HYDROGEOCHEMISTRY, SOURCE APPORTIONMENT AND RISK ASSESSMENT OF ARSENIC, FLUORIDE AND TRACE METALS IN DISTRICT RAHIM YAR KHAN

BY

QURAT UL AIN

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In

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APPROVAL CERTIFICATE

This is to certify that the dissertation entitled **"Hydrogeochemistry, Source Apportionment and Risk Assessment of Arsenic, Fluoride and Trace Metals in District Rahim Yar Khan"** submitted by **Qurat ul ain** is accepted in its present form by the Department of Environmental Sciences, Quaid-i-Azam University Islamabad, Pakistan, as satisfying the dissertation requirement for the degree of M.Phil in **Hydrogeochemistry**.

Supervisor:

Abida

Dr. Abida Farooqi
Assistant Professor,
Department of Environmental Sciences,
Quaid-i-Azam University Islamabad

External Examiner:

Dr. Maryam Ibrar
Senior Scientific Officer
PASTIC, QAU Campus Islamabad

Chairperson:

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

Dated: 12th March,2014

PLAGARISM CERTIFICATE

It is certified that Qurat ul ain of Department of Environmental has completed her thesis, **Hydrogeochemistry, source apportionment and risk assessment of arsenic, fluoride and trace metals in District Rahim Yar Khan,** her thesis has been checked for plagiarism on Turniton and found that it lies in the limit provided by HEC.

Supervisor: abida

Dr. Abida Farooqi
Assistant Professor,
Department of Environmental Sciences,
Quaid-i-Azam University Islamabad

Student Q-ain

Dedicated

To

My parents—

the spiritual teachers of mine…

for their

eternal love, encouragement & countless

prayers…

IN THE NAME OF ALLAH

بِسْمِ اللَّهِ الرَّحْمَٰنِ الرَّحِيمِ

The Most Merciful
The Most Beneficent
For those who believe in Allah,
No argument is necessary and
For those who do not believe in Allah
No argument is possible

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Qurat ul ain

List of Abbreviations

PCRWR	Pakistan Council for Research in Water Resources	EC	Electrical Conductivity
MMA^{V}	Monomethylarsonic acid	TDS	Total Dissolved Solid
DMA^{V}	Dimethylarsenic acid	mg/L	milligram per litre
MMA^{III}	Monomethylarsonous acid	µg/L	microgram per litre
DMA^{III}	Dimethylarsinous acid	GPS	Global Positioning System
AAS	Atomic Absorption Spectrophotometer	I_{geo}	Geoaccumulation Index
CDI	Chronic Daily Intake	B_n	Geochemical background Value
ADD	Average Daily Dose	EF	Enrichment factor
HQ	Hazard Quotient	C_{deg}	Degree of Contamination
DI	Average Daily Intake Rate	C_f	Contamination Factor
BW	Average Body Weight	DAP	Di-Ammonium Phosphate
IR	Water Ingestion Rate	ppm	parts per million
RfD	Oral Toxicity Reference Dose	WHO	World Health Organization
ED	Exposure Duration	BGS	British Geological Survey
EF	Exposure Frequency	CA	Component Analysis
AT	Average Life Time	PCA	Principal Component Analysis
CR	Cancer Risk	FA	Factor Analysis
CSF	Cancer Slope Factor	SEPA	State Environmental Protection Administration

Abstract

Release of soluble As species and F^- into the groundwater is a serious problem in many areas of the world. Natural and anthropogenic pollutants threaten the quality of groundwater. In order to investigate the extent of As, F^- and trace metal pollution and to evaluate the anthropogenic sources and the necessary geochemical triggers mobilizing As and F^- in groundwater a detailed study of groundwater and soil was carried out in District Rahim Yar Khan, Southern Punjab in Pakistan. Two tehsils of district Rahin Yar khan were selected for the present study; Site A (Tehsil Khan pur) which is an agricultural area and Site B (Rahim Yar Khan) which is an industrial area. About 51 groundwater and 33 samples of soil and sediments were collected from both sites. The major chemical composition of analyzed groundwater is characterized by Na^+-K^+-HCO_3^- type. 32.5 % groundwater exceeded the WHO standard (10 µg/L) for As and 100 % exceeded the WHO standard (1.5 mg/L) for F^-. The highly contaminated As (max. 107.23µg/L) and F^- (max. 26.4 mg/L) groundwaters were found from TRM (Tube well) and CK86 (Rotor pump). The contaminated ground waters were characterized by high pH (max.9.2), alkalinity (HCO_3^- up to 980mg/L), K^+ (max.55 mg/L), NO_3^- (max. 40.7mg/L). Fluoride concentrations showed positive correlations with depth and HCO_3^- and negative ones with Ca^{2+} and Mg^{2+} showing the calcite and dolomite precipitation under alkailine conditions. The basic mechanism supporting the higher levels of arsenic in the current study was desorption of arsenic via PO_4^{-3} at high pH. 70.5 % samples of groundwater exceeded the permissible limits of N (0.02ppm) and 100% samples groundwater crossed the permissible limits of Pb (0.01ppm) and Cd (0.003ppm). Based on the chemistry of those ground waters, soil pollution was suspected to cause the groundwater contamination. Thus, soils mostly from the Site A and Site B were chemically analyzed to figure out the relationship of water and soil contamination. The surface soils comprise permeable aeolian sediments on the terrace and coarse sand intercalating fine to very fine sand and silt layers on the flood plain. Positive correlation was observed between Pb(water)- Pb(soil) and Cd(water)-Cd(soil) for soil and water which shows the water pollution is affected by anthropogenic activities in the area. The HQ values of fluorides revealed severe health risk for the exposed population. With respect to As, F, Ni, Pb and Cd the area is highly contaminated and at high risk of health effects caused by these elements.

1. Introduction

Water, soil and sediments are the most important environmental compartments. Water is life and soil is the uppermost non consolidated portion of earth's crust that supports life. Sediment is the naturally occurring material that is broken down by various processes including weathering and erosion and is subsequently transported by the action of wind, water, glaciers or ice and/or by the force of gravity acting on the particle itself. The term suspended solid includes both the minerals and organic solids. While, sediment is restricted to the mineral fraction of the suspended solids load (Bartram and Ballance 1996). All of these matrices including water, soil and sediments have the great capacity to accumulate heavy metals, arsenic and fluoride. Soil and sediments contamination is the root cause for water pollution. Soil, sediments and water pollution are ultimately responsible for contamination in food chain which poses a significant risk to the human health. Thus, it is very important to analyze the level of heavy metals, fluoride and arsenic in all of these matrices (Bartram and Ballance 1996; An and Kampbell 2003).

Soil is the most environmental component because it is not only a geochemical sink for pollutants but also a natural buffer for the pollutants by controlling the transport of chemical elements and substances to the atmosphere, hydrosphere and biosphere (Kabata-Pendias 2004; Khan, Rehman et al. 2010). It has the capacity to accumulate heavy metals resulting from the deposition of particles emitted by urban and industrial activities, vehicular exhausts and industrial practices. Soil pollution with heavy metals is a serious environmental problem in the world. Elevated concentration of these metals can have adverse effects on soil biology and functions. Soil pollution can have implications to phytotoxicity at high concentrations and may also result in the transfer of heavy metals to the human diet through food chain, which pose a significant risk to human health. The heavy metals may be leached from soil into water and their availability to the plants and other organisms depends upon the soluble/exchangeable fraction of these metals (Rodríguez-Barroso, García-Morales et al. 2010; Wang, Liu et al. 2012). Measurement of total metal content in soil is a poor indicator of metal leachability, bioavailability, mobility and toxicity. Therefore, along with total metal concentrations, estimation of the biologically available fractions is important, which helps to assess the potential for mobilization of the metals at contaminated sites and their availability to other organisms (An and Kampbell 2003; Rodríguez-Barroso, García-Morales et al. 2010).

Sediment quality is an indicator of water pollution that manifests pollutant variations. Sediment provides a site for biogeochemical cycling and the foundation of the food web (Burton Jr, Baudo et al. 2001). Sediments have been used as an important tool to assess the health status of aquatic ecosystems (Birch, Taylor et al. 2001) and are an integral component for functioning of ecological integrity. Sediments like soil also act as a sink of organic as well as inorganic pollutants (heavy metals) and provide a history of anthropogenic pollutant input (Santos Bermejo, Beltrán et al. 2003) and environmental changes (Shomar, Müller et al. 2005). Heavy metals enter the aquatic ecosystems through point sources such as industrial, municipal and domestic waste water effluents as well as diffuse sources which include surface runoff, erosion, and atmospheric deposition.

Sediment pollution with heavy metals is a worldwide problem (Fernandes, Fontaínhas-Fernandes et al. 2008; Kucuksezgin, Uluturhan et al. 2008) and is considered to be a serious threat to the aquatic ecosystem because of their toxicity, ubiquitous and persistence nature, non-biodegradability and ability to bio-accumulate in food chain (Duman, Aksoy et al. 2007). Sediments serve as the largest pool of metals in aquatic environment. More than 90% of the heavy metal load in the aquatic systems has been found to be associated with suspended particulate matter and sediments (Zheng, Wang et al. 2008; Amin, Ismail et al. 2009). Metals in suspended particulates settle down and pool up in sediments (Kucuksezgin, Uluturhan et al. 2008), while the dissolved metals adsorb onto fine particles which may carry them to bottom sediments (Singh, Malik et al. 2005). Distribution of heavy metals is influenced by the mineralogical and chemical composition of suspended material, anthropogenic influences, deposition, sorption, enrichment in organism (Jain, Malik et al. 2007) and various physico-chemical characteristics (Singh, Malik et al. 2005). Although all of the metals adsorbed on the soils/sediments are not bioavailable, certain mechanisms such as, direct consumption from the benthic fauna, sediment re-suspension, desorption, redox reactions or biodegradation of the sorptive substance may induce the release of metals back to the water column (Hakanson 1980; Soares, Boaventura et al. 1999; Wright and Mason 1999).

Arsenic is found naturally in various minerals of soil and/or sediments (Welch, Westjohn et al. 2000; Smedley and Kinniburgh 2002). Moreover, the concentration of arsenic is increasing in these soils via irrigating them with As contaminated water. It has recently been recognized that such contaminated water may pose an equally serious health hazard to people eating food from the crops irrigated (Williams, Islam et al. 2006) and that As accumulating in irrigated soils poses a serious threat to sustainable agriculture in affected areas (Heikens 2006). This is commonly being practiced in various developing countries like Bangladesh, India (McArthur, Banerjee et al. 2004; Acharyya and Shah 2007) Nepal (Gurung, Ishiga et al. 2005) Cambodia (Buschmann, Berg et al. 2007) Vietnam (Postma, Larsen et al. 2007) and Taiwan (Liu, Zhu et al. 2006) where rice is the major crop being irrigated and thus, resulting in the accumulation of As at higher concentration in respective soils and crops.

There are various natural and geochemical processes responsible for the release of As into groundwater from soil and sediments. The natural sources include arsenic bearing sulphides, arsenic adsorbed on or co-precipitated with iron oxides or other mineral phases, and geochemical systems. However, the geochemical processes resulting in discharge of As into water include oxidative and reductive dissolution, desorption (Welch, Westjohn et al. 2000; Smedley, Kinniburgh et al. 2005) and concentration by evaporative enrichment (Welch, Westjohn et al. 2000). Among all of these mechanisms reductive dissolution is the most commonly occurred phenomenon responsible for arsenic-contaminated groundwater on the river deltas of Asia and this process is the most commonly evoked to explain elevated arsenic in groundwater (Islam, Gault et al. 2004).

1.1 : Drinking water quality of Pakistan

Pakistan is a water deficient country and the drinking water quality is poorly managed and monitored in our country. Like other developing nations of the world, Pakistan is also facing critical water shortage and pollution. The available water resources have already diminished in our country (PCRWR 2005). According to World Bank, the per capita water availability in Pakistan has decreased five times since 1947, which was around 5,000 cubic meters in 1947 but now stands at only 1,000 cubic meters, which is the lowest in the region (World Bank 2006). Moreover, it is expected that the per capita availability may be further reduced due to lack of development of new water efficient reservoirs and exponential increase of population in Pakistan. The situation might get worse in areas situated outside the Indus basin where the average per capita water availability per annum is already below 1000 m^3 (PAK-EPA 2005a).

Pakistan ranks at 80 among 122 nations regarding drinking water quality in the world. Drinking water sources, both surface and groundwater are contaminated with coliforms, toxic metals and pesticides throughout the country (Azizullah, Khattak et al. 2011). According to PCRWR's report, Pakistan is facing four major water quality tribulations: bacteriological contamination (27-100 %); arsenic (0-100 %); nitrate (0-54%); and fluoride (0-55%). It has been reported that according to the national statistics just 56% of our population has access to safe drinking water (Farooq, Hashmi et al. 2008) and according to International Standards for safe and drinkable water, only 25.61% (rural 23.5% and 30% urban) of our population have access to this basic need (Rosemann 2005).

1.2: Sources and health impacts of Heavy Metals, Arsenic and Fluoride

1.2.1: Heavy metals and their health impacts

The heavy metals are ubiquitous i.e., found everywhere in the environment. There are various geogenic and anthropogenic sources of these heavy metals. The most significant geogenic sources are weathering of rocks, ore deposits and volcanic activities. However, the anthropogenic sources are wastewater irrigation, solid waste disposal, sludge applications, vehicular exhaust, industrial activities, fertilizers and metal based pesticides (Singh, Mohan et al. 2004; Chen, Wang et al. 2005). However, wastewater irrigation and metal based pesticides are the most significant sources of heavy metals. In Pakistan about 32500 ha of land is irrigated with wastewater and there is no check and balance in our country on the use of wastewater from any industry. Moreover, the wastewater of just food industry is considered safe for irrigation purpose (Ensink, Mahmood et al. 2004).

The heavy metals are detrimental for human health even at very low concentrations because they are non-biodegradable and tend to accumulate and bio-magnify in different tissues and blood of human beings. Their toxic effects include headache, hypertension, irritability, abdominal pain, nerve damages, liver and kidney problems, sideroblastic anemia, and intellectual disabilities, fatal cardiac arrest and carcinogenesis (Järup 2003; Muhammad, Shah et al. 2011). The excessive ingestion of all these heavy metals including Cd, Cr, Co, Hg, Ni, Pb and Zn has carcinogenic effects on human health (Muhammad, Shah et al. 2011). The adverse effects of heavy metals include toxic, neurotoxic, carcinogenic, mutagenic and teratogenic effects depending upon the heavy metal species (Sharma, Agrawal et al. 2008; Patra, Wagh et al. 2010).

But, there are certain essential light metals and heavy metals required for the growth of human body in specific concentrations and may produce toxic effects whenever they cross the safe limits. These light and heavy metals are sodium (Na), potassium (K), calcium (Ca), magnesium (Mg), iron (Fe), Manganese (Mn), copper (Cu), cobalt (Co), and zinc (Zn).

1.2.2: Arsenic and their associated health effects:

Arsenic is a brittle-natured and gray or white-colored toxic metalloid that cannot be found as a free element in the earth's crust. There are more than 245 species of arsenic-bearing minerals, mostly ores containing sulphide along with copper, nickel, lead, cobalt and other metals as well as some oxides that exist in nature. There are also anthropogenic sources of arsenic such as insecticides, pesticides and wastes from mine, smelter and tannery industries (Rahman, Khanam et al. 2012). Overexposure to arsenic may cause a decrease in white and red blood cells production, gastrointestinal irritation, disrupt the heart rhythm, damage blood vessels and cause "pins and needles" sensation in hands and feet (Abernathy, Thomas et al. 2003). Long time exposure to arsenic can cause melanosis, leuko-melanosis, hyperkeratosis, cardiovascular disease, black foot disease, neuropathy and cancer (Caussy 2005).

Arsenic is classified as a Group I carcinogen (human carcinogen). It is the only carcinogenic substance which has carcinogenic risk in humans caused via ingestion and inhalation (IARC 2004). It is discovered via literature that the most of the ingested As is rapidly excreted via the kidney within a few days (Tam, Charbonneau et al. 1979; Vahter 2002) and higher levels of As are retained within the bones, skin, hairs, and nails of exposed humans for longer periods of time (Karagas, Tosteson et al. 2000). Moreover, studies conducted regarding As speciation in urine of exposed humans reported that the metabolites comprise 10–15% inorganic As (iAs) and monomethylarsonic acid (MMA^{V}) and a major proportion (60–80%) of dimethylarsenic acid (DMA^{V}) (Tam, Charbonneau et al. 1979; Vahter 2002). Monomethylarsonous acid (MMA^{III}) and dimethylarsinous acid (DMA^{III}) were found in trace quantities in human urine (Aposhian, Gurzau et al. 2000; Del Razo, Styblo et al. 2001). In general, MMA^{III} is more toxic than As (III) and As (V) (Petrick, Ayala-Fierro et al. 2000).

Arsenic appears in inorganic as well as organic species, and the main oxidation states are +III and +V, depending on pH and redox properties of the media. Inorganic species (iAs) are much more toxic in general than organic arsenical compounds, and iAs (III) species are of great environmental concern in view of a combination of high mobility and toxicity in comparison with the pentavalent species, which can be more easily adsorbed and retained by different surfaces (Litter, Morgada et al. 2010). The Eh and pH are the most important factors predicting inorganic As speciation. Under oxidizing conditions elevated As(V) (arsenate) concentrations in ground waters can be derived from oxidation of sulfide minerals, particularly arsenian pyrite, and arsenopyrite. In reducing natural ground waters, at near-neutral pH, As(III) (arsenite) is the dominant As species derived from desorption of As bound to mineral oxides and from the reductive dissolution of As-bearing Fe and Mn oxides (Welch, Westjohn et al. 2000; Smedley and Kinniburgh 2002).

1.2.3: Fluoride and its associated health hazards

Fluorine is the lightest halogen, one of the most reactive of all chemical elements (Kaminsky, Mahoney et al. 1990) and also the most electronegative element in nature (Helm 1985). It is a strong lithophile element and has an ionic radius very similar to that of OH^- and substitutes readily in hydroxyl positions during magmatic differentiation. It enters into silicate minerals at late stages because of the high partitioning coefficient for low temperature minerals. It is one of the most abundant elements available in the earth crust and combines with other elements to produce compound known fluoride (F). Fluoride is found naturally in rock, soil, water, plants and animals (Zhu, Ding et al. 2007; Ozsvath 2009). Drinking water is the largest contributor to the daily F intake. It is present in vegetables, fruits, black tea and fish bones. F is also found in dusts, industrial wastes and burning of coal. A number of studies have reported the ubiquitous distribution of organofluorine compounds in human and animal tissues (Borlongana 2005). Food, water and house dust are potentially significant source of these compounds. The widespread occurrence of perfluorinated compounds received worldwide attention recently because accumulation of these compounds in animal and human body can cause potential impairment of their health (Domingo 2012).

The average fluoride concentration in the earth's crust is estimated at 0.05–0.1% or 500–1000 mg/kg (Krauskopf and Bird 1967; Adriano 2001). However, the fresh surface waters have very low fluoride concentration ranging from 0.01-0.3 mg/L (Msonda, Masamba et al. 2007). The natural fluoride concentration ranges from trace quantities to over 25mg/L in groundwater (Harrison 2005). Fluoridation does not affect the appearance, taste and smell of water. It ranks at 13th position among the elements in terms of occurrence in nature (Krauskopf and Bird 1967; Adriano 2001).

The exposures of different forms of fluoride are critical and have shown to affect the fluoride content in body, thus increasing the risk of fluoride prone diseases. Fluoride can be beneficial or detrimental for our body depending on its concentration in the drinking water (Harrison 2005). F^- <1 mg/L reduces dental caries and the concentrations less than 0.5mg/L enhances the risk of dental caries. It may be harmful for our health at concentrations exceeding 1.5-2mg/L. However, F^- >2 mg/L causes discoloration of teeth and the higher concentration increase the risk of dental and skeletal flourosis depending on the level and period of exposure (Hileman 1988; Kaminsky, Mahoney et al. 1990). However, it may be responsible for crippling skeletal and dental flourosis and cancer at concentrations exceeding 10mg/L (Dissanayake 1991).

At higher a level (10mg/L) F is dangerous for soft tissues also and its continuous exposure leads towards the damaging effects on body tissues particularly the nervous system (Ozsvath 2009). It can also damage blood cells, blood vessels, lining of stomach and intestine and accelerate calcification of blood vessels (Ozsvath 2009). All of these abnormalities resulting from F toxicity ultimately accelerate the ageing process in human beings (Machoy-Mokrzyńska 2003). It is also responsible for reduction in the level of reproductive hormones in the serum of men (Ortiz-Pérez, Rodríguez-Martínez et al. 2003) miscarriage, birth abnormalities, mental retardation and cancer in bone, lungs, bladder and uterus (Grandjean, Olsen et al. 1992). F can penetrate into brain and it is an important component of the cerebrospinal fluid. At higher concentration it can produce harmful effects in the brain. Chronic flourosis seems to have a role in Alzheimer's disease (AD) because this disease is more common among people living in high F contaminated regions (Tang, Du et al. 2008).

There are both natural and anthropogenic sources of fluoride responsible for groundwater contamination throughout the world. The natural sources include fluoride-bearing minerals (fluorite, flourapatite, cryolite and apophyllite) as well as F^- replacing OH^- in the ferromagnesium silicates (amphiboles and micas), and clay minerals (Guo, Wang et al. 2007; Dey, Swain et al. 2012). Its concentration in underground water depends on the pH, the intensity of the weathering process, and the amount of clay in the aquifer material (Adriano 2001; Saxena and Ahmed 2003). However, the anthropogenic sources include, aluminum refining, fertilizer and semi-conductor manufacturing, glass and ceramic production, coal combustion, brick manufacturing, nickel, copper and steel smelting (Pickering 1985).

1.3: Analysis of drinking water quality parameters

In drinking water, the physio-chemical parameters are important and their high or low concentration directly or indirectly affects the human health. The pH is one of the important indicators of water quality and level of pollution in aquatic system (Jonnalagadda and Mhere 2001). Drinking water pH has no direct effects on human health but it has some indirect health effects by bringing changes in other water quality parameters such as metal solubility and pathogens survival. However, high range of pH attributes bitter taste to drinking water. The ideal pH for drinking water is 6.5-8.5 (US-EPA 2003).

The salt concentration or salinity of drinking water is determined by TDS and EC. According to USEPA, the permissible limit for TDS is 1000mg/L. The electrical conductivity (EC) qualitatively estimates the status of inorganic dissolved solids and ionized species in water (Jonnalagadda and Mhere 2001).

