sr > Cu > Ag > Cr > Cd > Zn > Li$. The metal levels in water samples were also compared with the guideline values proposed by various organizations such as WHO, USEPA and Pak-EPA. Mean levels of all the physicochemical parameters were within the guideline values while average concentrations of Cd, Co, Cr, Mn and Pb were found to be higher than the standard limits. Significant strong clusters were observed among Ag-Cr, Fe-Mn, Co-Li-Cu, Pb-Sr, Cd-Zn, Ca-Na and K-Mg. The major pollution sources identified by multivariate PCA and CA were agriculture runoff, domestic wastes, lithogenic sources, soil erosion, automobile emission or transportation and natural weathering processes. Health risk assessment was calculated in terms of exposure of metals through ingestion and dermal absorption. Among the metals, Cd, Co, Cr and Pb exceeded the safe limit of hazard quotient so they can pose non-carcinogenic health risk through ingestion of water from Tarbela Dam, while levels of these metals were within the safe limit when measuring exposure through dermal contact. Among trace metals, significant carcinogenic risk was associated with Pb, Cr and Cd as these metals exceeded the safe limit, suggesting lifetime carcinogenic risk through ingestion of the water from the study area.

Chapter 1

INTRODUCTION

1.1 Water Pollution

Water being vital for drinking, industry and agriculture is one of the most valued commodities. It has numerous applications in everyday life and society. It is essential for survival of life and maintaining personal hygiene. The global food production depends on the availability of water. Different potential applications of water depend on its quality. For example in industry, availability and application of water depend on the nature of industrial process such as some processes required polluted water and some required fresh water. Overall, water shortage should not be a major problem because it is continuously recycled through different hydrological cycles; however its quality may be deteriorated to a point where it becomes harmful, useless and even deadly. Water pollutants are generally defined as any biological, chemical and physical entities that are harmful to the living organisms when present at excessive levels in water. Water pollution has become one of the modern worldwide serious problems as it may affect many lakes, rivers and even some parts of the oceans. Water bodies such as rivers, lakes and oceans have their own self-purification capacity but when water pollution exceeds the self-purification ability of an aquatic environment it becomes a severe problem for all living organisms. Human activities for deterioration of water quality are more pronounced due to introduction of various polluting substances in water bodies. Water pollution generally amplifies with the development of human population (Chen, 2002; Radojevic and Bashkin, 1999; Rapant and Kracmova, 2007).

Primary and major sources of water pollution are anthropogenic in origin such as sewage, land drainage, oil spills and industrial waste waters, as well as natural in origin such as erosion, ore deposits and rocks weathering (Ajibade, 2004; Carpenter et al., 1998; Jarvie et al., 1998; Simeonov and Stratis, 2003). Many of these water pollutants are continuously discharging into aquatic environment on daily bases and their release in large quantities attracts public concern. Water pollutants can be physical, biological or chemical in nature. Thermal pollution is one of the common forms of physical water pollution. The main source of this pollution is industrially utilized water for cooling purposes. This water returned to water bodies at high temperature. Power stations are more pronounced for the

introduction of such hot water. These power stations use surface water to condense steam that is used to derive turbines for the production of electricity. The residual water is very hot and returned back to rivers, lakes, estuaries and seas causing thermal pollution (Heugens et al., 2002; Holmstrup, 2010; Hester and Doyle, 2011; Stewart et al., 2013). Biological water pollutants are basically bacteria such as coliform, protozoa, helminthes and phytoplankton population such as algal blooms. These pollutants enter into water bodies by different sources such as sewage, human and animal faecal contamination, and fertilizer rich farmland etc (Khan et al., 2013).

Major chemical water pollutants are organic chemicals, heavy metals, acids, nutrients, and radioactivity etc. Major sources of radioactivity are nuclear industries, nuclear tests and transport of nuclear materials. Herbicides and pesticides used in agriculture, marine oil pollution due to spillage of oil from oil tanker accident; and industrial and domestic wastes are some sources of organic chemical pollutants. Wastes from domestic households, agriculture and urban drainage are responsible for heavy metal contamination in water. Acidity of water arises due to acid deposition from atmosphere, drainage from mines and wastes from different industries. Although salinity of fresh water bodies is undesirable but it can be due to irrigation, industrial wastewaters, road drainage, brine from mines and oil wells and sea water penetration due to low runoff and high tides. Fertilizers and sewage from industries are major routes to increase concentration of nutrients in water bodies ((Azizullah et al., 2010; Radojevic and Bashkin, 1999).

Polluted water can cause serious health hazards for all living organisms. The pathogens are biological hazards and can be transmitted through water. These pathogens are responsible for different water born diseases, such as typhoid fever, dysentery, polio, cholera and hepatitis etc. A wide variety of chemicals such as pesticides, petroleum, detergents and hydrocarbons are discharged in water bodies and caused harmful effects on aquatic ecosystem (such as death of fishes and production of algal blooms etc.) and human health (such as different water born diseases). Many heavy metals including mercury, cadmium and lead can also produce potential harmful effects for all living organisms. Acidic pollution has many adverse effects like mobilization of toxic metals in water bodies, destruction of aquatic life ($\text{pH} < 4$), increased corrosion that effects plumbing systems, boats and structure hoisted in different water bodies and damage to the agriculture crops (Khan et al., 2013; Muhammad et al., 2011; Strachan, 2010).

Salinity in fresh water makes it useless for drinking and irrigation purposes. It can also cause death of many aquatic organisms as they are less adapted to high salinity.

Excess of nutrients especially nitrogen and phosphorus is responsible for eutrophication that leads to the formation of algal blooms. These algal blooms stop penetration of light into the water resulting in the death of algae growing beneath the surface. Decomposition of these algae consumes dissolved oxygen and fish die due to starvation of dissolved oxygen. In developed countries such as Europe and North America water pollution is not a major problem but in developing countries like Pakistan it has become one of the serious threats to the public health. A detailed investigation conducted by Pakistan Council of Research in Water Resources (PCRWR) in 23 major cities in four provinces from 2002-2006 indicated that an average of 84-89% of water sources have the water quality below the recommended standards for human consumption (PCRWR, 2010). A report released by UNO Secretary General on World Water Day 2002 indicated that 1.1 billion people lack access to safe drinking water followed by 2.5 billion people have no excess to proper sanitation and >5.0 million people die every year from water related diseases (WHO, 2011). Due to poor quality of drinking water, people are forced to acquire commercially available mineral water packed in bottles but those mineral waters are also not safe due to lack of proper monitoring of processing plants (Rosemann, 2005).

1.2 Water Quality

It is a technical term which is used to characterise the water for human consumption on the basis of different guideline values. World Health Organization (WHO) proposed many guidelines and standards with the aim to provide safe drinking water to all human beings. These standards and guidelines are based on different scientific researches and epidemiological findings and are consultative in nature. Although WHO recommended many water quality parameters, different countries have demonstrated their own standards in accordance to meet their national priorities based on political, economic, social, technical and cultural requirements (Hespanhol and Prost, 1994). Some important water quality aspects are described below:

1.2.1 Physical Aspects

Physical aspects of water include colour, taste, turbidity, odour, etc. Turbidity in water should be low for proper practice of disinfection as higher turbidity can stop the effects of disinfection against different micro-organisms and promotes bacterial growth. Colour of drinking water may be due to organic matter contamination so it should be

colourless. Industrial pollution, organic substances and biological activities are responsible to cause water odour. Change in treatment processes and water sources cause taste problems in the drinking water. Taste of water can be used for detection of different inorganic compounds (such as, Zinc, Magnesium, Copper, Calcium, Iron, Sodium, etc.). Organic substances like methyl tertiary-butyl ether can also affect the taste of water (Maddaus, 2007).

1.2.2 Chemical Aspects

Natural sources, agriculture and industrial practices are some sources of chemical contamination in water bodies. Toxic chemicals in drinking water have great potential for acute or chronic health effects. Acute effects are less common than chronic effects because levels of these toxic chemicals in drinking water are seldom higher enough for acute health effects. Animal studies in laboratory and human data from clinical reports can be used to estimate the adverse effects (Maddaus, 2007).

1.2.3 Microbial Aspects

Drinking water should not contain pathogens and bacteria as they are considered as scatological pollution. Coliform bacteria are a most common form of bacterial contamination and they can enter into the water bodies through faeces of warm blooded organisms. Chlorine is usually used as disinfectants, but it is not fully effective in some cases (Gray, 2005).

1.2.4 Biological Aspects

Biological aspects include parasitic protozoa and helminthes. Most common forms of parasitic protozoan are Giardia, Coliforms and Entamoeba. Human and animal faecal contamination is the main source for their introduction into the water bodies. Coliforms show great resistance toward inactivation by disinfection and hence cannot be used as direct indicators. Due to the lack of proper indicators to detect the presence or absence of parasitic protozoa, drinking water sources can be used for drinking purposes by ensuring that they are likely not to be contaminated by faecal matter. A single fertilized egg or mature larva of these parasites can be harmful to humans when transmitted through drinking water (Maddaus, 2007). According to the WHO standard concentration of coliforms in drinking water should be 0 counts/100 mL (WHO, 2011).

1.3 Physicochemical Parameters of Water

Water quality has many physical, chemical and biological characteristics (Mohsin *et al.*, 2013), and geological data of the particular region may provide fruitful information about it. Water is used for different purposes such as drinking, agriculture, household and industrial applications so its contamination with harmful micro-organism, toxic/heavy metals is one of the serious problems for all living organisms (Palanisamy, 2007). Consequently there is a need for some physicochemical parameters to monitor the quality of drinking water. Selection of these parameters depends on the nature of water use. These parameters include colour, taste, smell or odour, temperature, pH, electrical conductivity, total dissolved solids, total alkalinity, total hardness, dissolved oxygen, chlorides, etc. (Patil *et al.*, 2012).

1.3.1 Colour

Usually water is colourless and it is the basic requirement for drinking purposes, but sometimes it becomes coloured due to the presence of some organic matters and other constituents (Mohsin *et al.*, 2013).

1.3.2 Taste

Taste in water may be due to different living organisms, industrial wastes and decaying organic matters. It has three types including sweet, medium and brackish. Drinking water should not be brackish in taste (Mohsin *et al.*, 2013).

1.3.3 Smell/Odour

Industrial pollutants, organic substances and biological activities are responsible to cause water odour. It can be categories into three types including no smell, slightly smell and fast smell. Drinking water should have no smell. Slightly or fast smell water is generally considered unfit for drinking purposes (Mohsin *et al.*, 2013).

1.3.4 Temperature

Temperature plays a vital role to control the chemical reactions and metabolic activities of all living organisms (Patil *et al.*, 2012). It is responsible to affect the growth and activity of ecological life as well as solubility of oxygen in aquatic ecosystems (Kataria *et al.*, 2011). It is affected by many factors; water with high turbidity or dark

muddy bottoms usually has high temperature because they absorb more heat. Deep water requires more time to warm up that's why they are colder than shallow water. Trees covering river bank or lake shores shade their water from sunlight and prevent to raise the temperature of these water bodies on bright day. Size and quantity of water in a water body is also responsible for its temperature. Large quantity of water requires more time to heat up or cool down. Temperature of water can also rise by dumping heated effluents into the water ways. Temperature of the water body varies with seasons and environment of its origin. Warm water is toxic for aquatic organisms as it contains elevated levels of toxic substances and this toxicity is further increased when it coupled with low dissolved oxygen levels (Aecos, 2010).

1.3.5 pH

pH is used to measure the concentration of hydrogen ions and acidic/basic character of a substance. It is fundamentally negative logarithmic of hydrogen ions concentration with values ranges from 0 to 14. pH of a water body depends on the nature of substances dissolved in it and it influenced the chemical reactions and solubility of other substances in it. In the natural water reservoirs pH is affected by its age and chemical discharges from the surrounding environments. pH of lakes changes from basic to acidic with passage of time due to formation of acidic materials. Carbonic acid is most common acidic material that is formed by the chemical reaction of water with carbon dioxide. Many industrial processes are also influenced by change in pH of water and sometimes certain chemical or buffers are added to adjust the pH (Wellby et al., 2010). pH does not directly affect the human health but it affects some water parameters like pathogens survival and ionic mobility that caused harmful effects on human beings (Muhammad *et al.*, 2011; WHO, 2011). Lower pH is toxic in the sense that it increases corrosive nature and the solubility of certain chemicals and toxic metals in water (Gupta and Mumper, 2009; Patil *et al.*, 2012). Higher pH is also harmful because it causes bitter taste to water (Mohsin *et al.*, 2013).

1.3.6 Electrical Conductivity (EC)

Electrical conductivity is the measure of ability of water to conduct electricity. Pure water is insulator but it becomes conductor due to presence of certain inorganic dissolved solids (such as chlorides, phosphates, nitrates, sulphates, etc.), metal cations (such as aluminium, calcium, sodium, magnesium, etc.). The electrical conductivity of

water can also be used to determine its purity. Electrical conductivity is temperature dependent; it increases by increasing temperature thus it is reported at 25°C (Boman *et al.*, 2002). Conductivity of water also increases by increasing concentration of above ions (Mohsin *et al.*, 2013). It is also correlated with hardness, alkalinity, dissolved oxygen and total dissolved solids (Patil *et al.*, 2012).

1.3.7 Total Dissolved Solids (TDS)

Total dissolved solids is an important parameter which is used to measure the amount of erosion that took place upstream and surrounding areas of a water body. It can change composition of an aquatic ecosystem by stopping the penetration of sunlight that suppresses the photosynthetic activity of macrophytes, phytoplankton and algae, as well as declining the number of invertebrates that depend on such photosynthetic organisms and ultimately decreased fish populations. It is also responsible to decline number of filter-feeding invertebrates/zooplankton as their filter/feeding mechanisms are choked by the dissolved solids. Fish also feel respiratory problems as they are suffered by clogging and abrasive damages to gills tissues which may cause complete cessation of feeding followed by decrease resistance to diseases and excess of mucous secretion (Aecos, 2010).

1.3.8 Total Alkalinity

Alkalinity is the ability of water to neutralize acids, especially the salts of weak acids (Agdag and Sponza, 2005). As described above, pH measures the acidic/basic character of a substance but alkalinity determines the capacity of a solution to react with acid to buffer its pH. Due to its buffer action, alkalinity is very important parameter for fish and other aquatic life. Alkalinity also reduces the effects of acid rain. Alkalinity of water body may be due to the presence of some mineral salts that are introduced in it from surrounding environment. These are salts of bicarbonates, carbonates, phosphates, silicates, borates, etc. Hydroxide ions also contribute towards alkalinity. Most common forms of alkalinity are carbonates, bicarbonates and hydroxide and they are ranked on the basis of their association with greater pH values (Ramachandra and Solanki, 2007).

1.3.9 Total Hardness

Total hardness in water is due to the presence of bivalent metal cations and more pronounced among them are calcium and magnesium ions. Admissible concentration of total hardness in drinking water set by WHO is less than 500 mg CaCO₃ /L. Higher value

of hardness in water is not useful for drinking purposes and can also produced scaling in pipelines that in turn affect the water supply system (WHO, 2011).

1.3.10 Dissolved Oxygen (DO)

It reflects the concentration of dissolved oxygen in water. Oxygen dissolved in water mainly come either as a waste product of photosynthesis of aquatic plants or through aeration of water, but main source is diffusion from surrounding air. Dissolved oxygen is very fruitful to sustain the aquatic life. Fish and other aquatic fauna have no tendency to split dissolved oxygen from water and oxygen containing compounds. The concentration of dissolved oxygen can be reduced by factors such as temperature of the water body, bacteria, eutrophication, etc. DO generally decreases by increasing temperature because high temperature favours the escape of dissolved oxygen from water. Similarly greater number of bacteria and other aquatic animals consume more dissolved oxygen and hence reduced its concentration. Eutrophication is caused by excess of the nutrients in aquatic ecosystems mainly due to sewage and fertilizer rich farmland drainage. It is responsible for the formation of algal blooms and adverse effects of these algal blooms include death of algae due to absence of light. Decomposition of these algae consumed dissolved oxygen and reduced its concentration and ultimately caused death of fish that depend on it (Radojevic and Bashkin, 1999; Caduto, 1990).

1.3.11 Chlorides

Chloride is a major ion present in natural water where its concentration varies. It provides salty taste to water. More concentration of chlorides is found in salt water lakes and sea water while less concentration is found in mountain streams or lakes. Intermediate chloride concentration is found in estuarine water (Radojevic and Bashkin, 1999). According to WHO standards maximum admissible concentration of chloride in drinking water is 250 mg/L (WHO, 2011). Low concentration of chlorides is required for different physiological processes and body metabolism. Elevated concentration of chlorides (greater than 250 mg/L) make water salty and unfit for drinking purposes and also harmful for growing plants and humans. Higher contents of chlorides also affect the food crops and plant growth. Surface water usually has low concentration of chlorides than groundwater (Mohsin et al., 2013).

1.4 Trace Metals in Water

The elements required by living organisms in minute concentrations are termed as microelements or micronutrients or trace elements. Trace metals are natural components of the environment. These elements play an important role in chemical, biological, biochemical, metabolic, catabolic and enzymatic reactions in the living cells of plants, animals, and human beings (Pais and Jones, 1997; Stoeppler, 1992). Some trace metals such as copper and zinc are essential for living organisms but most of them are harmful and toxic at higher concentrations. They act as conservative pollutants and entered in aquatic ecosystem in large quantities during various processes due to human activities. Human beings settled in areas, contaminated by these heavy metals are more affected due to bioaccumulation of these pollutants (Tautkus *et al.*, 2004). In a water body trace metals are introduced by two major sources; natural and anthropogenic. Municipal/industrial effluents, mining, agriculture and human activities are major anthropogenic sources while weathering, erosion of ore bearing bed rocks, volcanic activities are some natural sources (Chatterjee *et al.*, 2007). Input from rivers and other non-point sources can also contribute to derive trace metals in aquatic ecosystem. Competing process between water and sediments, consumption by micro-organisms, removal by particle scrounge ring and river export to marine ecosystems are key factors for ultimate fate and biogeochemical cycling of these metals (Tang *et al.*, 2002). Trace metals are major sources of water pollution due to their bioaccumulation, toxicity, non-degradability and persistence (Page and Harbottle, 2014; Spanopoulos-Zarco and Inzunza, 2014). Water contamination with heavy metals such as cobalt, copper, zinc, chromium, cadmium, nickel, lead, manganese, different anions and pathogens are one of the serious problems for human health and environment (Avino *et al.*, 2011; Khan *et al.*, 2016, 2013; Lim *et al.*, 2008).

The presence of heavy metals in soil, water and atmosphere can cause serious threat to all organisms due to their bioaccumulation in the food chain and their pervasive nature that can be highly dangerous to human beings (Waseem *et al.*, 2014). It is recognized that malnourishment and diseases such as abdominal pain, anorexia, cardiovascular diseases, immune dysfunction, hypertension, liver and kidney related disorders, as well as various kinds of cancers could be caused not only by nutrient deficiency, but also by excessive intake of heavy metals in contaminated food and drinking water (Shah *et al.*, 2012; Muhammad *et al.*, 2011; Pekey *et al.*, 2004). It is also estimated that not only more than 250000 children die every year due to water born

diseases but these also caused an annual income loss of 25-58 billion in Pakistan. It is also observed that patients suffering from water related diseases occupied 20-40% of the hospital beds and these diseases are responsible for one third of all the deaths in Pakistan (WWF, 2007; PCRWR, 2010). Shortage of the fresh water and pollution in readily accessible resources are current major problems in many developing regions. In such regions limited water resources and poor sanitation condition with accelerated population growth and socioeconomic development are responsible to increase the risks of water born diseases (Khan *et al.*, 2013). Pollution of fresh water bodies due to heavy metals and contaminants is shrinking water resources for domestic purposes (Demir *et al.*, 2014).

Calcium (Ca) is natural and essential element for human body. It is an important structural constituent of different body parts such as skeleton, teeth and also present in soft tissues and body fluids. It comprises nearly 2% of total body weight in adult. It is also essential for various metabolic processes of the body; it regulates intracellular functions, regulates heart rhythm, nerve transmission, muscle contraction, blood coagulation, mitosis, cell adhesiveness, structural support of the skeleton, normal kidney function and lowers the blood pressure (Theobald, 2005; Bacher *et al.*, 2010; Miller *et al.*, 2001; Miller and Anderson, 1999). It is required for proper growth of plants (Dolman and Tepikin, 2006) and several other functions in plants such as cell division, nitrate uptake and metabolism, starch metabolism and enzymes activity (Lenntech, 2010). Calcium is also used to remove stomach acidity and digestive failure in the form of calcium carbonate. Hard water has high concentration of calcium and provides aid in strengthening teeth and bones. Calcium lactate provides support to the body during Ca deficiency (Kozisek, 2003). Its maximum admissible concentration in drinking water set by WHO in 100 mg/L (WHO, 2011). Generally short term intake of calcium is not harmful because gastrointestinal tract limits its absorption, but its long term intake has adverse effects. Adverse effects of calcium include hypercalcaemia, nausea, hypercalciuria, vomiting, suppression of bone remodelling, abdominal pain, calcification in soft tissues, constipation and acute renal failure due to nephrogenic diabetes insipidus. Hypercalcaemia is associated with high concentration of serum ionized calcium, while hypocalcaemia is a condition of low concentration of serum ionized calcium. Major adverse effect of hypocalcaemia are tetany (Heaney *et al.*, 1982; Maziarka and Pasternak, 2013), rickets, bone fracture and poor blood clotting (Mohsin *et al.*, 2013). Calcium deficiency is responsible for osteoporosis, osteomalacia and hypertension.

Cadmium (Cd) is toxic and non-essential element. According to WHO standard

for safe cadmium concentration in drinking water should be 0.003 mg/L and in air should be 5 ng/m³ (WHO, 2011). It is commonly found in combination with Zn in rocks and fossil fuels. Several anthropogenic sources such as mining, electroplating, effluent discharges from industries, incineration, fertilizers, fossil fuel and sewage sludge disposal are responsible for introducing cadmium in the environment (Saleem *et al.*, 2000). Respiration is also a source to introduce many heavy metals in the body and directly affects the lungs. Various studies from Pakistan show cadmium concentration below the admissible level in particulate matters; however it showed large variations ranging from below detection limit to 0.2 mg/L in surface water (Nazif *et al.*, 2006; Mastoi *et al.*, 2008). Although drinking water contributes only a few percent to the total intake of cadmium by all living organisms but this percentage increases in the areas located in the vicinity of heavily cadmium contaminated regions such as mining districts and cadmium emitting plants (Olsson *et al.*, 2002; Ilyasova and Schwartz, 2005). Cadmium being toxic has both acute and chronic impacts. Unfortunately human body has no excretion pathway for this toxic metal so it is accumulated in lungs, kidney, pancreas, skin and the liver (Nath *et al.*, 1984; Savolainen, 1995). Acute effects of cadmium include vomiting, diarrhoea (Nordberg, 2009) while chronic toxicity include kidney damage (Barbier *et al.*, 2005), bone damage (Kazantzis, 1979), cancer (Waalkes *et al.*, 1988) and reproductive problems (Frery *et al.*, 1993; Johnson *et al.*, 2003; Piasek and Laskey, 1999). Cadmium and its compounds are classified as Group-1 carcinogenic by International Agency for Research on Cancer (IARC) (IARC, 2012). Infamous disease *Itai itai* is also caused by the uptake of cadmium-polluted rice.

Cobalt (Co) is the main constituent of vitamin B-12 and it is required for physiological growth of human and animals (Muhammad *et al.*, 2011; Strachan, 2010). Cereals, green leafy vegetables and fish are major food items to provide this dietary mineral. In the body it is stored in red blood cells, plasma, pancreas, spleen, liver and kidney. It is used to treat anaemia by stimulating the formation of red blood cells (Lenntech, 2010), and also used to normalize lipoprotein and cholesterol level (Nicoloff *et al.*, 2006). Cobalt is involved in methionine metabolism and controls the homocystein methyl transferase (Prashanth *et al.*, 2015). Natural activities (such as weathering of rocks and volcanic eruption) and anthropogenic activities (such as alloys production and burning of fossil fuels) are responsible for its contamination in aquatic ecosystem (Gal *et al.*, 2008; Izah *et al.*, 2016). It also becomes toxic at high concentration and caused many pathological problems such as over production of red blood cells, increased activity in

bone marrow, heart problems, thickened blood, vision problems, vomiting, nausea, right coronary problems, thyroid damage and cancer (Robert and Mari, 2003).