Nitrates and nitrites are found naturally in water. High nitrate (NO_3) concentration is toxic especially for bottle fed babies causing blue baby syndrome. The toxicology of nitrate to humans is mainly attributable to its reduction to nitrite. The major biological effect of nitrite is its involvement in the oxidation of normal hemoglobin to methaemoglobin, which is unable to transport oxygen to the tissues. The dominant human health risk associated with nitrate consumption is considered to be of methaemoglobin aemia by nitrate-derived nitrite (Gupta, Gupta et al. 2000).

The adults average daily intakes of potassium (K) through water ingestion is generally <0.1%. For normal body functions, like other light elements, sufficient amount of K is also very significant. The low concentration of K can cause heart problems, hypertension, muscle weakness, bladder weakness, kidney diseases, asthma, while its high concentration can cause rapid heartbeat, cystitis, ovarian cysts, reduced renal function and abnormal metabolism of protein. Minerals deposits are the main sources of sodium (Na) in water. Low concentrations of Na can cause numerous health problems such as mental apathy, low blood pressure, fatigue, depression, and dehydration, while its high concentration is responsible for edema, hypertension, stroke, headaches, kidney damages, stomach problems and nausea (Mari 2003). The deficiency of base cations like calcium (Ca) and magnesium (Mg) in drinking water has been associated with cardiovascular diseases (Yang, Chang et al. 2006). Iron (Fe) is one of the human essential elements and needed for hemoglobin, myoglobin and a number of enzymes. However, high concentration of Fe is also toxic and characterized by the vomiting, diarrhea, with subsequent effect on cardiovascular and central nerves systems, liver, kidney and blood (Goldhaber 2003).

1.4: Heavy metals, arsenic and fluoride in Pakistan and worldwide

1.4.1: Heavy metal contamination in Pakistan and worldwide

The heavy metals pollution in water, soil and sediments is a great challenge for different developing countries like Pakistan of the world. There are various studies in literature reporting the metals contamination in soil/sediments or water but, there are few researches focusing on the heavy metals contamination in all of these matrices at the same time. Rather there are papers available in literature focusing on only one matrix like water or soil/sediments in terms of heavy metals.

The distribution of heavy metals in urban soils has been studied in many big cities of the world such as Glasgow (Farmer and Lyon 1977), London (Kelly, Thornton et al. 1996), Hong Kong (Li, Lee et al. 2004), New Orleans (Mielke, Gonzales et al. 2000), and Oslo (Tijhuis, Brattli et al. 2002). Similarly, the heavy metals contamination in sediments of the world has been reported in the Po River, Italy (Viganò, Arillo et al. 2003), the River Gomti, India (Singh, Malik et al. 2005), the Songhua River, China (Lin, He et al. 2008), and the Shur River (Karbassi, Monavari et al. 2008) and the Khoshk River (Salati and Moore 2010) in Iran.

There are numerous studies in Pakistan focusing on the assessment of heavy metal concentration and their risk assessment in different matrices including water, soil and sediments. For instance until now the drinking water quality in terms of heavy metals has been evaluated in Manchar lake (Kazi, Jamali et al. 2009) Charsadah (Khan, Shahnaz et al. 2013) Rawal Lake (Iqbal, Shah et al. 2013) Kohistan region (Muhammad, Shah et al. 2011) and Swat District (Khan, Lu et al. 2013). However, various soils of Pakistan have been analyzed in terms of the heavy metals in Hattar industry (Manzoor, Shah et al. 2006) Swat District (Khan, Lu et al. 2013) Peshawar (Jan, Ishaq et al. 2010) Islamabad (Iqbal and Shah 2011) Faisalabad (Parveen, Ghaffar et al. 2012) Kohistan Region (Muhammad, Shah et al. 2011) Mangla lake (Saleem, Iqbal et al. 2013) Swat Valley (Nafees, Jan et al. 2009) Kurrang Nullah, feeding tributary of Rawal lake (Zahra, Hashmi et al. 2014).

1.4.2: Arsenic contamination in Pakistan and worldwide

Arsenic is a great challenge for various nations in the world. More than 70 countries of the world have drinking water supplies naturally contaminated with arsenic and majority of these nations belong to South Asia and South East Asia. It has been reported that about 150million people are affected via consumption of As contaminated water worldwide (Ravenscroft, Brammer et al. 2009).

Elevated levels of As (>50μg/L) has been reported in drinking water in various countries of the world including Bangladesh, India, China, Hungary, Pakistan, Argentina, Chile, Mexico, Taiwan, Vietnam and many parts of USA (Smedley and Kinniburgh 2002). Similarly, high levels of As (>5 mg/kg) in soils have been reported in many parts of the world, including Argentina, Bangladesh, Chile, China, Hungary, parts of India, Mexico, Taiwan, Vietnam, and many parts of the United States (Smedley and Kinniburgh 2002).

In Pakistan, there are numerous researches focusing on the drinking water contamination with As and these studies were conducted in Jamshoro (Baig, Kazi et al. 2009) Manchar lake (Arain, Kazi et al. 2008; Arain, Kazi et al. 2009) Lahore and Kasur (Farooqi, Masuda et al. 2007) Muzaffargarh District (Nickson, McArthur et al. 2005) and Tharparkar (Brahman, Kazi et al. 2013). In 2004, more than 40 people were died in Hyderabad city due to the usage of drinking water contaminated with high level of As and other toxic metals (Arain, Kazi et al. 2008).

However, there is very less data focusing on the arsenic contamination in soil and sediments of Pakistan and worldwide. In Pakistan so far, only two studies have been conducted in this regard i,e., in District Punjab (Farooqi, Masuda et al. 2009) and District Nagarparkar (Brahman, Kazi et al. 2013).

India and Bangladesh are among the worst As affected areas of the world. In, both of these nations various studies have been conducted and their results were quite alarming. It has been reported that in West Bengal, India and Bengal Basin of Bangladesh at least 100million people are at risk of cancer and other As-related diseases (Bhattacharya, Jacks et al. 2002; Bhattacharya, Welch et al. 2004). During the past few years, As has also been detected in ground waters of the sedimentary aquifers of the Terai Belt in Southern Nepal (Bhattacharya, Tandukar et al. 2003) Red River Delta and Mekong Basin of Vietnam and Cambodia (Berg, Tran et al. 2001; Berg, Stengel et al. 2007). Recently, As concentration was determined in water, soil and sediments of Western Snake River Plain of Idaho, USA (Busbee, Kocar et al. 2009). Ravenscroft et al., (2009) defined four As affected regions in South and Central America including the high volcanic mountains of the Andes, the arid Pacific coastal plains, the tropical river basins of Amazonia, and the semiarid Chaco-Pampean plain. Arsenic is also reported in ground waters of Australia (O'Shea, Jankowski et al. 2007) and Guam, a small island in Western Pacific Ocean (Vuki, Limtiaco et al. 2007). Moreover, the sediments of Bangladesh (Seddique, Masuda et al. 2011) India (Nath, Chakraborty et al. 2009) and Taiwan (Lu, Liu et al. 2010) have been analyzed in terms of arsenic contamination.

1.4.3: Fluoride contamination in Pakistan and worldwide

Fluoride in drinking water is a serious concern for different nations in the world. High levels of fluoride concentration in groundwater are affecting millions of people in many countries such as China, India, Pakistan, Sri Lanka, Ghana, Ivory Coast, Senegal, Algeria, Kenya, Uganda, Tanzania, Ethiopia, Mexico and Argentina. Fluorosis is endemic in at least 25 countries around the world (Rafique, Naseem et al. 2009).

In Pakistan, large variation in fluoride concentration is documented in drinking water due to different geological characteristics of different areas. Fluoride levels can even differ significantly in water samples from different wells within the same area (Ahmed, Hussain et al. 2004). Some areas of Pakistan like Karachi and Faisalabad even had fluoride concentration less than the minimum recommended level of 0.7mg/L for human health (Rubina Kausar 2003; Siddique, Mumtaz et al. 2006). However, the areas of Pakistan having high fluoride concentration include Naranji (Shah and Danishwar 2003) Nagar Parkar town (Naseem, Rafique et al. 2010) Lahore and Kasur (Farooqi, Masuda et al. 2007) East Punjab (Farooq, Yousafzai et al. 2007) Tharparkar (Brahman, Kazi et al. 2013). But, there is very little research regarding fluoride contamination in soils and sediments of Pakistan and so far only two studies have been conducted in this aspect i.e., Punjab (Farooqi, Masuda et al. 2009) and Nagarparkar (Brahman, Kazi et al. 2013).

India is one of the most badly affected nations of the world in terms of fluoride contamination in the drinking water. As, 50% of groundwater supplies are contaminated with fluoride and more than 90% of ground water is used for drinking purpose in India. Flourosis is reported in 22 states of India thus affecting 40million people (Karthikeyan, Pius et al. 2005; Susheelaa and Moolenburghb 2007).

Dental and skeletal flourosis was found to be 76.9% and 47.5% in different villages of Rajasthan. It was also observed that flourosis was more common in the poor communities and male members using tobacco, beetle nuts and alcoholic drinks (Hussain, Hussain et al. 2010). The results of a study conducted in various villages of Jhajjar District of Haryana, India showed that about 30-94.85% of children were affected with dental flourosis children in the high fluoride villages and from 8.8-28.2% in low/normal-fluoride villages. India is among the several nations of the world where severe health problems due to fluoride toxicity are prevalent because most of the people have calcium deficiency in their diet (Yadav, Lata et al. 2009).

China is also among the severely affected nations with fluoride of the world and various studies have been conducted in this regard. Fluorosis is a widespread problem in the Yuncheng Basin, northern China and approximately 20% of people are affected by the disease in the last two decades (Currell, Cartwright et al. 2011). Recently, study was also conducted in North Jordan for analyzing the fluoride in groundwater and the results showed that it had fluoride concentration even less than minimum recommended level of 0.5mg/L (Abu Rukah and Alsokhny 2004).

1.5: Importance of study

District Rahim Yar Khan is a neglected and poor area of Pakistan. In this area, there is not even a single study focusing on arsenic, fluoride and trace metals levels in drinking water and their effect on human health. Only initial screening was done by PCRWR and declared District Rahim Yar Khan, as the worst hit arsenic contaminated area in Pakistan (Islam-ul-Haq. 2007). Moreover, this is the first systematic and scientific study conducted in the study area. Hence, there is an urgent need to focus on the analysis of soil, sediments and drinking water quality in District Rahim Yar Khan. This study will provide the foundation for various future researchers focusing on the analysis of water quality in Pakistan.

1.6 :Aims and objectives of study

- Determination of various physio-chemical properties, arsenic, fluoride and trace metals in water, soil and sediments and their comparison with the permissible limits set by WHO/EPA.
- Determination of health risk assessment of arsenic, fluoride and trace metals in drinking water via Chronic Daily Intake and Hazard Quotients and in soil and sediments via Geoaccumulation Index, Enrichment Factor, Contamination Factor and Degree of Contamination.
- To propose the possible sources of heavy metals, arsenic and fluoride in groundwater.

2. Study Area

2.1: General Description

Rahim Yar Khan District lies between 27.40' - 29.16' north latitudes and 60.45' - 70.01' east longitudes. The total area of the district is about 11.880 sq km with a total population of about 340,810. The river Indus flows on the north-west side of the district and forms its boundary with Rajanpur and Muzaffargarh districts. There is no other river, Nallah or lake in this district. It is divided into four Tehsils including Rahim Yar Khan, Sadiqabad, Liaquat pur and Khan pur. The district is surrounded on the north by Muzaffargarh district, on the east by Bahawalpur district, on the south by Jasilmir (India) and Ghotki district of Sindh province and on the west by Rajanpur district. A very prominent feature of the area is that sub-soil water level on river side of main line of Pakistan Railways is generally sweet, but, on the other side it is brackish. This fact had its repercussion on all the completed as well as proposed water projects in the area (District Census Report of Rahim Yar Khan, 1998).

The present study is designed for the analysis of soil, sediments and drinking water quality in the district Rahim Yar Khan. In the district, both ground and surface water are used for drinking purpose. But, the major source of drinking water is ground water including hand pumps, motor pumps or rotor pumps. Surface water including canal water is generally used for drinking purpose only in those areas having brackish water. However, canal water is the major source of irrigation in the area. But, groundwater in the form of tube well is also used for irrigation purpose in some areas of this region. Moreover, in the desert area of the district there is very critical situation regarding the availability of drinking water. The ground water of this region is unfit for drinking purpose due to its brackish nature. Hence, in this region the contaminated canal water is collected in various pools or ponds known as 'Tubas or Tobas' which is supplied to homes of that area via various hand pumps. Moreover, both animals and human beings use this contaminated water for drinking purpose. In the present study, two Tehsils including Khan pur and Rahim Yar Khan were selected because River Indus mainly flows in the Tehsil Khan pur while the major industries are located in the Tehsil Rahim Yar Khan (District Census Report of Rahim Yar Khan, 1998).

2.1.1: Hydrogeochemistry

The study area consists of a thickened sequence of unconsolidated flood plain deposits and aeolian deposits of Pleistocene to Present age. The former comprises of both abandoned and active flood plain deposits consisting mainly of loose to friable, well packed, and fine to medium-grained sand, silt and clay. Calcium carbonate concretions (Kankar) of irregular shape, but of regular size and distribution are associated with these sediments (Farooq, Yousafzai et al. 2007). Data obtained from several wells and surroundings show that alluvium is more than 1500m thick. According to the previous studies in the region, the alluvium complex is of heterogeneous nature and shows limited horizontal and vertical extension of beds. The south-eastern part of the district comprised of aeolian deposits of Cholistan desert. The sand plain consists of high sand ridges and inter-dunal hollows, which are sub recent to older channels of Hakra River. The aeolian deposits are youngest in the area and active westward moving dunes 7-20ft high. These deposits consist of fine sand and silt with well rounded and well sorted grains. Most of the material is derived from the adjacent arid zone by wind action (Farooq, Yousafzai et al. 2007).

The aeolian deposits occur above the water table and have no hydrological significance except at a few places where the zone of saturation may be within them. The sediments formed as channel infills, levees and overbank flood plain deposits, show lateral and vertical variation. This is due to cyclic shifting in the course of Indus River and its tributaries which laid down these sediments. The grain size decreases from northeast to southwest, which points to heterogeneous conditions of deposition and cause for variation in the permeability values of the layers. The absence of continuous clay layers in general, is the indication of the presence of unconfined aquifers in the fluvial sediments. However, the presence of 5-15ft thick clay lenses at some places suggests that confined and unconfined conditions are present locally (Farooq, Yousafzai et al. 2007).

In most of the area, the depth of water table is between 6 and 8ft. the coefficient of transmissivity in various parts of the aquifers (calculated from equilibrium and non equilibrium conditions from pumping tests, sieve analysis and specific capacities and specific yield values range from 1952-2423m^2/day and 4.16×10^{-3}-1.6×10^{-3}, respectively. The geologic factors that influence permeability and transmissitivity are lateral lithological changes, variation in sand thickness and grain size distribution. In order to control the effects of groundwater exploitation, the depths to water table should be frequently monitored in wells (Farooq, Yousafzai et al. 2007).

2.1.2: Topography

The district is divided into three main parts. These are the riverain area, canal irrigated area and the Cholistan area. The riverain area lies close to the river Indus and Punjnad. To the south-west of this area lies the canal irrigated area. It is separated by main Minchan bund. The land in this area is higher than that of the riverain area. The approximate height of this area is 150-200m above the sea level. The desert area lies in the south-west of the district which is known as Cholistan area. It extends into Bahawalpur and Bahawalnagar districts (District Census Report of Rahim Yar Khan, 1998).

2.1.3: Climate

District Rahim Yar Khan has very hot and dry climate in summers. It has cold and dry climate in winters. The maximum temperature touches 49.7 °C. The minimum temperature recorded is 6.8°C. The average rainfall is 165mm. The summer season is comparatively longer. It starts in April and continues until October. The winter season goes from November to March. However, November and March are pleasant. Dust storms are frequent during the summer season (District Census Report of Rahim Yar Khan, 1998).

2.1.4: Sources of drinking water and irrigation water

Around 16.5% of the housing units are using piped water, majority of which has that facility in their own houses. About 76% of population is using hand pumps for drinking purposes. Only 1.4% households are using portable water taken out from wells. Such facility is mostly being available in rural areas where there percentage share is around 1.7. Agriculture, in Rahim Yar Khan, mainly depends upon canal irrigation. However, other modes of land irrigation like pumps and tube wells are also used. The major canals used for irrigation purpose are Pajnad Canal and Abbasia Canal. Table 1, given below, shows the total irrigated area of District Rahim Yar Khan by different modes of irrigation.

Table 2.1: Area Sown, Un-Irrigated and Irrigated by Mode of Irrigation (Thousand Hectares)

District	Total area sown	Un-irrigated area	Irrigated area					
			Total	Canals	Well	Tube wells	Canal wells	Canal tube wells
Rahim Yar Khan	795	385	787	385	5	49	5	352

Source: Bureau of statistics, Punjab, Lahore

2.1.5: Major food crops

Agriculture is the occupation of 65% people living in Rahim Yar Khan. The main crops are cotton, wheat, rice and sugar cane. Mangoes, citrus, guavas and dates are the major fruits of this city. However, the main vegetables are cauliflower, onion, tomato, carrot, turnip and ladyfinger (District Census Report of Rahim Yar Khan, 1998).

Table 2.2: Cropping pattern, 1997-98

Kharif	Cotton	Garden	Sugarcane	Rice	Fodders and others	Total
	64%	10%	6%	4%	16%	100%
Rabi	Wheat	Garden	Oil seeds		Fodders and others	
	71%	10%	5%		14%	100%

2.1.6: Industries

The major industries of Rahim Yar Khan include fertilizer, cosmetics, glass manufacturing, cotton production and processing, large textile units, flour mills, sugar and oil mills and large-scale power generation projects. Cotton production in Punjab Province starts from this area. Cottage industries includes; ginning, pottery/clay products, agricultural machinery, handicrafts, and embroidery. Above all there is an industrial unit of Lever Brothers at Rahim Yar Khan and F.F.C plant at Matchi Goth, Tehsil Sadiqabad. There are total 319 industrial units in the district Rahim Yar Khan (District Census Report of Rahim Yar, 1998).

2.2: Sampling

2.2.1: Sampling plan

Sampling was done from two Tehsils, Rahim Yar Khan and Khan pur. Both, of these Tehsils are interconnected with each other. Rahim Yar Khan is the largest Tehsil and the major industrial unit of the district. However, River Indus flows through Tehsil Khan pur. Moreover, one of the major canals of the district used for irrigation purpose including Pajnad Canal starts from Tehsil Khan pur and extends throughout the district.

Tehsil Khan pur was divided into 10 equal agricultural lands for the purpose of sampling and the each agricultural land was selected after a distance of 3-4km. The distance between the agricultural land and the agriculture land was not greater than 1km. The samples were collected from both the rural and urban areas. The rural areas comprised of drinking water and irrigation water and from the urban areas only the drinking water samples were collected. However, from Tehsil Rahim Yar Khan some of the drinking water samples and all of the industrial soil samples were collected. Global Positioning System (GPS) was used for locating each sampling site via latitude and longitude during sampling.

2.2.2: Water sampling and sample preparation

About 51 samples of groundwater were collected in plastic bottles from both Tehsil Khan pur and Tehsil Rahim Yar Khan (Figure 2.1). Among all of these samples, about 7 samples were of irrigation water and the rest of the 44 samples were of drinking water (Table 2.3). The field parameters of all water samples are summarized in Table A.1 (Annexure A). We have categorized these two Tehsils as:

Site A (Khan Pur, agricultural area)

Site B (Rahim Yar Khan, Industrial area)

a) Site A

The Site A is the agricultural area of Tehsil Khan pur which included about 44 groundwater. Out of the total 44 samples of Site A there were 7 irrigation water samples collected from various agricultural lands/farmlands and rest of the 37 samples were the drinking water samples collected from various households in each sampling location. These samples were further divided into deep and shallow groundwater samples. The shallow groundwater included samples having the depth of about 20-100ft and deep groundwater included samples having depth of about 145-200ft. There were only 4 deep groundwater samples and rests of the 40samples were shallow groundwater samples.

b) **Site B**

The Site B is the industrial area of Tehsil Rahim Yar Khan. About 7 shallow groundwater samples were collected from the Site B. These drinking water samples were located near the industrial area of this region.

All of these samples were collected via following standard procedures (Khan, Shahnaz et al. 2013). All of these samples were divided into two equal parts. One part of each sample was acidified with few drops of nitric acid for the analysis of cations while the second part of the sample was non-acidified for analysis of anions. All of the water samples were stored at 4°C.

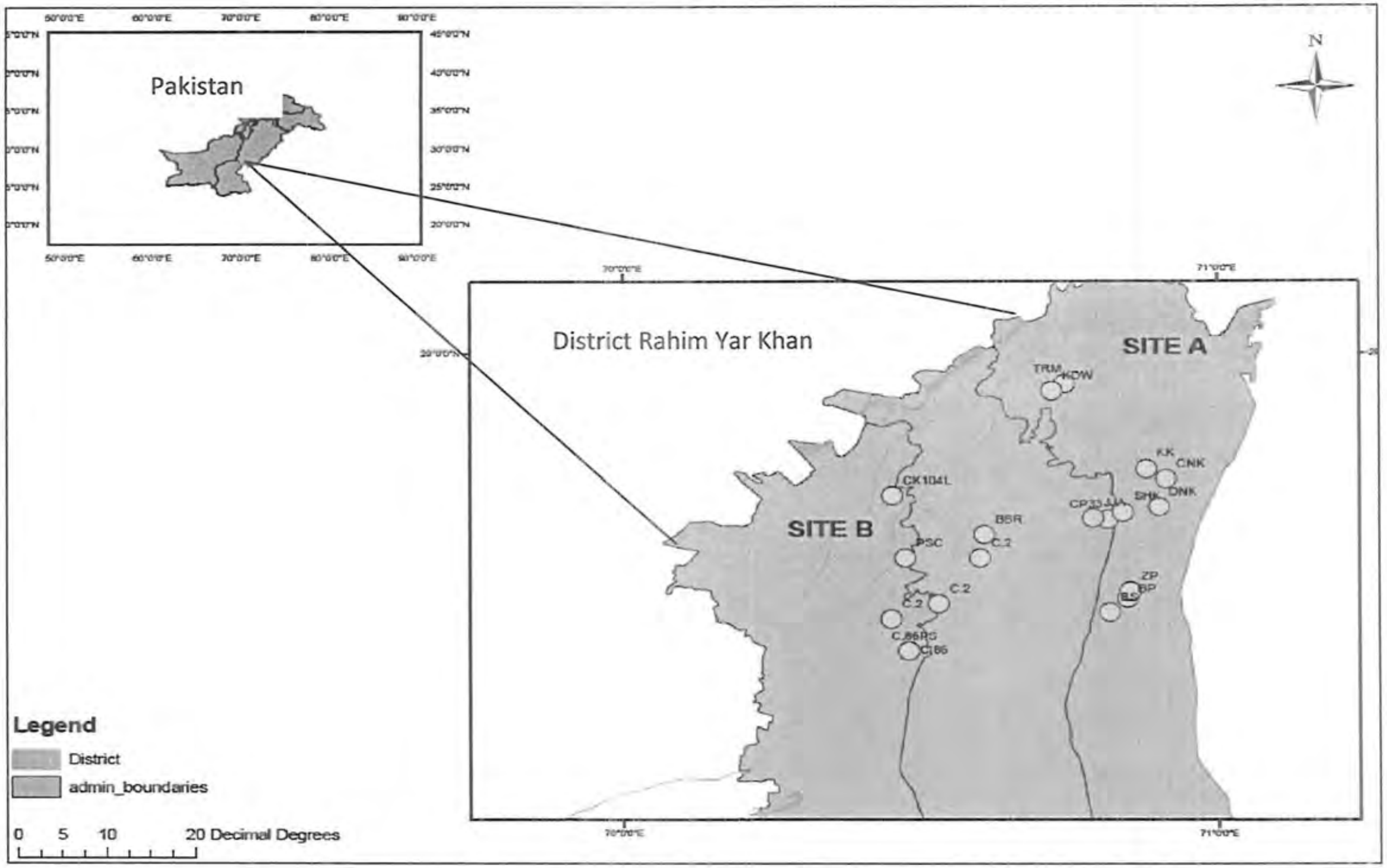


Figure 2.1: Location map showing the sampling points of groundwater samples of District Rahim Yar Khan

Table 2.3: Description of location and sampling points of water samples

Site	Sampling location	Sample ID	Depth (ft)	Type of water	Type of depth	Source	Area/region	Agricultural land/household
SITE A	Basti Chak CK 104L	CK104L	30	Hand pump	Shallow	Drinking water	Desert area	Household
		CK104L	70	Tube well	Shallow	Irrigation water	Desert area	Agricultural land
	Basti Chak CP33	CP33	60	Tube well	Shallow	Irrigation water	Desert area	Agricultural land
		CP33	20	Hand pump	Shallow	Drinking water	Desert area	Household
		CP33	20	Motor pump	Shallow	Drinking water	Desert area	Household
	Basti Sheikhan	SHK	55	Hand pump	Shallow	Drinking water	Desert area	Household
		SHK	55	Hand pump	Shallow	Drinking water	Desert area	Household
		SHK	55	Motor pump	Shallow	Drinking water	Desert area	Household
		SHK	55	Motor pump	Shallow	Drinking water	Canal irrigated area	Household
	Basti Dharecha Nagar Khakwani	DNK	60	Hand pump	Shallow	Drinking water	Canal irrigated area	Household
		DNK	60	Motor pump	Shallow	Drinking water	Canal irrigated area	Household
		CMK	70	Hand pump	Shallow	Drinking water	Canal irrigated area	Household
	Basti Chah Nssrullah Khan	CNK	150	Tube well	Deep	Irrigation water	Canal irrigated area	Agricultural land
	Basti Khokran	KK	200	Tube well	Deep	Irrigation water	Canal irrigated area	Agricultural land
		KK	60	Hand pump	Shallow	Drinking water	Canal irrigated area	Household
		KK	60	Motor pump	Shallow	Drinking water	Canal irrigated area	Household
		KK	60	Rotor pump	Shallow	Drinking water	Canal irrigated area	Household
	Jajah Abbaia	JJA	200	Tube well	Deep	Irrigation water	Canal irrigated area	Agricultural land
		JJA	40	Hand pump	Shallow	Drinking water	Canal irrigated area	Household
		JJA	40	Motor pump	Shallow	Drinking water	Canal irrigated area	Household
		JJA	40	Rotor pump	Shallow	Drinking water	Canal irrigated area	Household
	Basti Bukhari Sharif	BS	60	Hand pump	Shallow	Drinking water	Riverain area	Household
		BS	60	Rotor pump	Shallow	Drinking water	Riverain area	Household
		BS	60	Tube well	Shallow	Irrigation water	Riverain area	Agricultural land
	Basti Pahore	BP	25	Hand pump	Shallow	Drinking water	Canal irrigated area	Household
		BP	25	Motor pump	Shallow	Drinking water	Canal irrigated area	Household
		BP	25	Rotor pump	Shallow	Drinking water	Canal irrigated area	Household
		TRM	145	Tube well	Deep	Irrigation water	Canal irrigated area	Agricultural land

SITE A	Basti Taranda Molvian	TRM	50	Hand pump	Shallow	Drinking water	Canal irrigated area	Household
		TRM	50	Hand pump	Shallow	Drinking water	Canal irrigated area	Household
		TRM	50	Hand pump	Shallow	Drinking water	Canal irrigated area	Household
		TRM	50	Hand pump	Shallow	Drinking water	Canal irrigated area	Household
		TRM	50	Motor pump	Shallow	Drinking water	Canal irrigated area	Household
		TRM	50	Motor pump	Shallow	Drinking water	Canal irrigated area	Household
		TRM	50	Motor pump	Shallow	Drinking water	Canal irrigated area	Household
	Zahip pir	ZP	55	Hand pump	Shallow	Drinking water	Canal irrigated area	Household
		ZP	55	Rotor pump	Shallow	Drinking water	Canal irrigated area	Household
		ZP	55	Motor pump	Shallow	Drinking water	Canal irrigated area	Household
	Adda Bagobahar	BBR	20	Hand pump	Shallow	Drinking water	Canal irrigated area	Household
		BBR	20	Motor pump	Shallow	Drinking water	Canal irrigated area	Household
		BBR	20	Rotor pump	Shallow	Drinking water	Canal irrigated area	Household
	Majeed Colony	MC	50	Hand pump	Shallow	Drinking water	Canal irrigated area	Household
	Madina Town	MT	50	Hand pump	Shallow	Drinking water	Canal irrigated area	Household
	Railway Colony	RC	50	Hand pump	Shallow	Drinking water	Canal irrigated area	Household
	Muhala Loharan	ML	50	Hand pump	Shallow	Drinking water	Canal irrigated area	Household
SITE B	Pul Sanni Colony	PSC	70	Hand pump	Shallow	Drinking water	Canal irrigated area	Household
	Pul Sanni	PS	70	Hand pump	Shallow	Drinking water	Canal irrigated area	Household
	Chak 86	CK 86	70	Hand pump	Shallow	Drinking water	Canal irrigated area	Household
	Chak 86	CK 86	70	Hand pump	Shallow	Drinking water	Canal irrigated area	Household
	Colony No.2	C.2	70	Hand pump	Shallow	Drinking water	Canal irrigated area	Household
	Colony No.2	C.2	70	Hand pump	Shallow	Drinking water	Canal irrigated area	Household
	Colony No.2	C.2	70	Hand pump	Shallow	Drinking water	Canal irrigated area	household

2.2.3: Soil and sediment sampling and sample preparation

About 33 soil and sediments samples as shown in Figure 2.2 were collected from both Tehsil Khan pur and Tehsil Rahim Yar Khan via following standard procedures (Carson 2001). The detail of each sample is summarized in Table 2.4. The field parameters of all soil and sediment samples are summarized in Table A.2 (Annexure A).

a) Site A

The Site A is the agricultural area of Tehsil Khan pur. The Site A comprised of 11 agricultural soil samples and 15 sediment samples. Thus, this site comprised of total 26 samples of agricultural soils and sediments. Composite samples of soil and sediments were collected at the depth of 0-30cm. The agricultural soils were collected from 11 agricultural lands and each agricultural land was divided into 5 equal parts. About 200g of soil sub-sample was collected from middle and all of the 4 corners of each agricultural land and mixed. While, the deposited sediment samples were collected from the head, middle and tail section of the respective water bodies like canals and River Indus.

b) Site B

The Site B is the industrial area of Tehsil Rahim Yar Khan. Seven industrial soil samples were collected from this Site. In the case of industrial soils, about 500g of soil sub-sample was collected from dumping site and about 500g was collected at a distance of 1km away from the dumping site of each industry and mixed.

All of the soil and sediment samples were air dried, grounded, homogenized and sieved via 2mm sieve. These were sealed in clean polythene bags and then were stored in refrigerator until further processing (Kumar, Kaur et al. 1998).

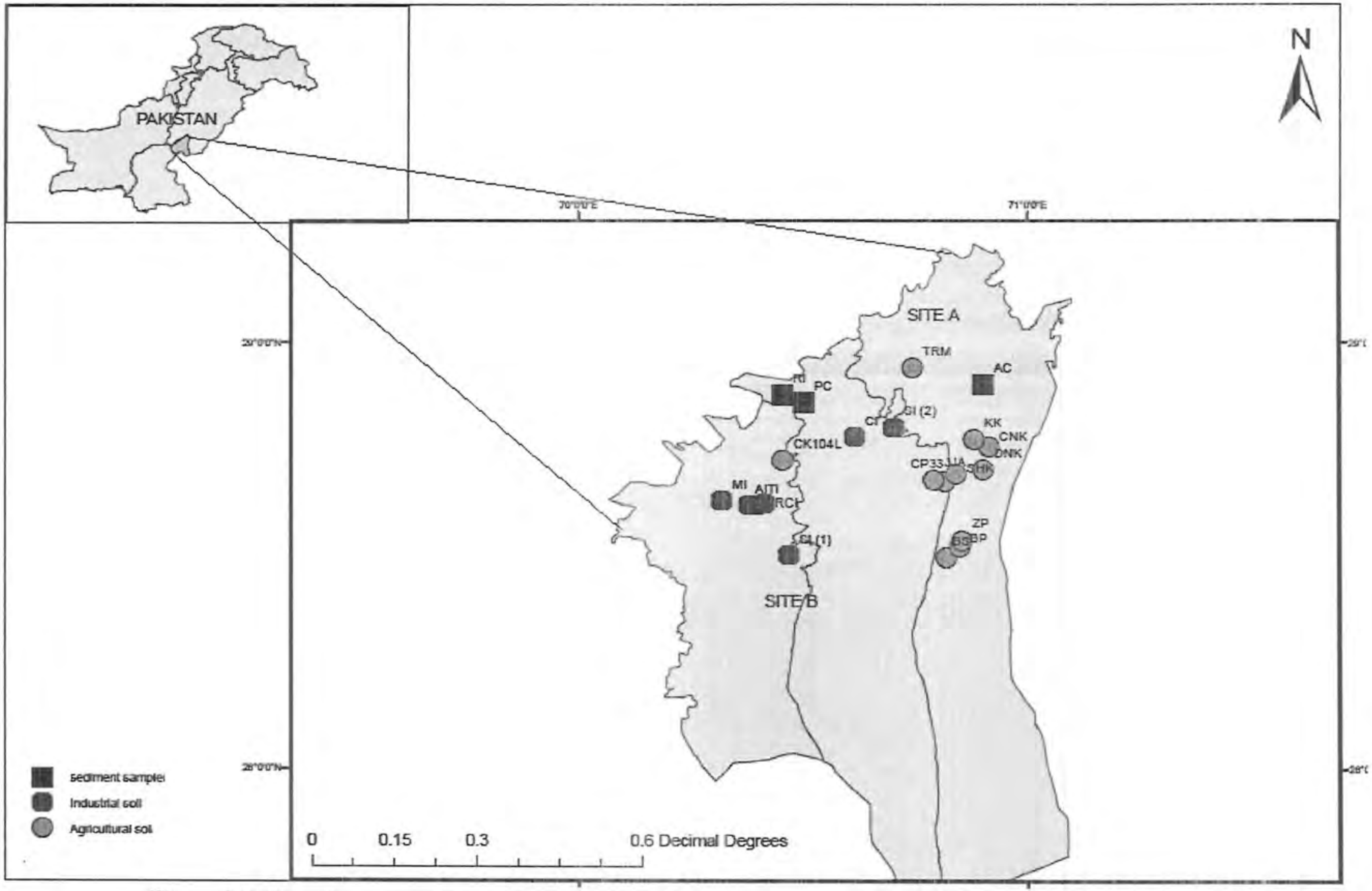


Figure 2.2: Location map and sampling points of soil and sediment samples of District Rahim Yar Khan

Table 2.4: Description of sampling points of soil and sediment samples

Site	Sampling location	Sample ID	Type of sample	Depth (cm)	No. of samples taken
SITE A	Basti Chak 104L	CK104L	Agriculture soil	0-30cm	1
	Basti Chak P33	CP33	Agriculture soil	0-30cm	1
	Basti Sheikhan	SHK	Agriculture soil	0-30cm	1
	Basti Dhareja Nagar Khakwani	DNK	Agriculture soil	0-30cm	1
	Basti Chah Nasrullah Khan	CNK	Agriculture soil	0-30cm	1
	Basti Khokaran	KK	Agriculture soil	0-30cm	1
	Jajah Abbasia	JJA	Agriculture soil	0-30cm	1
	Basti Bukhari Sharif	BS	Agriculture soil	0-30cm	1
	Basti Pahore (BP)	BP	Agriculture soil	0-30cm	1
	Basti Taranda Molvian (TRM)	TRM	Agriculture soil	0-30cm	1
	Zahir pir	ZP	Agriculture soil	0-30cm	1
	Pajnad Canal	PC	Sediment	0-30cm	5
	Abbasia Canal	AC	Sediment	0-30cm	5
	River Indus	RI	Sediment	0-30cm	5
					Total = 26
SITE B	Al Noor Factory, Zari-e-Aalat (Industry of Agriculture Instruments)	AI	Industrial soil	0-30cm	1
	Umar and Husnain Marble factory (Marble Industry)	MI	Industrial soil	0-30cm	1
	Itehad Soap Factory (Soap Industry)	SI (1)	Industrial soil	0-30cm	1
	Baloch RCC Piped Industry	RCI	Industrial soil	0-30cm	1
	Naveena Industry (Textile Industry)	TI	Industrial soil	0-30cm	1
	Itehad Sugar Mills (Sugar Industry)	SI (2)	Industrial soil	0-30cm	1
	Ginning Press Factory (Cotton Industry)	CI	Industrial soil	0-30cm	1
					Total = 7

2.3: Investigation of physico-chemical parameters of water, soil and sediments

a) pH

In order to measure pH of soil and sediment samples, a solution in the ratio of 1:9 was prepared and filtered via Whatman filter paper No.42. The pH of all water, soil and sediment samples was done with pH meter (pH meter W2015).

b) EC (Electrical conductivity)

The procedure of sample preparation was same for soil and sediment samples as used for the measurement of pH. The EC of all water, soil and sediment samples was determined via EC meter (EC meter, W2015).

c) TDS (Total Dissolved Solids)

The samples of soil and sediment were prepared in exactly the same manner as used for pH and EC. The TDS of all water, soil and sediment samples was determined via EC meter (TDS meter, W2015).

d) Dissolved Oxygen (DO)

The Dissolved Oxygen of all the water samples was determined via DO meter (DO meter, W2015).

e) Alkalinity

The alkalinity of all water samples in the form of bicarbonates was calculated by titration method using concentrated H_2SO_4 solution and bromophenol blue as an indicator (Eaton and Franson 2005). The alkalinity was calculated by the following formula:

$$\boldsymbol{Total\ alkalinity = \frac{(ml \times N)\,of\ H_2SO_4 \times 50 \times 1000}{ml\ of\ sample\ taken}}$$

f) Chlorides

The chlorides of all water samples was determined via Mohr's titration method in which silver nitrate solution and potassium chromate was used as an indicator (Eaton and Franson 2005). The concentration of chlorides in water was calculated by the following formula:

$$\boldsymbol{Chlorides\ (mg/L) = \frac{(ml \times N) of\ AgNO_3 \times 35.5 \times 1000}{ml\ of\ sample\ taken}}$$

g) Calcium

The concentration of calcium of all acidified water samples was determined via Atomic Absorption Spectrophotometer (AAS) (VARIAN).

h) Magnesium

The concentration of magnesium of all acidified water samples was determined via Atomic Absorption Spectrophotometer (AAS) (VARIAN).

i) Sodium

The concentration of sodium of all acidified water samples was determined by AAS (VARIAN).

j) Potassium

The concentration of potassium of all acidified water samples was determined by AAS (VARIAN).

k) Iron

The concentration of iron of all samples including water, soil and sediments was determined by AAS (VARIAN).

l) Manganese

The concentration of manganese of all samples including water, soil and sediments was determined by AAS (VARIAN).

m) Nitrates

The content of nitrates in all water samples was analyzed via UV/Vis Spectrophotometer (Hach DR UV 5000) by using phenol disulphonic acid as a dye and potassium nitrate as the standard stock solution (Eaton and Franson 2005).

n) Sulphates

The sulphates concentration of all water samples was determined through UV/Vis Spectrophotometer (Hach DR UV 5000) via using sodium sulphate as a standard solution and conditioning reagent as a dye (Eaton and Franson 2005).

o) Phosphates

The phosphate content of all water samples was determined via UV/Vis Spectrophotometer (Hach DR UV 5000) via using ammonium molybedate as standard and stannous chloride as standard (Eaton and Franson 2005).

p) Fluorides

UV/Vis Spectrophotometer (Hach DR UV 5000) was used for the analysis of fluoride content in all water samples via using zirconyl acid as the standard solution and alzarine red as a dye (Eaton and Franson 2005).

q) Arsenic

All of the water samples were preserved with HCl and KI solution for the analysis of arsenic. About 2ml of HCl and 1.75ml of KI was added in 15-20ml of water sample. Hydride generator AAS (VARIAN) was used for the analysis of arsenic in all of the water samples (US-EPA 2003).

r) Organic Matter

The organic matter of all soil and sediment samples was analyzed by titration method via using ferrous ammonium sulphate solution and diphenyl amine as an indicator (Kandeler and Gerber 1988). The organic matter was calculated by the formulas:

$$\%\, \textbf{\textit{Organic Matter}}\, (M) = \frac{\mathbf{10}}{\boldsymbol{Vb}}$$

$$\%\, \textbf{\textit{Oxidizable Carbon}} = (\boldsymbol{Vb} - \boldsymbol{Vs}) \times \mathbf{0.3} \times \boldsymbol{M} \div \boldsymbol{Wt}$$

$$\%\,Total\ organic\ carbon\ \left(\frac{W}{W}\right) = 1.334\ \times\ \%\,oxidizable\ organic\ carbon$$

$$\%\,Organic\,Matter\ \left(\frac{W}{W}\right) = 1.724\ \times \%\,Total\ organic\ carbon$$

s) Soil Texture

The soil texture of all soil and sediment samples was determined by Bouyocous Method (Kandeler and Gerber 1988). In this method hydrogen peroxide and sodium oxalate solution was used while using the hydrometer for determination of soil texture. The textural class was determined by using the USDA textural triangle. The percentage of sand, silt and clay in all of the soil and sediment samples was determined by the following formulas:

$$1st\ Hydrometer\ reading\ = silt + clay$$

$$2nd\ Hydrometer\ reading = \%\ clay$$

$$\%\,Sand\ = 100 - (silt + clay)$$

$$\%\,Silt = 100 - (sand + clay)$$

t) Determination of Heavy metals in water, soil and sediment samples

The heavy metals in all of the water, soil and sediment samples were analyzed through Atomic Absorption Spectrophotometer AAS (VARIAN). The water samples acidified with nitric acid were directly analyzed via AAS. While, the soil and sediment samples were digested on the hot plate for 3 hours by using a freshly prepared acid mixture: 9mL HNO_3 and 3mL HCl. The digested samples were than filtered via fine filters and made up to 100ml with distilled water and stored at 4°C (US-EPA 2003).

2.4: Human health risk assessment of arsenic, fluoride and heavy metals

2.4.1: Health risk assessment of heavy metals and fluoride in water

According to US-EPA (2003), the health risk assessment of heavy metals and fluoride in water can be calculated via chronic daily intake (CDI) or average daily dose (ADD) and Hazard Quotient (HQ). The exposed population is considered safe when HQ<1. Both of these values are calculated by the following formulas:

$$CDI = C\ \times\ DI/BW$$

Where, C is the concentration of heavy metals in water (μg/L)

DI is the average daily intake rate (2L/day)

BW is the average body weight (72kg)

Or average daily dose (ADD) can be calculated by the following formula:

$$ADD = C \times IR/BW$$

Where, C is the concentration of heavy metals in water (mg/L)

IR is the water ingestion rate (2L/day)

BW is the average body weight (73kg)

$$HQ = CDI/RfD$$

Where, CDI is the chronic daily intake and

RfD is the oral toxicity reference dose

2.4.2: Arsenic risk assessment in water

a) Exposure assessment

Arsenic enters into human body through several pathways including food chain, dermal contact and inhalation but in comparison with oral intake all others are negligible. The average daily dose (ADD) through drinking water intake was calculated according to the following formula (US-EPA 2003).

$$ADD = C \times IR \times ED \times EF/BW \times AT$$

Where, C is the concentration of arsenic in water (mg/L)

IR is the water ingestion rate (2L/day),

ED is the exposure duration (assumed 67 years),

EF is the exposure frequency (365 days/year),

BW is the body weight (72kg)

AT is the average life time (24, 455 days), respectively.

b) Human health risk assessment of Arsenic

In this study, both the chronic and carcinogenic risk levels were also assessed. HQ was calculated by the following equation (US-EPA 2003).

$$HQ = ADD/RfD$$

Where, the As toxicity reference dose (RfD) is 0.0003 mg/kg/day. The health risk generally occurs when the HQ values were >1 (US-EPA 2003).

The cancer risk (CR) was calculated using the formula:

$$CR = ADD \times CSF$$

According to (US-EPA 2003) database, the cancer slope factor CSF is 1.5mg/kg/day.