Chromium (Cr) is necessary for human body in small amount but it becomes toxic at high concentration. It is used to stabilize blood glucose level in coordination with insulin, reduce triglyceride and cholesterol level from arteries (ATSDR, 2012; Anderson, 2000). Its admissible concentration for drinking water set by WHO is 0.05 mg/L (WHO, 2011). It is an important element for various industries such as pigments, spray painting, stainless steel, leather tanning, chromate and chromium plating etc. (Kabata-Pendias, 2011). Waste water discharges from these industries (especially leather tanning and dyestuff) are a major route of chromium pollution in natural water reservoirs (Waseem *et al.*, 2014). Some other natural sources for chromium contamination in water are runoff, dry fall-out, wet precipitation and weathering of chromium rocks (Kotas and Stasicka, 2000). Chromium is generally present in two forms; trivalent chromium and hexavalent chromium. Hexavalent form is more toxic and carcinogenic than trivalent forms. In fact small dose (25-35 µg/day) of trivalent form is essential for human beings as its deficiency is associated with diabetes and cardiovascular diseases. Drinking water, meats, breads and vegetables are sources of this dietary mineral (Zhitkovich, 2011). Hexavalent chromium is classified as Group-1 carcinogenic by IARC (IARC, 2012), especially for lungs and nasal cavity (Kim *et al.*, 2004; Sunderman, 2001). It is also a potent teratogen (Rana, 2008) and is responsible for many other diseases including small intestine ulcer, sperm damage, nose irritation and stomach tumours (Tchounwou *et al.*, 2012).

Copper (Cu) is also an essential trace metal which act as cofactors for many important enzymes such as ascorbate oxidase, cytochrome c-oxidase, dopamine hydroxylase, superoxide dismutase and lysyl oxidase. These enzymes are used for cellular redox mechanisms. Copper is also used to transport electrons in biological systems. It is absorbed from diet through small intestine and stored in liver by the high affinity human copper transporter (Kuo *et al.*, 2007; Van and Klomp, 2010; Stern, 2010). The recommended dietary allowance for human is 0.9 mg/day (DRI, 2001), and its maximum admissible concentration in drinking water set by WHO is 2 mg/L (WHO, 2011). Many studies indicate that in Pakistan its concentration is less than the maximum admissible concentration in both surface and groundwater (Azizullah *et al.*, 2010). Adverse health effects associated with high copper levels can be acute and chronic. Chronic effects include Parkinson's disease, neurodegenerative disease, Alzheimer's disease, diabetes, atherosclerosis, various types of cancer (such as breast, ovarian, prostates, leukaemia,

lungs and cervical) (Gupta and Mumper, 2009; Kang, 2011; Brewer, 2007; Jomova *et al.*, 2010). Acute effects include vomiting, diarrhoea and epigastric burns (Spitalny *et al.*, 1984; Knobeloch *et al.*, 1994). It can also interfere with Zn hence disturb digestive enzymes (Ebrahim *et al.*, 2011; Kim *et al.*, 2010, Stargrove *et al.*, 2008). It is also involved in the development of coronary artery disease due to oxidation of high density lipoprotein (HDL) that is a cardio protective protein (Jomova and Valko, 2011; LaMarca *et al.*, 2008).

Iron (Fe) is most abundant metal and essential for normal physiology of living organisms. Its maximum admissible concentration in drinking water 0.3 mg/L (WHO, 2011; USEPA, 2009). It acts as a catalyst and is an important constituent of many enzymes, haemoglobin and many other proteins such as ferritin, myoglobin, haemosiderin and cytochrome (Gurusamy, 2007; Eisenstein and Blemings, 1998; Lasheras *et al.*, 2003). It is also involved in brain development, immune system and production of red blood cells (Insel *et al.*, 2003). Concentration of iron in human body is approximately 3-4 g and two-third of this concentration is present in red blood cells that can be recycled by the destruction of red blood cells and 1-2 mg of iron is absorbed in the intestinal tract (Andrews, 1999). Iron is usually present into two stable forms; ferrous ion and ferric ion. The two forms are interconvertable to each other due to electron donating and accepting ability (Kurz *et al.*, 2011). Deficiency and overloading of iron both have adverse effects on all living organisms; deficiency of iron causes fatigue, behavioural changes in childhood, anaemia, pallor and difficulty in maintaining body temperature (Powell, 2002; Sullivan, 1996). Elevated level of iron is responsible for hypertension, rheumatoid arthritis, hypoxia, atherosclerosis, inflammation, neurodegenerative disorders, severe damage to organs/tissues and cancer (Fleming and Ponka, 2012; Oshiro *et al.*, 2011; Gambling and McArdle, 2011; Altamura and Muckenthaler, 2009).

Potassium (K) is an essential metal and required in adequate amount for normal body metabolism. It acts as an electrolyte and takes part in the electrical and cellular function of the body. It is also a constituent of Na-K pump which regulate the intracellular potassium concentration that is necessary for proper functioning of muscles, nerves and hearts (Farouque *et al.*, 2004). Potassium is involved in various body functions such as neurotransmission, regulates blood pressure, promotes healthy skin, proper supply of oxygen to brain, body waste balance, regulate heartbeat, protein synthesis, nucleic acid formation, energy production and glucose metabolism (Lawton *et al.*, 1990). Deficiency of potassium has severe adverse effects including hypokalaemia, nervous disorders, cardiac

failure, respiratory failure, muscle weakness, poor reflexes, intolerance, tiredness and electrolyte imbalance (Naismith and Braschi, 2003; Parekh, 2010; Insel *et al.*, 2003).

Lithium (Li) is essential for the development of behavioural changes (Anke *et al.*, 1990). It is also involved in neurotransmitters and phospholipids metabolism. It is used for the treatment of various diseases such as anorexia, bulimia (eating disorders) and anaemia. Its deficiency causes depressed fertility, poor functioning of endocrine system, altered activities of several enzymes and increased mortality rate (Grandjean and Jean-Michel, 2009; Neilsen, 1998). Although lithium is less toxic due to low bio-accumulation in human and environment but sometimes it causes toxicity to kidney and nervous system. Some other toxicity of lithium includes bipolar disorder, ataxia, memory loss and speech impairment (Gelenberg *et al.*, 1989; Aral and Vecchio-Sadus, 2008).

Magnesium (Mg) is also an important metal for normal metabolic activities and a variety of physiological functions. In body 50% of its concentration is present in bones and remaining 50% is equally distributed between other parts of the body such as muscle and non-muscular soft tissues. Only 1% of total magnesium is present in blood (Volpe, 2013; Greenwood and Earnshaw, 1997; Arnaud, 2008). It is also involved in approximately 300 metabolic reactions (Chakraborti *et al.*, 2002; Eby and Eby, 2010). It has the ability to regulate the formation and degradation of proteins and DNA and also participates in neurotransmission, immune system, bone formation and muscle contraction (Chubanov *et al.*, 2005; Nisha, 2006; Wacker, 1980). Maximum admissible concentration of magnesium in drinking water set by WHO is 150 mg/L (WHO, 2011). Concentration of magnesium in adult human body is 21-28 g. Deficiency of magnesium is responsible for heart diseases, heart failure, metabolic syndrome, insulin resistance, sickle cell anaemia, diabetes mellitus type-2, hypertension, polycystic ovary syndrome, Alzheimer's, depression, Parkinson's anxiety, growth retardation, obsessive-compulsive disorder, tuberculosis pleurisy, multiple sclerosis, chronic kidney diseases, epilepsy and prostate cancer (Glasdam *et al.*, 2016). Mild magnesium concentration is responsible for diarrhoea, nausea, double vision, weakness and abdominal cramps. High concentration of magnesium causes muscular paralysis, difficulty in breathing, cardiac arrest and kidney failure (Saris *et al.*, 2000; USDA, 2003; Jaing *et al.*, 2002).

Manganese (Mn) is essential and naturally occurring trace element in surface and groundwater. Its maximum admissible amount for safe use in drinking water set by WHO is 0.1 mg/L (WHO, 2011). In some cases human activities are also responsible for its introduction in drinking water (USEPA, 2009; Emsley, 2003). It regulates many enzymes

like superoxide dismutase, glutamine synthetase and pyruvate carboxylase in the body (Crossgrove and Zheng, 2004; Michalke *et al.*, 2007). It is involved in bone growth and reproduction. It is mostly concentrated in bones, brain, liver and pancreas. Anthropogenic activities such as mining, agrochemicals, ferro-Mn operations, alloy production/processing and welding are responsible for its introduction into the water body. Deficiency of manganese causes digestive problems, convulsions, dizziness, ataxia, impaired growth, reduced fertility, abnormal glucose tolerance, skeletal defects, blindness and deafness (Lenntech, 2010; Chu *et al.*, 1995; Bowler *et al.*, 1999; Davies, 1999; Dobson *et al.*, 2004). Toxicity of manganese include manganism, muscle stiffness, nervous disorders (such as Schizophrenia), respiratory and swallowing problems, liver abnormalities, neuromuscular disorders, tremble, learning disabilities and difficulty in walking (Mergler *et al.*, 1999; Collipp *et al.*, 1983; Ono *et al.*, 2002; Pal *et al.*, 1999; Aschner and Aschner, 1991).

Sodium (Na) is an essential metal and required to maintain the balance of the body fluid system. It is also involved in the proper functioning of muscles and nerves. Its concentration in drinking water should be less than 200 mg/L (WHO, 2011). Saline and brackish nature of a water body, carbonate precipitation and cation exchange reaction with bivalent ion such as calcium are responsible to increase the concentration of sodium in aquatic ecosystem. High concentration of sodium in a water body makes it useless for drinking and irrigation purposes and also exerts osmotic stress on water biota (Raza *et al.*, 2007; Farooqi *et al.*, 2007). High concentration of sodium in water form sodium hydroxide fumes, that causes irritation to eye, nose, skin and throat, which are responsible for coughing and sneezing. If salty water is consumed by human, it causes hypertension and high blood pressure (Kawasaki *et al.*, 1978).

Lead (Pb) is naturally occurring and notorious element for all living organisms. It has many applications such as lead acid batteries, metal products, ammunitions and X-ray shields (Tchounwou *et al.*, 2012). Although it is naturally occurring metal but different anthropogenic activities such as mining and processing of lead ores, burning of fossil fuels, tyre wear (David *et al.*, 2013) and wastes from different pharmaceutical and batteries production industries are also responsible for the introduction of lead in a water body (Izah *et al.*, 2016). Toxicity of lead inhibits the absorption of essential elements, cardiovascular diseases (Navas-Acien *et al.*, 2007; Nawrot *et al.*, 2002; Poreba *et al.*, 2011, Telisman *et al.*, 2001), hypertension (Bhatnagar, 2006), promoting oxidative stress, lowering vasodilator prostaglandins, increasing endothelin production and arteriosclerosis

(Vaziri, 2008; Gump *et al.*, 2011). Presence of elevated level of lead in blood of patients with irreversible brain and spinal cord damage indicate that lead is also a neurotoxin metal (Khan *et al.*, 2015). In children high concentration of lead is responsible for reduced growth, muscle weakness, blood anaemia, inattention, hallucination, decreased mental ability and brain damage (Muhammad *et al.*, 2014; Naseem and Tahir, 2001). It is classified as group-1 carcinogenic by IARC (IARC, 2012).

Strontium (Sr) has similarity with Ca and Ba in physicochemical properties. Naturally it is found in the form of carbonate mineral or celestite (SrCO_3) and sulphates minerals or strontianite (SrSO_4). It is present in trace amount in almost all fresh water reservoirs. Strontium-90 is radioactive in nature and emits high energy radiation, hence can be used to generate electricity (Skougstadt and Horr, 1960). Strontium is non-essential alkaline earth metal. It is bone seeking element and decreases the chances of bone fracture in osteoporotic patients. It also prevents caries in teeth (Prejac *et al.*, 2017). Adverse effects of Sr include hypocalcaemia, rickets, atherosclerosis and cardiovascular diseases (Morohashi *et al.*, 1994; Skoryna and Fuskova, 1985; Mercado and Jaimes, 2007).

Zinc (Zn) is also an essential element for human beings (Solomons and Ruz, 1998). It is the constituent of more than 70 different enzymes that are involved in different metabolic reactions of lipids, carbohydrates and proteins. It is also involved in development of immune system and also increases the action of insulin and maintains glucose level in human body. It is also a cofactor of more than 200 enzymes, which are used for the synthesis of DNA and RNA. It also plays an important role to protect damage of lipids, proteins and nucleic acid by controlling the antioxidant activities and formation of free radicals (Farzin *et al.*, 2009; Devasagayam *et al.*, 2004; Soinio *et al.*, 2007; Powell, 2002). It is redox inert metal and thus does not contribute in redox reaction (Chasapis *et al.*, 2012). Its admissible concentration set by WHO is 3 mg/L (WHO, 2011). Deficiency of zinc is associated with growth retardation, loss of appetite, reduced taste acuity, hypogonadism, poor immune function, delayed wound healing, white spot on finger nails, fatigue and delayed sexual maturity (Prasad, 2003; Sandstead *et al.*, 1998; Oricha, 2010). Zinc toxicity includes poor Cu absorption, dizziness and gastric distress (Yadrick *et al.*, 1989).

1.5 Water Reservoirs in Pakistan

Water reservoirs can be natural and artificial and regulate a large quantity of water.

They are created by constructing a dam across the way of a flowing stream (Somani, 1992). The basic purpose of water reservoirs is to store a large volume of water for its later uses, whenever it is needed. They have many advantages such as provide water for cities, irrigation, to generate power and to sustain fisheries. They are also used to control flood by storing excess water and minimize the rate of flow of water downstream. Reservoirs are also a source of general enjoyment of nature such as boating, fishing, swimming, hiking and photography. Construction of dam to preserve and store water is an ancient practice. For constructing a dam it is necessary to consider the following aspects; catchment's area of the dam, runoff, distribution of rainfall, soil and rock condition. The embankment should be masonry or of loose rocks. Earth forms good retaining walls, but they must be sealed by a core of clay and their faces should be covered by masonry to prevent the chances of erosion (Chernow and Vallasi, 1993; Parker, 1997). The size and depth of a water reservoir depend on various factors such as shape of the land surface, purposes of the reservoir, height and the amount of the water flow blocked by a dam constructed on that reservoir. Water loss from a reservoir can be either through seepage or evaporation and it depends on the area of the reservoir and ecological factors (Jain and Singh, 2003).

Tarbela Dam is constructed on Indus River under Indus Basin Project. The basic purpose for its construction was to store the water of Indus River for irrigation, electricity generation and flood control. Pakistan is among some major arid countries of the world. 75% of its total area receives less than 250mm and 20% receives less than 125mm of annually rainfall. So economy of Pakistan is totally dependent on agriculture blessed by the potential and most extensive irrigation network known as Indus Basin Irrigation System (IBIS). Agriculture gross contributed to 23% of the GDP of overall economy of Pakistan. Before construction of Tarbela Dam, the country had power deficit of around 5000MW and after its construction no big project was initiated which indicates that needs of irrigation and power generation could have been met. Water availability for irrigation in Pakistan was increased up to 15.7% after construction of Tarbela Dam. It can also generate 6298 megawatts of electricity from the irrigation release and also used to control flood that is usually occur in July and August. It is an amazing and key source for fishing, boating, entertainment and tourism. The dam also has significant role towards improvement of standard of living in terms of job opportunities (Tariq, 2010; Brouwer and Hofkes, 2008).

1.6 Major Objectives of the Present Study

Pakistan is a developing country and it is facing various problems related to water pollution such as scarcity of fresh water and a large number of deaths due to water born diseases. The adverse effect of water pollution on human beings and environment is a major issue of present time. Consequently, the present study is intended to envisage the water quality of the country's largest water reservoir, Tarbela Dam. Followings are the major objectives of the present study:

1. To quantify the prevailing levels of selected trace metals in the surface water of Tarbela dam.
2. To estimate various physicochemical characteristics of the water reservoir.
3. To evaluate the baseline data on the current status of trace metals contamination and different physicochemical parameters in the study area.
4. To investigate the mutual relationships among the trace metals and various physicochemical parameters in water of Tarbela Dam.
5. To employ the multivariate statistical methods of analysis for the identification and apportionment of major pollution sources.
6. To assess the possible adverse effects associated with elevated levels of these pollutants on human health.
7. To compare the data of present study with the standard data provided by World Health Authorities and those reported from other areas around the world.

Chapter 2

EXPERIMENTAL METHODOLOGY

2.1 Study Area

The present study is conducted on Tarbela Dam, Pakistan. It is the largest man made earth/rock filled dam by structure and volume in Pakistan and ranked at 5th position in the list of largest dam in the world by volume. It is located in Tarbela Town, Swabi district of Khyber Pakhtunkhwa Province and approximately 50 km (31 miles) from northwest of Islamabad. It was constructed on the Indus River which is the largest river of Pakistan. Indus River is originated from the “land of glaciers” on northern slopes of Kailash, about 17,000 feet (5182 meters) above sea level and it is also known as “Abbasin” or ‘father of rivers’. It has a source near the Lake Mansrowar in the Himalayan catchments area. Indus River flows into an area of 2900 km and ultimately outfalls in Arabian Sea with draining area of approximately 964,261 km². The dam was constructed under ‘Indus Basin Project’ after signing ‘Indus Water Treaty’ between Pakistan and India in 1960. World Bank accepted its construction project in 1965. It was constructed between 1968 and 1976 with a cost of \$1.5 billion. The dam is situated at latitude of 34°05' 23.00" N and longitude of 72°41' 54.00" E. The dam has height of about 485 feet (148 m) from river level, with surface area of approximately 250 km². Its length is 2743 meters and total water storage capacity is 13.69 km³, which is declined up to 33.5% since its construction due to massive sedimentation. Its structural volume is about 153×10^6 m³ and reservoir volume is 13.7×10^9 m³. Shyok River and Siran River joined Indus River near Skardu and Tarbela respectively and they are main Indus River tributaries upstream of the Tarbela Lake. It has 2 spillways that are on auxiliary dam rather than main dam. Discharge capacity of main spillway is 18406 m³/s while auxiliary spillway has discharged capacity of 24070 m³/s. Five tunnels were constructed on Tarbela Dam and among them 1-3 tunnels are used for hydroelectricity generation and 4, 5 tunnels were initially used for irrigation purposes but now they are also converted to hydropower tunnels to enhance Tarbela Hydroelectricity generation capacity. Maximum installed capacity for these tunnels is 6298 MW. The life span of dam is estimated as 85 year that will complete in 2060 (WAPDA, 1968).

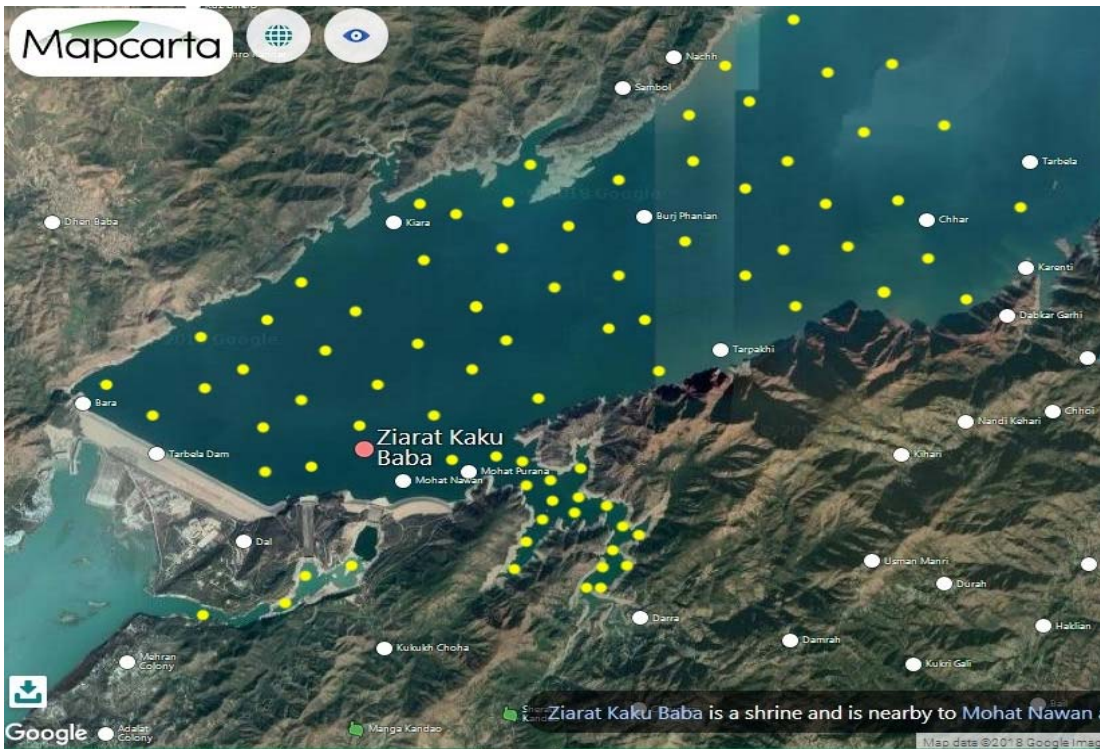


Figure 1. Location map of the study area with yellow point as sampling sites from upstream and downstream region

2.2 Sampling Protocol

Sample collection is first and most crucial step which defines the scope of the successive work, therefore proper sampling procedures are mandatory for environmental investigations. Sampling procedure is often not a problem for those parameters that can be measured in situ. Such parameters are not subjected to an error while collecting samples from the study area and transporting them to the laboratory. However condition becomes more critical for those parameters which show variation in both space and time and in such cases regular and telemetered recordings are necessary. Material for research project and related information about study area are critical need for any environmental investigation (Parker *et al.*, 2007). Sampling can be defined as any technique of selecting and collecting a small portion of sample in volume or weight that can be transported and handled in an analytical laboratory and can accurately represent the part of a sampling site. Sampling is very important procedure in a sense that it has significant influence to the overall error in any analytical process. Sampling procedure has some plans that are termed as sampling protocol which is very important for proper sampling and has following essential aspects:

- Selection of place, time and proper methods for sampling.
- Calibration and maintenance of sampling equipment.
- Washing and storage of sample containers.
- Suitable sample analysis techniques.
- Record of the results of sample analysis.

Sampling protocol has many advantages such as it provides guidelines for sampling, it provides standard operational techniques for sampling and it avoids problems associated with change in sampling personnel (Madrid and Zayas, 2007). Sampling protocol should be simple enough to minimize any kind of contamination or interferences (Worsfold *et al.*, 2005). It is also mandatory to consider the location of the sampling site when developing a sampling plan (Ansa-Asare *et al.*, 2000). Sample containers should be neat and clean as their walls are main source of contamination (Gardolinski *et al.*, 2001). Following steps were adapted for cleaning of sample containers (Australia-EPA, 2002):

- Washed sample container along stoppers with tap water.
- Dipped sample containers and stoppers in a detergent solution overnight.
- Washed thoroughly with tap water.
- Dipped both sample containers and stoppers in acidic solution (10% HNO₃) for at least 2 h.
- Rinsed with plentiful distilled water.
- Allowed the sample containers to air dry.

2.3 Sample Collection, Storage and Preparation

Surface water samples were collected in 500 mL polyethylene plastic bottles from different sites of the main reservoir of Tarbela Dam. Before collecting the sample, the storage bottles were properly washed. During collection of sample, reduced the flow of water to avoid splashing and rinsed the bottles with sampled water for three to four times before final collection. Samples were properly coded and location of each sample was mentioned on corresponding sampling bottle. Samples were transferred to the analytical laboratory on the same day and stored at 4°C. Temperature, EC, DO and pH of each sample were recorded on the same day of sample collection. Each sample was divided into two parts; one for the measurement of physicochemical parameters and second for trace metals analysis using Atomic Absorption Spectrometry. The sample code and details of sampling points included in the present study are shown in Table 1.

Table 1. Description of the sampling points included in the present study

Sample Code	Location	Latitude/Longitude
WT-101	Bara (Near Spillways)	N 34.098181°/ E 72.688291°
WT-102	Bara (Near Spillways)	N 34.090717°/ E 72.699277°
WT-103	Bara (Near Spillways)	N 34.084178°/ E 72.712238°
WT-104	Bara (Near Spillways)	N 34.088016°/ E 72.712410°
WT-105	Bara (Near Spillways)	N 34.093916°/ E 72.705200°
WT-106	Bara (Near Spillways)	N 34.102090°/ E 72.697389°
WT-107	Bara	N 34.099033°/ E 72.702110°
WT-108	Bara	N 34.094058°/ E 72.710006°
WT-109	Bara	N 34.086168°/ E 72.717903°
WT-110	Bara	N 34.087945°/ E 72.717989°
WT-111	Bara	N 34.086452°/ E 72.727116°
WT-112	Bara	N 34.093205°/ E 72.714984°
WT-113	Bara	N 34.101663°/ E 72.709320°
WT-114	Ziarat Kaku Baba	N 34.108415°/ E 72.706058°
WT-115	Mohat Nawan	N 34.103653°/ E 72.710950°
WT-116	Ziarat Kaku Baba	N 34.095551°/ E 72.717989°
WT-117	Kiara	N 34.086879°/ E 72.724083°
WT-118	Kiara	N 34.095622°/ E 72.719190°
WT-119	Kiara	N 34.107349°/ E 72.711208°
WT-120	Kiara	N 34.109836°/ E 72.713697°
WT-121	Kiara	N 34.103724°/ E 72.719705°
WT-122	Kiara	N 34.095622°/ E 72.729232°
WT-123	Mohat Purana	N 34.088656°/ E 72.737215°
WT-124	Mohat Purana	N 34.092565°/ E 72.739103°
WT-125	Mohat Purana	N 34.097612°/ E 72.737644°
WT-126	Mohat Purana	N 34.103937°/ E 72.730949°
WT-127	Kiara	N 34.109196°/ E 72.729147°
WT-128	Kiara	N 34.119713°/ E 72.728632°
WT-129	Kiara	N 34.119713°/ E 72.734211°
WT-130	Kiara	N 34.116303°/ E 72.750690°
WT-131	Kiara	N 34.108912°/ E 72.750347°
WT-132	Tarpakhi	N 34.103369°/ E 72.753780°
WT-133	Tarpakhi	N 34.101095°/ E 72.760475°
WT-134	Tarpakhi	N 34.125540°/ E 72.755668°
WT-135	Burj Phanian	N 34.118150°/ E 72.758415°
WT-136	Burj Phanian	N 34.110049°/ E 72.761161°
WT-137	Burj Phanian	N 34.101237°/ E 72.765281°
WT-138	Tarpakhi	N 34.106354°/ E 72.770088°
WT-139	Tarpakhi	N 34.112607°/ E 72.767341°
WT-140	Tarpakhi	N 34.124403°/ E 72.767170°

Sample Code	Location	Latitude/Longitude
WT-141	Burj Phanian	N 34.133639°/ E 72.764595°
WT-142	Burj Phanian	N 34.128808°/ E 72.768714°
WT-143	Nachh	N 34.121419°/ E 72.772834°
WT-144	Chhar	N 34.115592°/ E 72.778499°
WT-145	Chhar	N 34.110760°/ E 72.785022°
WT-146	Chhar	N 34.121561°/ E 72.786224°
WT-147	Dabkar Garhi	N 34.134918°/ E 72.784679°
WT-148	Dabkar Garhi	N 34.143727°/ E 72.782791°
WT-149	Karanti	N 34.151683°/ E 72.781246°
WT-150	Tarbela	N 34.151683°/ E 72.783649°
WT-151	Tarbela	N 34.145148°/ E 72.785194°
WT-152	Tarbela	N 34.137618°/ E 72.790687°
WT-153	Nachh	N 34.129092°/ E 72.796009°
WT-154	Tehli	N 34.117440°/ E 72.805622°
WT-155	Tehli	N 34.114171°/ E 72.812660°
WT-156	Tehli	N 34.119998°/ E 72.814033°
WT-157	Tehli	N 34.125113°/ E 72.814891°
WT-158	Mohat Purana	N 34.087874°/ E 72.740390°
WT-159	Mohat Purana	N 34.0908660°/ E 72.743137°
WT-160	Mohat Purana	N 34.088869°/ E 72.744854°
WT-161	Mohat Purana	N 34.086595°/ E 72.745025°
WT-162	Mohat Purana	N 34.087305°/ E 72.747943°
WT-163	Mohat Purana	N 34.083893°/ E 72.747085°
WT-164	Mohat Purana	N 34.085599°/ E 72.750003°
WT-165	Mohat Purana	N 34.089011°/ E 72.752750°
WT-166	Mohat Purana	N 34.084320°/ E 72.751033°
WT-167	Mohat Purana	N 34.079059°/ E 72.746399°
WT-168	Mohat Purana	N 34.074936°/ E 72.743652°
WT-169	Mohat Purana	N 34.082756°/ E 72.752750°
WT-170	Mohat Purana	N 34.083751°/ E 72.756355°
WT-171	Dara	N 34.080908°/ E 72.756870°
WT-172	Dara	N 34.080090°/ E 72.757728°
WT-173	Dara	N 34.080801°/ E 72.760131°
WT-174	Dara	N 34.077673°/ E 72.756612°
WT-175	Dara	N 34.074900°/ E 72.756612°
WT-176	Dara	N 34.074189°/ E 72.753780°
WT-177	Dara	N 34.071559°/ E 72.754638°
WT-178	Dal (Downstream)	N 34.075967°/ E 72.723568°
WT-179	Dal (Downstream)	N 34.074403°/ E 72.723224°
WT-180	Dal (Downstream)	N 34.075043°/ E 72.720821°
WT-181	Dal (Downstream)	N 34.073550°/ E 72.721422°

2.4 Chemicals and Glassware

All chemicals used were of analytical grade with certified purity of greater than 99.9%. Distilled water was used for the dilution of sample and preparation of all standards. All glassware used was chemically inert Pyrex of high quality. Glassware was carefully washed to avoid any chance of contamination during sample collection, storage and analysis. Certified standard solutions of the metals were used for the preparation of working standards on the day of analysis. Standard reference material was also used to ensure the reliability of the quantified data.

2.5 Measurement of Physicochemical Parameters

Physicochemical parameters of the water samples were estimated using different standard methods of analysis (APHA, 2006). Temperature, pH, EC and DO of the samples were measured on the same day of sampling, using mercury thermometer, pH meter, conductivity meter and DO meter, respectively. Brief methodology for the measurement of different physicochemical parameters is given below:

2.5.1 pH

pH is an important physicochemical parameter of water for acid-base neutralization, coagulation, water softening and precipitation. It is also used for alkalinity and electrical conductivity measurement. Carbon dioxide dissolved in water from air and its equilibrium between $\text{CO}_2 - \text{HCO}_3^{-1} - \text{CO}_3^{-2}$ is responsible to control the pH in a water body. pH range in natural water lies between 4 to 9 while in drinking water its admissible value is 6.5 to 8.5. pH of water sample was measured using digital pH meter which was firstly calibrated using two points calibration with buffer solution of pH 4 and 7. For calibration purposes buffer solutions of pH 4 and 7 were prepared by dissolving the buffer tablets of corresponding pH in 100 mL distilled water. For instrumental calibration, rinsed the electrode of pH meter with distilled water and dip firstly in buffer solution of pH 7 and then in pH 4 following procedure provided in manufacturer's guidebook. After calibration the electrode was rinsed again with distilled water and immersed in water sample and recorded the stabilized reading on data sheet. This procedure was repeated for all water samples and after each sample rinsed the electrode with distilled water before immersing in next sample (Radojevic and Bashkin, 1999; APHA, 2006).

2.5.2 Electrical Conductivity (EC)

Generally, EC depends on the availability and mobility of free ions in a solution and temperature of measurement. Solutions of inorganic compounds have more value of EC as compared to the solutions of organic compounds because of low dissociation of organic compounds (Wu *et al.*, 1987; Jasper, 1988; Schoemaker *et al.*, 1989; Tchobanoglous and Schroeder, 1985). EC is also used to measure TDS and other ionized ions in water (Saleem *et al.*, 2015). EC of water samples was measured using digital EC meter. Calibration of EC meter was carried out using 0.01 M and 0.1 M standard KCl solution, following procedure provided in manufacturer's guidebook. The electrode of EC meter was dipped in 0.01 M and 0.1 M KCl solution and noted the stabilized readings. After calibration immersed the prewashed electrode in water sample and noted stabilize reading on data sheet. Repeated this procedure for all water samples and after each sample rinsed the electrode with distilled water before immersing in next sample (APHA, 2006).

2.5.3 Total Dissolved Solids (TDS)

TDS is very important parameter for physical and biological wastewater treatment process. High quantity of TDS in water makes it unpalatable and unfavourable for drinking purposes. Maximum admissible concentration of TDS in drinking water is 500 mg/L (USEPA, 2009). TDS in drinking water can be measured by different ways such as gravimetric analysis, using EC meter or from values of EC. In current study TDS were measured from the values of EC using following standard relationship:

$$\text{TDS (mg/L)} = K_e \times \text{EC} \quad [1]$$

where, K_e is an empirical or correlation factor and its value is 0.64 (APHA, 2006).

2.5.4 Dissolved Oxygen (DO)

Quantity of DO in water depends on physical, chemical and biochemical activities in an aquatic ecosystem. Temperature, pressure and salinity are some factors that affect the amount of DO in water. Rain water can also increase concentration of DO in surface water (Radojevic and Bashkin, 1999). DO of water sample was estimated using digital DO meter. Simply switched on DO meter and allowed it to stabilize for about 10 minutes. Rinsed the electrode with distilled water and immersed in the water sample. Noted the reading that was stabilized for at least 5 seconds. Repeated this procedure for all water samples and after each sample rinsed the electrode with distilled water before immersing

in next sample (APHA, 2006).

2.5.5 Total Alkalinity

Alkalinity is also a useful parameter in treatment of natural and wastewater. Carbonates, bicarbonates, hydroxides, borates, phosphates and sulphates are some species that provide alkaline nature to water. However carbonates, bicarbonates and hydroxides are major contributors towards alkalinity. It is also influenced by $\text{CO}_2 - \text{HCO}_3^{-1} - \text{CO}_3^{-2}$ equilibrium in water. It is measured as mg of CaCO_3/L . There are three forms of alkalinity; carbonate alkalinity, bicarbonate alkalinity and hydroxide alkalinity. Carbonate alkalinity is due to the presence of carbonates in water. It is also called phenolphthalein alkalinity because here phenolphthalein is used as indicator. In case of carbonate alkalinity pH of water sample is greater than 8.5. Bicarbonate alkalinity is due to the presence of bicarbonates. It is also called methyl orange alkalinity because here methyl orange is used as indicator. In case of bicarbonates alkalinity pH of water sample is between 4.5 to 8.5. Hydroxide alkalinity is due to the presence of hydroxide ions and it is also called caustic alkalinity. Combination of carbonate, bicarbonate and hydroxide alkalinity is termed as total alkalinity.

There are various methods for the measurement of total alkalinity of water but in the current study titration method was employed. Titration of water sample was carried out against standard 0.02 N HCl solution using phenolphthalein and methyl orange as indicators. In the first step titrant was prepared and standardized against 0.05 N standard Na_2CO_3 solution. Afterward, standard acid was taken in a burette and 50 mL water sample was taken in titration flask; 1 drop of freshly prepared phenolphthalein indicator was added in water sample. If colour of the sample changed to violet, titrated it until colour disappeared (end point). Noted volume (A) of the standard acid used on data sheet and from that volume calculated phenolphthalein alkalinity by the following relationship:

$$\text{Alkalinity (mg CaCO}_3/\text{L)} = (A \times N \times 50000) / \text{mL of sample} \quad [2]$$

In second step, 2-3 drops of freshly prepared methyl orange indicator were added in same water sample and colour changed to yellow which was titrated against standard acid solution until colour changed to orange or red (end point). Noted volume (A) of the standard acid (N) used on data sheet and from that volume calculated methyl orange alkalinity by the following relationship:

$$\text{Alkalinity (mg CaCO}_3/\text{L)} = (A \times N \times 50000) / \text{mL of sample} \quad [3]$$

Total alkalinity was calculated by adding the values of phenolphthalein alkalinity and methyl orange alkalinity or using the following relationship (APHA, 2006):

$$\text{Total Alkalinity (mg CaCO}_3\text{/L)} = (V_t \times N \times 50000) / V_s \quad [4]$$

V_t = volume of titrant used for both phenolphthalein and methyl orange alkalinity

N = Normality of standard acid

V_s = volume of sample taken.

(APHA, 2006).

2.5.6 Total Hardness

Water hardness is sum of concentrations of all bivalent cations in water; Ca and Mg ions are the major contributors toward total hardness of water. It is also expressed as mg CaCO₃/L. It can be either temporary hardness or permanent hardness. Temporary hardness is due to the presence of carbonates and bicarbonates of bivalent cations especially Ca and Mg. It is also classified into carbonate and bicarbonate hardness. When numerical value of phenolphthalein and methyl orange alkalinity is greater than hardness value then phenolphthalein and methyl orange alkalinity value equal to hardness value is carbonate hardness and remaining excess value is bicarbonate hardness. Permanent hardness is due to presence of sulphates and chlorides of bivalent ions especially Ca and Mg. In current study we measured only temporary hardness by complexometric titration. Here titrant used was 0.01 M EDTA solution that was standardized against 0.01 M standard CaCO₃ solution. Eriochrome Black-T (EBT) was used as indicator in this titration. Standard EDTA solution was taken in burette and 50 mL of water sample was taken in titration flask; added 2-3 mL of buffer solution (pH 10) and then 2-3 drops of freshly prepared EBT indicator with the appearance of purple colour. Started titration against standard EDTA titrant until colour changed to blue (end point). Noted volume of the EDTA titrant used and calculated total hardness by the following relationship:

$$\text{Total Hardness (mg CaCO}_3\text{/L)} = (V_t \times M \times 1000) / V_s \quad [5]$$

V_t = Volume of EDTA titrant used; M = Molarity of EDTA; V_s = Volume of sample taken (APHA, 2006).

2.5.7 Chlorides

It is one of the major ions present in natural and wastewater and provides salty taste to water. If it is present with Na ions then it has a detectable salty taste even at low concentration (250 mg/L) but if it is present with calcium or magnesium then it has no taste even at high concentration of 1000 mg/L. Concentration of chlorides in water can be estimated by argentometric titration method, ion chromatography or potentiometric method. In the present study argentometric titration method was followed; titrant used was 0.0141 M silver nitrate solution and indicator was 0.01 M K₂CrO₄. Firstly, silver nitrate

solution was standardized against 0.0141 M NaCl solution. Standard titrant solution was taken in burette and water sample in titration flask. Added 2-3 drops of freshly prepared indicator solution and colour changed to yellow. Started titration against standard silver nitrate solution until colour changed to brick red (end point). Following relationship was used to calculate chloride concentration in water:

$$\text{Chloride (mg/L)} = (V_t \times N \times \text{eq. weight of Cl}^- \times 1000) / V_s \quad [6]$$

V_t = volume of titrant used; N = Normality of AgNO_3 ; V_s = volume of sample taken.

(APHA, 2006).

2.6 Analysis of Selected Trace Metals

Atomic spectrometric method is one of the most powerful and widely adopted methods for quantitative analysis of metals in different types of environmental samples. Various kinds of atomic spectrometric techniques used for quantification of metals include atomic fluorescence spectrometry (AFS), electrothermal atomic absorption spectrometry (ETAAS), flame atomic absorption spectrometry (FAAS), inductively coupled plasma mass spectrometry (ICP-MS) and inductively coupled plasma optical emission spectrometry (ICP-OES) (Smichowski, 2008). These types differ only on the basis of nature of radiations and the use of heat for atomization. Atomic absorption spectrometry (AAS) is most commonly used atomic spectrometric technique because of its element selective nature and provides sensitive result at parts per million levels and less. Basic principle of atomic absorption spectrometry includes atomization of constituent molecules or ions and absorption of electromagnetic radiation by these gaseous atoms. Amount of radiations absorbed is directly proportional to the concentration of metals in the sample. Atomic absorption spectrometry has less interference than any other technique and these interferences can be minimized by matrix matching of samples to standards, proper choice of filter media and solvent (Lagalante, 2004). Flame atomic absorption spectrometry (FAAS) was used in the present study. It is considered as standard technique since 1960's because of its sample introduction method through high-efficiency nebulization systems (Ivanova *et al.*, 2004). In this technique the water sample was first vaporized by the flame and trace metals in the sample were converted into atomic form by the dissociation of chemical bonds. Metals in atomic form absorbed radiation of characteristic wavelength. A hollow cathode lamp provided electromagnetic radiations. As each element absorb radiation of a particular wavelength, so various light sources are used in FAAS and only one element is determined at one time using a particular light source. Water samples were

analyzed for selected trace metals including Ag, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Pb, Sr and Zn using a Shimadzu Atomic Absorption Spectrophotometer (Model AA-670, Japan) under optimum instrumental condition as shown in Table 2.

Table 2. Optimum analytical conditions for the analysis of selected trace metals on atomic absorption spectrophotometer (Shimadzu AA-670, Japan) using air-acetylene flame

Metal	Wavelength (nm)	HC lamp current (mA)	Slit width (nm)	Fuel-gas flow rate (L/min)	1% Absorption concentration (ppm)
Ag	328.1	4.0	0.6	2.2	0.06
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
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

2.7 Statistical Analysis

Trace metals data were subjected to univariate and multivariate statistical analysis. In univariate method, basic statistical and correlation analysis was conducted. The basic statistical parameters included minimum, maximum, mean, median, standard error, standard deviation, skewness and kurtosis. Spearman correlation analysis was used to monitor the mutual relationship among different variables. Univariate analysis provided information about distribution pattern and mutual combination of the measured variables. Principle component analysis (PCA) and cluster analysis (CA) are included in multivariate method. Multivariate analysis was used to study the effect of external parameters on the

distribution of metals, defining source profiles and their interpretation in terms of combined influence of several measured variables. PCA was conducted to determine the multiple relationships and apportionment among the selected metals in the water sample. CA was employed to classify the elements of multiple sources on the basis of similarities in their chemical behaviour. Consequently multivariate analysis proved very fruitful tool for identification/apportionment of various sources and covariation of trace metals in the environment. Generally, the multivariate methods help to understand mutual association of a set of variables (Iqbal *et al.*, 2012).

2.8 Health Risk Assessment

Trace metals in a water body have numerous health risks. There are three major pathways to introduce trace metals in human body; direct ingestion through food, inhalation through nose or dermal absorption through skin. But major contribution is from ingestion and dermal absorption. In current study, health risk assessment of metals was conducted using following relationships:

$$\text{Exp}_{\text{ing}} = C_{\text{water}} \times \text{IR} \times \text{EF} \times \text{ED} / \text{BW} \times \text{AT} \quad [7]$$

$$\text{Exp}_{\text{derm}} = C_{\text{water}} \times \text{SA} \times \text{Kp} \times \text{ET} \times \text{EF} \times \text{ED} \times \text{CF} / \text{BW} \times \text{AT} \quad [8]$$

where, Exp_{ing} = Exposure dose ($\mu\text{g}/\text{kg}\text{-day}$) through ingestion; Exp_{derm} = Exposure dose ($\mu\text{g}/\text{kg}\text{-day}$) through thermal absorption; C_{water} = Concentration ($\mu\text{g}/\text{L}$) of trace metals in water; IR = ingestion rate (2.2 L/day and 1.8 L/day for adult and children, respectively); EF = Exposure frequency (365 days/year); ED = Exposure duration (70 year and 6 year for adult and children, respectively); BW = Average body weight (70 kg for adult and 15 kg for children); AT = Average time (25,550 days and 2190 days for adult and children, respectively); SA = Exposed skin area (18000 and 6600 cm^2 for adult and children, respectively); ET = Exposure time (0.58 h/day and 1h /day for adult and children, respectively); CF = Conversion factor (0.001 L/cm^3); Kp = Dermal permeability coefficient (0.001 cm/h for Cd, Cu, Fe, Mn, Li; 0.002 for Cr; 0.004 for Co, Pb; 0.006 for Zn).

Non carcinogenic risk of trace metals was assessed by the following relationship:

$$\text{HQ}_{\text{ing/derm}} = \text{Exp}_{\text{ing/derm}} / \text{RfD}_{\text{ing/derm}} \quad [9]$$

where, $\text{HQ}_{\text{ing/derm}}$ = Hazard quotient through ingestion and dermal absorption; $\text{RfD}_{\text{ing/derm}}$ = Reference dose ($\mu\text{g}/\text{kg}\text{-day}$) for both ingestion and dermal absorption.

HQ is used for numeric estimation of potential toxicity induced by a single metal.

Hazard index (HI) is an integrated form of computed hazard quotient for each metal. HI is used to estimate the overall non-carcinogenic effect posed by more than one trace metals using following relationship:

$$HI_{\text{ing/derm}} = \sum HQ_{\text{ing/derm}} \quad [10]$$

If value of Hazard quotient and hazard index exceeds by 1, then there is potential for human health risk associated with exposure of trace metals. Carcinogenic risk of trace metals was estimated by the following relationship:

$$CR_{\text{ing}} = \text{Exp}_{\text{ing}} \times SF_o \quad [11]$$

where, CR_{ing} = Carcinogenic risk through ingestion; SF_o = Carcinogenic slope factor ($\mu\text{g/g-day}$)⁻¹. It is only available for carcinogenic metals; therefore it was only estimated for Cd, Cr and Pb in the current study. It is used to monitor lifetime risk potential for cancer in local population. Its value for Cd is 6.1 E+03, for Cr is 5.0 E+02 and for Pb is 8.5 E+00. Maximum admissible value for CR_{ing} is 1.0 E-04 for carcinogenic effects of the metals (such as Cd, Cr and Pb). If value of carcinogenic risk exceeds to 1.0 E-04 than there is potential risk for cancer in the individuals which are exposed to these carcinogenic metals for lifetime (USEPA, 2009; Wu *et al.*, 2009, 2010; Iqbal *et al.*, 2012; Saleem *et al.*, 2014).

Chapter 3

RESULTS AND DISCUSSION

3.1 Distribution of Selected Trace Metals

Basic statistical parameters associated with the distribution of selected essential and toxic metals in surface water samples of Tarbela Dam collected in the present study are shown in Table 3. Overall, the data exhibited considerable variation in concentrations of various metals in the water samples. On comparative basis, higher contribution was observed for Mg (4.351 mg/L), Ca (4.312 mg/L) and Na (4.150 mg/L), followed by moderately lower concentration of K (2.693 mg/L). However, lowest mean concentration was observed for Li (0.012 mg/L), followed by Zn (0.035 mg/L), Cd (0.061 mg/L), Cr (0.071 mg/L), Ag (0.073 mg/L), Cu (0.073 mg/L), Sr (0.132 mg/L), Mn (0.261 mg/L), Fe (0.365 mg/L), Co (0.500 mg/L) and Pb (0.685 mg/L). The table also revealed variations in mean and median levels with moderate to low SD and SE values for most of the metals in water sample with exception of Li and Sr that showed approximately comparable values of their mean and median levels. SD and SE values demonstrated higher dispersion for Ca (2.829 and 0.314, respectively), followed by moderate dispersal for Mg (1.195 and 0.133, respectively). Rest of the metals showed relatively lower dispersion in the water samples. Kurtosis and Skewness indicated considerably higher asymmetry in the distribution of Zn, Cd, Cu and Mn whereas somewhat symmetric variations were noted for Ag, Mg, Pb and Cr in the water samples of Tarbela Dam.

Comparison of the average trace metal levels in the water samples collected during the present study are shown in Figure 2, which revealed dominant concentrations of Ca, Mg and Na while least concentration of Li. On the average selected metals in water samples exhibited following decreasing order: Mg > Ca > Na > K > Pb > Co > Fe > Mn > Sr > Ag > Cr > Cu > Cd > Zn > Li. Consequently, Ca, Mg and Na were major contributors in water samples from Tarbela Dam. Figure 3 displayed quartile distribution of selected trace metal levels in the form of box and whisker plot. Overall, the study indicated random and broad distribution of selected metals in water samples. Highest spread was observed for Cd, followed by Ag, Co, Cr, Cu, Fe, Pb, Sr and Zn while least scattering was observed for K and Na. This diverse distribution was a clear indication of anthropogenic and natural intrusion of metals in the study area that will be studied in detail in impending section.