2.4.3: Health risk assessment of heavy metals in soils and sediments

There are various methods used for evaluating the degree of pollution in various soils and sediments. The health risk assessment of heavy metals in soil and sediments was calculated via the following statistical formulas.

a) Geoaccumulation Index

The index of geoaccumulation (I_{geo}) enables the assessment of contamination by comparing the current and pre-industrial concentrations. It was computed by using the following Eq. (1):

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

Where, C_n is the mean concentration of the element in the examined soil

B_n is the geochemical background value in the crust.

b) Enrichment Factor

The enrichment factor (EF) represents the contamination level in the soil and is a good tool to differentiate between the anthropogenic and natural sources of the metals. EFs are usually taken as double ratios of the target metal and a reference metal in the examined soil and earth crust.

Usually, Al, Mg, Ca, Mn and Fe are used as the reference. The most commonly used reference metal is Fe. It was calculated by using the following equation:

$$EF = \frac{[X/F_e]_{sample}}{[X/F_e]_{crust}}$$

Where $[X/Fe]_{sample}$ refer to the ratio of mean concentration of the target metal and Fe in the soil (mg/kg, dry weight)

$[X/Fe]_{crust}$ refers to the ratio of mean concentration of the target metal and Fe in the continental crust.

c) *Degree of contamination*

The assessment of soil contamination can also be carried out by using the contamination factor (C_f) and degree of contamination (C_{deg}). The contamination factor was calculated by using the following formula:

$$C_f^i = \frac{C_i}{C_n}$$

Where, Ci and C^i_n, refer to the mean concentration of a pollutant in the examined site and the pre-industrial soil, respectively. The C^i_f is the single element index.

The sum of contamination factors for all elements examined represents the contamination degree (C_{deg}) of the environment which was calculated as by the following formula:

$$C_{deg} = \sum_{i=1}^{i=n} C_f^i$$

2.5: Statistical Analysis

The statistical analysis was carried out by using the software's IBM SPSS Statistics 20 and MVSP 3.2. The correlation matrix and descriptive statistics was calculated for the data set via using SPSS (version 20) and multivariate analysis techniques including CA and PCA were applied on the data set via MVSP (version 3.2). Aquachem software (version 4.0.264 Waterloo Hydrogeologic Inc., 2003) was used to create the Piper plot to determine water type and for the determination of saturation indices for selected minerals in the groundwater samples PHREEQC soft-ware (version 2.1) was used.

2.6: Field survey

A questionnaire based field survey was also conducted in order to determine the most important environmental problems of district Rahim Yar Khan. The questionnaire had various demographic and general questions regarding the district. These questions were asked from different people of various age groups in each village. Moreover, the data regarding various common diseases in district was also collected from the Sheikh Zayed Hospital of District Rahim Yar Khan.

The chapter of Results and Discussion is divided into two major sections A and B. The section A comprised the results of water and section B included results of soil and sediments.

Section A-Water

All of the water samples were categorized into 2 major groups/sites Site A and Site B. The Site A comprised samples of Tehsil Khan pur and Site B comprised the samples of Tehsil Rahim Yar Khan. The groundwater samples of Site A on the basis of their different depths were further divided into two major categories i.e., shallow and deep groundwater. The shallow groundwater samples were between 20-100ft depth and deep groundwater samples were of about 145-200ft.

3.1: Physio-chemical parameters

The results of all physio-chemical parameters are summarized in Table B.1 (Annexure B) and the results comprising mean values of each sampling site are summarized in Table 3.1a. The overall results showed the following order for all physio-chemical parameters except DO i.e., Site A < Site B.

3.1.1: Site A

The pH of all the water samples was alkaline. The mean and range value for pH was 8.6 and 7.9-9.2 respectively. The values were slightly greater than the permissible limits for drinking water in 39.2% samples. Highest value of pH was found in the sample of BP (Rotor pump i.e., 25ft) and smallest value of pH was recorded in CP33 (Tube well i.e., 60ft). The following order for pH values was observed in all of the sampling points i.e., CNK < CP33 < SHK < KK < CK104L < TRM < JJA < DNK < KDW < BS < BP < BBR < ZP. The previous studies have demonstrated that there are many factors responsible for changing the drinking water quality and cause health problems (Tamasi and Cini 2004; Mora, Mac-Quhae et al. 2009). The pH is one of the most important parameter which has no immediate direct effects on human health but has some indirect health effects by bringing changes in other water quality parameters such as solubility of metals (Ho, Chow et al. 2003). The pH values were higher than the previous study reported in Multan and Muzaffargarh (Nickson, McArthur et al. 2005).

While, EC values crossed the permissible limits in 11.7% samples and had a mean value of EC 1093.7μS/cm and it ranged between 550-1950μS/cm. While, the TDS values were within the permissible limits in all of the groundwater samples. The mean and range value of TDS was

533.6ppm and 195-1320ppm. Largest value of both EC and TDS was reported in SHK (hand pump) and smallest value was found in ZP (motor pump i.e., 55ft). The ascending order for both EC and TDS values was ZP < KK > BP < JJA < BBR < BS < CNK < CP33 < TRM < CK104L < DNK < KDW < SHK. The results showed that the samples located near the River Indus had higher values of EC and TDS than those located far from River Indus. The EC and TDS values in all of the water samples were lower than those reported in Multan and Muzaffargarh (Nickson, McArthur et al. 2005).

The DO level in water affects the oxidation-reduction state of many chemicals including nitrates, ammonia, sulphates, sulphites and iron. The mean and range of DO values was 7.3ppm and 6.3-8.2ppm respectively. The lowest and highest value was reported in CNK (hand pump i.e., 70ft) and JJA (rotor pump i.e., 40ft). The DO values were much higher than those reported in Multan and Muzaffargarh (Nickson, McArthur et al. 2005). The ascending order for DO values was ZP > CK104L > KK > CNK > BBR > CP33 > DNK > SHK > TRM > KDW > BS > BP > JJA. The shallow groundwater samples had higher values of all these physio-chemical parameters than the deeper groundwater samples.

3.1.2: Site B

All of the groundwater samples were alkaline in nature and the pH values were slightly higher than the safe limits in about 85.7% samples. The mean and range pH values was 8.6 and 8.3-8.8. The pH values were slightly greater than the permissible limits in majority of the samples. The highest and lowest value was reported in the C.2 (water supply i.e., 70ft) and PSC (hand pump i.e., 70ft). The pH values were higher than the previous study reported in Multan and Muzaffargarh (Nickson, McArthur et al. 2005). The ascending order was found to be C.2 < CK86 < PSC. The EC and TDS values were within the permissible limits in all of the groundwater samples. The mean and range for EC was 1150.3μS/cm and 950-1380 μS/cm. While, the mean and range value of TDS was 575/5ppm and 475-690ppm. The highest and lowest value of EC and TDS was reported in CK86 (motor pump i.e., 70ft) and C.2 (rotor pump i.e., 70ft). The ascending order for both EC and TDS was C.2 < CK86 < PSC. The EC and TDS values were lower than the previous study reported in Multan and Muzaffargarh (Nickson, McArthur et al. 2005). The DO had a mean and range value of 7.1ppm and 6.4-8ppm. The values were higher than those reported in Multan and Muzaffargarh districts (Nickson, McArthur et al.

2005). The samples were arranged in this ascending order in terms of DO values i.e., C.2 < CK86 < PSC.

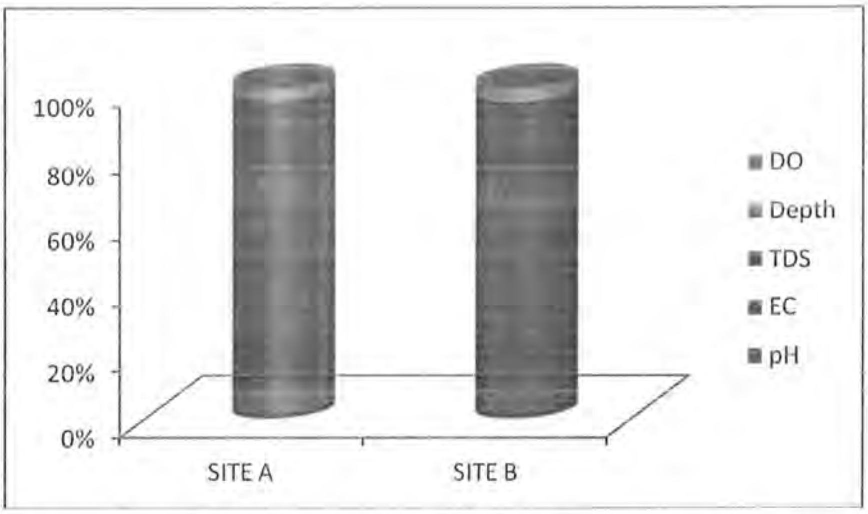


Figure 3.1a: Physio-chemical parameters of groundwater samples of Site A and B

Table 3.1a: Mean, maximum and minimum values of all physio-chemical parameters

Site	SAMPLE ID	Depth (ft)			pH			EC (uS/cm)			TDS (mg/L)			DO (mg/L)		
		Mean	Max	Min	Mean	Max	Min	Mean	Max	Min	Mean	Max	Min	Mean	Max	Min
SITE A	CK104L (n=2)	30	70	50	8.5	8.7	8.6	1321.5	1343	1300	660.7	671.5	650	6.5	6.6	6.5
	CP33 (n=3)	33.3	60	20	8.2	8.5	7.9	1075	1100	1050	537.5	550	525	7.3	7.6	7.1
	SHK (n=4)	55	55	55*	8.3	8.4	8.2	1926.3	1950	1870	963.1	975	935	7.5	7.6	7.1
	DNK (n=2)	60	60	60*	8.6	8.8	8.3	1425	1500	1350	712.5	750	675	7.3	7.5	7.1
	CNK (n=2)	110	150	70	8.2	8.2	8.1	1075	1200	950	537.5	600	475	6.7	7	6.3
	KK (n=4)	87.5	200	50	8.5	8.6	8.3	719.3	900	602	359.6	450	301	6.6	7	6.5
	JJA (n=4)	80	200	40	8.5	8.6	8.4	759.8	915	604	379.9	457.5	302	8.1	8.2	8
	BS (n=3)	60	60	60*	8.6	8.7	8.6	820	939	631	410	469.5	315.5	7.7	7.8	7.5
	BP (n=3)	36.7	60	25	8.7	9.2	8.4	742.7	928	600	371.3	464	300	7.7	7.8	7.7
	TRM (n=7)	61.4	145	45	8.5	8.8	8.2	1277.1	1620	1020	638.6	810	510	7.5	7.6	7.5
	ZP (n=3)	55	55	55*	8.8	9.1	8.6	573.3	620	550	286.7	310	275	6.4	6.5	6.3
	BBR (n=3)	20	20	20*	8.8	8.9	8.7	790	900	670	395	450	335	7	7.7	6.4
	KDW (n=4)	50	50	50*	8.6	8.6	8.5	1480	1720	1380	740	860	690	7.7	8.2	7.3
SITE B	PSC 9n=2)	70	70	70*	8.7	8.8	8.7	1165	1180	1150	582.5	590	575	7.3	7.4	7.3
SITE B	CK.86 (n=2)	70	70	70*	8.6	8.8	8.5	1215	1380	1050	607.5	690	525	7	7.5	6.4
SITE B	C.2 (n=3)	70	70	70*	8.5	8.67	8.29	1097.3	1362	950	548.7	681	475	7	8	6.4

Where *means that all of the samples had similar depths in the same sampling location and n = number of samples.

3.2: Major Ionic Composition of water

The results of major cations and anions present in all water samples are discussed in Table B.2 (Annexure B) and the mean values of each sampling site are summarized in Table 3.2a. The following ascending order was observed for the major anions in groundwater i.e., $NO_3^- < PO_4^{-3} < SO_4^{-2} < Cl^- < HCO_3^-$ and the following order was observed for the major cations in the groundwater i.e., $K^+ < Ca^{+2} < Mg^{+2} < Na^+$.

a) Chlorides

The chlorides concentration was within the permissible limits set by WHO (i.e., 250ppm) in most of the water sample. 5% samples just crossed the permissible limits. The results showed that Site B < Site A in terms of the chloride concentration. The mean and range of the chlorides was 101.4ppm and 5-564.8ppm respectively for Site A. The results showed that the shallower groundwater samples were more contaminated with chlorides than the deeper groundwater samples of Site A. Similar pattern was found in the previous study of East Punjab (Farooqi, Masuda et al. 2007). TRM (Hand pump i.e., 45ft) had the greatest concentration of chlorides and KK (Rotor pump i.e., 50ft) had the smallest concentration of chlorides. The ascending order of all sampling points of Site A was BP < CK104L < CNK < KK < BBR < BS < SHK < KDW < CP33 < JJA < DNK < TRM < ZP. The Site B had a mean and range value of 80.7ppm and 10-179ppm. In Site B, the smallest and largest value was recorded in PS (hand pump i.e., 70ft) and CK86 (rotor pump i.e., 70ft). The ascending order of all sampling locations of Site B was PSC < C.2 < CK86. The agriculture area (Site A) had higher values of chlorides than the industrial area (Site B) as shown in Figure 3.2a.

Cl^- showed positive correlation with SO_4^{-2} (r = 0.317) and Ca^{+2} (r = 0.382) as shown in Figure 3.3a and Table D.1 (Annexure D). The results of the current study were in agreement with previous study reported in East Punjab (Farooqi, Masuda et al. 2007). Chlorides occur in areas having saline water and are widely available in the form of NaCl, KCl and $CaCl_2$ salts (Ullah, Malik et al. 2009). The major sources of chlorides are dissolution of salt deposits, industrial effluents, oil well operation, irrigation drainage and sewage discharges (Ullah, Malik et al. 2009; Azizullah, Khattak et al. 2011). The possible sources of chlorides might be the dissolution of salt deposits and sewage discharges in the brackish and saline areas of the study area.

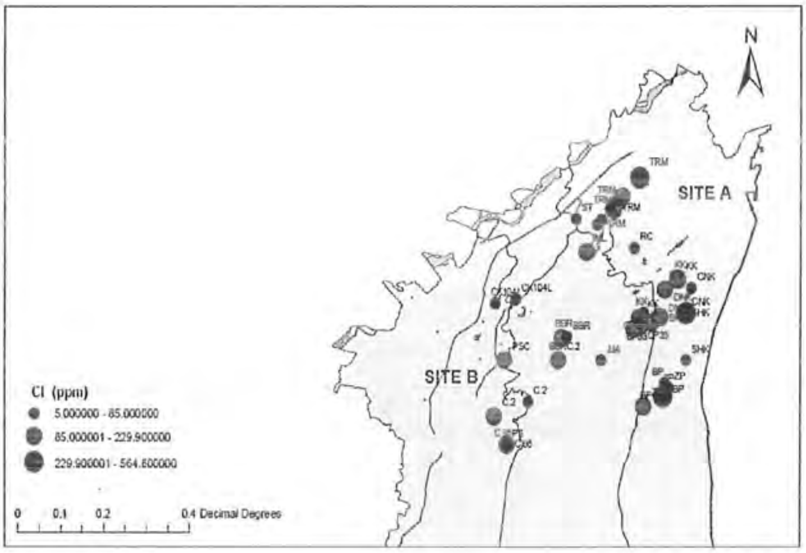


Figure 3.2a: Spatial distribution of chlorides in groundwater of District Rahim Yar Khan

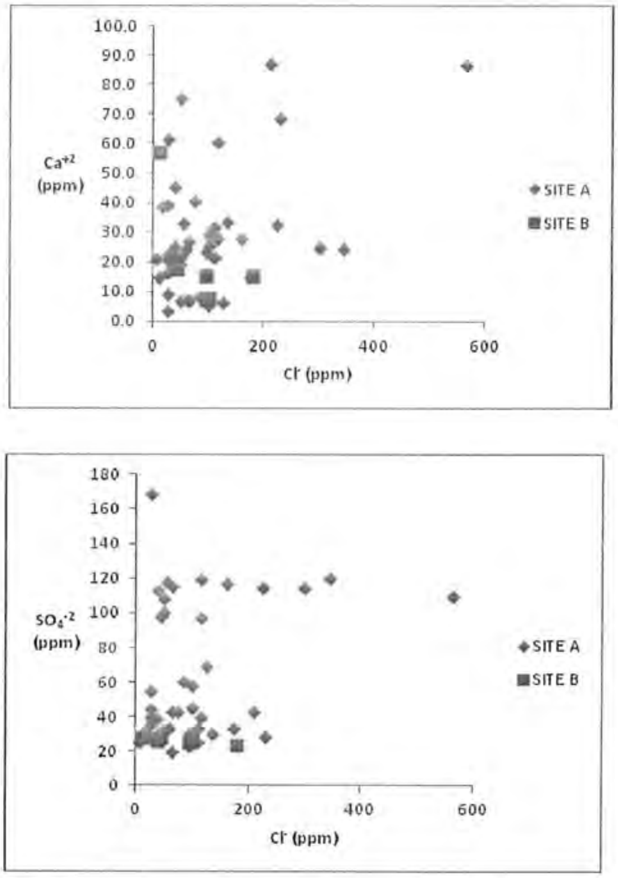


Figure 3.3a: Relationship of a) Cl^- with Ca^{+2} and b) Cl^- with SO_4^{-2}

b) Bicarbonates

The bicarbonates ranged between 210-980ppm and had a mean value of 561.3ppm for Site A. The highest value of bicarbonates was found in the sample of SHK (hand pump i.e., 55ft) and the smallest value was recorded in the sample of ZP (hand pump i.e., 55ft). The sampling points were arranged in this ascending order i.e., ZP < KK < BP < JJA < DNK < BS < BBR < CNK < CP33 < TRM < KDW < CK104L < SHK. The shallow groundwater samples were more contaminated than deep groundwater samples of Site A. This similar trend was observed in the previous study of East Punjab (Farooqi, Masuda et al. 2007).

The mean and range value for bicarbonates in Site B was 573.7ppm and 470-671ppm. The highest and lowest value was observed in C.2 (water supply i.e., 70ft) and C.2 (rotor pump i.e., 70ft). The sampling points of Site B showed this order i.e., C.2 < PSC < CK86. This order was observed for the sites i.e., Site A < Site B as shown in Figure 3.4a.

The bicarbonates had positive correlation with Mg^{+2} (r = 0.360), K^{+} (r = 0. 344) and TDS (r = 0.923) as shown in Figure 3.5a. The bicarbonates values were much less than the previous studies of Muzaffargarh (Nickson, McArthur et al. 2005) and East Punjab (Farooqi, Masuda et al. 2007).

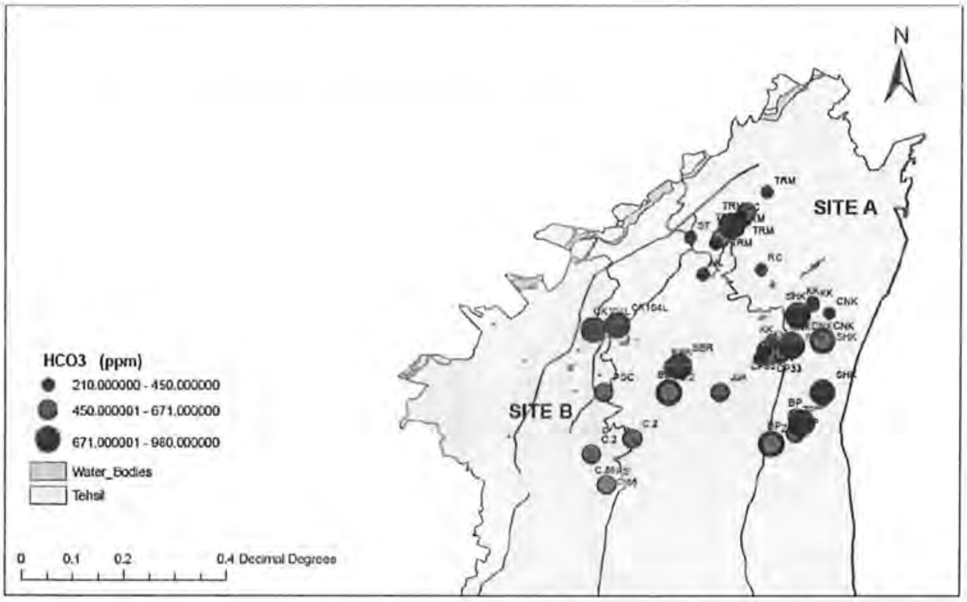


Figure 3.4a : Spatial distribution of bicarbonates in groundwater of District Rahim Yar Khan

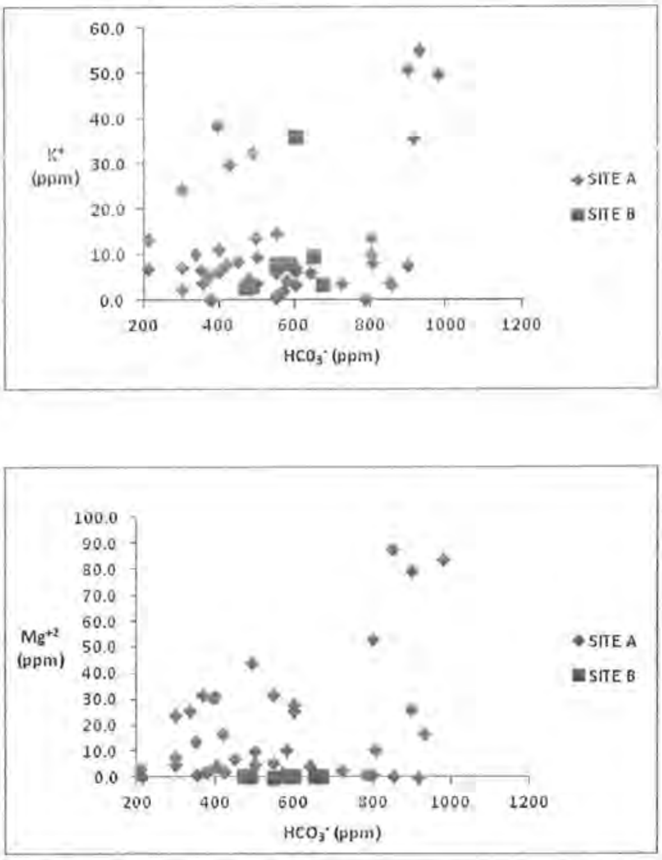


Figure 3.5a: Relationship of a) HCO_3^- vs. K^+ and b) HCO_3^- vs. Mg^{+2}

c) Nitrates

The results of nitrates were very critical in the current study, as the nitrates concentration crossed the permissible limits set by WHO i.e., 10ppm in all of the water samples. The mean and range value of nitrates for Site A was 24.5ppm and 13.2-40.7ppm respectively. The shallow groundwater samples were more contaminated than deeper groundwater samples of Site B. The lowest and highest value was recorded in the samples CNK (tube well i.e., 150ft) and TRM (tube well i.e., 145ppm). The sampling points followed this order i.e., CNK < SHK < KK < JJA < DNK < CK104L < BS < CP33 < BBR < TRM < ZP < KDW < BP. The Site B had a mean and range value of 24.7ppm and 21-27ppm. The highest and lowest concentration was reported in the samples PSC (hand pump i.e., 70ft) and CK86 (hand pump i.e., 70ft). The sampling points observed the following order i.e., CK86 < C.2 < PSC. The following order was observed for the sites i.e., Site A < Site B as shown in Figure 3.6a. The nitrates concentration was much higher than the previous studies conducted in Muzaffargarh (Nickson, McArthur et al. 2005) East Punjab (Farooqi, Masuda et al. 2007) and India (Chauhan, Nickson et al. 2009).