Table 3. Basic statistical parameters for the distribution of selected metal levels (mg/L) in the water samples

	Min	Max	Mean	Median	SD	SE	Kurtosis	Skewness
Ag	0.001	0.261	0.073	0.052	0.063	0.007	1.096	1.277
Ca	0.757	12.17	4.312	3.588	2.829	0.314	0.185	0.930
Cd	0.001	0.431	0.061	0.036	0.073	0.008	9.032	2.652
Co	0.007	1.651	0.500	0.400	0.388	0.043	0.275	0.899
Cr	0.001	0.250	0.071	0.067	0.056	0.006	1.622	1.200
Cu	0.002	0.393	0.073	0.057	0.065	0.007	7.793	2.326
Fe	0.012	1.669	0.365	0.296	0.312	0.035	4.035	1.697
K	1.787	3.171	2.693	2.749	0.339	0.038	-0.367	-0.589
Li	0.001	0.029	0.012	0.011	0.006	0.001	-0.245	0.323
Mg	0.761	6.080	4.351	4.481	1.195	0.133	1.147	-1.007
Mn	0.035	1.020	0.261	0.233	0.174	0.019	7.422	2.320
Na	2.873	5.076	4.150	4.219	0.460	0.051	-0.311	-0.371
Pb	0.019	2.912	0.685	0.353	0.715	0.079	1.557	1.457
Sr	0.001	0.293	0.132	0.131	0.065	0.007	-0.730	0.113
Zn	0.001	0.271	0.035	0.016	0.048	0.005	10.176	2.851

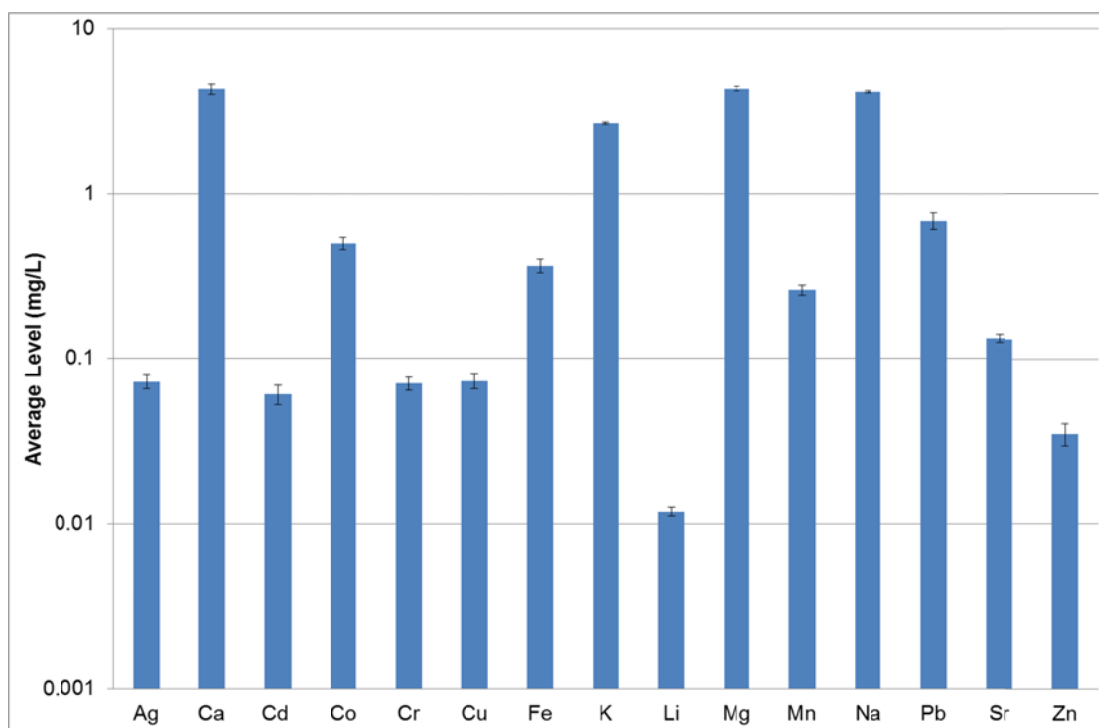


Figure 2. Comparison of the average trace metal levels (\pm SE, mg/L) in the water samples

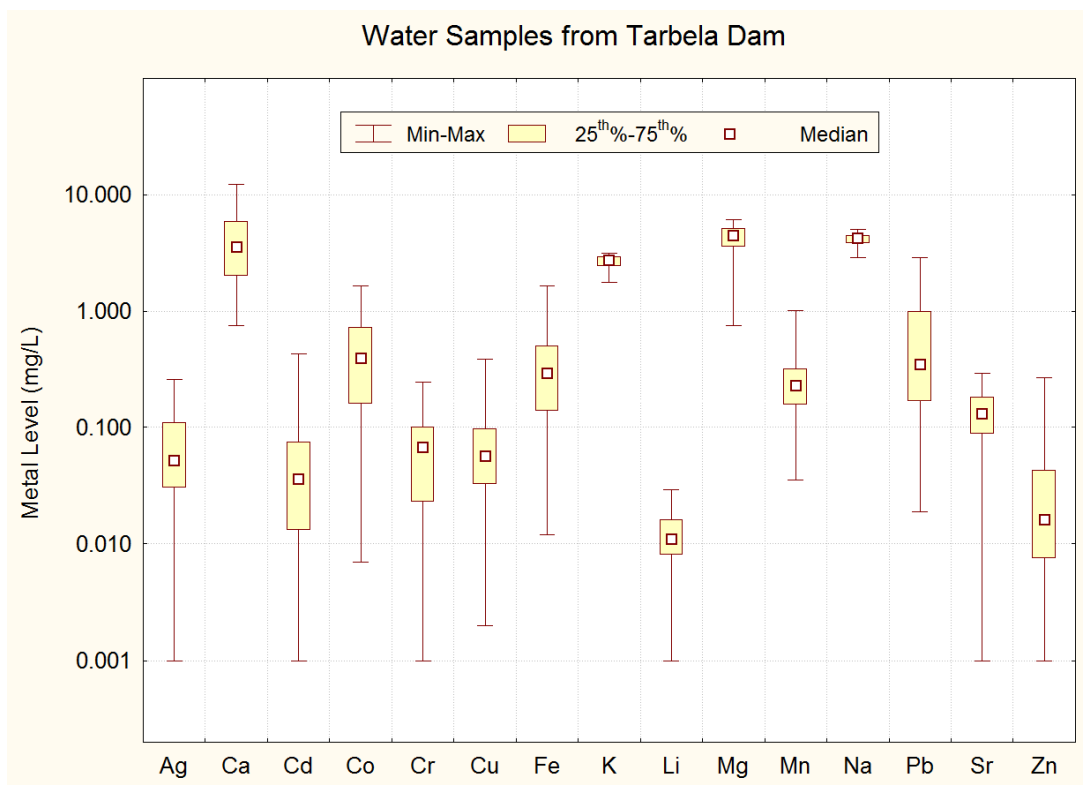


Figure 3. Quartile distribution of selected trace metal levels (mg/L) in the water samples

3.2 Distribution of Physicochemical Parameters

Statistical summary for the physicochemical parameters measured in the water samples from Tarbela Dam is shown in Table 4. The pH value ranged from 7.380 to 7.890 with an average value of 7.781. Thus pH value indicated slightly alkaline nature of the water samples. EC and TDS values showed moderate variation with mean values of 227.2 $\mu\text{S}/\text{cm}$ and 145.4 mg/L, respectively. DO is an important parameter to measure the quality of drinking water; it ranged from 9.710 mg/L to 12.15 mg/L with mean and median levels of 10.50 mg/L and 10.44 mg/L, respectively. A general criterion for drinking water to accumulate DO is 5 to 14 mg/L (WHO, 2011); accordingly the results indicated that water samples were well aerated with excellent DO level for drinking purposes. Greater DO level in water samples was due to the fact that water samples were mainly surface water samples. Alkalinity of water samples was measured as mg CaCO_3/L . Its value ranged from 47.60 to 65.80 mg CaCO_3/L with the average level of 61.86 mg CaCO_3/L during the present study. Alkalinity values showed moderate variation with slight changes in pH values. Similarly hardness contents ranged from 65.34 to 112.9 mg CaCO_3/L with mean value of 106.4 mg CaCO_3/L . Chloride contents were recorded between 9.855 and 14.78

mg/L. Mean value for chloride contents was 12 mg/L. Overall, the results of physicochemical parameters pointed out that water samples collected in the present study belonged to the class of “soft water” because values of all parameters laid within the “permissible safe limit for drinking water” provided by several regulatory organization. Comparative variations of various physicochemical parameters based on their average values are shown in Figure 4. Highest levels were observed for EC, followed by TDS and hardness, while least level was observed for pH.

Table 4. Statistical summary of the physicochemical parameters in the water samples

	Min	Max	Mean	Median	SD	SE	Kurtosis	Skewness
pH	7.380	7.890	7.781	7.790	0.103	0.011	8.188	-2.766
EC ($\mu\text{S}/\text{cm}$)	157.0	239.0	227.2	230.0	15.95	1.773	15.382	-4.051
TDS (mg/L)	100.5	153.0	145.4	147.2	10.21	1.134	15.382	-4.051
DO (mg/L)	9.710	12.15	10.50	10.44	0.425	0.047	2.275	1.085
Alkalinity (mg CaCO_3/L)	47.60	65.80	61.86	63.00	3.269	0.363	7.356	-2.373
Hardness (mg CaCO_3/L)	65.34	112.9	106.4	108.9	9.111	1.012	13.082	-3.593
Chloride (mg/L)	9.855	14.78	12.00	11.83	1.401	0.156	-0.749	0.195

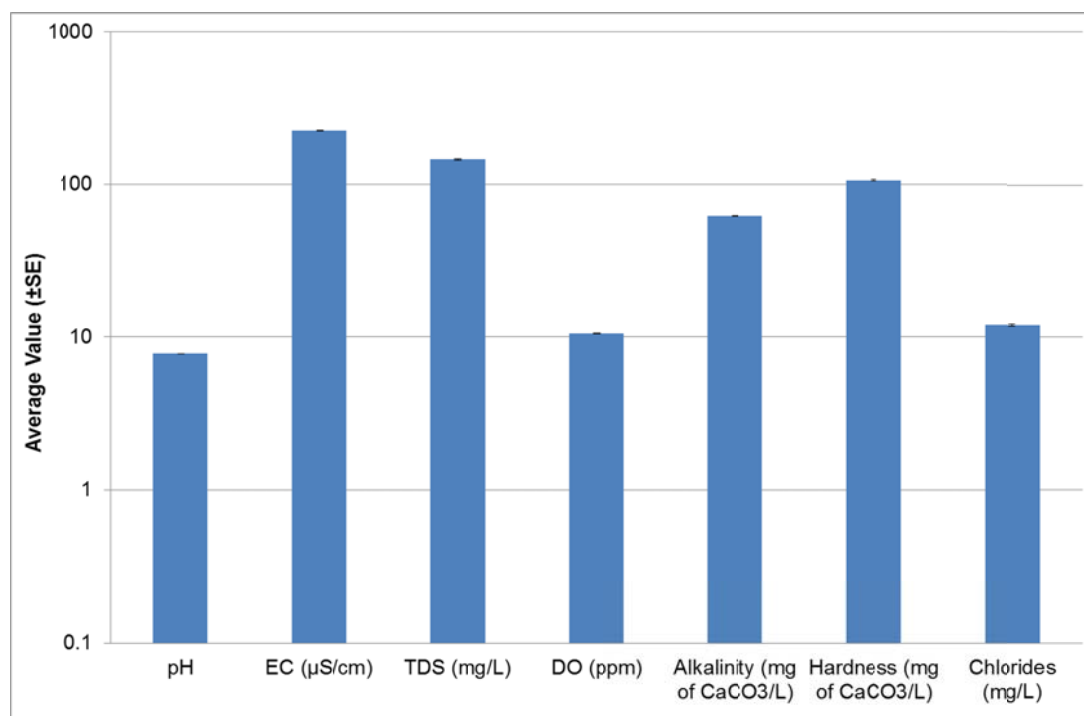


Figure 4. Comparison of the physicochemical parameters in the water samples

Table 5. Correlation coefficient* matrix for selected trace metal levels in the water samples

	Ag	Ca	Cd	Co	Cr	Cu	Fe	K	Li	Mg	Mn	Na	Pb	Sr	Zn
Ag	1.000														
Ca	0.111	1.000													
Cd	-0.032	-0.080	1.000												
Co	-0.028	-0.226	-0.085	1.000											
Cr	0.134	0.012	-0.153	0.067	1.000										
Cu	-0.078	0.097	-0.003	0.120	0.016	1.000									
Fe	-0.002	-0.114	-0.033	0.211	0.006	0.082	1.000								
K	0.077	0.170	-0.104	0.104	-0.330	-0.079	-0.118	1.000							
Li	-0.178	0.122	-0.046	0.048	-0.208	-0.045	-0.097	-0.002	1.000						
Mg	-0.073	0.350	-0.204	-0.006	-0.192	-0.133	-0.084	0.744	0.048	1.000					
Mn	0.076	-0.201	0.045	0.139	0.042	-0.068	0.216	-0.216	-0.059	-0.204	1.000				
Na	0.071	0.654	-0.068	-0.117	0.193	0.017	-0.105	0.049	0.175	0.374	-0.047	1.000			
Pb	0.043	-0.081	-0.021	-0.026	-0.005	-0.116	-0.045	-0.052	-0.001	-0.185	0.016	-0.227	1.000		
Sr	0.004	0.084	-0.022	0.004	-0.134	-0.182	0.064	0.201	-0.051	0.171	-0.170	-0.101	-0.037	1.000	
Zn	0.034	-0.098	0.308	-0.163	-0.162	0.043	0.120	-0.275	0.079	-0.395	0.073	-0.253	0.144	-0.126	1.000

*the coefficient values shown in bold are significant at $p < 0.05$

3.3 Correlation Study of Selected Trace Metals

Correlation coefficient matrix for selected trace metals in the water samples is shown in Table 5. Bold values in the table referred to the coefficient values which were significant at $p < 0.05$. The correlation study showed only few significant correlations between metals; K was strongly correlated with Mg ($r = 0.744$), Ca was positively correlated with Mg ($r = 0.350$) and Na ($r = 0.654$), Mg was positively correlated with Na ($r = 0.374$) and inversely correlated with Zn ($r = -0.395$), Cd showed significant correlation with Zn ($r = 0.308$), while Cr was negatively correlated with K ($r = -0.330$). Rest of the metal pairs showed insignificant relationships which revealed their independent variations in water samples of Terbela Dam. The correlation study thus indicated mutual associations among the major contributors (K, Ca, Mg and Na) in the water reservoir which might be due to their common origin in the study area. However, trace metals (Cr and Zn) exhibited inverse relationships with the major contributors which indicated their opposing distribution and hence diverse origin in the surface water. Generally, Cd contamination is associated with Zn in the environment and this association was established in the water samples of Tarbela Dam as Zn was significantly correlated with Cd (Table 5).

3.4 Correlation Study of Physicochemical Parameters

Correlation coefficient matrix for physicochemical parameters in the water samples is shown in Table 6. The coefficient values shown in bold were significant at $p < 0.05$. It was observed that most of the physicochemical parameters exhibited strong and significant relationship among them; pH showed significantly strong correlations with EC ($r = 0.861$), TDS ($r = 0.861$), alkalinity ($r = 0.826$) and hardness ($r = 0.853$). EC and TDS showed same behaviour of correlation with alkalinity and hardness ($r = 0.844$ and 0.947 , respectively). Similarly alkalinity also showed strong positive correlation towards hardness ($r = 0.838$). Higher coefficient values among these parameters showed the presence of elevated concentrations of dissolved materials that contributed towards these parameters. Overall, the correlation study indicated that pH, EC, TDS, DO and alkalinity showed strong mutual associations in the water samples; it may be attributed to the prevailing elevated levels of dissolved materials/minerals in the study area.

Table 6. Correlation coefficient* matrix for the physicochemical parameters in the water samples

	pH	EC	TDS	DO	Alkalinity	Hardness	Chloride
pH	1.000						
EC	0.861	1.000					
TDS	0.861	1.000	1.000				
DO	0.150	0.238	0.238	1.000			
Alkalinity	0.826	0.844	0.844	0.134	1.000		
Hardness	0.853	0.947	0.947	0.243	0.838	1.000	
Chloride	0.104	0.107	0.107	0.041	0.118	0.053	1.000

*the coefficient values shown in bold are significant at $p < 0.05$

3.5 Correlation Study among Trace Metals and Physicochemical Parameters

Correlation coefficient matrix among trace metal levels and physicochemical parameters in the water samples is also computed and the results are mentioned in Table 7. Among trace metals, Cd showed inverse correlation with hardness ($r = -0.312$) while a significant positive correlation was found between Fe and DO ($r = 0.354$). Similarly K was found to be significantly and positively correlated with pH ($r = 0.409$), EC and TDS ($r = 0.502$), alkalinity ($r = 0.330$) and hardness ($r = 0.463$). Likewise, Mg exhibited strong relationship with pH ($r = 0.576$), EC and TDS ($r = 0.640$), alkalinity ($r = 0.482$) and hardness ($r = 0.617$). Among other metals Na was significantly associated with pH ($r = 0.396$), EC and TDS ($r = 0.426$), alkalinity ($r = 0.444$) and hardness ($r = 0.391$), while Zn was inversely correlated with pH ($r = -0.537$), EC and TDS ($r = -0.505$), alkalinity ($r = -0.489$) and hardness ($r = -0.488$). Rest of the metals including Ag, Ca, Co, Cr, Cu, Li, Mn, Pb and Sr showed no significant relationship with any of the physicochemical parameters so they exhibited independent variations. Overall from the results of correlation study it was concluded that most of the metals showed weak and insignificant correlations with physicochemical parameters in the present study. However some metals (K, Mg and Na) exhibited strong and positive relationship with physicochemical parameters with only one exceptional case of Zn that was negatively associated with the physicochemical parameters in the water samples.

Table 7. Correlation coefficient* matrix for selected trace metal levels and physicochemical parameters in the water samples

	pH	EC	TDS	DO	Alkalinity	Hardness	Chloride
Ag	-0.121	-0.066	-0.066	0.144	-0.022	-0.048	0.090
Ca	0.013	0.004	0.004	-0.054	-0.002	0.015	-0.028
Cd	-0.272	-0.275	-0.275	-0.120	-0.191	-0.312	-0.014
Co	0.215	0.163	0.163	0.059	0.269	0.133	-0.009
Cr	0.235	0.082	0.082	0.060	0.170	0.105	0.103
Cu	-0.192	-0.195	-0.195	0.128	-0.164	-0.264	0.032
Fe	-0.072	-0.078	-0.078	0.354	-0.061	-0.059	-0.027
K	0.409	0.502	0.502	0.129	0.330	0.463	0.061
Li	-0.036	0.079	0.079	-0.002	0.056	0.040	-0.161
Mg	0.576	0.640	0.640	0.081	0.482	0.617	0.155
Mn	-0.087	-0.120	-0.120	-0.018	-0.072	-0.113	-0.058
Na	0.396	0.426	0.426	0.116	0.444	0.391	0.170
Pb	-0.219	-0.213	-0.213	-0.017	-0.231	-0.201	0.047
Sr	0.132	0.075	0.075	0.077	0.029	0.102	-0.252
Zn	-0.537	-0.505	-0.505	-0.065	-0.489	-0.488	0.058

*the coefficient values shown in bold are significant at $p < 0.05$

3.6 Spatial Variations of Selected Trace Metals in the Study Area

Data obtained from the analysis of selected metals in water samples exhibited spatial variation in their levels from point to point. Spatial variations of Ag levels in the water samples from study area are shown in Figure 5. Highest concentration was found in the water sample collected from the sites near to Tarbela WAPDA Harbour House and the least concentration was observed in the water samples collected from Burj Phanian and Dara. Measured concentration of Ca in all water samples is shown in Figure 6 for comparative assessment. Highest concentration was observed in the water sample collected from Ziarat Kaku Baba in the study area, followed by the water samples collected from Bara, Kiara, Tehli and Dara, while least concentration was observed in the water samples collected from Tarbela and Dara.

Spatial variations in the concentration of Cd in the water samples are shown in Figure 7. Highest concentration was noted in the water sample collected from Mohat Purana followed by the water sample collected from Burj Phanian in the study area. Least concentration was also observed in some water sample collected from Mohat Purana.

Comparative assessment of the concentrations of Co in the water samples is shown in Figure 8. Higher level of Co was observed in the water sample collected from Tehli, followed by the water samples collected from Tarpakhi and Mohat Purana whereas lowest level was observed in water sample collected from Dal (downstream).

Spatial variations of Cr levels in the water samples are shown in Figure 9. Elevated content of Cr was observed in the water samples collected from Kiara and Chhar, followed by the water samples collected from Mohat Purana and Dara; least Cr content was found in Dabkar Garhi samples. Comparative evaluation of Cu levels in water sample is shown in Figure 10. Highest concentration of Cu was found in the water sample collected from Chhar while least amount was found in the water samples collected from Tehli, Ziarat Kaku Baba, Kiara, Burj Phanian and Chhar. Spatial variations of Fe levels in the water samples are shown in Figure 11. Highest concentration was found in the water samples collected from Tarbela followed by Chhar, while least amount was found in the Bara, Burj Phanian and Dara samples.

Comparative assessment of the concentrations of K in the water samples is shown in Figure 12. Data in the figure indicated high to moderate concentration of K in almost all water samples with relatively lower content in the water samples collected from Dal (downstream) in the study area. Figure 13 showed the spatial variations of Li levels in water samples from study area. Highest concentration was observed in the water sample collected from Dara, while lowest Li content was found in the water samples collected from Bara, Dabkar Garhi and Dal. Spatial variation of Mg levels in the water samples is mentioned in Figure 14. Mg also showed moderate to high concentration in almost all water samples collected from upstream region. Water samples collected from downstream regions showed relatively lower concentration of Mg.

Comparative evaluation of Mn content in the water samples is shown in Figure 15. Highest concentration of Mn was observed in the water sample collected from Kiara whereas lower content of Mn was found in the water sample collected from Bara. Spatial variation of Na levels in the water samples from the study area are shown in Figure 16. Data in the figure showed moderate to high level of Na in almost all water samples collected from upstream and downstream regions. Comparative assessment of the average concentrations of Pb in the water samples is shown in Figure 17. Considerably elevated level of Pb was observed in the water samples collected from Mohat Purana and Dara while lowest concentration was found in the water samples collected from Bara, Tarpakhi and Chhar.