The major anthropogenic sources of nitrates in water are septic tanks, nitrogen rich fertilizers, livestock, manure, agricultural processes and atmospheric sources (Tahir and Rasheed 2008). The current study area is an agricultural area and industrial area where nitrogen rich fertilizers including urea and DAP are extensively applied. Moreover, livestock rearing is a common practice. Thus, the possible sources of nitrates in the current study could be attributed to nitrogen rich fertilizers, agricultural practices and livestock.

The consumption of high level of nitrates via drinking water is associated with various health problems especially among children's and is responsible for methemoglobinemia (blue baby syndrome) and may also increase the risk for respiratory tract infections and goiter development in children (Gupta, Gupta et al. 2000). In literature, there are different views regarding the significant health effects of nitrates in adults. According to one opinion, nitrates in water are also linked with high probability for bladder and ovarian cancer, insulin dependent diabetes mellitus and genotoxic effects at the chromosomal level (Ward, Mark et al. 1996). While the second opinion is that the adult individuals can tolerate high levels of NO_3 with little or no documented adverse health effects and may be able to drink water with nitrate concentrations considerably greater than 10ppm with no acute toxicity effects (Bruning-Fann and Kaneene 1993).

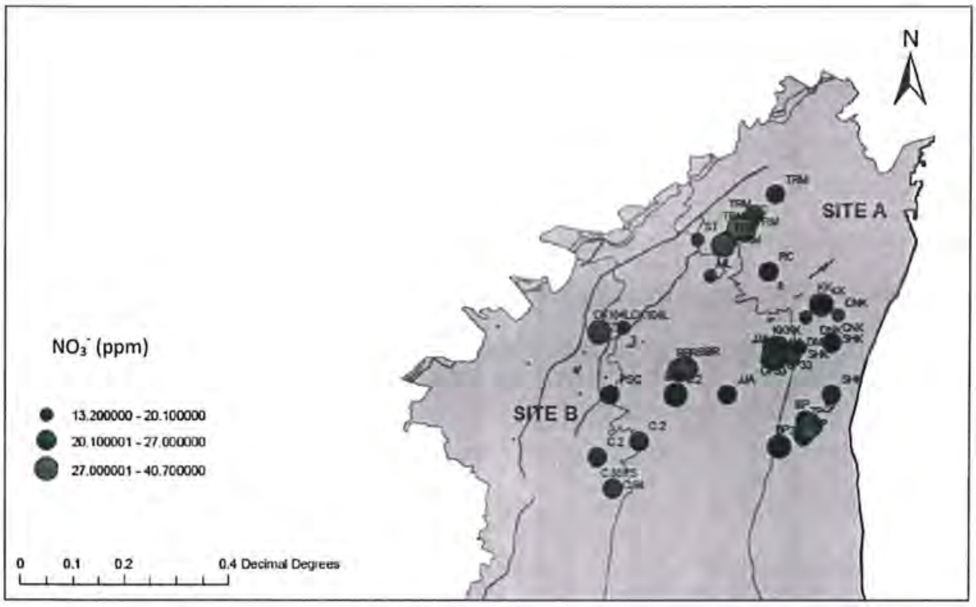


Figure 3.6a: Spatial distribution of nitrates in groundwater in District Rahim Yar Khan

d) Sulphates

The sulphates concentration was within the permissible limits set by WHO i.e., 250ppm in all of the water samples. The Site A had a mean and range of 61.7ppm and 19.8-168.6ppm, respectively. The highest and lowest value was detected in CNK (tube well i.e., 150ft) and CK104L (hand pump i.e., 30ft). The order for sulphates concentration for each sampling points was found as i.e., KK < JJA < DNK < BS < BP < CK104L < BBR < SHK < CP33 < KDW < CNK < ZP <TRM. The deeper groundwater samples were more contaminated with sulphates than shallow groundwater samples and this trend was opposite to previous study conducted in East Punjab (Farooqi, Masuda et al. 2007).

The Site B had a mean and range value of 26.6ppm and 24-29.8ppm. PSC (hand pump i.e., 70ft) had the highest value and CK86 (hand pump i.e., 70ft) had the lowest value of sulphates. The sampling sites were arranged in the following ascending order i.e., CK86 < C.2 < PSC. For sulpates the following order was found i.e., Site B < Site A as shown in Figure 3.7a. The sulphates concentration was much lower than those reported in Muzzafargarh and Multan (Nickson, McArthur et al. 2005). The sulphates showed positive correlation with chlorides (r = 0.317).

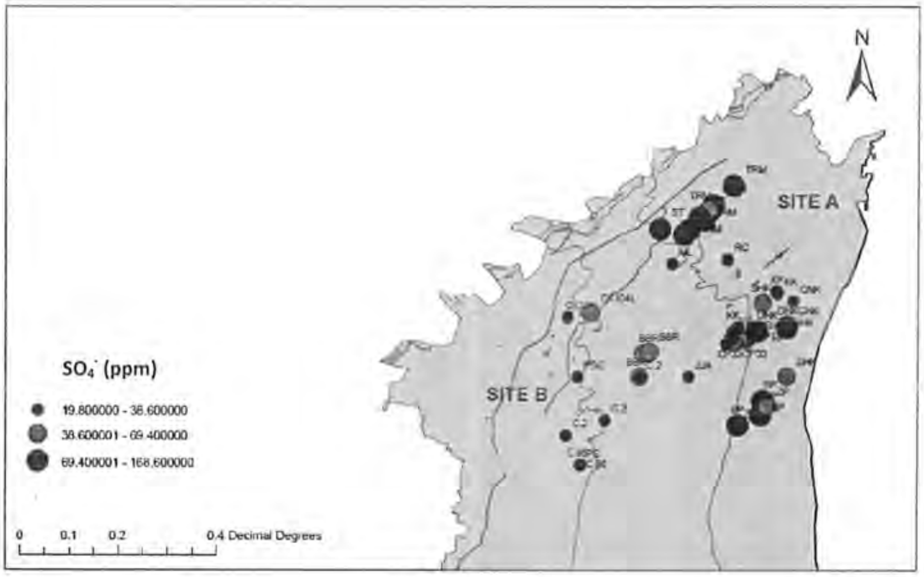


Figure 3.7a: Spatial distribution of sulphates in groundwater of District Rahim Yar Khan

e) Phosphates

The phosphates concentration at Site A ranged from 24.4-62.4ppm with a mean value of 45.6ppm. The highest and lowest value was reported in CP33 (hand pump i.e., 20ft) and BS (rotor pump i.e., 60ft). The shallow groundwater samples were more contaminated than the deeper groundwater samples. The similar pattern was found in the previous study of East Punjab (Farooqi, Masuda et al. 2007). The ascending order for sampling points was observed as BP < BS < CNK < KDW < BBR < KK < SHK < JJA < DNK < CK104L < TRM < ZP < CP33.

The phosphates had mean value of 54.7ppm and it ranged between 44.8-60ppm of Site B. Highest and lowest value of phosphates was recorded in the water samples of C.2 (motor pump i.e., 70ft) and CK86 (hand pump i.e., 70ft) respectively. The sampling points observed the following order i.e., CK86 < PSC < C.2. For phosphates, the following order was observed i.e., Site A < Site B and the phosphate levels were much higher in the industrial area as compared to the agriculture area as shown in the Figure 3.8a. The phosphate levels are much higher than those reported by the previous studies conducted in East Punjab (Farooqi, Masuda et al. 2007) and India (Chauhan, Nickson et al. 2009).

The WHO/EPA has not set any limit for phosphates in drinking water but according to EPA, the phosphate level should not exceed 0.1ppm in streams/rivers and 0.025ppm in the lakes/reservoirs. The phosphate levels greater than 1ppm may interfere with coagulation in water treatment plants. Digestive problems could occur from extremely high level of phosphates and phosphate itself does not have notable adverse health effects (Kotoski 1997).

The major sources of phosphates in drinking water are decomposition of organic matter or phosphorus rich bed rock, animal and human waste, laundry detergents, cleaning solutions, leaking septic tanks, industrial effluents and fertilizers (Kotoski 1997). The possible sources of phosphates in water might be attributed to the disproportionate usage of phosphatic fertilizers like DAP, animal and human waste, detergents and leaking septic tanks.

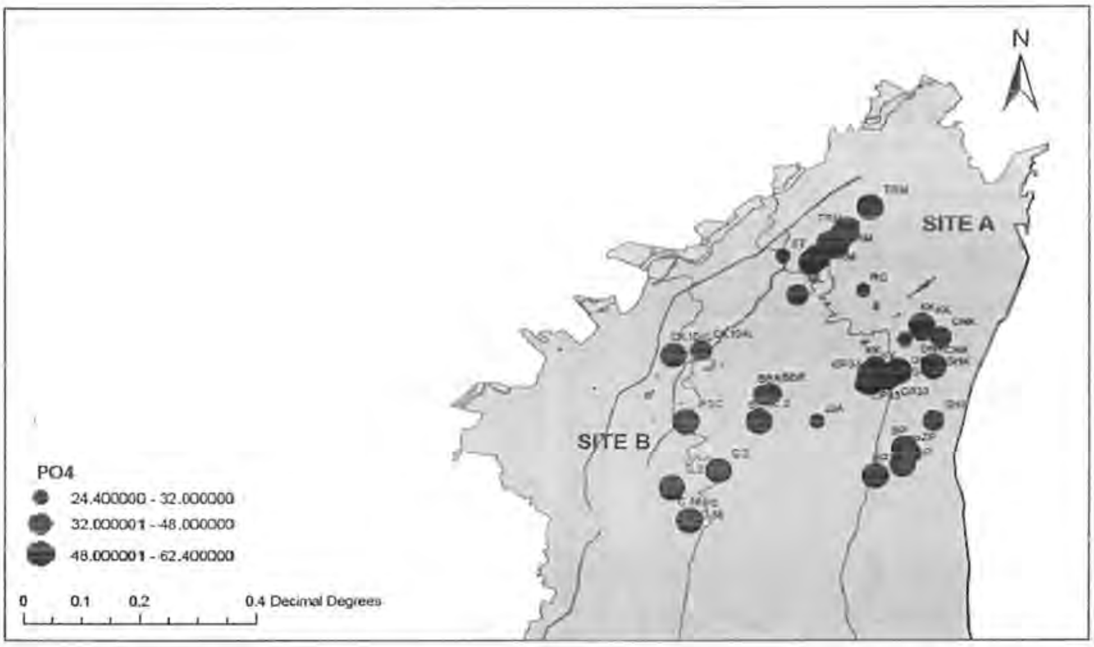


Figure 3.8a: Spatial distribution of phosphates in groundwater of District Rahim Yar Khan

e) Sodium

The concentration of sodium was within the safe limits set by WHO (i.e., 200ppm) in all of the water samples. The Na^+ concentration had a mean value of 41.8ppm and ranged between 1.6-80ppm for Site A. The sample SHK (motor pump i.e., 55ft) had the highest concentration and CK104L (tube well i.e., 70ft) had the lowest concentration. The sampling points showed the following order i.e., CK104L < CP33 < TRM < BBR < JJA < DNK < ZP < KK < KDW < SHK < BS < BP < CNK. The shallow groundwater showed higher concentration of sodium as compared to deeper. The results of the previous study of East Punjab showed similar pattern. The mean and range value for Site B was 24.8ppm and 3.3-57.3ppm. The sample PSC (hand pump i.e., 70ft) had the highest concentration and C.2 (motor pump i.e., 70ft) had the lowest concentration. The sampling sites showed the following order i.e., C.2 < CK86 < PSC. The following order was observed for the major sites i.e., Site B < Site A as shown in Figure 3.9a.

Na^+ showed positive correlation with K^+ (r =0.473) and Mg^{+2} (r =0.366) as shown in Figure 3.10a. The Na^+ concentration was much lower than the previous studies conducted in Muzaffargarh (Nickson, McArthur et al. 2005) and East Punjab (Farooqi, Masuda et al. 2007).

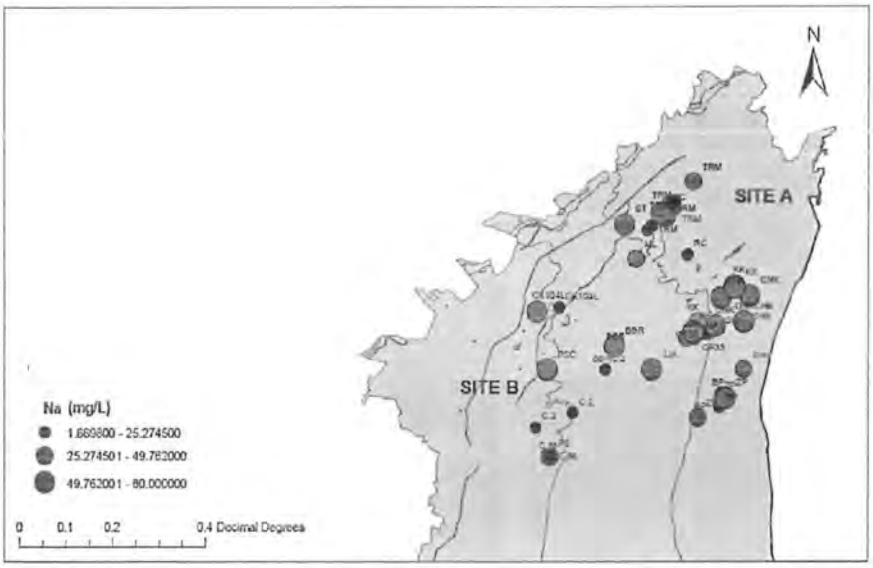
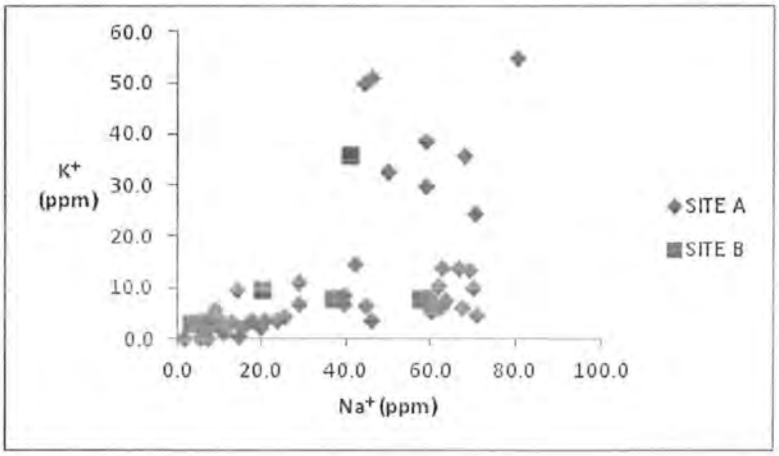


Figure 3.9a: Spatial distribution of Na^+ in groundwater in District Rahim Yar Khan



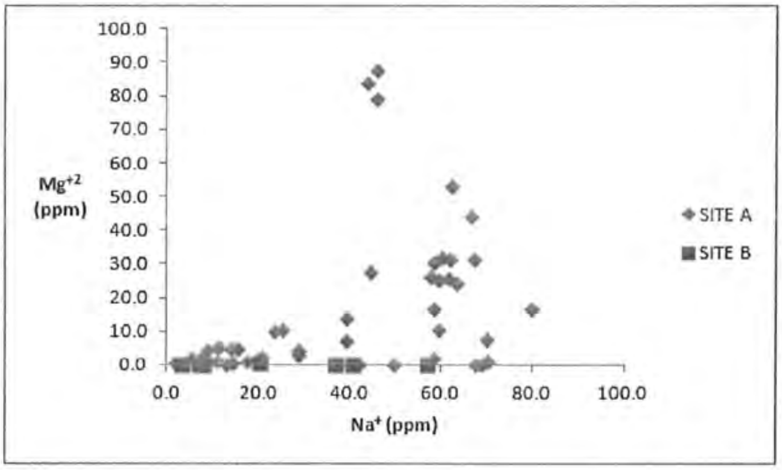


Figure 3.10a: Relationship of a) Na^+ vs. K^+ and b) Na^+ vs. Mg^{+2}

f) Potassium

The concentration of K^+ crossed the safe limits in 27.4% samples. The mean and range value of Site A was 12.3ppm and 0.1-55ppm. SHK (motor pump i.e., 55ft) had the largest concentration and CK104L (tube well i.e., 30ft) had the lowest concentration. The ascending order of all sampling points for potassium was observed as CP33 < TRM < JJA < DNK < KK < CNK < CK104L < ZP < BS > KDW < BBR < BP < SHK. The deep groundwater was less contaminated than the shallow groundwater in Site A. The Site B had a mean and range value of 10.1ppm and 3-36ppm. The highest and lowest value was found in PS (hand pump i.e., 70ft) and C.2 (motor pump i.e., 70ft). The following order was observed for the sampling points i.e., C.2 < CK86 < PSC. The following order was observed i.e., Site B < Site A as shown in Figure 3.11a.

K^+ showed positive correlation with EC ($r = 0.356$), HCO_3^- ($r = 0.344$), Na^+ ($r = 0.473$) and Mg^{+2} (0.371). K^+ like Na^+ is also an alkali metal and both of them have the similar physical and chemical properties. K^+ is also an important component of many fertilizers (Shaposhnik 2007). The possible sources of K^+ in the present study could be attributed to the extravagant usage of potassium rich fertilizers. The concentration of K^+ was quite lower than the previous studies reported in Faisalabad and Kasur (PCRWR 2005).

Higher levels of potassium in our body is associated with rapid heartbeat, cystitis, ovarian cysts, reduced renal function and abnormal metabolism of protein (Toro 1997).

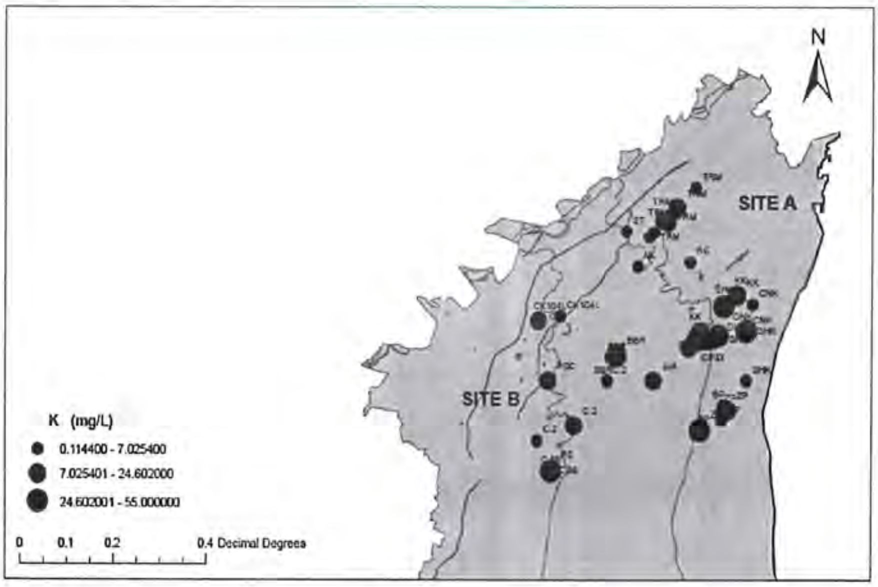


Figure 3.11a: Spatial distribution of K^+ in groundwater of District Rahim Yar Khan

g) Calcium

The concentration of Ca^{+2} was within the permissible limits set by WHO (i.e., 100pm) in all of the samples. The mean and range value for calcium was 29.1ppm and ranged between 3.4-87.2ppm. The highest and lowest value was reported in CP33 (hand pump i.e., 20ft) and CK104L (tube well i.e., 145ft). The deep groundwater showed less calcium levels than the shallow groundwater in Site A. The similar trend was observed in East Punjab (Farooqi, Masuda et al. 2007). The ascending order for sampling locations was KDW < CK104L < BBR < KK < CNK < BS < BP < SHK < TRM < CP33 < JJA < DNK < JJA for Site A. The Site B had a mean and range value of 20ppm and 7-57.2ppm. The highest and lowest value was observed in CK86 (rotor pump i.e., 70ft) and C.2 (motor pump i.e., 70ft). The ascending order for sampling locations was C.2 < CK86 < PSC. The following order was observed for the sites i.e., Site B < Site A as shown in Figure 3.12a. The calcium concentration was less than those reported by the previous study of Muzaffargarh and Multan (Nickson, McArthur et al. 2005). Calcium showed positive correlation with Cl^- ($r = 0.382$).

The primary source of calcium is various minerals including calacite and dolomite. The intense cation exchange reaction between Ca^{+2} and Na^+ decreases the Ca^{+2} levels in groundwater and HCO_3^- concentrations at alkaline pH also promote the precipitation of Ca^{+2} as calcite and Mg^{+2} as dolomite (Sarma and Rao 1997). Thus, low calcium levels in the current study might have resulted from the precipitation of Ca^{+2} as calcite, as of the water samples were had alkaline in nature and had higher HCO_3^- concentrations.

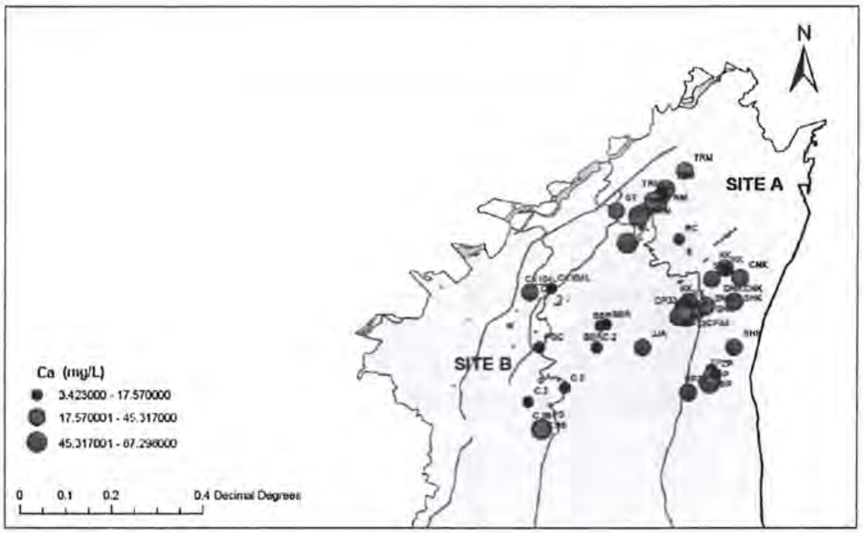


Figure 3.12a: Spatial distribution of calcium in groundwater of District Rahim Yar Khan

h) Magnesium

Mg^{+2} concentrations were above the prescribed limits of WHO (i.e., 50ppm) in 7.8% of water samples. Magnesium had a mean value of 16.8ppm and ranged between 0.09-87.5ppm for Site A. The highest and lowest value was found in SHK (H.P i.e., 55ft) and ML (H.P i.e., 50ft). It was arranged in this increasing order in terms of its mean value of each site i.e., KDW < BBR < ZP < TRM < JJA < DNK < BP < CP33 < KK < BS < CK104L < CNK < SHK. The deep groundwater samples were less contaminated than the shallow groundwater samples. The similar pattern was found in the previous study of East Punjab (Farooqi, Masuda et al. 2007) . The Site B had a mean and range value of 0.3ppm and 0.1-0.4ppm. The highest and lowest concentration was found in C.2 (water supply i.e., 70ft) and C.2 (motor pump i.e., 70ft). The sampling points followed this order i.e., CK86 < PSC < C.2. For Mg^{+2}, the following order was found i.e., Site B < Site A as shown in Figure 3.13a. Mg^{+2} showed positive correlation with EC (r = 0.405), HCO_3^- (r = 360), Na^+ (r = 0.366) and K^+ (r = 0.371).

The magnesium concentration was lower than the study reported in Multan and Muzaffargarh Districts (Nickson, McArthur et al. 2005). According to Sharma and Rao, 1997, higher HCO_3^- concentrations at alkaline pH promote the precipitation of Mg^{+2} as dolomite which might be the possible reason of low magnesium levels as compared to the previous study of Muzaffargarh.

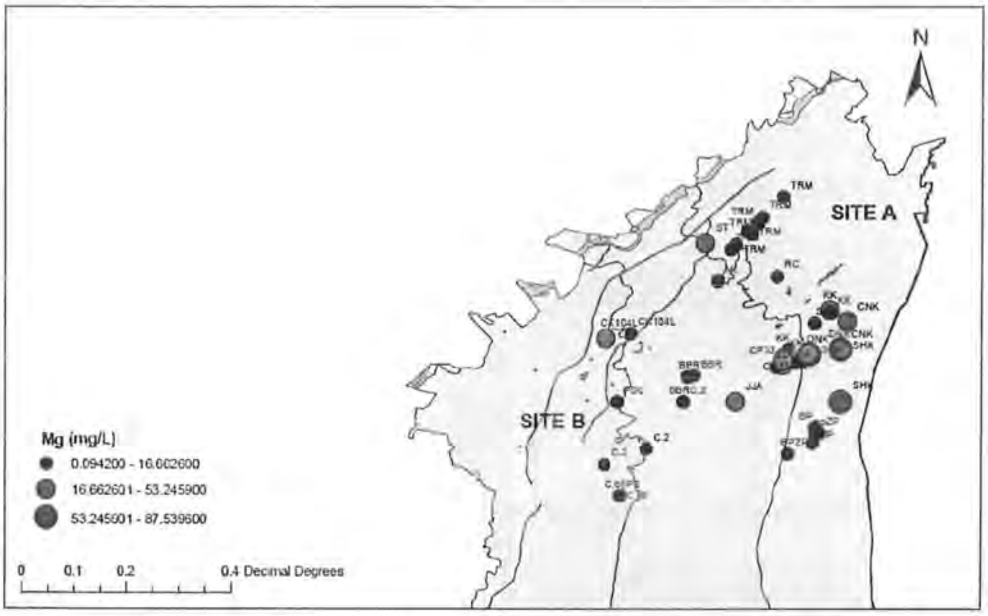


Figure 3.13a: Spatial distribution of Mg^{+2} in groundwater of District Rahim Yar Khan

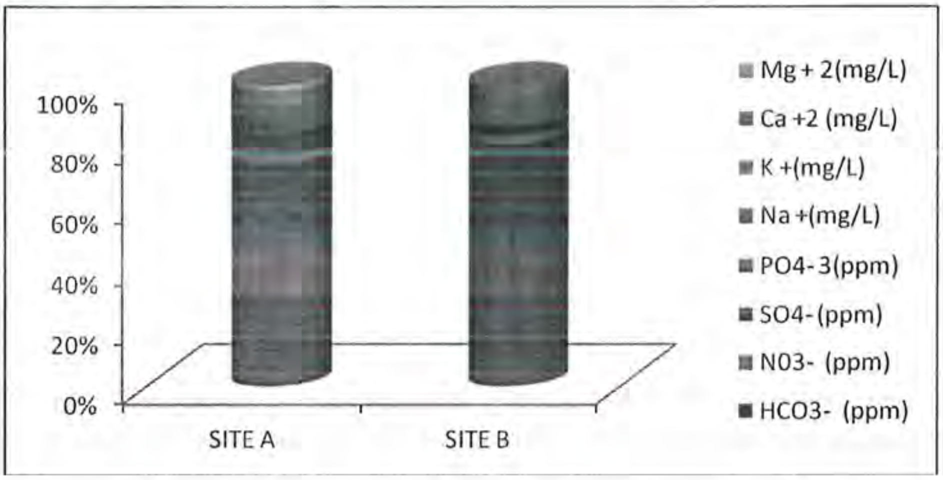


Figure 3.14a: Major ionic composition of Site A and B of District Rahim Yar Khan

3.2.1: Major Groundwater Chemistry

The major groundwater chemistry of all water samples was determined via piper plot. A piper diagram is a graphical representation of the chemistry of a water samples. The piper plots were constructed for the determination of the dominant cations and anions present in water, thus indicating the major water types found in the study area. The cations and anions are shown by separate ternary plots. The apexes of the cation plot are calcium, magnesium and sodium plus potassium cations. The apexes of the anion plot are sulfate, chloride and carbonate plus hydrogen carbonate anions. The two ternary plots are then projected onto a diamond. The diamond is a matrix transformation of a graph of the anions (sulfate + chloride/ total anions) and cations (sodium + potassium/total cations).

The piper plot resulted in the formation of 3major groups i.e., the group 1 comprised shallow groundwater samples of Site A, group 2 included deep groundwater samples of Site A and group 3 included the samples of Site B. The results showed that the dominant anion in all of the water samples was HCO_3^-. In case of the cations, there was no dominant cation, as majority of samples fell in the category of triangle B indicating the presence of no dominant cation. However, some of the samples fell in the triangle D showing the presence of Na^+ and K^+ in water. Thus, groundwater chemistry was categorized by two major types i.e., Na^+-HCO_3^- and K^+-HCO_3 as described in Figure 3.15a and Figure 3.16a.

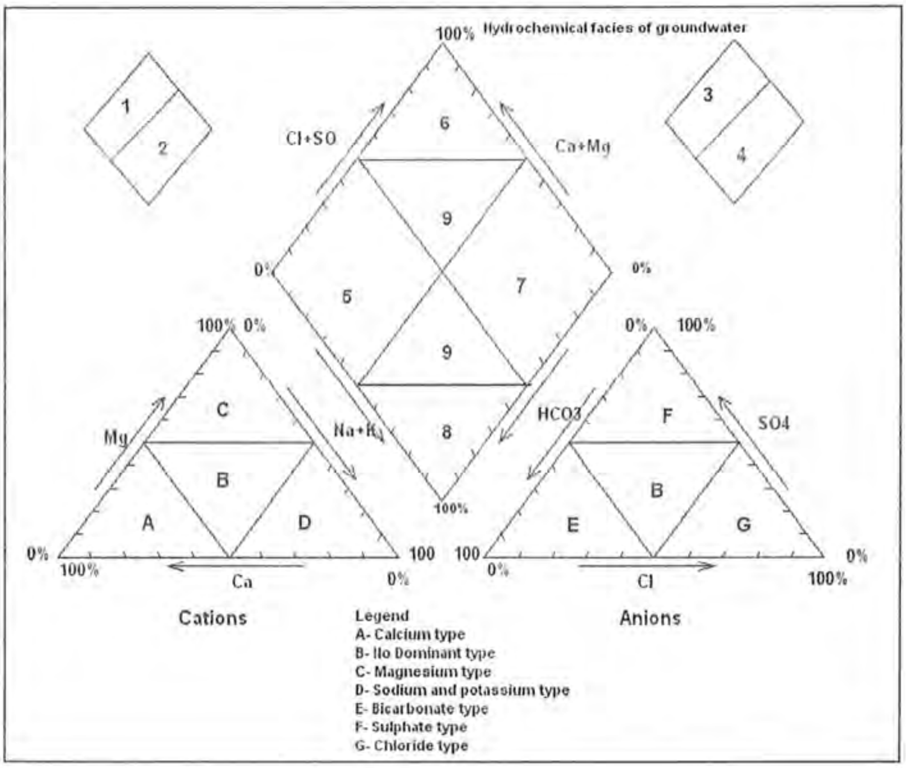


Figure 3.15a: Classification diagram for anion and cation facies in the form of major-ion percentages. Water types are designed according to the domain in which they occur on the diagram segments. By Piper and Hill

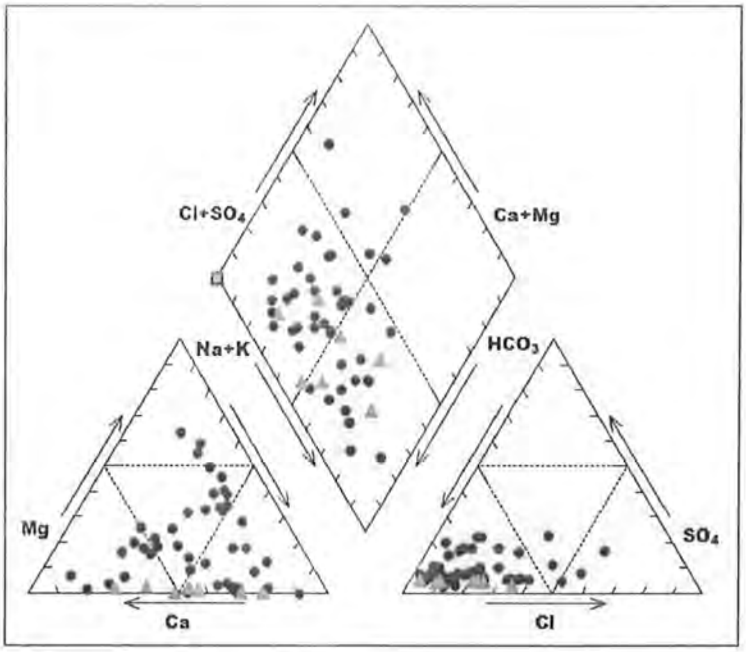


Figure 3.16a: Piper plot showing the major water types

Table 3.2a: Major Ionic Composition of groundwater samples of Site A and B of District Rahim Yar Khan

Site	SAMPLE ID	Cl^- (ppm)			HCO_3^- (ppm)			NO_3^- (ppm)			SO_4^{-2} (ppm)			$P0_4^{-3}$ (ppm)			Na^+ (ppm)			K^+ (ppm)			Ca^{+2} (ppm)			Mg^{+2} (ppm)		
		Mean	Max	Min	Mean	Max	Min	Mean	Max	Min	Mean	Max	Min	Max	Max	Min	Mean	Max	Min	Mean	Max	Min	Mean	Max	Min	Mean	Max	Min
SITE A	CK104L (n=2)	45	65	25	792.5	800	785	22.7	31.2	14.2	32	44.1	19.8	49	59.9	38	1.7	62.6	32.1	7.0	13.8	0.1	15.0	26.6	3.4	27.0	53.2	0.7
	CP33 (n=3)	116.6	209.9	25	576.7	600	550	25.3	28.4	20.1	45.9	55	39.7	53.6	62.4	36.5	27.1	44.7	11.3	4.0	6.4	1.3	41.4	87.3	9	14.6	27.6	5.5
	SHK (n=4)	77.5	110	25	915	980	850	19.8	23.2	15	39.3	45	33	46.2	57.2	32	54	80	44	39.9	55	3.7	35.1	40.5	29	66.8	87.5	16.6
	DNK (n=2)	135	229.9	25	392.5	500	300	22.4	30	13.2	29	33	25.5	46.6	56.9	37.5	34.3	58.7	15.4	5.3	8.1	2.5	41.5	68.5	14.6	11.4	16.7	4.9
	CNK (n=2)	47.5	50	45	475	550	400	18.8	23.8	13.7	103.1	108.1	98.13	33.1	41.1	25	64.7	67.4	62	6.2	6.3	6.1	19.2	19.3	19.1	31.4	31.5	31.3
	KK (n=4)	47.5	95	5	362.5	400	300	21.4	27.8	16.1	27.3	30	23.3	44.1	55.6	28	40	63.5	7.4	6.1	11.1	0.3	19	24.8	6.8	15.5	31.6	1.9
	JJA (n=4)	134.9	229.9	25	392.5	500	300	22.4	30	13.2	29	33	25.5	46.6	56.9	37.5	34.3	58.7	15.4	5.3	8.1	2.5	41.5	68.5	14.6	11.4	16.7	4.9
	BS (n=3)	70	135	25	426.7	495	335	24.5	31.9	19.7	30	32.01	28	32.4	46.4	24.4	55.9	66.6	39.3	11.0	13.9	8.7	25.2	33.5	20.6	25.7	44.2	7.2
	BP (n=3)	28.3	60	10	373.3	425	300	30.5	33	28.9	31.5	33.12	30.1	31.3	35	28.8	62.5	70.2	58.5	31.1	38.7	24.6	26	38.8	14.8	13.5	30.5	2.3
	TRM (n=7)	146.4	564.8	25	613.3	805	475	27.5	40.7	21	122.9	168.6	110	52.5	56	50.1	28.4	70.6	8.8	5.2	9.7	0.5	35.5	86.5	6.6	3.6	10.5	0.5
	ZP (n=3)	155	299.9	50	259.3	355	210	27.5	29.2	24.8	103.7	114.6	96.7	53.2	54	52	38.5	69	17.7	8.1	13.4	3.7	53.4	75.2	24.7	1.5	3.2	0.2
	BBR (n=3)	66.7	100	35	471.7	550	375	25.6	26.7	24.5	36.8	43	28.7	43.8	49.5	40	32.4	49.8	5.4	15.9	32.7	0.3	17.5	25.4	7.4	0.8	2.1	0.2
	KDW (n=4)	83.8	125	25	784.8	915	570	30.3	33.6	28	56.9	69.4	40	42.3	45	40.2	42.5	70	13	12.9	35.9	2.3	9.0	16.2	5.2	0.7	1.3	0.1
SITE B	PSC (n=2)	52.5	95	10	592.5	600	585	26	27	25	28.8	29.8	27.7	56.3	57	55.6	49.1	57.3	40.8	22	36	7.9	36.2	57.2	15.1	0.2	0.3	0.2
	CK.86 (n=2)	110	179.9	40	610.5	671	550	23	25	21	25	26	24	47.4	50	44.8	21.9	36.7	7.0	5.7	8	3.4	17.8	20.3	15.2	0.2	0.3	0.1
	C.2 (n=3)	80	100	45	536.7	650	470	24.9	27	23	26.3	28	25	58.3	60	56.9	10.6	20.3	3.3	5.2	9.6	3.0	10.7	17.6	7.0	0.3	0.4	0.2

3.3: Fluoride in Groundwater

3.3.1: Spatial variation of Fluoride

The fluoride concentration crossed the permissible values of WHO (1.5ppm) in all of the water samples (Table 3.3 and Table B.3; Annexure B). The Site A had a mean value of 7.6ppm and it ranged between 5.2-20.4ppm. KK (T.W i.e., 200ft) had the largest value of F^- and BS (M.P i.e., 60ft) had the smallest value of F^-. The Site A showed the following ascending order for the sampling points i.e., KDW < SHK < ZP < BP < BBR < CK104L < KK < BS < CNK < TRM < CP33 < JJA < DNK. The Site B had a mean and range value of 10.6ppm and 5.8-26.4ppm. The largest and smallest value was reported in CK86 (M.P i.e., 70ft) and C.2 (R.P i.e., 70ft). The Site B showed the following ascending order for the sampling points i.e., CK86 < C.2 < PSC.

The following order was observed for the sites i.e., Site A < Site B (Figure 3.17a). The industries present in Site B could be the contributing source towards high fluoride concentrations besides other natural sources. Fluoride concentration was much higher than the previous studies conducted in Sialkot (Ullah, Malik et al. 2009) D.G Khan (Malana and Khosa 2011) and North Jordan (Abu Rukah and Alsokhny 2004). Recently PCRWR has declared 6 cities as the most affected areas of Punjab in terms of fluoride levels which include Multan, Bahawalpur, Sheikhopura, Gujranwala, Kasur and Lahore (PCRWR 2005) and the current study area is bounded to Multan and Bahawalpur districts in Southern Punjab.

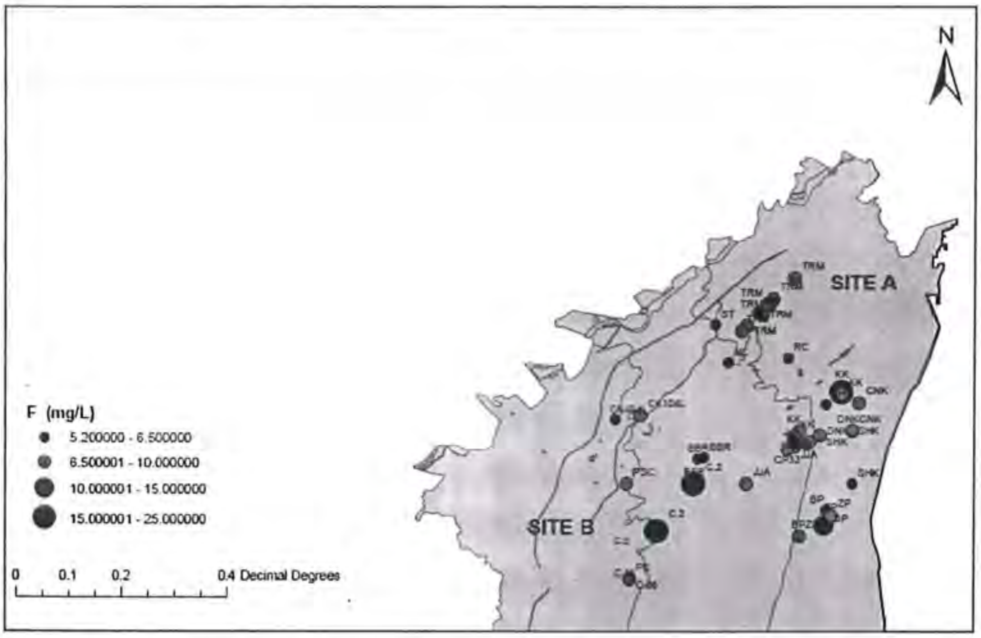


Figure 3.17a: Concentration map showing spatial distribution of fluoride in groundwater

3.3.2: Health Risk Assessment of Fluoride

The health risk assessment of F via HQ is summarized in Table 3.3a and Table B.3 (Annexure B). The Site A had a mean and range value of ADD 0.2 mg/kg/day and 0.1-0.6 mg/kg/day. While, mean and range of HQ for Site A was 3.5 and 2.4-9.3. The mean and range value of ADD for Site B was 0.3 mg/kg/day and 0.2-0.7 mg/kg/day. The mean and range value of HQ for Site B was 4.9 and 2.7-12.2. The following order was observed for HQ values of F i.e., Site A < Site B as shown in Figure 3.18a. Moreover, the ADD and HQ values of fluoride indicated severe contamination of fluoride in all of the water samples. The HQ values of all the samples were greater than 1 thus indicating significant health risk in the current study area. Thus, all of the drinking water samples were considered unsafe in terms of fluoride concentration.

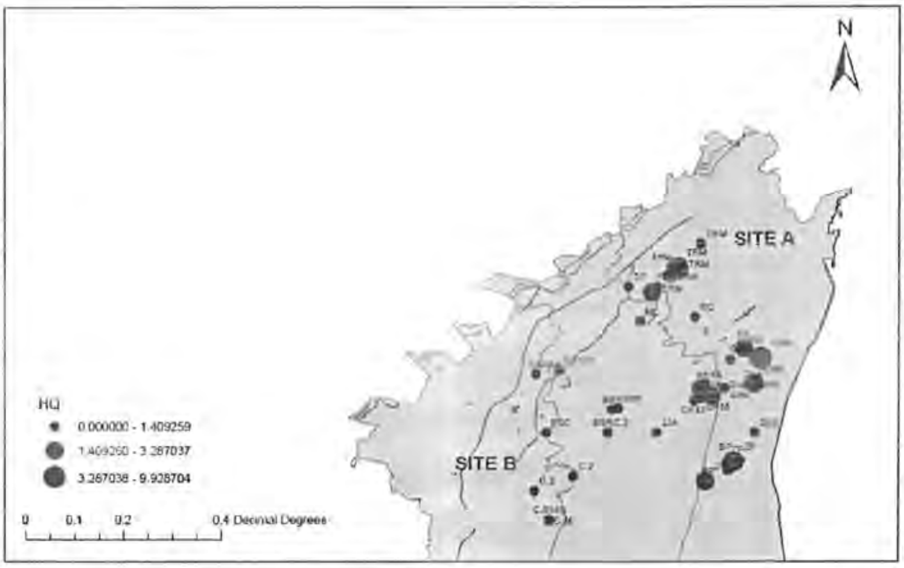


Figure 3.18a: Concentration map showing the health risk assessment of F via HQ

3.3.3: Relationship of Fluoride with depth of water

The concentration of fluoride in groundwater depends upon the depth of water (Guo, Zhang et al. 2012). There were about 92% shallow groundwater samples and only 8% deep groundwater samples. It was observed that the F concentration increased with depth of water and significant positive correlation existed between F-depth of water (r = 0.321) as shown in Figure.3.19a. But, highest F concentration was found at the depth of 70ft.