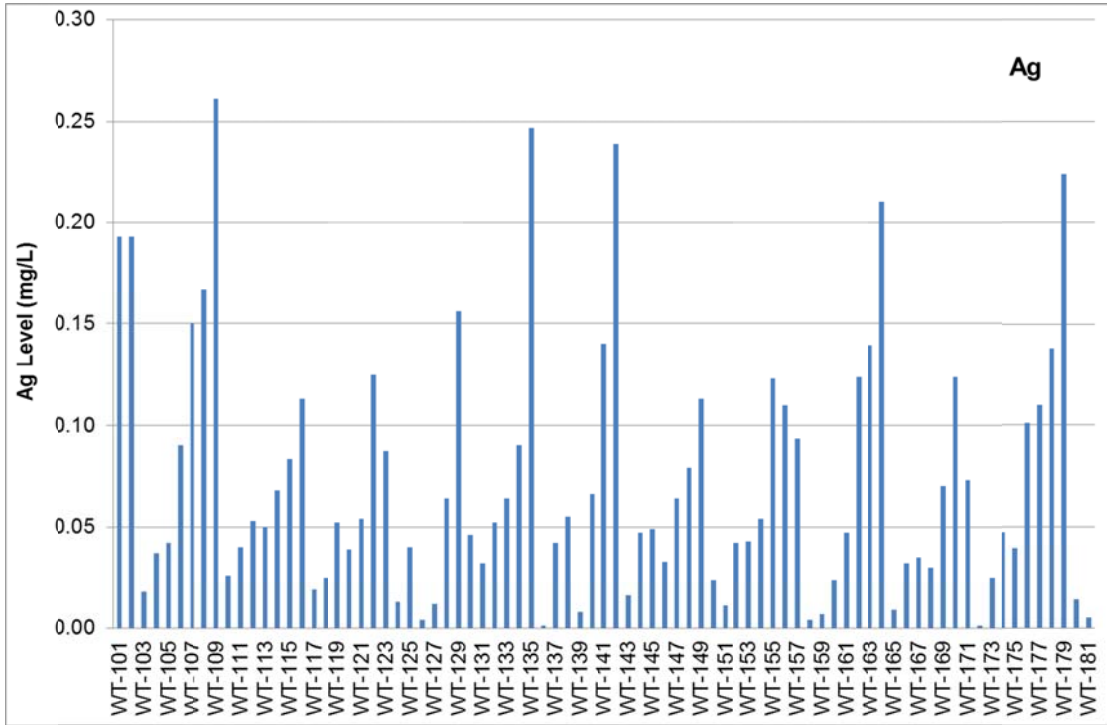


Figure 5. Spatial variations of Ag levels (mg/L) in the water samples from Tarbela dam

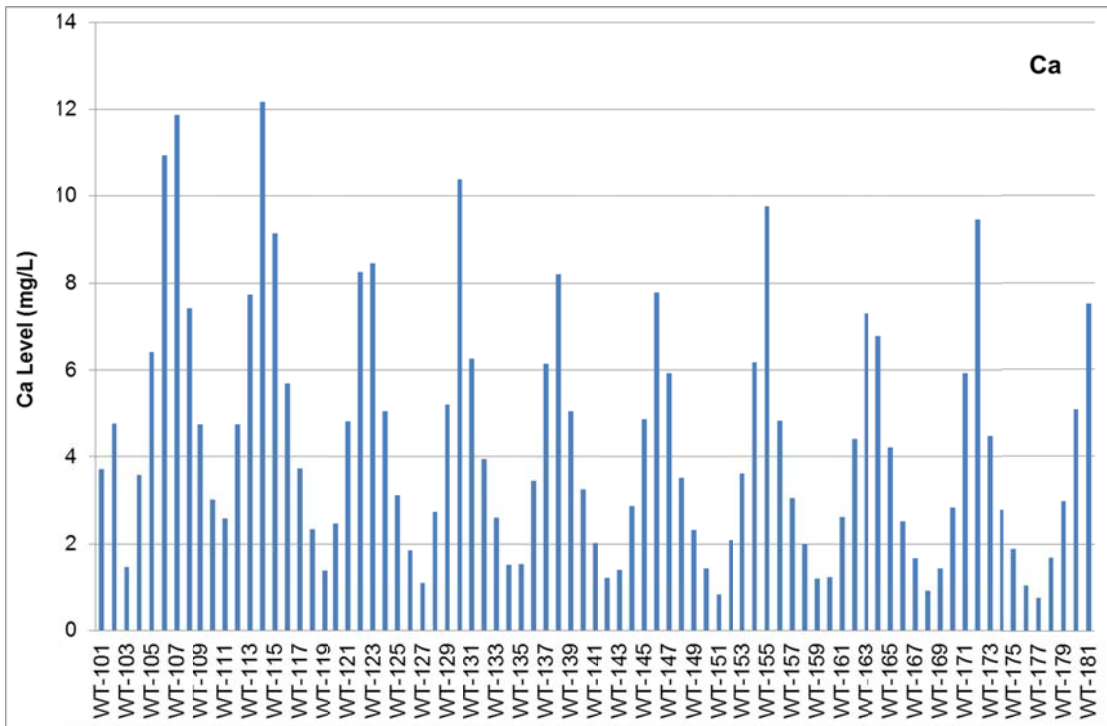


Figure 6. Spatial variations of Ca levels (mg/L) in the water samples from Tarbela dam

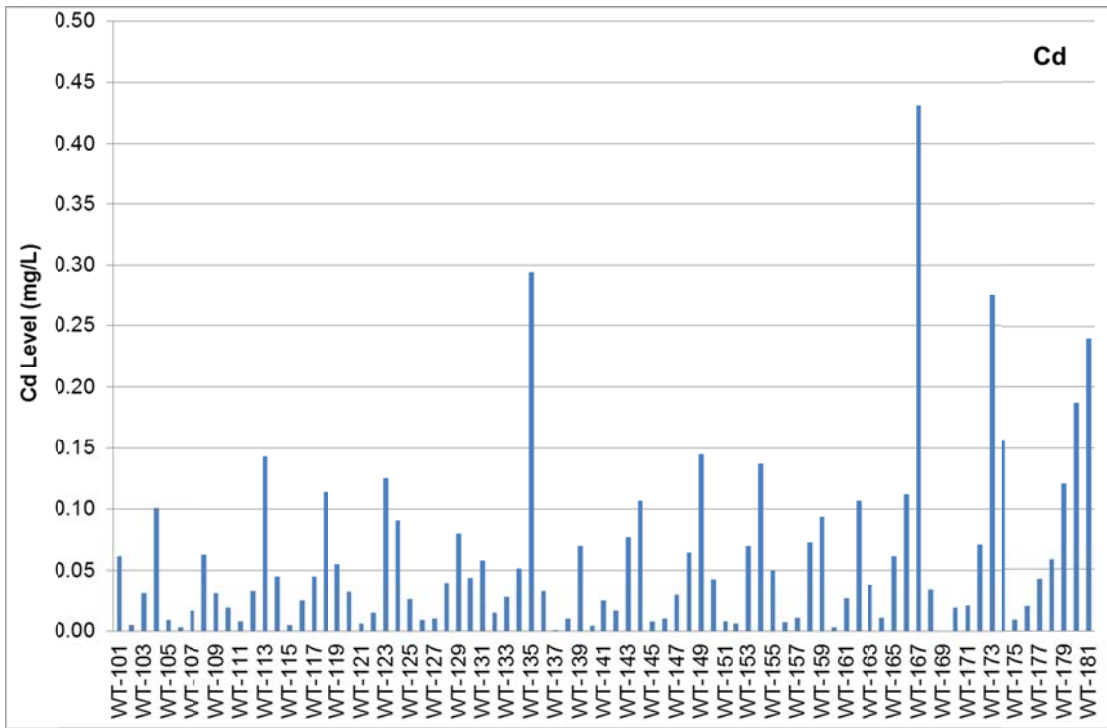


Figure 7. Spatial variations of Cd levels (mg/L) in the water samples from Tarbela dam

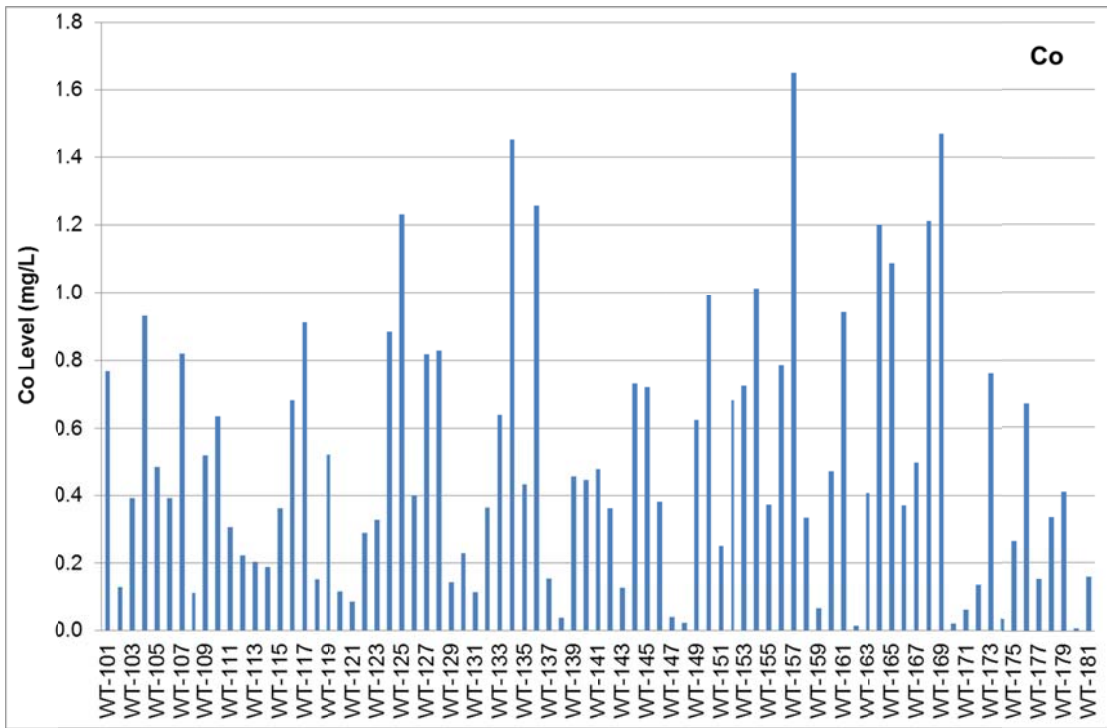


Figure 8. Spatial variations of Co levels (mg/L) in the water samples from Tarbela dam

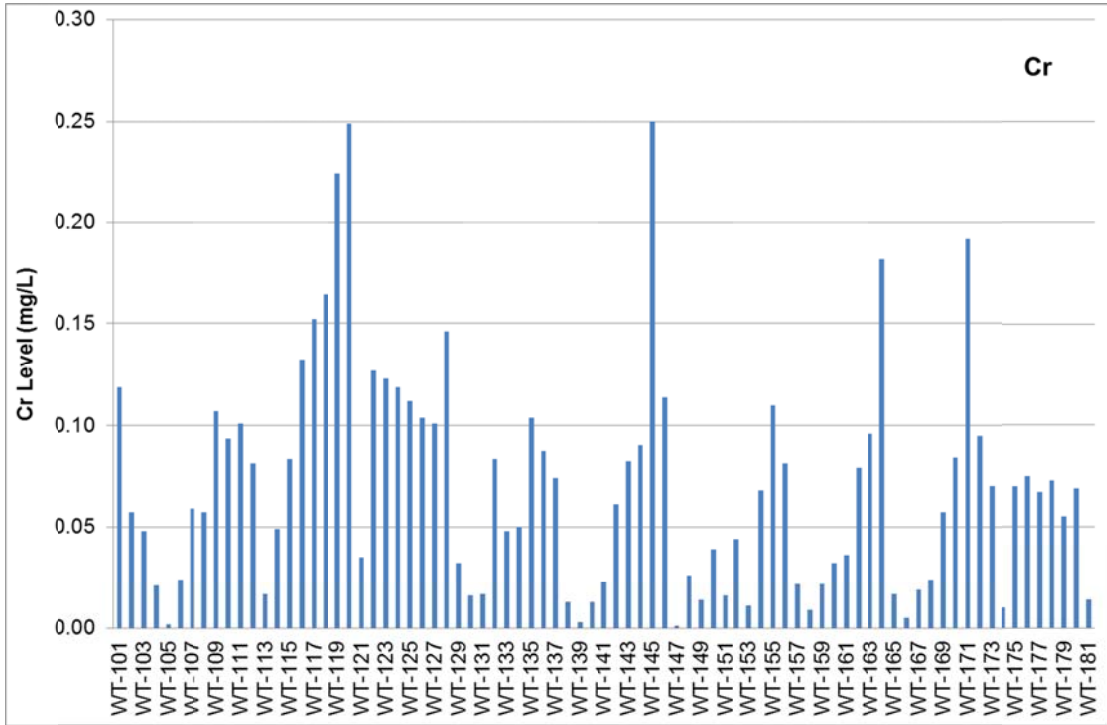


Figure 9. Spatial variations of Cr levels (mg/L) in the water samples from Tarbela dam

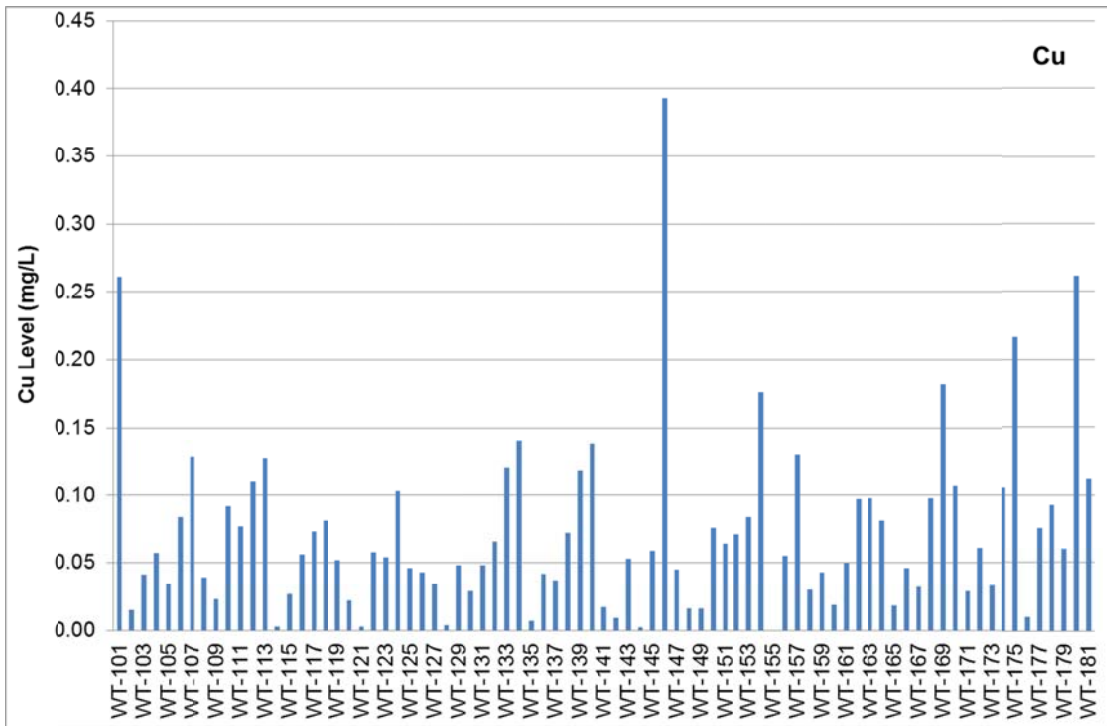


Figure 10. Spatial variations of Cu levels (mg/L) in the water samples from Tarbela dam

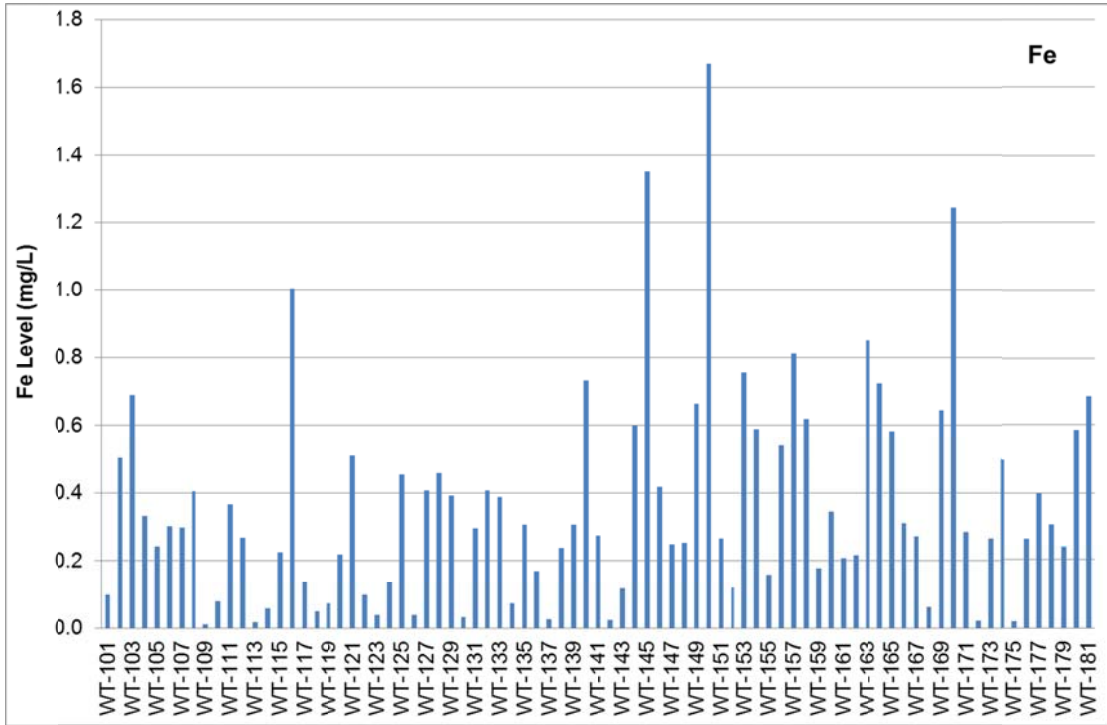


Figure 11. Spatial variations of Fe levels (mg/L) in the water samples from Tarbela dam

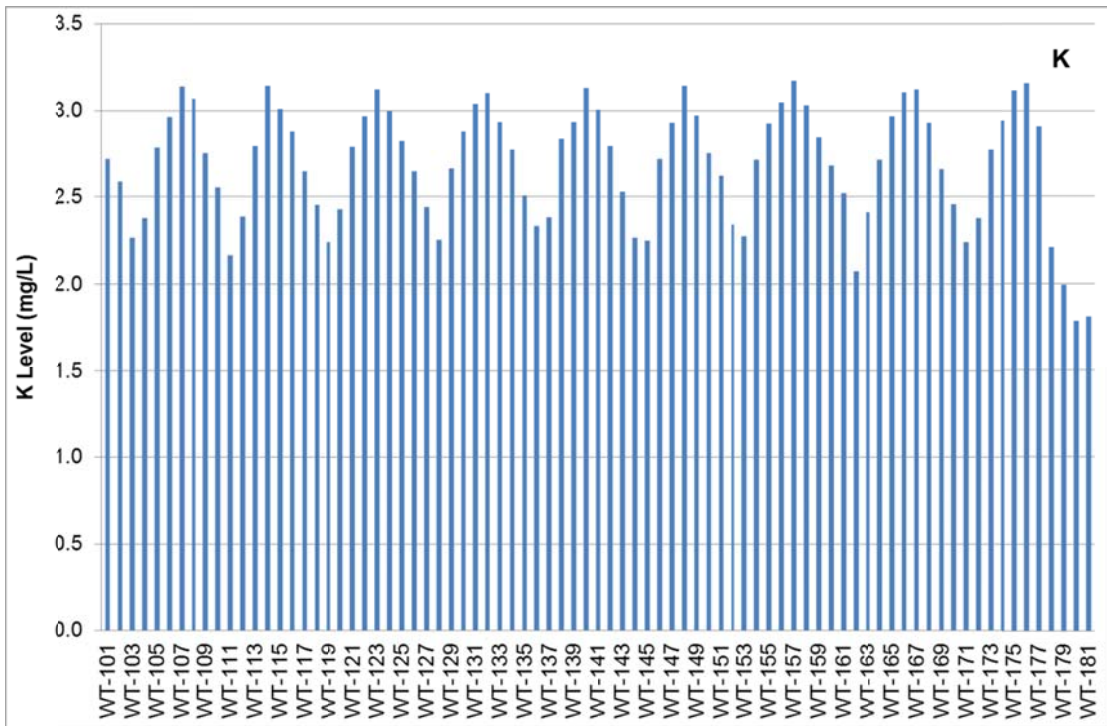


Figure 12. Spatial variations of K levels (mg/L) in the water samples from Tarbela dam

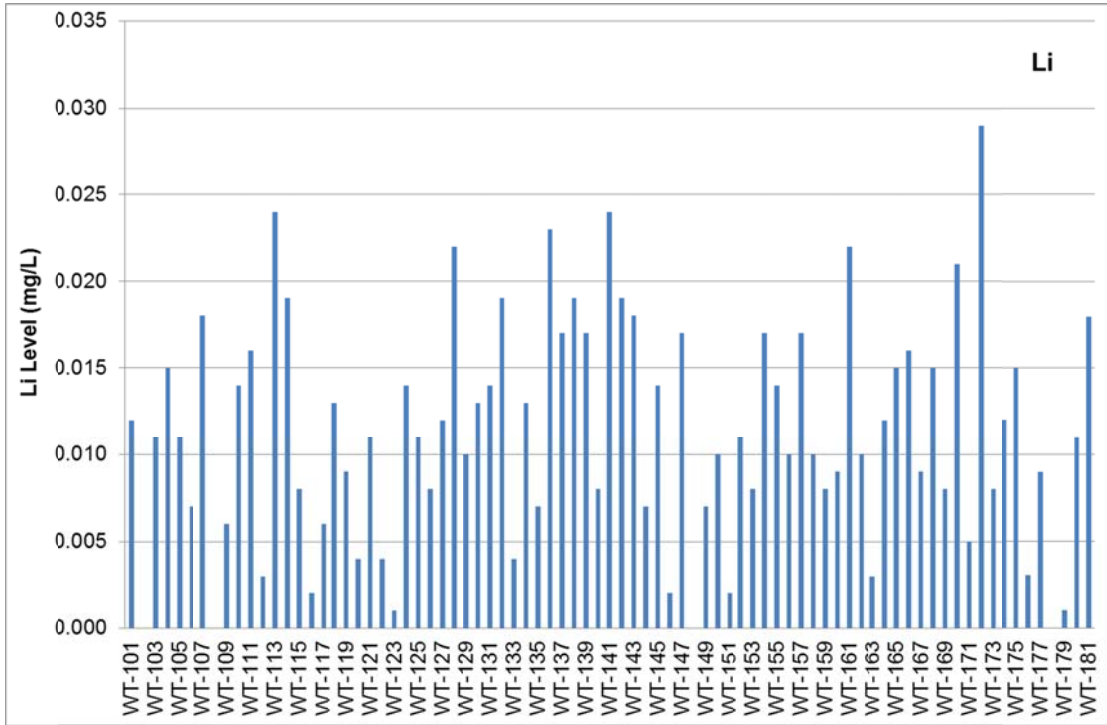


Figure 13. Spatial variations of Li levels (mg/L) in the water samples from Tarbela dam

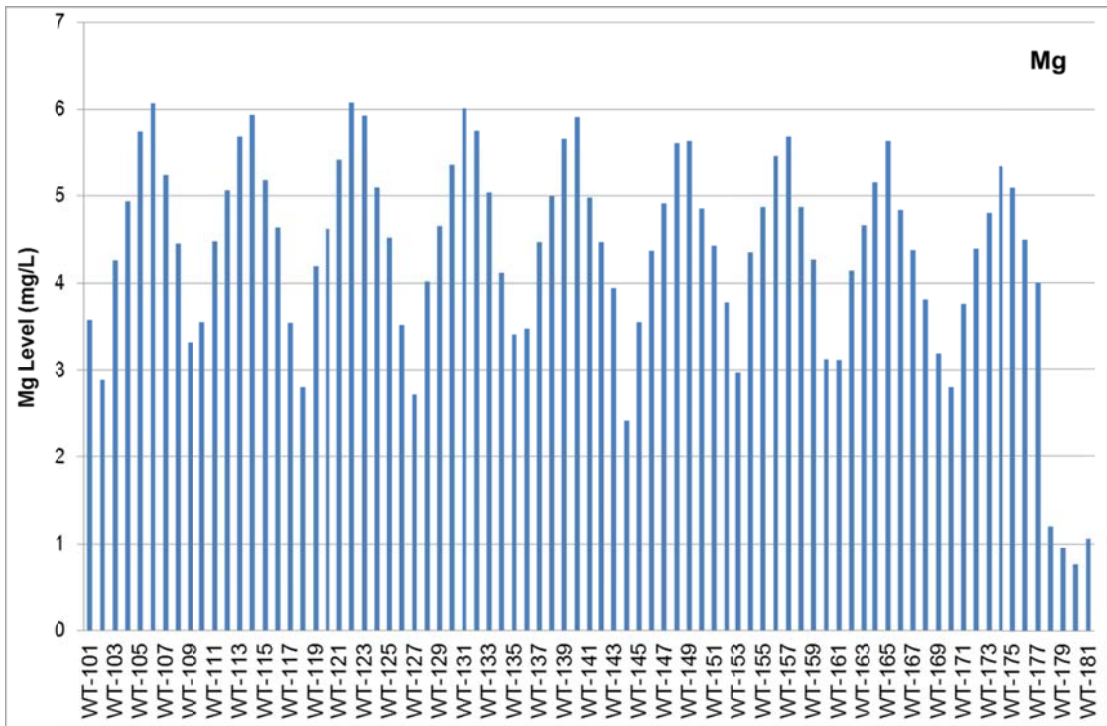


Figure 14. Spatial variations of Mg levels (mg/L) in the water samples from Tarbela dam