In literature it is reported that the F concentration generally decreases with depth of water as observed in Pakistan i.e., East Punjab (Farooqi et al. 2007b) Lahore and Kasur (Farooqi et al.

2007a) and in rare cases the F concentration increases with the depth of water which was also observed in China (Li et al. 2012). The possible reason for this trend might be the absence of clay in the unconfined aquifers of the study area (Farooq, Yousafzai et al. 2007) which is responsible for leaching of F from shallow to deeper layers of aquifers (Ohio-EPA 2012) and another reason might be the geogenic sources of F bearing minerals in the study area (Romić, Habuda-Stanić et al. 2011).

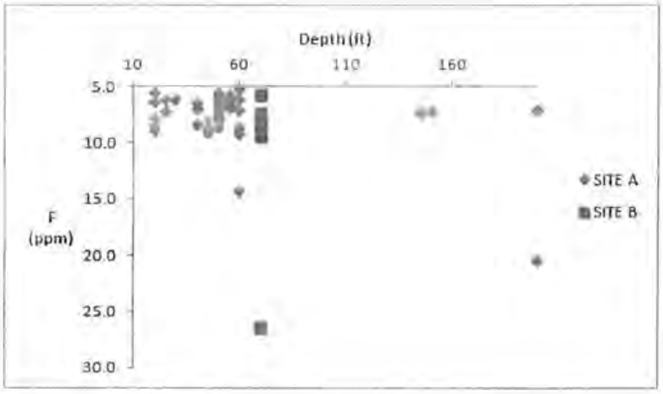


Figure 3.19a: Relationship of F with depth of water

3.3.4: Possible mechanism for F in groundwater

Higher F levels in groundwater were categorized by higher HCO_3^- and Na^+ along with lower values of Ca^{+2} and Mg^{+2} at high pH. The intense cation exchange reaction between Ca^{+2} and Na^+ decreases the Ca^{+2} levels in groundwater (Sarma and Rao 1997). High HCO_3^- concentrations and alkaline pH also promote the precipitation of Ca^{+2} as calcite (Sarma and Rao 1997) and Mg^{+2} as dolomite. Fluoride ions are absorbed by clays in acidic solution and are desorbed in alkaline solution. Thus, an alkaline pH is favorable for F^- dissolution (Saxena and Ahmed 2003). Fluoride shows negative correlation with Ca^{+2} and Mg^{+2} and Cl^- (Figure 3.20a and Table D.2; Annexure D).

There are 2 important mechanisms used to explain the possible reasons of high fluoride levels in groundwater throughout the world and these processes include dissolution of fluoride bearing minerals, ion exchange and evaporative concentration (Agrawal, Vaish et al. 1997) (Apambire, Boyle et al. 1997) (Saxena and Ahmed 2003). One of the mechanisms of high F^- concentrations in groundwater in arid and semiarid regions is the condensation of soluble components due to evaporation and evapo-transpiration (Jacks, Bhattacharya et al. 2005). But, this mechanism could not be explained for the present study due to the small study area and lack of positive correlation between F⁻ and Cl⁻ (r = -0.249) as shown in Figure 3.20a, which is the most conservative element during evaporation and condensation.

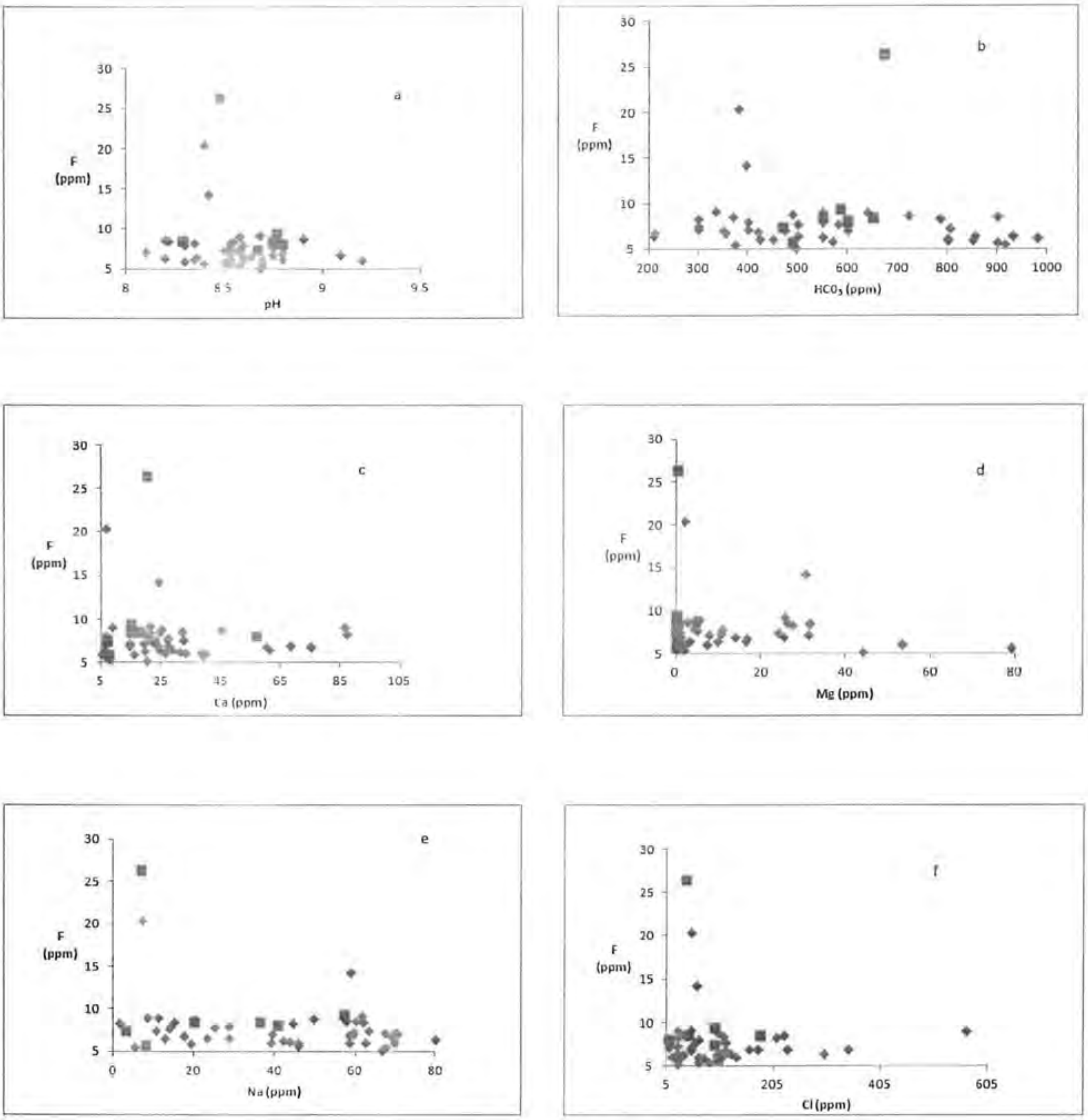


Figure 3.20a: Relationship of F with various other drinking water quality parameters

3.3.5: Dissolution of fluorite and hydrolysis of F rich minerals

Fluoride in groundwater can originate from the dissolution of F- bearing minerals including fluorite, fluorapatite, cryolite and apophyllite, ferromagnesium silicates (amphiboles and micas) and clay minerals (Guo, Wang et al. 2007). F showed negative correlation with Ca^{+2} (r = -0.137) as shown in Figure 3.21a. The negative correlation between Ca^{+2} and F suggests that fluorite solubility may enhance F concentration ($K_{fluorite} = 10^{-10.6}$)(Parkhurst and Appelo 1999) and dissolution of fluorite (Eq. 1)) in high HCO_3 groundwater has been described as follows (Guo, Wang et al. 2007):

$$CaF_2 + 2HCO_3^- = CaCO_3 + 2F^- + H_2O + CO_2.$$

Mineral saturation indices calculated with PHREEQC 2.1 (Parkhurst and Appelo 1999) showed that all groundwater samples were saturated with respect to fluorite, suggesting the dissolution of fluoride in groundwater (Figure 3.21a). The SI of fluorite > 0 for 78.4% samples; SI of fluorite < 0 for 21.5% samples and SI > 1 for only 0.01% samples. However, the mineral saturation indices calculated with PHREEQC (Parkhurst and Appelo 1999) showed that all groundwater samples were oversaturated with respect to calcite, as the SI of calcite > 0 in all of the groundwater samples suggesting the precipitation of calcite (Figure 3.21a). Precipitation of calcite would lower the dissolved Ca^{+2} concentration and favor dissolution of fluorite in groundwater.

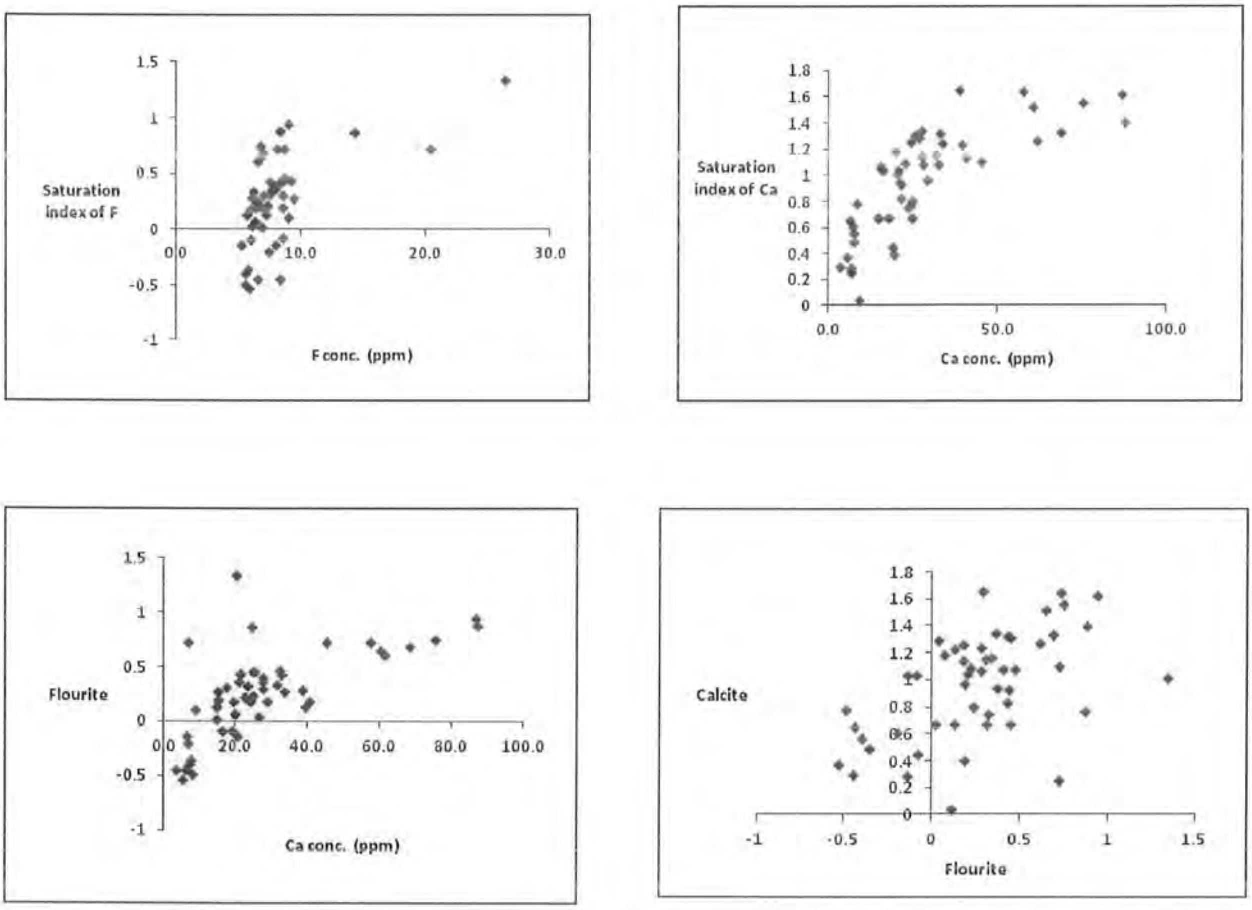


Figure 3.21a: Saturation index of F and calcium and relationship of calcite vs. fluorite and F vs. calcium

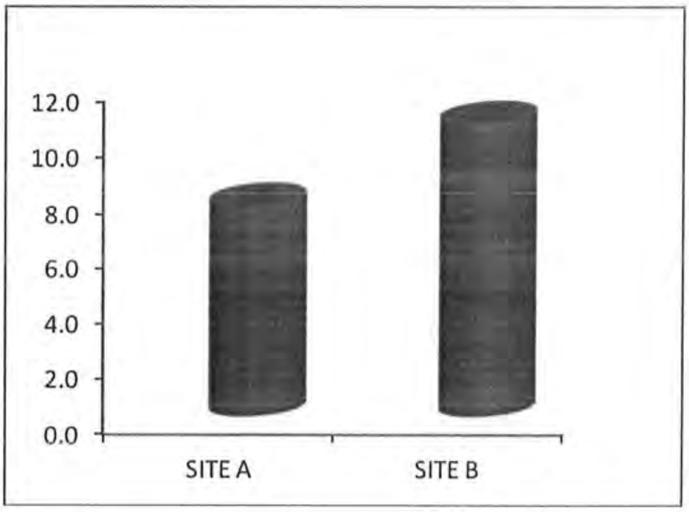


Figure 3.22a: Fluoride in groundwater of Site A and Site B

3.4: Arsenic in groundwater

3.4.1: Spatial variation of arsenic

The results of arsenic were less critical as compared to fluoride and the arsenic concentration crossed the permissible limits of WHO (10ppb) in 35.2% of drinking water samples (Table 3.3a and Table B.3; Annexure B). In some of the samples arsenic was not even detected. These included SHK (H.P i.e., 55ft) and SHK (M.P i.e., 55ft). The Site A had a mean and range value of 15.3ppb and 0-107.23ppb. The sample TRM (T.W i.e., 154 ft) had the largest concentration of arsenic. The ascending order for sampling points of Site A was i.e., BP <SHK < JJA < DNK < BBR < KDW < CK104L < CP33 < KK < TRM < ZP < BS < CNK. The Site B had a mean and range value of 3.7ppb and 0-6.1ppb. The sampling points showed the following order i.e., CK86 < PSC < C.2. Highest and lowest value was observed in the sample C.2 (water supply i.e., 70ft) and PS (hand pump i.e., 70ft). The following order was observed for the sites i.e., Site B < Site A as shown in Figure 3.23a.

The groundwater samples located near River Indus were highly enriched with As than the samples located far from it and these results were comparable to previous studies reported in Pakistan i.e., Muzaffargarh and Multan (Nickson, McArthur et al. 2005) and worldwide i.e., Bengal delta of Bangladesh (Berg, Tran et al. 2001) Ganga-Mehgna Brahmaputra plain of India (Das, Sengupta et al. 2008) Red River Delta and Mekong basin of Vietnam and Cambodia (Berg, Stengel et al. 2007) and Western Snake River Plain of Idaho, USA (Busbee, Kocar et al. 2009).

Active flood plain areas like Indus alluvial basin in Pakistan have considerably higher levels of As due to the dissolution of arsenic compounds arising from Himalaya through the Indus river and settled down over the years which then introduced into groundwater by various geothermal, geo hydrological and bio geo chemical processes (Smedley and Kinniburgh 2002; Singh 2006). Moreover, this situation might have aggravated due to the excessive usage of As containing insecticides and herbicides for agriculture purposes and seepages from hazardous waste sites (Smedley and Kinniburgh 2002).

Although in 35.2 % samples As concentrations crossed the permissible limit of WHO, the As concentration are much lower than the previous studies conducted in Pakistan i.e East Punjab (Farooqi, Masuda et al. 2007) Lahore and Kasur (Farooqi, Masuda et al. 2007) and Muzaffargarh (Nickson, McArthur et al. 2005) and worldwide i.e., China (Li, Wang et al. 2012) and Argentina (Raychowdhury, Mukherjee et al. 2013). The possible reason for lower As levels in the current study might be the oxidizing conditions (categorized by higher HCO_3^-, NO_3^-, SO_4^{-2}, PO_4^{-3}, Fe and DO at high pH) prevailing in all of the groundwater samples, as the As concentration is generally higher in the reducing environments as compared to the oxidizing environments (British Geological Survey 2001) and the oxidized sediments have a high capacity for adsorbing dissolved As, and thus leading towards lower As concentration in groundwater (Burgess, Hoque et al. 2010).

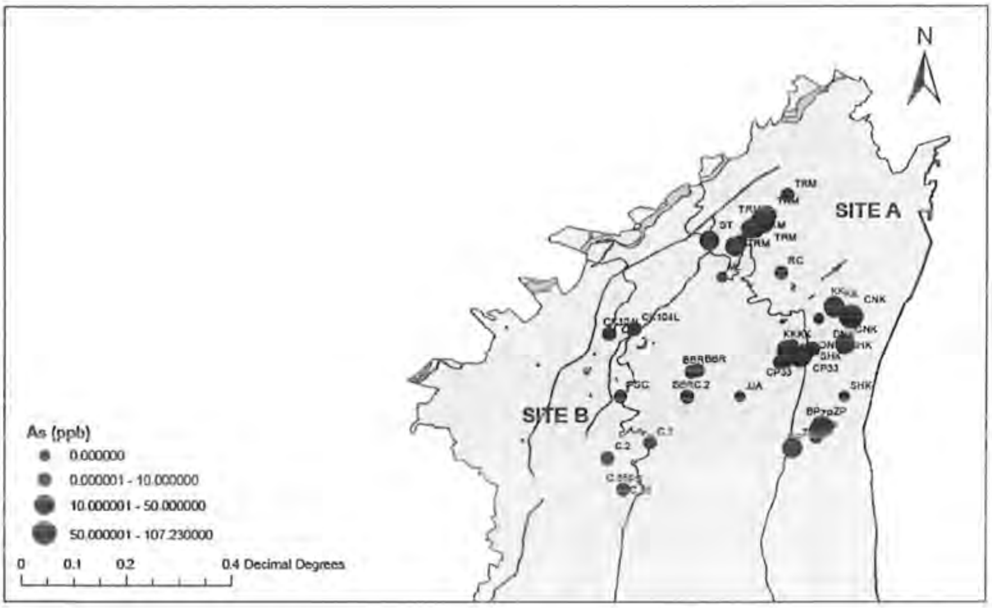


Figure 3.23a: Concentration map showing spatial distribution of arsenic in groundwater

3.4.2: Health Risk Assessment of Arsenic

The results of health risk assessment of As are summarized in Table 3.3a and Table B.3 (Annexure B). The mean and range of ADD value for Site A was 0.0004mg/kg/day and 0-0.003mg/kg/day. The mean HQ value for arsenic was 1.4 and it ranged between 0-9.9. The cancer risk for arsenic in drinking water ranged between 0-0.004. ADD had a mean and range value of 0.0001mg/kg/day and 0-0.0002mg/kg/day for Site B. The mean and range value of HQ for Site B was 0.3 and 0-0.6. The cancer risk ranged between 0-0.0003. The following order for HQ values of As was observed i.e., Site B < Site A as shown in Figure 3.24a.

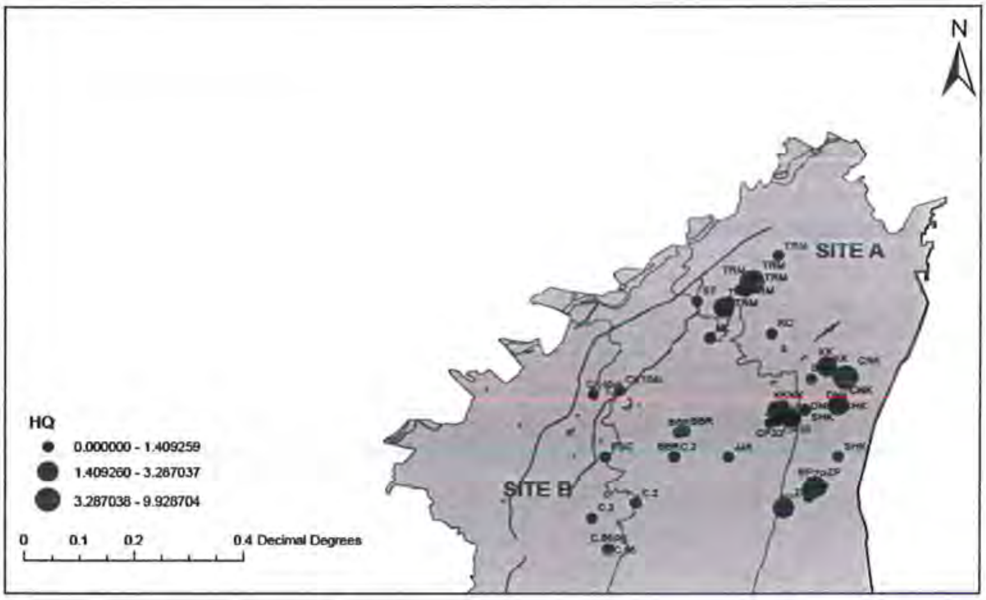


Figure 3.24a: Concentration map showing the health risk assessment of arsenic via HQ values

3.4.3: Relationship of Arsenic with depth of water

The concentration of As is dependent on depth of water (Guo, Zhang et al. 2012). Out of 51 groundwater samples, there were 47(92 %) shallow groundwater samples (20-100ft) and only 4 (8%) deep groundwater samples (145-200ft). The highest concentration of As was found at the depth of 145 ft and at 200 ft. Overall positive correlation existed between As and depth of water (r = 0.471) as shown in Figure 3.25a and it was observed that the arsenic concentration increased with depth of water. Generally, the As concentration decreases with the depth of water as observed in Pakistan i.e, East Punjab (Farooqi, Masuda et al. 2007) Lahore and Kasur (Farooqi, Masuda et al. 2007), India (Chauhan, Nickson et al. 2009) and in the rare cases the As level increases with the depth of water which was observed in Bangladesh (Halim, Majumder et al. 2010) China (Li, Wang et al. 2012) India (Mukherjee, Fryar et al. 2011) and Croatia (Romić, Habuda-Stanić et al. 2011). The possible reason for the trend observed in the current study was the absence of clay in the unconfined aquifers of the study area (Farooq, Yousafzai et al. 2007) which is responsible for leaching of arsenic from shallow to deeper layers of aquifers (Warren, Burgess et al. 2005) and another reason might be the geogenic sources of As bearing minerals (Romić, Habuda-Stanić et al. 2011). Thus, it can be inferred from the results of the current study that the As concentration are not dependent upon the depth of water.