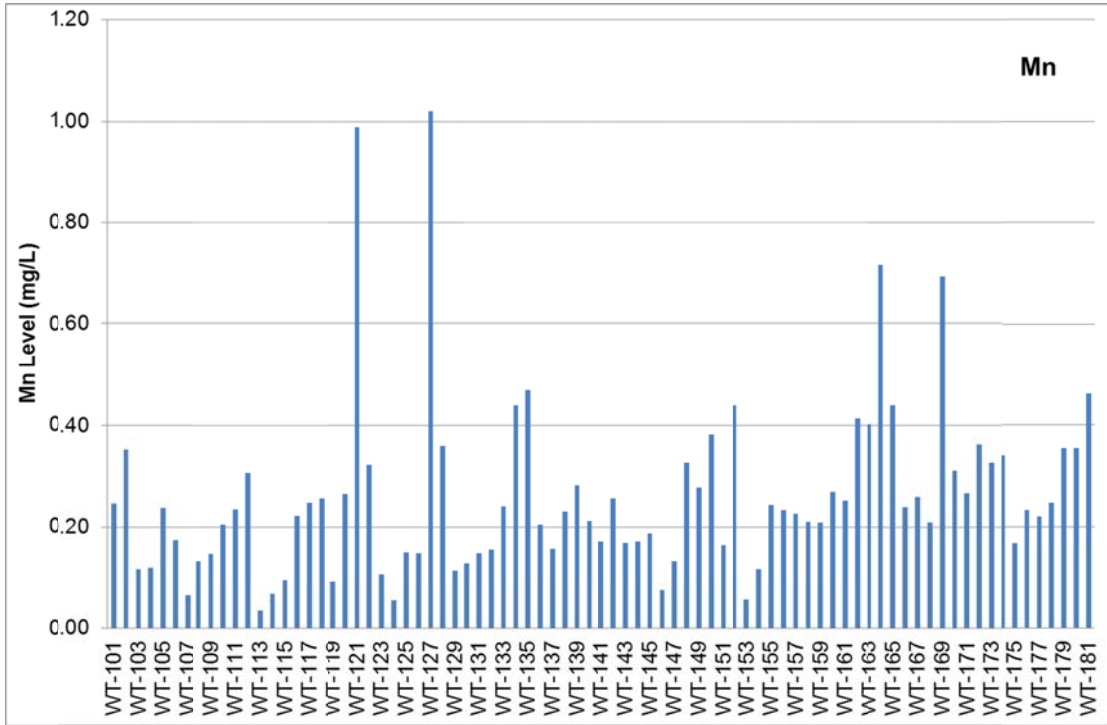


Figure 15. Spatial variations of Mn levels (mg/L) in the water samples from Tarbela dam

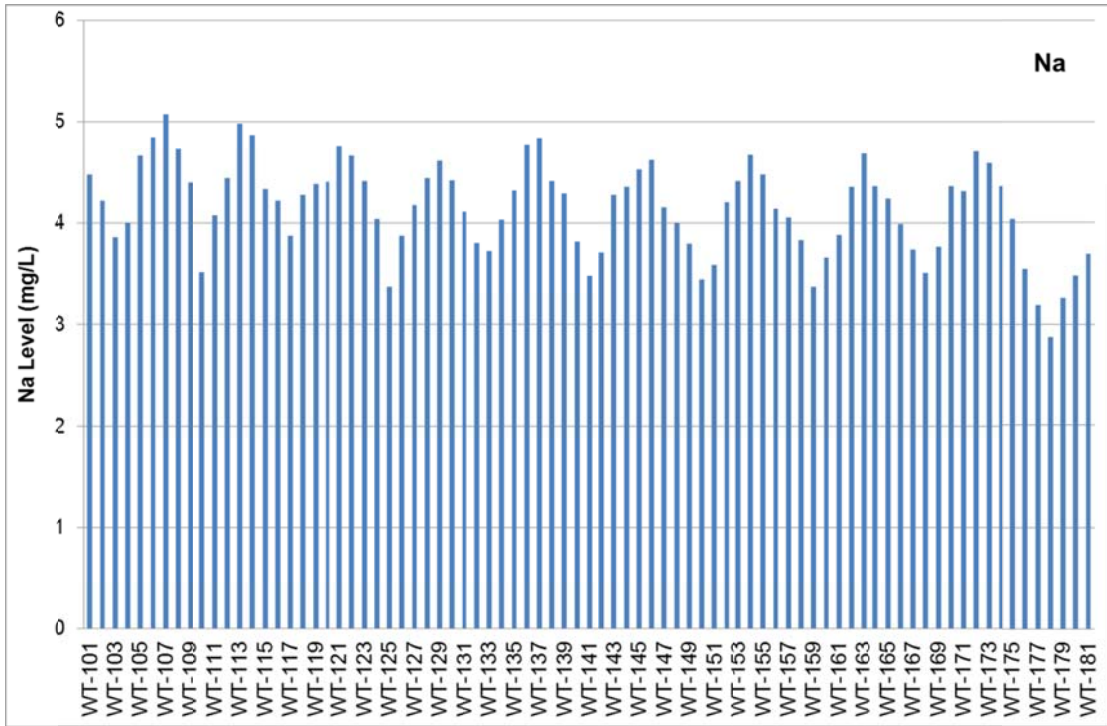


Figure 16. Spatial variations of Na levels (mg/L) in the water samples from Tarbela dam

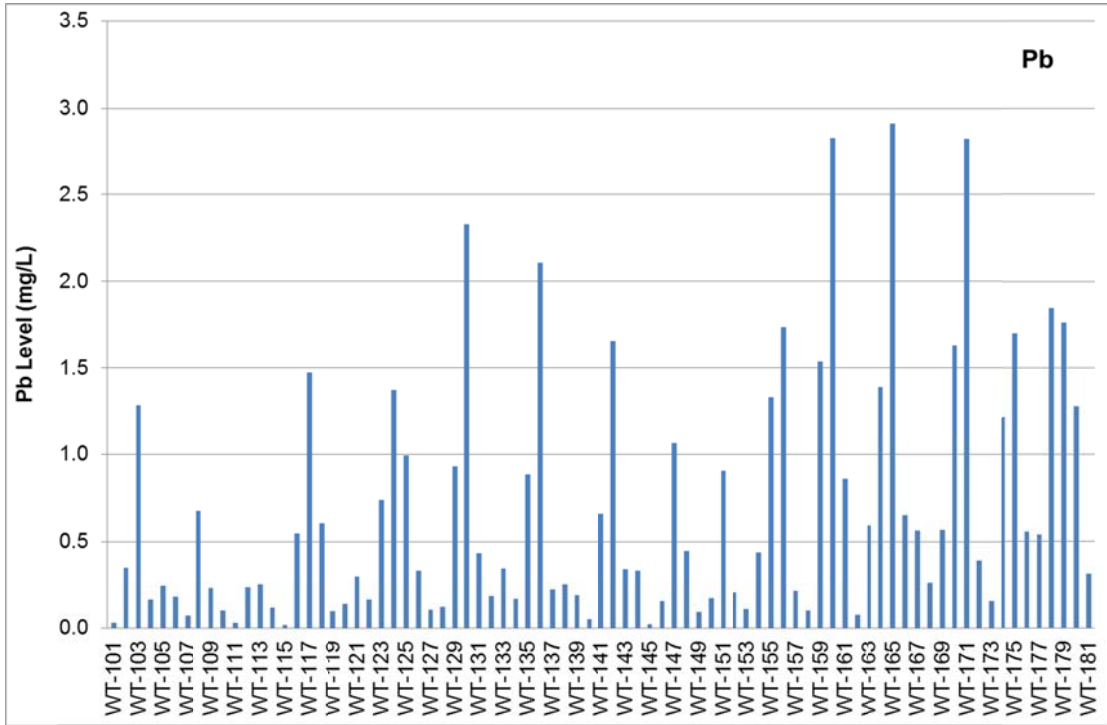


Figure 17. Spatial variations of Pb levels (mg/L) in the water samples from Tarbela dam

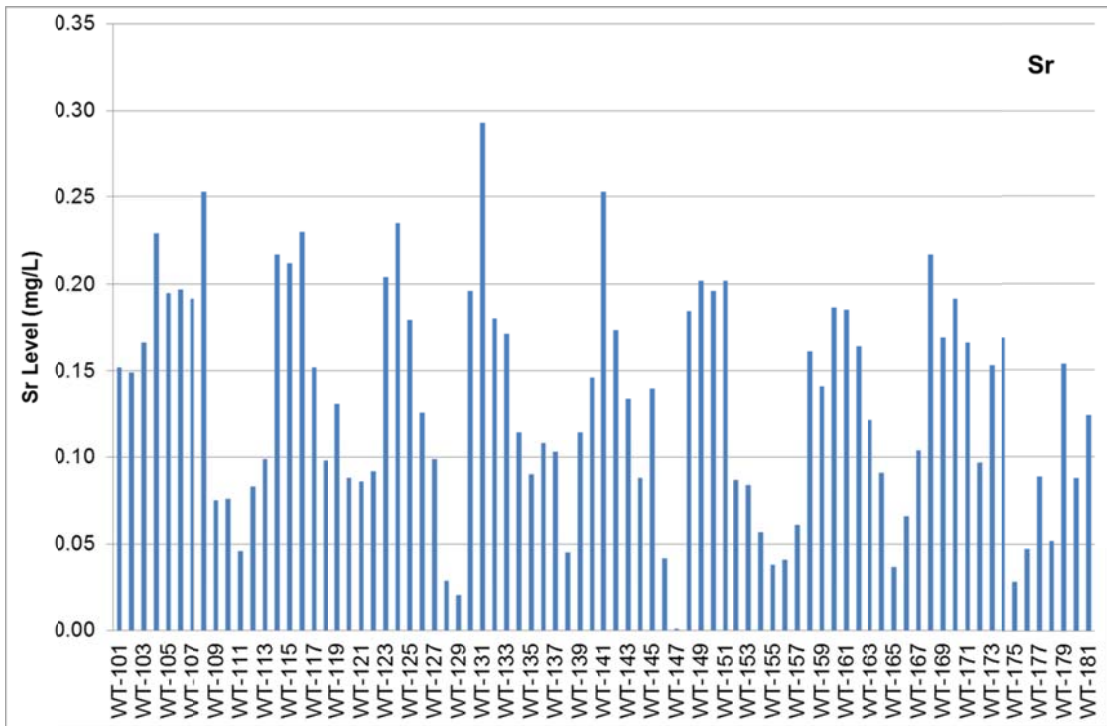


Figure 18. Spatial variations of Sr levels (mg/L) in the water samples from Tarbela dam

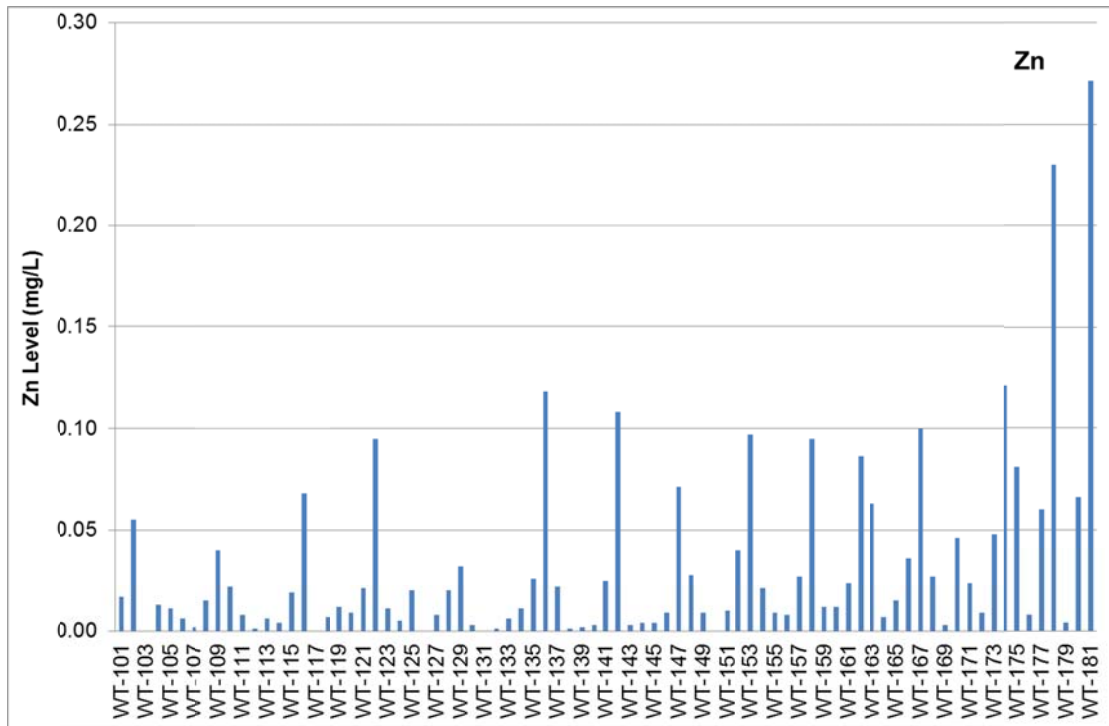


Figure 19. Spatial variations of Zn levels (mg/L) in the water samples from Tarbela dam

Spatial variation of Sr levels in the water samples is shown in Figure 18. Highest content of Sr was observed in the water sample collected from Kiara and lowest quantity was found in the water sample collected from Dabkar Garhi. Figure 19 illustrated spatial variation of Zn levels in the water samples from Tarbela Dam. Elevated level of Zn was observed in the water samples collected from downstream regions while most of the samples collected from upstream region showed relatively lower level of Zn.

3.7 Spatial Variations of Physicochemical Parameters in the Study Area

Spatial variations of physicochemical parameters in the water samples from the study area were also investigated. Results of spatial variations of pH are mentioned in Figure 20. Water samples collected from upstream region showed comparable pH value ranging from 7.1 to 7.9. Highest pH was observed in the water samples collected from Mohat Purana and lowest value was observed in the water sample collected from Dabkar Garhi. The samples collected from downstream region showed relatively lower pH value ranging from 7.1 to 7.4. As it was observed that water was nearly stagnant in upstream

region while in downstream region it was well aerated and showed relatively lower value of pH. Spatial variation of EC values in the water samples is shown in Figure 21. EC also showed same phenomena as observed for pH. Water samples collected from upstream region showed higher value of EC ranging from 230 to 240 $\mu\text{S}/\text{cm}$, while water samples collected from downstream region showed minimum value of EC ranging from 150 to 155 $\mu\text{S}/\text{cm}$. Highest value of EC was observed in the water sample collected from Dabkar Garhi in the study area. Higher values of EC in upstream region relative to downstream region indicated the presence of high mineral contents in upstream region. Figure 22 portrayed comparative assessment of the TDS in the water samples. Highest concentration of 155 mg/L was observed in the water sample collected from Dabkar Garhi and lowest concentration was found in the water samples collected from downstream region.

Spatial variations in DO levels in the water sample are mentioned in Figure 23. Almost all water samples showed comparable values of DO either collected from upstream region or from downstream region. Elevated levels of DO indicated that water samples collected from study area were well aerated. Spatial variations of alkalinity in the water samples are mentioned in Figure 24. Water samples collected from upstream region and downstream regions showed same behaviour towards alkalinity as observed for DO. Values of alkalinity ranged from 60 to 63 mg CaCO_3/L in the water samples collected from upstream region and 48 to 50 mg CaCO_3/L in the water samples collected from downstream region. Figure 25 revealed comparative assessment of hardness in the water samples. Highest value of hardness was found in the water samples collected from upstream region with values between 102 and 110 mg CaCO_3/L while least contents were observed in the water samples collected from downstream with values ranging from 68 to 73 mg CaCO_3/L . Spatial variations in chloride contents are portrayed in Figure 26. Chloride concentrations in the water sample showed irregular spatial variation and varied from moderate to high levels. Chloride contents in water samples ranged between 9.9 to 14.5 mg/L.

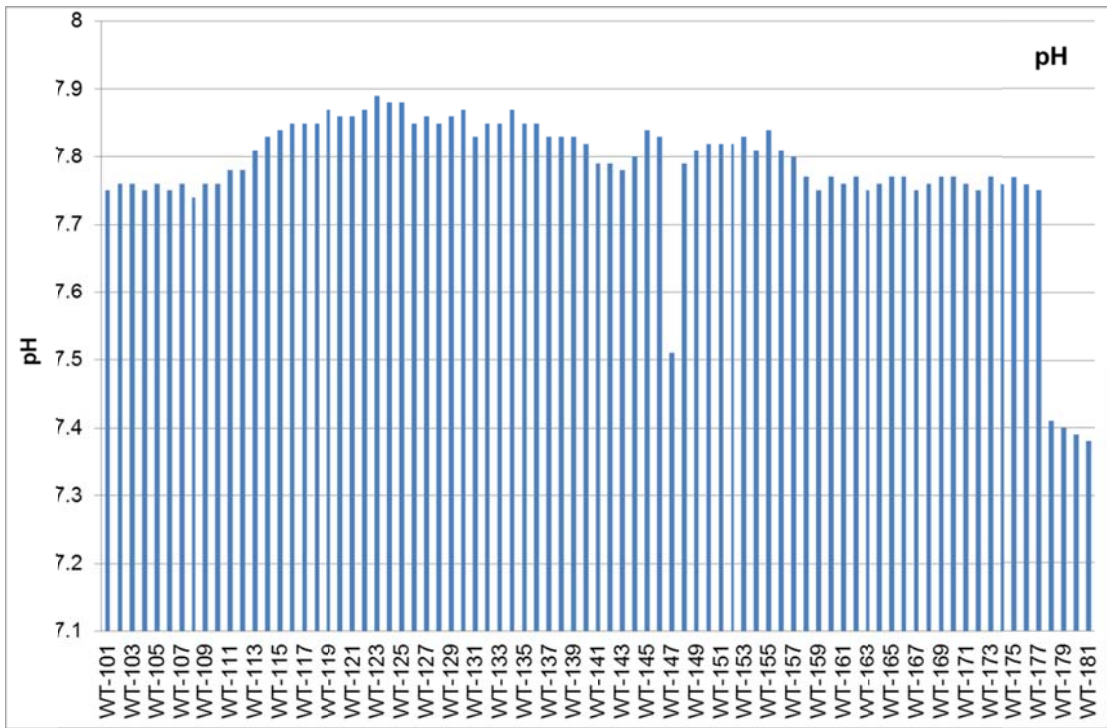


Figure 20. Spatial variations of pH values in the water samples from Tarbela dam

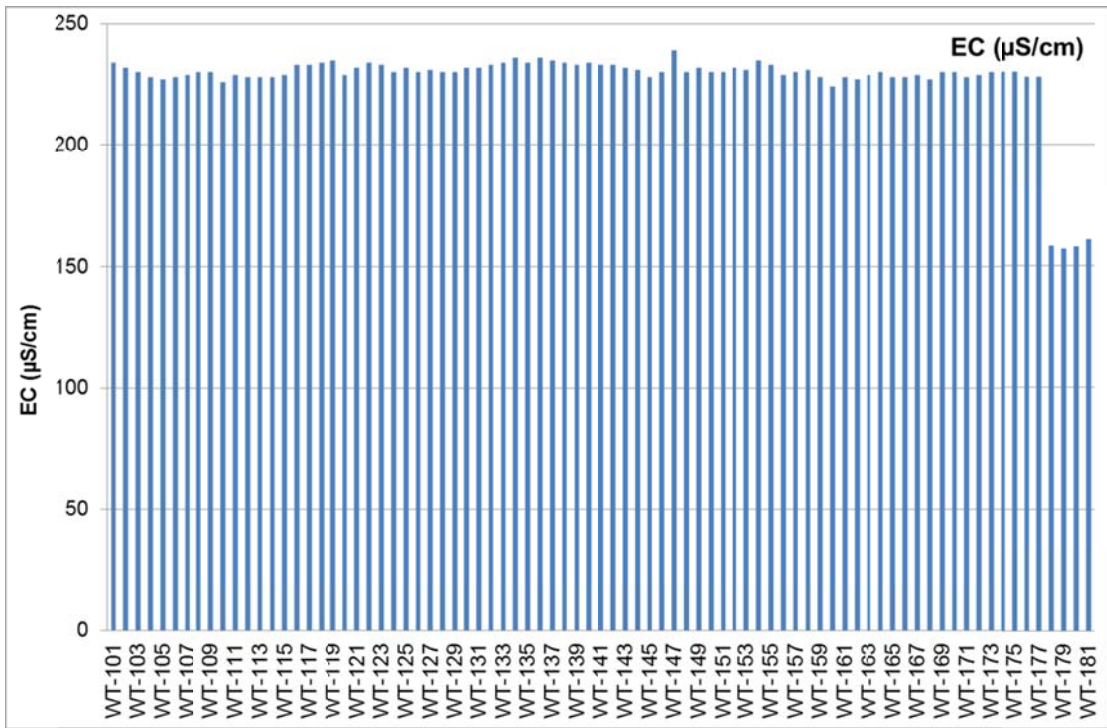


Figure 21. Spatial variations of EC values (µS/cm) in the water samples from Tarbela dam

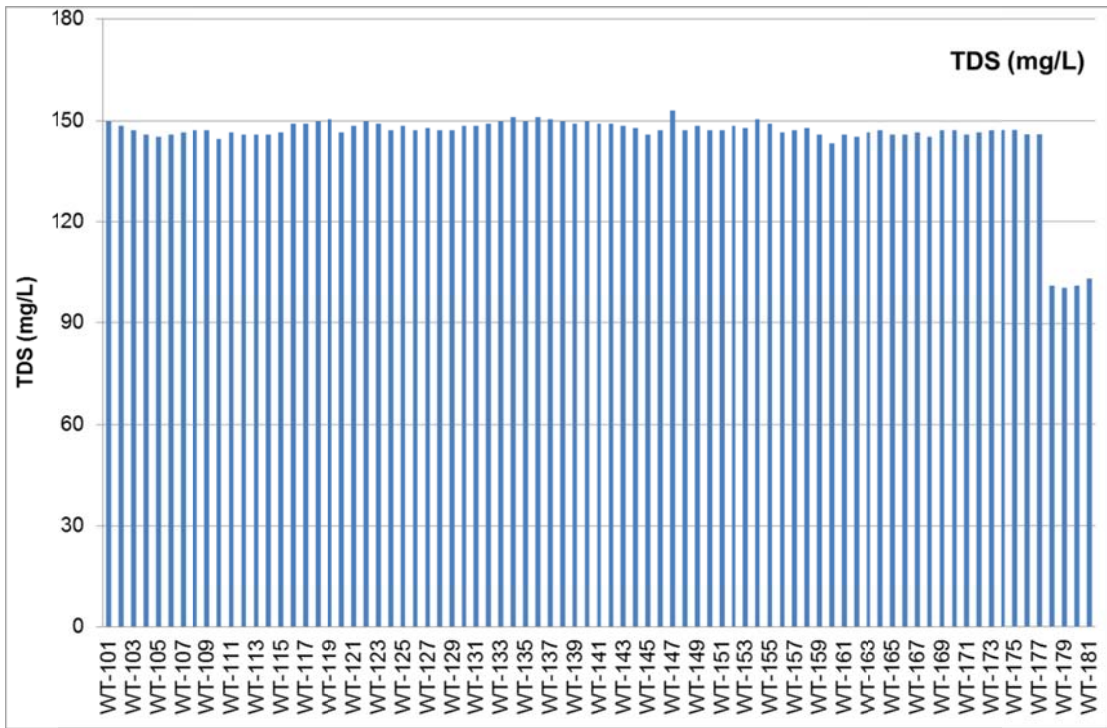


Figure 22. Spatial variations of TDS levels (mg/L) in the water samples from Tarbela dam

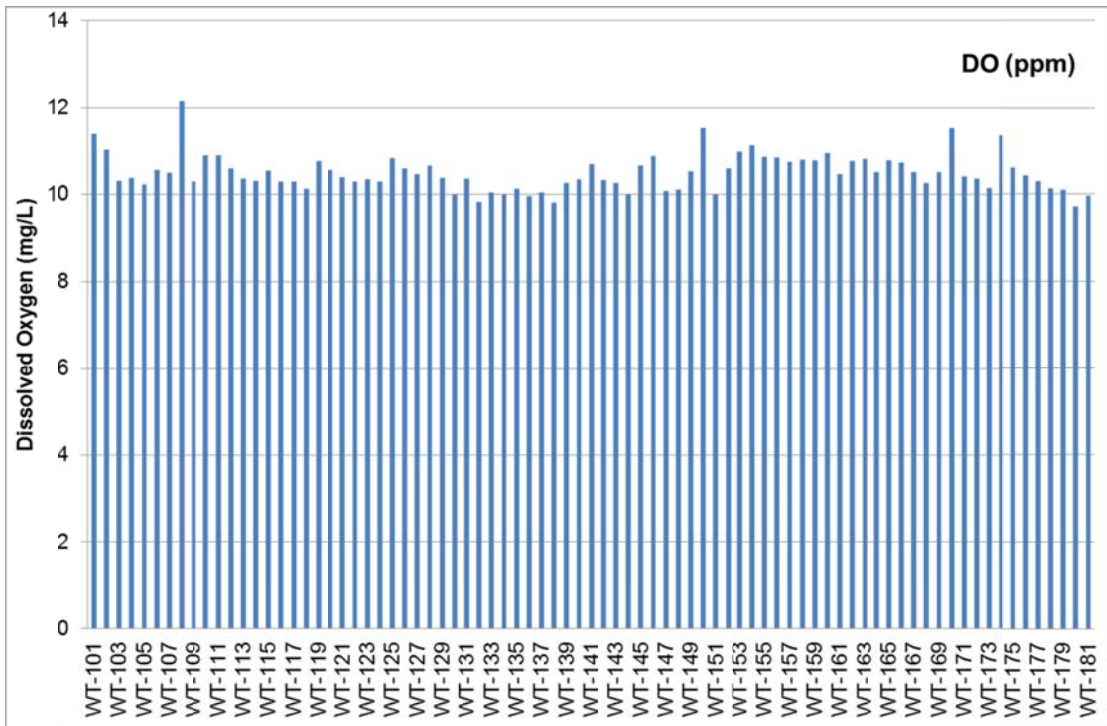


Figure 23. Spatial variations of DO levels (mg/L) in the water samples from Tarbela dam

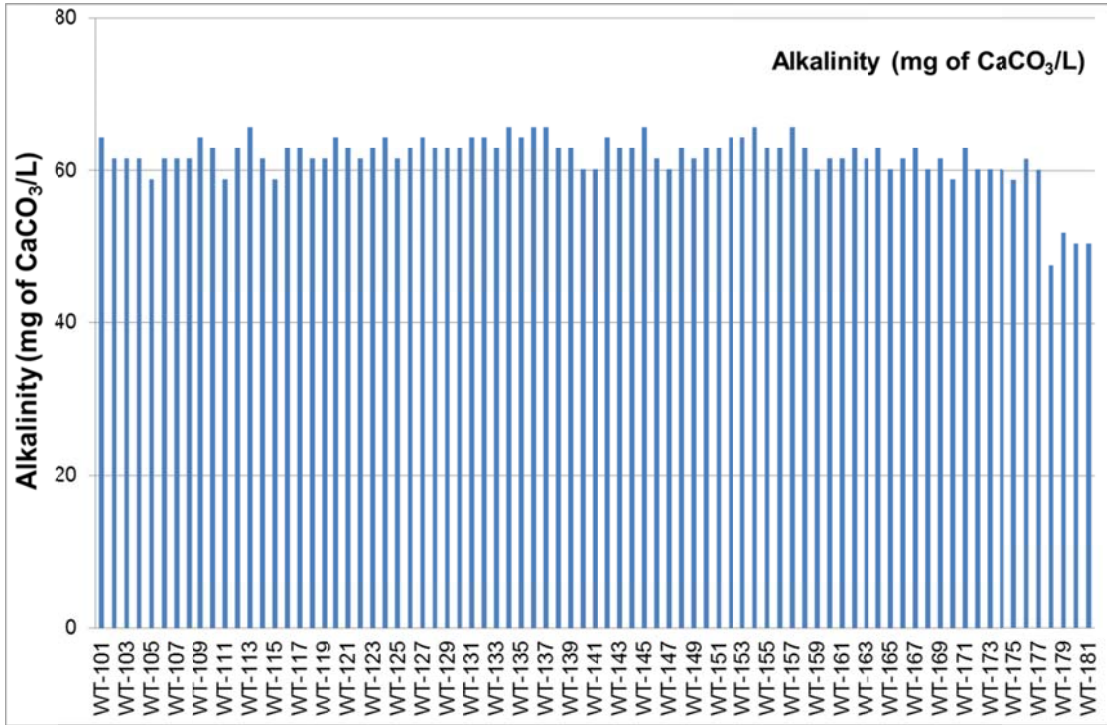


Figure 24. Spatial variations of alkalinity (mg CaCO₃/L) in the water samples from Tarbela dam

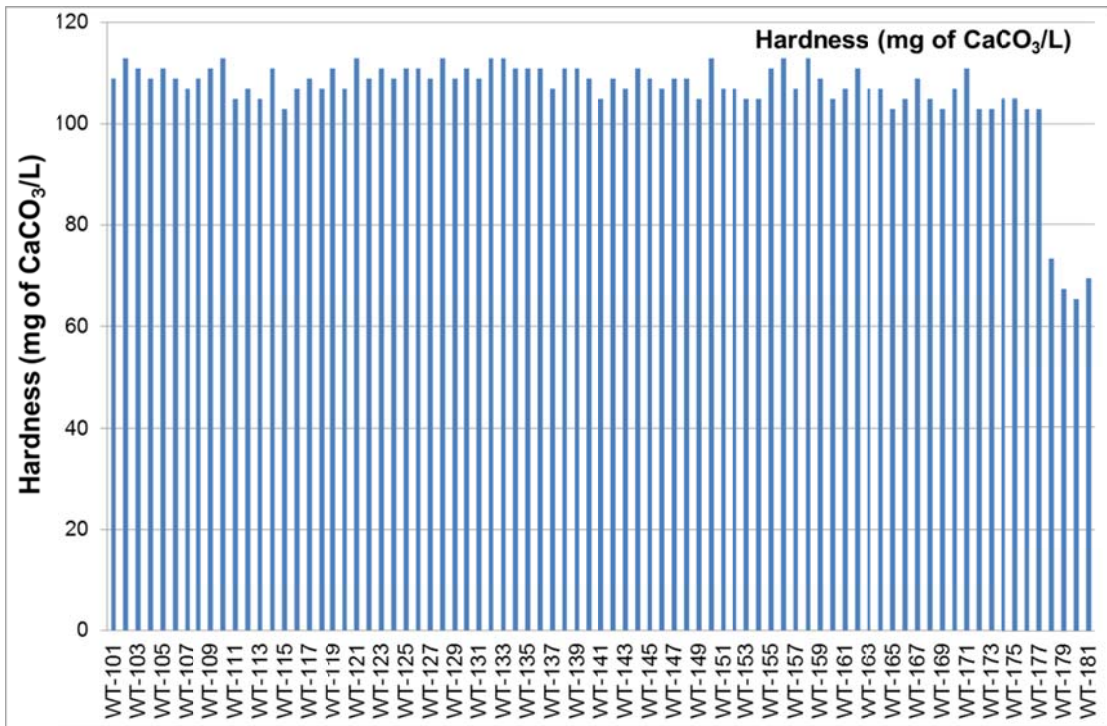


Figure 25. Spatial variations of hardness (mg CaCO₃/L) in the water samples from Tarbela dam

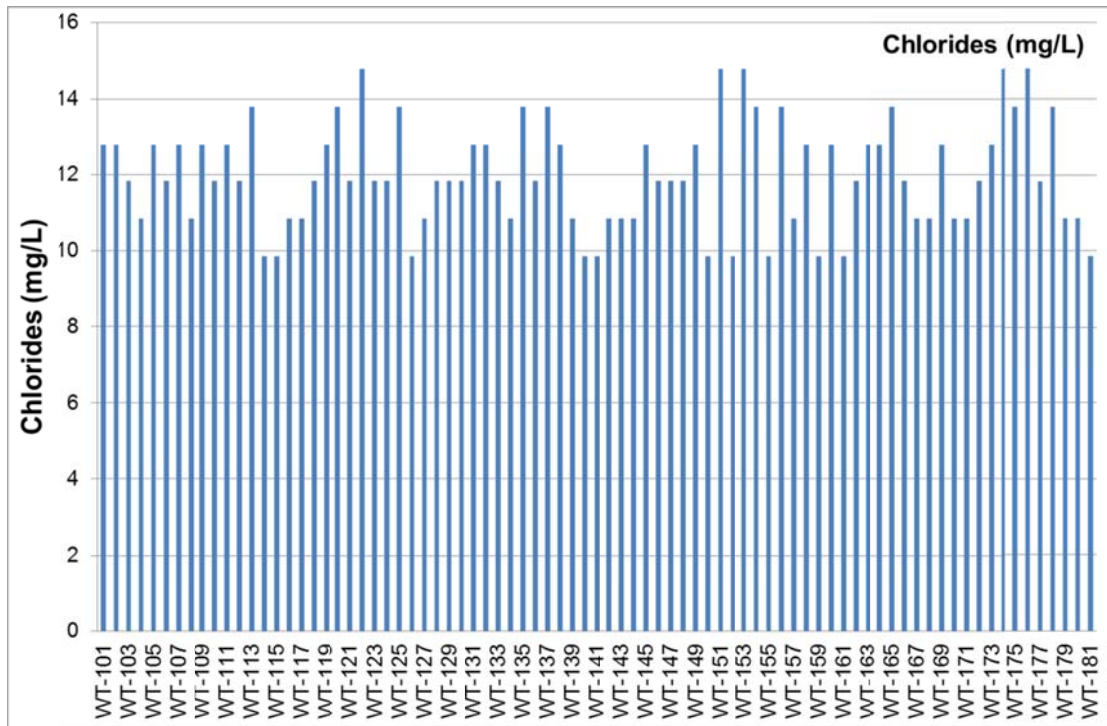


Figure 26. Spatial variations of chloride levels (mg/L) in the water samples from Tarbela dam

3.8 Multivariate Analysis of Trace Metals in Water

One of the important aspects of the present study was source identification and apportionment of selected trace metals in the study area. Several multivariate statistical models have been reported in literature to this effect but in the current study principle components analysis (PCA) and cluster analysis (CA) were used for identification and apportionment of trace metals' source in the water samples. Principle component analysis (PCA) for selected trace metals levels in the water sample extracted by varimax normalized rotation of the data-set is shown in Table 8. PCA yielded seven principle components (PC) with eigen values greater than unity and cumulative variance of about 70%. Cluster analysis of selected trace metals in the water samples is shown in Figure 27 as dendrogram which showed very strong clusters of Ag-Cr, Fe-Mn, Co-Li-Cu, Pb-Sr, Cd-Zn, Ca-Na and K-Mg.

PC 1 exhibited maximum loading for K (0.912) and Mg (0.817) while PC 2 showed maximum input for Na (0.878) and Ca (0.862) which were in very good agreement with the CA results. These PCs were contributed by agricultural run-offs and

domestic wastes in the catchments area, respectively. PC 3 indicated elevated loading for Zn (0.789) and Cd (0.713) while PC 4 showed significant loading for Li (0.815) and Ag (0.679). These metals were mostly derived from soil erosion and lithogenic sources. PC 5 exhibited maximum loading for Cu (0.814) and Pb (0.548) which were mostly derived from anthropogenic automobile emissions and transportation sources. PC 6 showed elevated loading for Fe (0.801) and Co (0.634) while in PC 7 maximum loading was found for Sr (0.791) and Mn (0.675). These metals were predominantly contributed by natural soil/rock weathering together with some anthropogenic intrusions in the upstream region. Overall, the PCA results were in good agreement with the CA findings and both multivariate methods demonstrated significant anthropogenic contributions of trace metals in the water samples collected from Tarbela Dam.

Table 8. Principal component analysis of selected trace metals in the water samples

	PC 1	PC 2	PC 3	PC 4	PC 5	PC 6	PC 7
Eigen value	2.521	1.788	1.579	1.279	1.164	1.149	1.011
Total Variance (%)	16.81	11.92	10.53	8.525	7.757	7.657	6.742
Cumulative Eigen value	2.521	4.309	5.888	7.166	8.330	9.478	10.49
Cumulative Variance (%)	16.81	28.72	39.25	47.78	55.53	63.19	69.93
Ag	-0.041	-0.125	0.018	0.679	0.174	-0.124	-0.034
Ca	0.117	0.862	0.024	0.010	0.102	-0.058	-0.222
Cd	-0.048	-0.108	0.713	-0.091	0.054	-0.127	0.057
Co	0.181	-0.257	-0.332	0.135	0.069	0.634	0.046
Cr	0.560	-0.173	0.490	0.350	-0.039	-0.030	-0.072
Cu	-0.138	0.008	0.054	0.073	0.814	0.097	-0.091
Fe	-0.150	0.058	0.149	-0.137	0.068	0.801	0.007
K	0.912	-0.027	-0.114	-0.072	0.010	0.005	-0.138
Li	0.020	0.203	-0.009	0.815	-0.172	0.082	0.052
Mg	0.817	0.334	-0.257	-0.031	0.010	-0.061	-0.045
Mn	-0.147	-0.027	0.116	-0.118	-0.329	0.283	0.675
Na	0.017	0.878	-0.154	0.037	0.109	-0.031	0.187
Pb	0.135	0.179	-0.034	-0.061	0.548	0.018	0.158
Sr	-0.093	-0.013	-0.001	0.093	0.293	-0.134	0.791
Zn	-0.186	0.019	0.789	0.090	-0.036	0.144	0.027

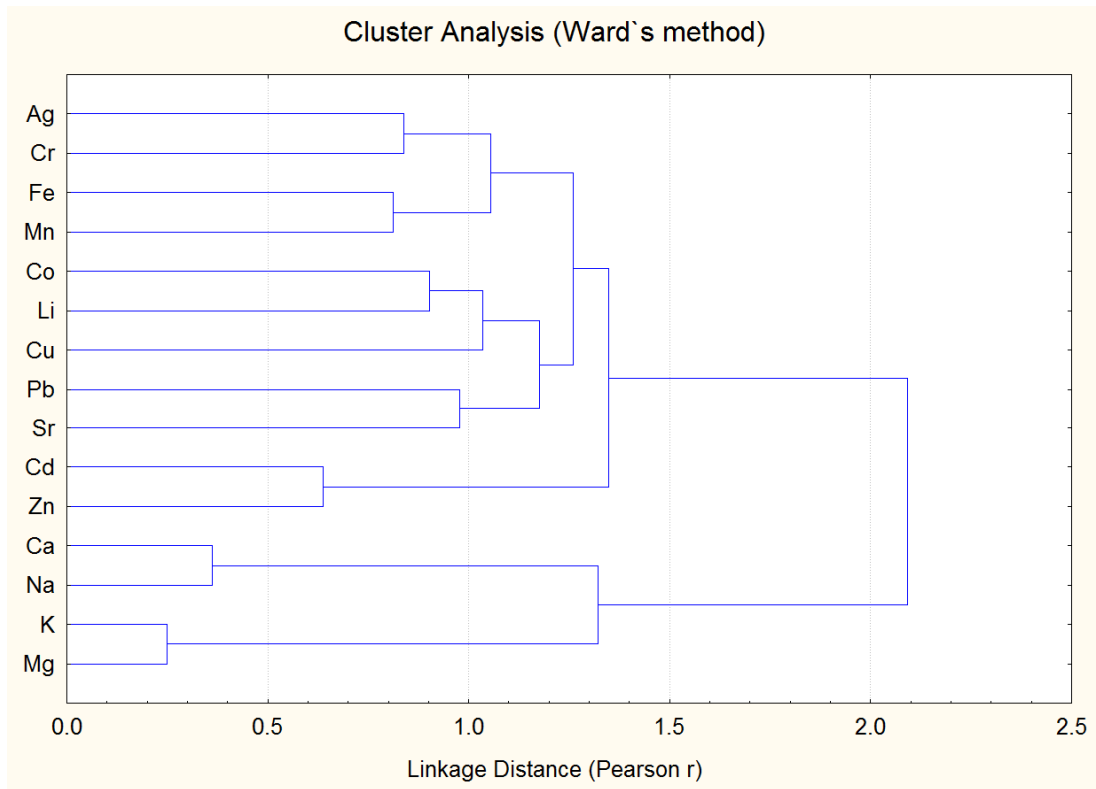


Figure 27. Cluster analysis of selected trace metals in the water samples

3.9 Health Risk Assessment of Trace Metals

Health risk assessment for the trace metal levels in the water sample was investigated with reference to the recommended intake both for the children and adult. The risk assessment was carried out both for ingestion and dermal absorption. Figure 28 showed health risk assessment by exposure through ingestion. As shown in the Figure calculated risk for Cd, Co, Cr, Mn and Pb were higher in comparison to the reference dose; consequently these metals showed significant health risk for both children and adult. It was also observed that children are at higher risk with respect to these metals than adult. Some of the metals (such as Cu, Fe, Li, Sr and Zn) showed calculated values less than the reference values, thus these metals exhibited no significant risk for both children and adults. Health risk assessment of trace metals in the water samples by exposure through the dermal contact was also calculated and results are displayed in Figure 29. It was observed that almost all selected metals showed calculated values significantly lower than the reference dose. In case of Co calculated value was slightly approaching the standard reference dose thus it may cause some health risk in children.

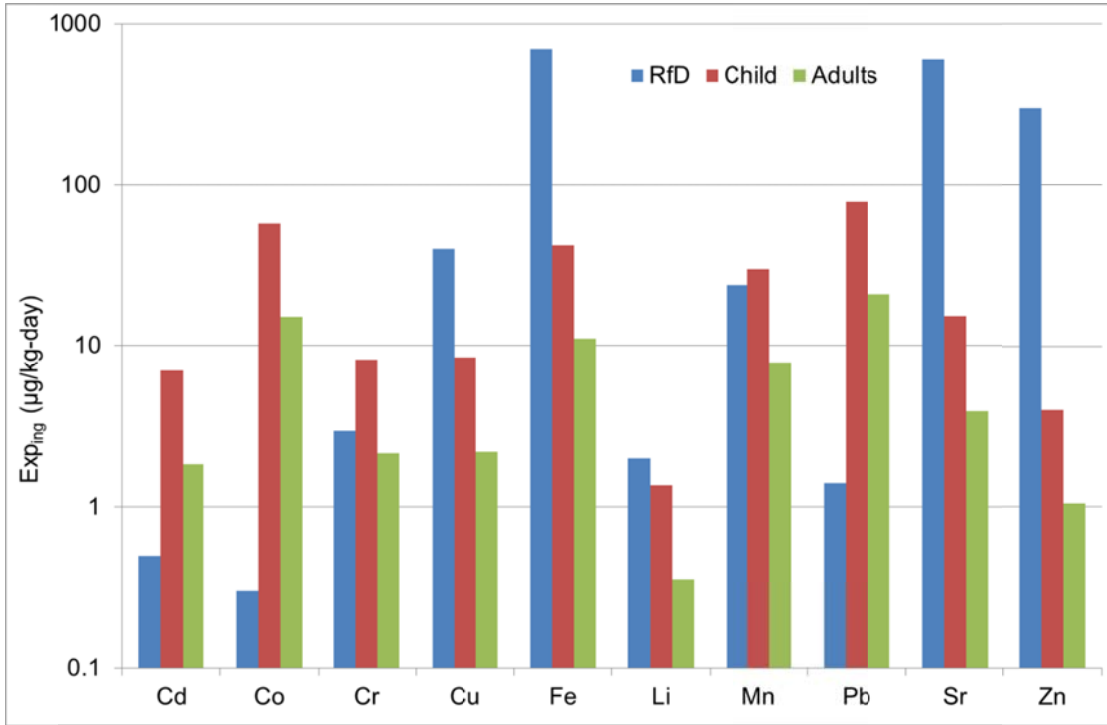


Figure 28. Health risk assessment of selected trace metals in the water samples by exposure through ingestion

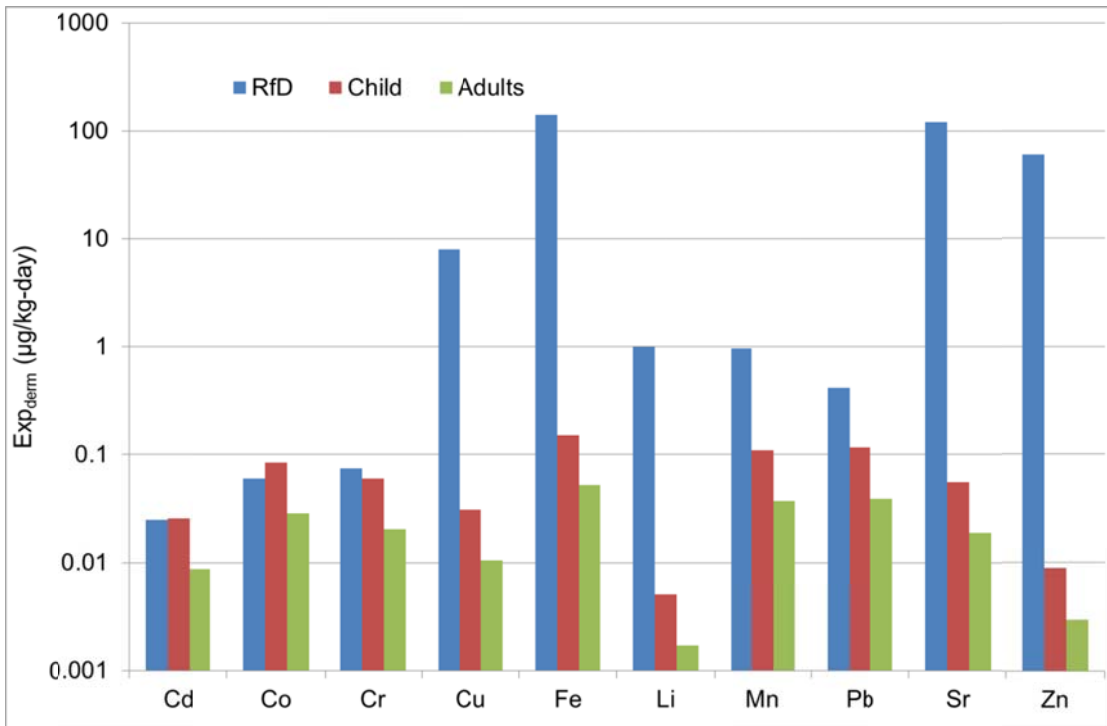


Figure 29. Health risk assessment of selected trace metals in the water samples by exposure through the dermal contact

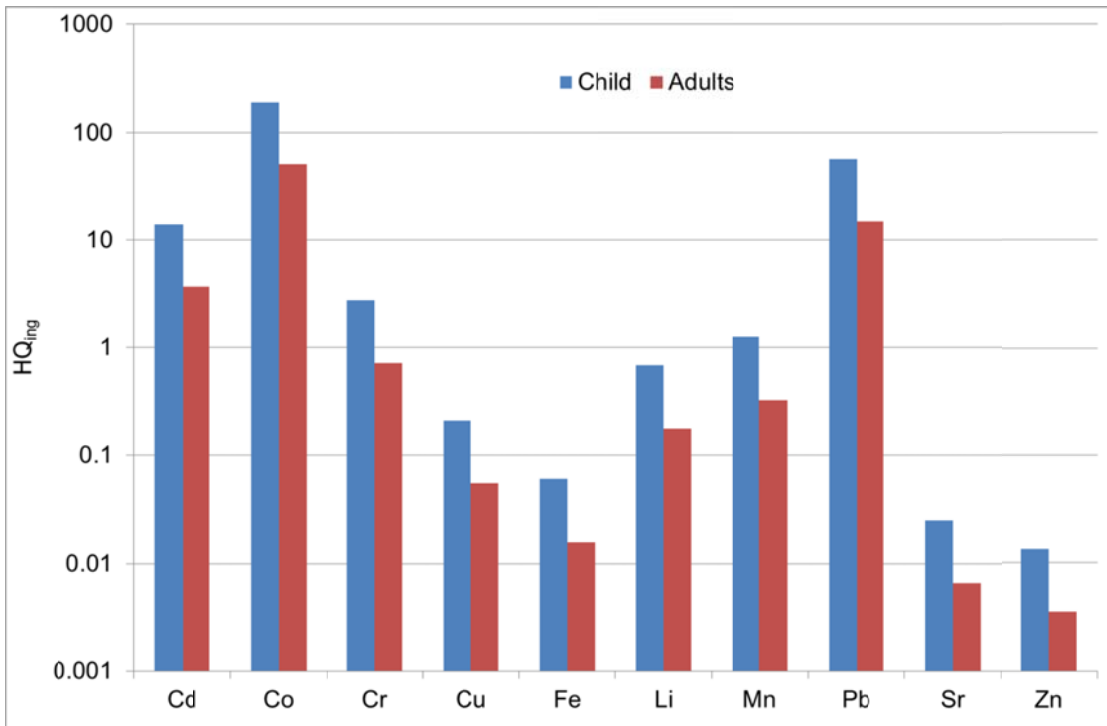


Figure 30. Hazard quotient of selected trace metals in the water samples through ingestion

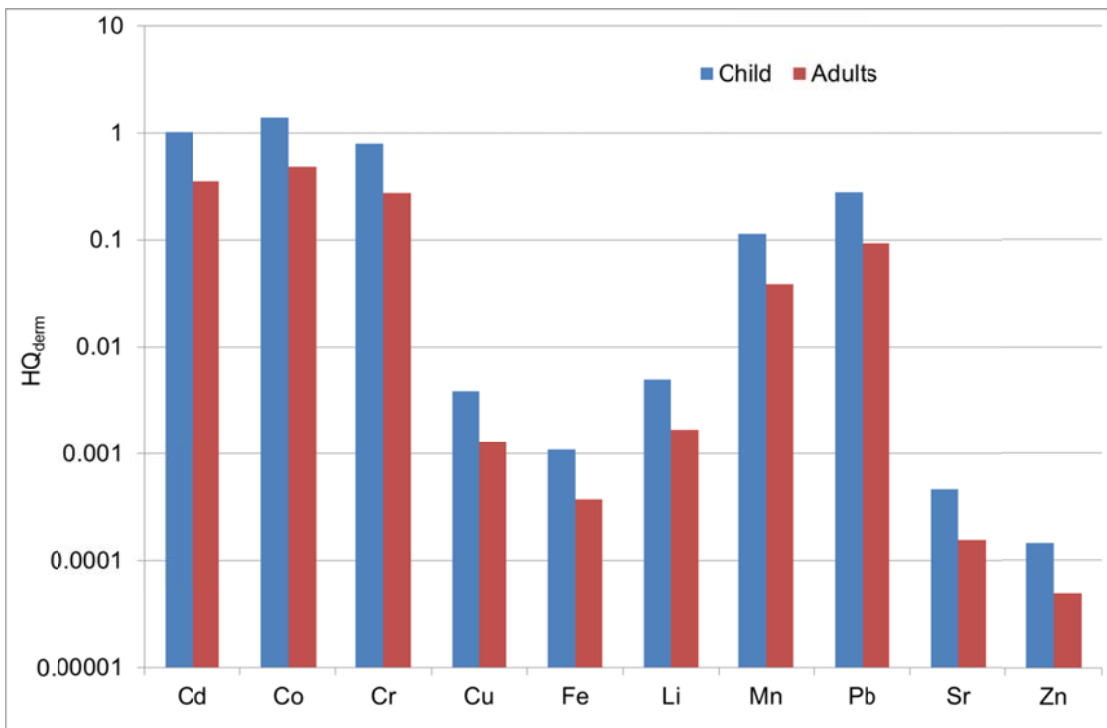


Figure 31. Hazard quotient of selected trace metals in the water samples through dermal adsorption

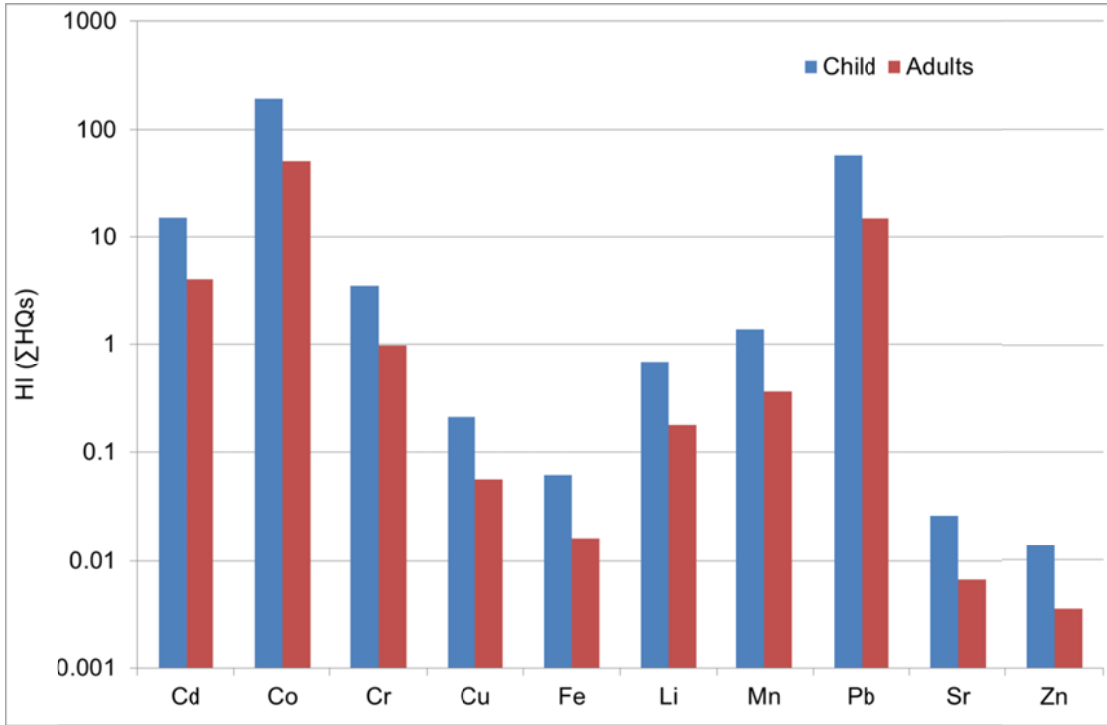


Figure 32. Hazard index (showing non-carcinogenic risk) of selected metals in the water samples

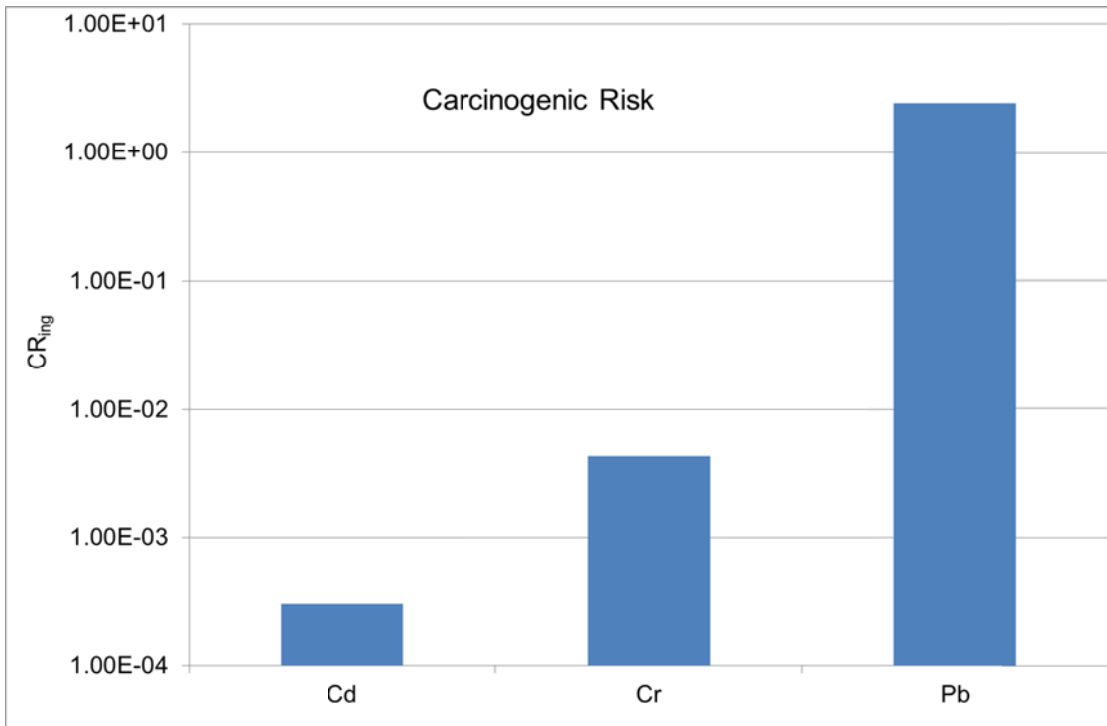


Figure 33. Carcinogenic risk of toxic trace metals in the water samples through ingestion

Hazard quotient (HQ) and hazard index (HI) were also evaluated to estimate the overall non-carcinogenic effects posed by trace metals in the water samples. Generally admissible safe limit for HQ and HI is unity and values greater than unity are associated with non-carcinogenic risk. Hazard quotient of selected trace metals in the water samples through ingestion is shown in Figure 30. Some of the trace metals such as Cd, Co, Cr and Pb were found to have values of HQ greater than unity for both children and adults. Accordingly these metals can be associated with possible non-carcinogenic health risk while rest of the metals showed values of HQ less than or equal to unity indicating no significant health hazards through their ingestion. Similarly, hazard quotient of selected trace metals in the water samples through dermal adsorption is shown in Figure 31 which indicated no significant hazards in both children and adults. From both Figures of HQ it can be concluded that HQ values (ingestion and dermal absorption) were considerably greater for children so children were at more risk compared to the adults.

Hazard index showing cumulative non-carcinogenic risk of selected trace metals in the water samples is shown in Figure 32. The calculated values were higher than unity (safe limit) for Cd, Co, Cr and Pb; these metals were associated with non-carcinogenic risks. Again, as discussed above significant hazards were more prominent in children than adults. Carcinogenic risk of toxic trace metals in the water samples through ingestion was also investigated and results are portrayed in Figure 33. All trace metals are not carcinogenic so in the present study only three carcinogenic metals (Cd, Cr and Pb) were evaluated. Generally, safe value through ingestion for cancer risk is less than 1.00×10^{-4} . It was observed that the calculated carcinogenic risks for Cd, Cr and Pb were higher than the safe limit thereby indicating lifetime carcinogenic risk to the consumers. Highest risk was found for Pb, followed by Cr and Cd in the water samples. So consumption of water for a long time can cause significant carcinogenic risk to the local population.

3.10 Comparison with National and International Standards

The average values of various physicochemical parameters measured in the water samples were compared with the recommended/reference values proposed by World Health Organization (WHO), United State Environmental Protection Agency (USEPA) and Pakistan Environmental Protection Agency (Pak-EPA) as shown in Table 9. The tabulated data revealed that average values of all physicochemical parameters in the present study were within the guideline values proposed by various organizations.

Therefore, consumption of water from Tarbela Dam can be considered safe with respect to the physicochemical parameters.

Table 9. Comparison of the physicochemical parameters in the water samples from Tarbela dam with national/international standards

	Tarbela dam	WHO	USEPA	Pak-EPA
pH	7.781	6.5-8.5	6.5-8.5	6.5-8.5
EC	227.2	200-600	200-600	200-600
TDS	145.4	1000	500	1000
DO	10.50	6	4-6	6
Alkalinity	61.86	200	200	200
Hardness	106.4	>500	-	500
Chloride	12.00	250	250	250
Ref.	Present study	WHO, 2011	USEPA, 2009	Pak-EPA, 2008

Table 10. Comparison of the average trace metal levels (mg/L) in the water samples from Tarbela dam with national/international standards

	Tarbela dam	WHO	USEPA	Pak-EPA
Ag	0.073	-	-	-
Ca	4.312	100	-	200
Cd	0.061	0.003	0.005	0.010
Co	0.500	0.04	-	-
Cr	0.071	0.05	0.01	0.05
Cu	0.073	2	1.3	2
Fe	0.365	0.3	0.3	-
K	2.693	12	-	-
Li	0.012	-	-	-
Mg	4.351	50	-	-
Mn	0.261	0.1	0.05	0.5
Na	4.150	200	20.0	-
Pb	0.685	0.01	0.015	0.05
Sr	0.132	-	-	-
Zn	0.035	3	5	5
Ref.	Present study	WHO, 2011	US-EPA, 2009	Pak-EPA, 2008

Similarly average concentrations of selected metals in water samples from Tarbela Dam were compared with various national and international guideline values as presented in Table 10. Average concentrations of some of the metals such as Cd, Co, Cr and Pb were considerably higher than the proposed levels by WHO, USEPA and Pak-EPA. Mean level of Mn was found to be greater than the recommended level of WHO and USEPA but less than the proposed level of Pak-EPA. Rest of the metal levels were within the safe limit of national and international guideline values. Nonetheless, Cd, Cr and Pb revealed a gross pollution status in the aquatic ecosystem; their average levels were noticeably higher than the guideline values of WHO, USEPA and Pak-EPA. This showed an alarming condition because these trace metals are carcinogenic and are associated with numerous human health risks. Therefore, it is high time to design and manage a proper pollution abatement strategy to control the pollutant levels in the water reservoir and to educate the local communities about the environmental hazards over a long time exposure which may result in chronic effects.

3.11 Comparison of the Trace Metals with the Reported Levels from Other Areas

Comparison of the average trace metal levels in the water samples from Tarbela dam with some reported levels from Pakistan is shown in Table 11. Mean level of Ca in the present study was found to be lower than that reported from Khanpur Lake, Mangla Lake and Simly Lake. Average concentration of Cd was also found to be lower than the reported levels from River Korang, Swat, Bara River, Canal Water Nowshera and Hudaira Drain Lahore, but the current Cd levels was relatively higher than the reported levels from other areas of Pakistan. Cd level in the present study was also higher than that reported level from the same study area in 1991. Mean level of Co was also higher than the reported level from Khanpur Lake. Mean concentration of Cr in the water samples was found to be lower than the levels reported from Swat, Malir River Karachi, Canal water Nowshera, Bara River Noshera and Simly Lake. Similarly, same areas showed elevated level of Cu compared to the estimated content in the present study. Mean concentration of Fe was observed to be higher than the reported levels from Khanpur Lake, Mangla Lake, Chashma Reservoir, Lloyd Reservoir, Ravi River, Chenab River and Manchar Lake. Average levels of K, Mg, Na and Sr were found to be higher in Khanpur Lake, Mangla Lake and Simly Lake than the water samples in present study area. Average concentration

of Mn was higher in Swat and Chenab River while Pb showed elevated level in the present study compared to those reported from some other areas of Pakistan. Mean level of Zn was more or less moderate in comparison with the already reported levels from various regions of Pakistan.

Average trace metal levels in the water samples from Tarbela Dam were also compared with the reported levels from other regions of world and results are shown in Table 12. Mean concentration of Cd was found to be higher in Taihu Lake China, Korotoa River Bangladesh and Nigerian water supply Nigeria but lower in Qilihai Reserve China, Dashen Tang Reserve China, Tunceli Turkey, Yellow River China and Lerma River Mexico compared to the present study. Average level of Co was also found to be higher in the present study in comparison to those reported from Thessaloniki Greece, Nigerian water supply Nigeria and Himalayan River Nepal. However, Taihu Lake China, Thessaloniki Greece, Korotoa River Bangladesh and J. A. Alzate Reservoir Mexico showed higher level of Cr compared to the measured level in Tarbela Dam. Mean value of Cu was also observed to be higher in the water samples from Tarbela Dam than those already reported from Taihu Lake China, Tunceli Turkey, Lerma River Mexico and J. A. Alzate Reservoir Mexico. Average concentrations of Fe and K in the present study were found to be relatively lower than the reported levels from some other regions of the world. Mean level of Mn was considerably higher in Taihu Lake China, Loktak Lake India, Gracanica River Kosovo and Yellow River China compared to the present study area. Present Pb concentration in water samples of Tarbela Dam was found to be lower than those reported from Taihu Lake China and J. A. Alzate Reservoir Mexico, while Sr level was found to be lower than those reported from Thessaloniki Greece and Yellow River China. Average concentration of Zn in the present study was found to be higher than the reported level from Yangtze River China, Pearl River China, Nigerian Water Supply Nigeria and Himalayan River Nepal. From comparison of the trace metal levels in the present study with the reported levels from other areas it was concluded that on the whole average concentrations of Ca, Cr, Pb and Zn were relatively lower in the present study compared to those reported from other national and international areas. Nonetheless, mean levels of Co and Cu were relatively higher in the study area than those reported from other national and international areas. Average concentrations of some of the trace metals such as Fe, K, Mg, Mn and Sr were higher in the study area compared to those reported from other areas of Pakistan and in some cases lower than the reported levels from other areas of the world as shown in Tables 11 and 12.

Table 11. Comparison of the average trace metal levels (mg/L) in the water samples from Tarbela dam with the reported levels from Pakistan

Location	Ag	Ca	Cd	Co	Cr	Cu	Fe	K	Li	Mg	Mn	Na	Pb	Sr	Zn	Ref.
Tarbela Dam	0.073	4.312	0.061	0.500	0.071	0.073	0.365	2.693	0.012	4.351	0.261	4.150	0.685	0.132	0.035	Present study
River Korang	-	-	0.234	-	-	0.024	-	-	-	-	-	-	0.284	-	0.034	Ali <i>et al.</i> , 2014
Khanpur Lake	-	16.50	0.034	0.303	0.241	0.046	0.255	2.570	-	15.23	0.077	5.784	0.565	1.148	0.063	Iqbal <i>et al.</i> , 2012
Mangla Lake	-	43	0.03	-	0.07	0.02	0.13	1.3	-	4.9	0.02	6.8	0.34	0.22	0.03	Saleem <i>et al.</i> , 2015
Swat	-	-	11.6	-	440.28	9.92	-	-	-	-	13644	-	-	-	21.04	Khan <i>et al.</i> , 2013
Tarbela Dam	-	-	0.004	-	0.003	0.04	0.012	-	-	-	0.018	-	0.107	-	0.028	Ashraf <i>et al.</i> , 1991
Chashma Reservoir	-	-	0.003	-	0.071	0.004	0.004	-	-	-	0.004	-	0.058	-	0.029	Ashraf <i>et al.</i> , 1991
Lloyd Reservoir	-	-	0.002	-	0.002	0.004	0.012	-	-	-	0.018	-	0.107	-	0.028	Ashraf <i>et al.</i> , 1991
Ravi River	-	-	0.0008	-	0.0008	0.004	0.084	-	-	-	0.006	-	0.001	-	0.022	Tariq <i>et al.</i> , 1994
Palosi Drain, Peshawar	-	-	0.004	-	-	0.000	0.56	-	-	-	0.130	-	0.34	-	0.239	Illyas and Sarwar, 2003
Different Site in NWFP	-	-	0.02	-	0.04	0.20	0.19	-	-	-	0.22	-	0.16	-	0.04	Haq <i>et al.</i> , 2005
Malir River, Karachi	-	-	0.04	-	0.10	0.31	0.78	-	-	-	0.33	-	0.19	-	0.16	Haq <i>et al.</i> , 2005
Chenab River	-	-	-	-	-	-	0.18	-	-	-	0.28	-	-	-	-	Nickson <i>et al.</i> , 2005
Canal Water, Nowshera	-	-	0.115	-	0.15	0.66	0.96	-	-	-	0.66	-	0.385	-	0.045	Nazif <i>et al.</i> , 2006
Bara River, Nowshera	-	-	0.175	-	0.225	1.05	1.52	-	-	-	0.81	-	0.525	-	0.04	Nazif <i>et al.</i> , 2006
Kalar Kahar Lake, Chakwal	-	-	0.03	-	-	0.605	2.83	-	-	-	-	-	0.155	-	1.63	Raza <i>et al.</i> , 2007
MNVD, Jamshoro	-	-	0.009	-	-	0.006	0.015	-	-	-	-	-	0.007	-	0.006	Mastoi <i>et al.</i> , 2008
Manchar Lake, Jamshoro	-	-	0.001	-	-	0.010	0.013	-	-	-	-	-	0.020	-	0.020	Mastoi <i>et al.</i> , 2008
Hudaira Drain, Lahore	-	-	0.18	-	0.07	0.45	8	-	-	-	0.85	-	0.03	-	1.7	Kashif <i>et al.</i> , 2009
Warsak Dam, KPK	-	-	-	-	0.051	0.042	-	-	-	-	-	-	0.009	-	0.087	Yousafzal <i>et al.</i> , 2008
Phulali Canal, Hyderabad	-	-	0.004	-	0.0082	0.063	1.451	-	-	-	0.596	-	0.026	-	0.167	Wattoo <i>et al.</i> , 2006
Simly Lake, Islamabad	-	18.1	0.02	0.21	0.16	0.05	0.20	3.87	0.01	11.5	0.04	15.3	0.31	0.62	0.05	Iqbal and Shah, 2012

Table 12. Comparison of the average trace metal levels (mg/L) in the water samples from Tarbela dam with the reported levels from other regions of world

Location	Ag	Ca	Cd	Co	Cr	Cu	Fe	K	Li	Mg	Mn	Na	Pb	Sr	Zn	Ref.
Tarbela Dam, Pakistan	0.073	4.312	0.061	0.500	0.071	0.073	0.365	2.693	0.012	4.351	0.261	4.150	0.685	0.132	0.035	Present study
Taihu Lake, China	-	-	1.06	-	1.91	5.08	629	-	-	-	48.3	-	6.72	-	18.07	Liang <i>et al.</i> , 2011
Qilihai Reserve, China	-	-	0.003	-	0.024	-	-	-	-	-	-	-	0.010	-	-	Zhang <i>et al.</i> , 2017
DashenTang Reserve, China	-	-	0.0001	-	0.0005	-	-	-	-	-	-	-	0.003	-	-	Zhang <i>et al.</i> , 2017
BinHai Reserve, China	-	-	-	-	0.0006	-	-	-	-	-	-	-	0.0004	-	-	Zhang <i>et al.</i> , 2017
Yellow River, China	-	-	0.0004	-	0.023	0.036	-	-	-	-	0.597	-	0.019	0.941	0.052	Hang <i>et al.</i> , 2016
Yangtze River, China	-	-	-	-	0.005	0.003	-	-	-	-	-	-	0.001	-	0.010	Yin <i>et al.</i> , 2016
Pearl River, China	-	-	-	-	0.002	0.001	-	-	-	-	0.001	-	-	-	0.004	Geng <i>et al.</i> , 2015
Loktak Lake, India	-	-	-	-	-	0.038	0.627	-	-	-	0.481	-	0.396	-	-	Maibam and Majeti, 2016
Subarnarekha River, India	-	-	-	-	0.0008	0.005	-	-	-	-	0.007	-	-	0.018	-	Giri and Singh, 2014
Tunceli, Turkey	-	-	0.002	-	0.006	0.200	-	-	-	-	-	-	0.003	-	-	Demir <i>et al.</i> , 2014
Thessaloniki, Greece	-	-	-	0.003	0.119	-	4.870	3.778	-	-	-	28.290	-	0.272	0.098	Fotini and Panagiotis, 2016
Ghana River, Ghana	-	-	-	-	0.003	-	-	-	-	-	-	-	-	-	-	Asante <i>et al.</i> , 2007
Crater Lake, Ghana	-	-	-	-	0.026	-	0.334	-	-	-	-	-	0.12	-	0.151	Noah <i>et al.</i> , 2016
Korotoa River, Bangladesh	-	-	0.011	-	0.083	0.073	-	-	-	-	-	-	0.035	0.0005	-	Islam <i>et al.</i> , 2015
Alzate Reservoir, Mexico	-	-	-	-	79	70	6923	-	-	-	-	-	61	-	68	Perez <i>et al.</i> , 1999
Lerma River, Mexico	-	-	0.001	-	0.05	0.246	-	-	-	-	0.288	-	0.078	-	0.066	Brito <i>et al.</i> , 2015
Himalayan River, Nepal	-	-	-	0.001	0.003	0.002	-	-	0.007	-	0.013	-	0.001	0.045	0.012	Lekhendra <i>et al.</i> , 2016
Water Supply, Nigeria	-	-	0.08	0.163	0.14	0.043	1.81	-	-	-	0.107	-	0.163	-	0.32	Gregory <i>et al.</i> , 2014
Gracanica River, Kosovo	-	-	0.001	-	0.049	0.004	-	-	-	-	2.948	-	0.007	-	0.132	Gashi <i>et al.</i> , 2017

3.12 Salient Findings of the Present Study

Salient features of the present study are:

- Water samples demonstrated relatively alkaline pH and comparatively high DO contents.
- EC, TDS, Alkalinity and Hardness values showed moderate variations with respect to each other. Moreover they revealed overall broad asymmetric dispersion in all water samples.
- Physicochemical parameters indicated some significant and strong correlations with each other.
- Some of the metals (Ca, Mg, Na, Cd, Zn, Cr, K and Mg) showed significant correlations with each other.
- Assessment of the physicochemical parameters in water samples expressed that values of these parameters in present study were within the guideline values proposed by various organization.
- Assessment of selected metals revealed that among the selected metals, Cd, Co, Cr and Pb showed comparatively higher average concentrations than proposed by WHO, USEPA and Pak-EPA.
- The HQ_{ing} levels of Cd, Co, Cr and Pb were found to be greater than the safe limit whereas the HQ_{derm} values of the metals were within the safe limits.
- Concentrations of carcinogenic metals (Cd, Cr and Pb) were higher than the safe limit ($1.00E-04$).
- Some of the metals (Fe, K, Mg, Mn and Sr) exhibited relatively higher concentrations in the study area as compared to that reported levels from other areas in Pakistan.

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