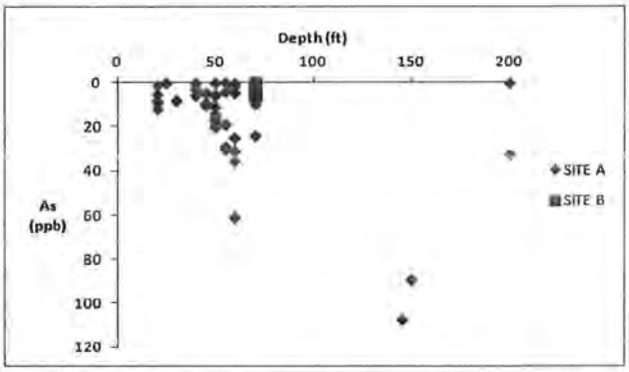


Figure 3.25a Relationship of As with depth of water

3.4.4: Possible mechanism for Arsenic in groundwater

Higher levels of As were categorized by higher HCO_3^-, NO_3^-, SO_4^{-2} and PO_4^{-3} at high pH, which was an indication of oxidizing environment although the redox potential was not calculated. Arsenic shows significant positive correlation with SO_4^{-2} (r = 0.421) and slight positive correlations with NO_3^- while negative correlation is observed between PO_4^{-3}, Fe and Mn as shown in Figure 3.26a and Table D.1 (Annexure D).

There are four basic geo-chemical mechanisms responsible for the release of arsenic in water including oxidative and reductive dissolution (McArthur, Ravenscroft et al. 2001) (Nickson, McArthur et al. 1998) desorption (Smedley, Kinniburgh et al. 2005) and concentration by evaporative enrichment (Welch, Westjohn et al. 2000). The desorption of As can also be promoted by increased pH (>8.5) or competitive anion-promoted desorption, especially by PO_4^{-3} (Dixit and Hering 2003).

Among all of these mechanisms, reductive dissolution and evaporative concentration was ruled out because in the current study positive correlation not existed between As-Fe (Figure.9f) and As-Cl^- (Figure.9e). The findings of the current study can be supported by oxidative dissolution to some extent as oxidative dissolution is characterized by high concentrations of HCO_3^- (>500ppm), SO_4^{-2} (>250ppm) at pH (>7.5) and desorption of arsenic via PO_4^- at high pH via application of phosphate fertilizers (Davenport and Peryea 1991; Campos 2002). Water quality survey conducted by PCRWR in the study area revealed higher PO_4^{-3}, concentration in drinking water (Water quality status in Pakistan, 2003). Hence preferential adsorption of phosphate on sediments can also be held responsible for the release of arsenic in the current study. Moreover, it is necessary to conduct advance studies in the current study area by expanding the sample size, area and examination of As levels in soils and sediments; in order to confirm various mechanisms responsible for the release of As in groundwater.

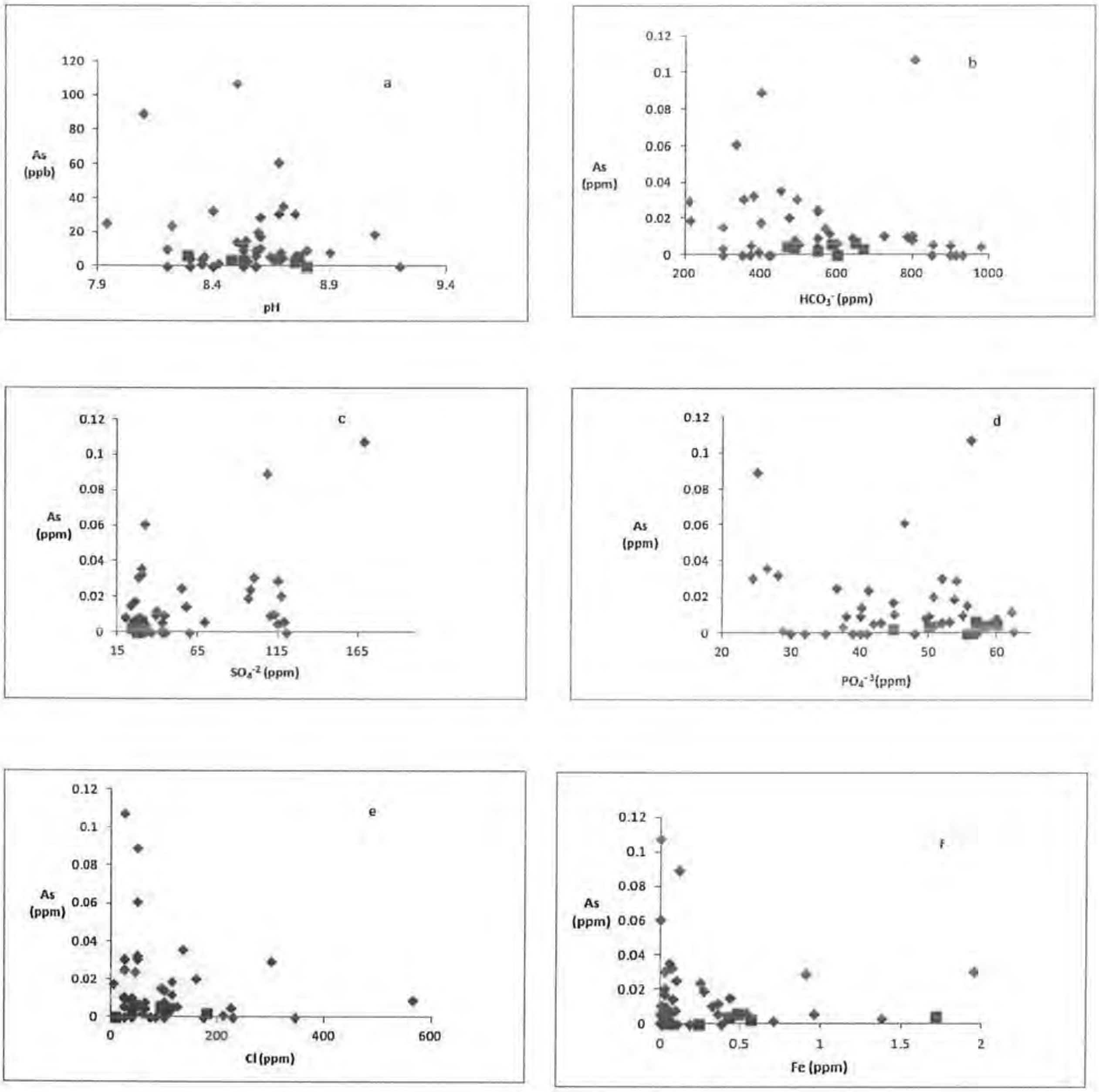


Figure 3.26a: Relationship of As with various other drinking water quality parameters

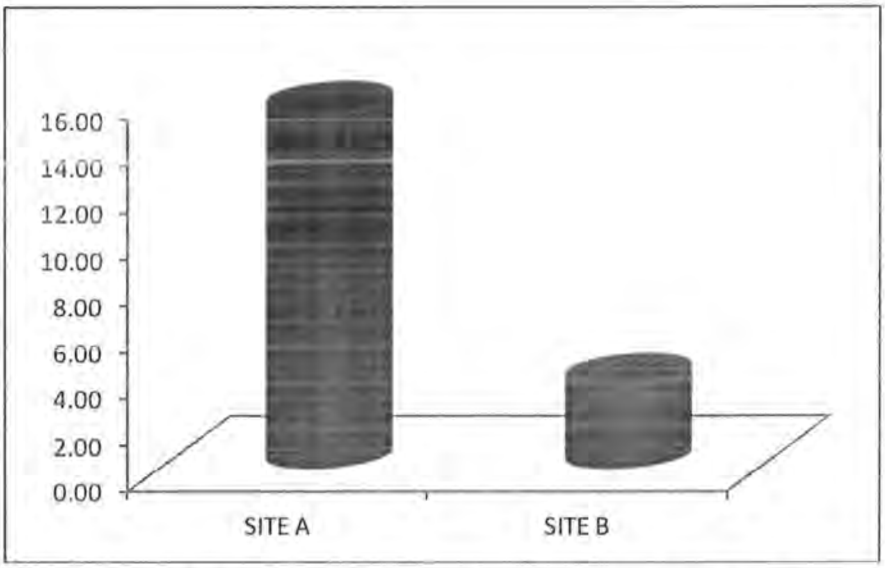


Figure 3.27a: Arsenic in groundwater of Site A and Site B

3.4.5: Co-occurrence of Arsenic and Fluoride in Groundwater

As and F were poorly correlated with each other in the current study as shown in Figure.3.28a. However; both these elements were enriched in deep groundwater samples, suggesting the contribution of common source or pathway for both pollutants in the current study. Both, arsenic and fluoride showed significant positive correlation with depth of water.

According to Farooqi et al., 2007, it is reported that coincidental occurrence of high F^-, As, and SO_4^- in the studied groundwater implies that air pollutants originating from coal combustion at brick factories scattered in the study area a source of these elements. Burning mineralized coal is known to exit toxic elements such as As and F^- (Finkelman, Orem et al. 2002). The results of the current study were in agreement with the study of Farooqi et al., 2007 but showed opposite trend. As, in the current study, it was observed that SO_4^- showed significant positive correlation with As and depth of water. Although, the sulphates levels were within the permissible limits in all of the samples but even than it was present in sufficient amount along with As and F in all of the samples. The results of both previous and present study suggest that the common source for the coincidental occurrence of both these elements i.e., As and F^- in the deep groundwater samples might be the coal combustion at brick factories as the brick factories are abundantly located in the current study area, where coal combustion is commonly practiced.

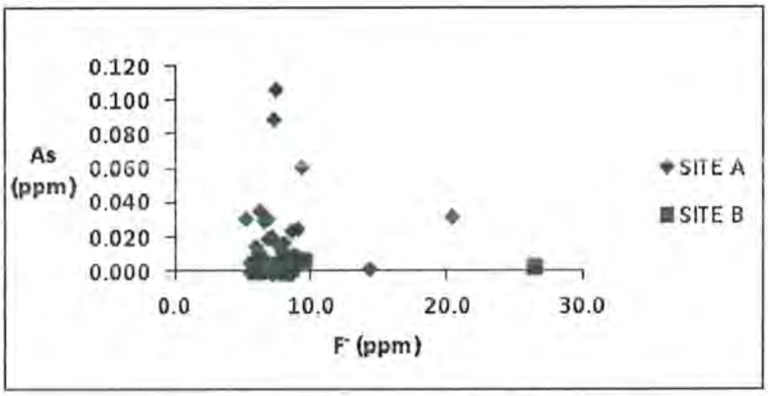


Figure 3.28a: Relationship of As vs.F

Table 3.3a: Arsenic and Fluoride Risk Assessment in drinking water

SITE	Site's code	Depth (ft)	F^- (mg/L)	CDI/ADD	HQ	As(μg/L)	ADD	HQ	CS
SITE A	CK104L	65	7.2	0.2	3.33	8.85	0	0.82	0
			6.1-8.3	0.17-0.23	2.82-3.84	8.09-9.61	0.00022-0.00027	0.74-0.89	0.0003-0.0004
	CP33	50	8.4	0.2	3.9	12.7	0	1.2	0
			7.8-9	0.2-0.3	3.6-4.2	1.2-24.9	0.00003-0.0006	0.11-2.30	0.00005-0.0010
	SHK	80	6.1	0.2	2.8	0.5	0	0	0
			6-6.4	0.1-0.2	2.8-3	0-2.1	0-0.0001	0-0.39	0-0.0001
	DNK	60	7.8	0.2	3.6	2.4	0	0.2	0
			7-8.6	0.19-0.2	3.2-4	2.4-4.9	0-0.0001	0-0.452	0-0.0002
	CNK	145	7.9	0.2	3.6	56.5	0	5.2	0
			7.2-8.5	0.21-0.23	3.3-3.9	23.8-89.1	0.0006-0.002	2.21-8.25	0.001-0.003
	KK	100	11.1	0.3	5.15	16.26	0.0004	1.5	0.0006
			7.5-20.4	0.2-0.5	3.4-9.4	0-32.4	0-0.0009	0-3.007	0-0.001
	JJA	220	7.2	0.2	3.3	2.3	0	0.2	0
			6.5-8.4	0.1-0.2	3-3.8	0-5.8	0-0.0001	0-0.53	0-0.0001
	BS	60	6.8	0.2	3.2	42.4	0	3.9	0
			5.2-9.2	0.1-0.2	2.4-4.2	30.6-60.9	0-0.001	2.83-5.63	0.001-0.002
	BP	25	9.2	0.3	4.3	0.6	0	0.1	0
			6.1-14.3	0.1-0.3	2.8-6.6	0-1.7	0-0.00005	0-0.16	0-0.00007
	TRM	117.5	7.9	0.2	3.7	20.3	0	1.9	0
			9-Jul	0.1-0.2	3.2-4.1	4.5-107.2	0.0001-0.002	0.41-9.92	0.0001-0.004
SITE A	ZP	55	6.7	0.19	3.1	26.23	0	2.43	0
			6.5-6.8	0.18-0.19	3.01-3.15	18.9-30.5	0.0005-0.0008	1.75-2.82	0.0007-0.001
	BBR	20	6.9	0.19	3.18	7.6	0	0.7	0
			5.5-8.8	0.15-0.24	2.5-4.07	5.3-9.2	0.0001-0.0002	0.49-0.85	0.0002-0.0003
	KDW	50	6	0.17	2.77	7.67	0	0.71	0
			5.5-6.5	0.15-0.18	2.5-3	0-14.3	0-0.0004	0-1.33	0-0.0006
SITE B	PSC	70	8.8	0.7	7.7	3	0.007	0.9	0.0004
			8.2-9.4	0.2-0.4	3.4-12.1	0-5.9	0.004-0.01	0.2-0.5	0.0001-0.0002
	CK86	70	2.9	0.2	3.3	0.04	0.0002	0.4	0.0003
			2.2-3.4	0.1-0.2	3.2-3.4	0.04-0.1	0.0001-0.0002	0.6-0.9	0.0002-0.0004
	C.2	70	7.2	0.29	4.7	4.8	0.0003	1.05	0.0004
			5.8-8.5	0.28-0.29	4.6-4.8	0.1-6.1	0.0001-0.0004	0.6-1.4	0.0002-0.0006

3.5: Trace Metals Concentration and their Health Risk Assessment

The concentration of trace metals in all of the water samples are summarized in Table 3.4a, 3.5a and Table B.4 (Annexure B). The health risk assessment of all these trace metals was also calculated via ADD and HQ. The exposed population is considered safe when HQ <1. The trace metals were arranged in the following ascending order in terms of their concentration and health risk assessment in water samples i.e., Cu > Cr > Mn > Ni > Fe > Pb > Cd. The metals Cu and Cr were below the detection limits in majority of the samples and they were detected in negligible amount in just few samples. The spatial distribution of trace metals was determined via various concentration maps as shown in the below section. The person correlation was also applied in order to determine the relationship of these trace metals with each other and other physio-chemical parameters. The correlation was not detected for various metals including Cu, Cr, Ni and Mn due to their lower and constant values in various samples. Positive correlation was found between Pb-Fe (r = 0.380) and Pb-Cd (r = 0.745).

a) Nickel

The concentration of Ni crossed the safe limits of WHO (0.02ppm) in 70.5% water samples. But, the exposed population was considered safe in terms of Ni concentration because their HQ values were less than 1 in all of the water samples. The Site A had a mean and range value of 0.05ppm and 0.007-0.1ppm. The highest and lowest value was recorded in the samples TRM (motor pump) and KK (tube well). The shallow groundwater samples were more contaminated with Ni as compared to deep groundwater samples. The Site A observed the following order for the groundwater samples i.e., DNK < KDW < KK < SHK < BS < BBR < TRM < CP33 < JJA < BP < CNK < CK194L < ZP. The Site B had a mean and range value of 0.04ppm and 0.01-0.1ppm. The smallest and highest value was recorded in the samples C.2 (water supply) and PSC (hand pump). The Site B followed this order for sampling sites i.e., PSC < CK86 < C.2. The major sites showed this order i.e., Site B < Site A as shown in Figure 3.29a. The Ni values were less than those reported in Sialkot (Ullah, Malik et al. 2009). The anthropogenic sources of Ni include production of electroplating, high grade steel alloy, fabrication, electronic component, automobiles, batteries, coins, jewellery, surgical implants, kitchen appliances, sinks and utensils (ASTDR 2005). Ni exposure through drinking water can cause allergy and hand eczema (Filon, D'Agostin et al. 2009). The possible sources of elevated Ni in drinking water could be attributed to automobiles, batteries, electronic equipments and kitchen appliances which are widely used in the current study area.

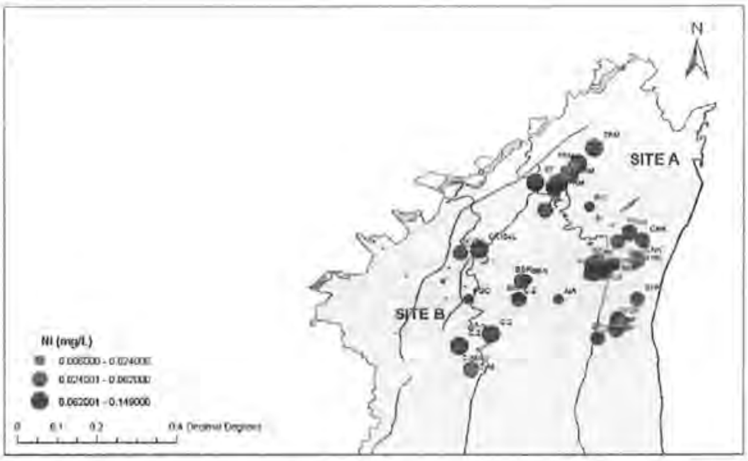


Figure 3.29a: Spatial distribution of Ni in groundwater of District Rahim Yar Khan

b) Mangenese

The concentration of Mn was within the safe limits of WHO (i.e., 0.1ppm) in all of the water samples. Moreover, the ADD and HQ values for Mn were within the prescribed limits. The mean and range value of Mn for Site A was 0.008ppm and 0.001-0.05ppm. The smallest and highest value was found in the samples ML (hand pump i.e., 55) and BBR (rotor pump i.e., 20ft). The following ascending order for the sampling sites was observed i.e., CP33 < KDW < TRM < ZP < KK < CNK < BP < SHK < BS < CK104L < JJA < DNK < BBR. The deep groundwater had less concentration of Mn than shallow groundwater. The Site B had a mean and range value of 0.2ppm and 0.002-0.1ppm. Highest and lowest value was observed in the samples C.2 (water supply i.e., 70ft) and C.2 (rotor pump i.e., 70ft). The sampling sites were arranged in the following order for Site B i.e., CK86 < PSC < C.2. Mn values showed the following order for the sites i.e., Site B < Site A as shown in Figure 3.30a.

The results of the current study were in agreement with various studies of Pakistan because Mn is not a great challenge for drinking water in most of the parts of our nation. However, the highest concentration of Mn was reported in Faisalabad City of Punjab (Mahmood and Maqbool 2006). The Mn concentration was less than the previous study reported in Multan and Muzaffargarh (Nickson, McArthur et al. 2005) . The possible reason for low level of Mn in the present study might be due to the aerobic conditions of water samples. As, in literature it is reported that in aerobic conditions, manganese is found in its stable oxidized form, generally as MnO_2, which is highly insoluble (Howe, Malcolm et al. 2004).

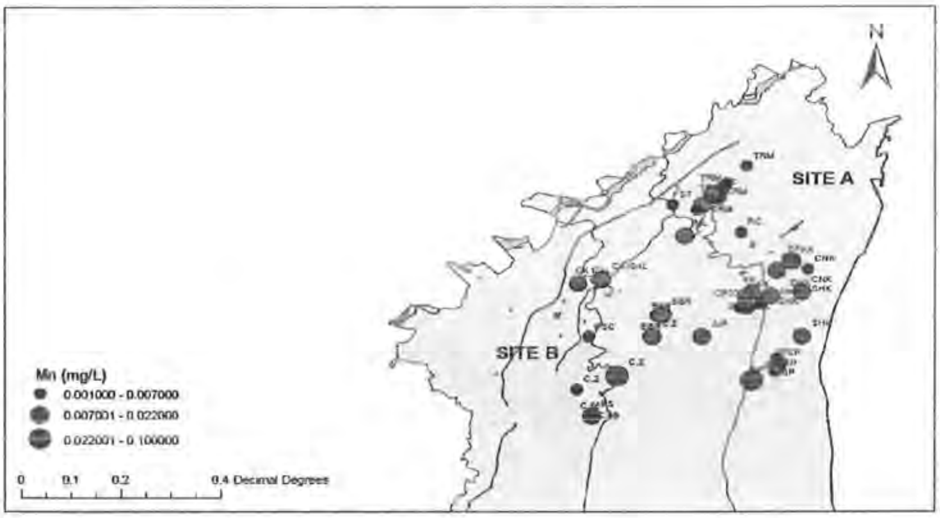


Figure 3.30a: Spatial distribution of Mn in groundwater of District Rahim Yar Khan

c) Iron

However, iron was present in sufficient amount in all of the drinking water samples. In fact, the concentration of Fe crossed the safe limits of WHO (0.3ppm) in 29.4% samples. The Site A had a mean and range value of 0.2ppm and 0.001-1.9ppm. The highest and lowest value was observed in the samples in ZP (hand pump) and BS (tube well). The shallow groundwater had higher concentration of Fe than the deep groundwater of Site A. the sampling sites followed this order i.e., BS < BBR < DNK < CK104L < KDW < SHK < KK < CP33 < CNK < TRM < BP < JJA < ZP. Site B had a mean and range value of 3.1ppm and 0.05-18.1ppm. The highest and lowest value was recorded in the sample C.2 (water supply i.e., 70ft) and CK86 (rotor pump i.e., 70ft). The ascending order of sampling sites for Site B was CK86 < PSC < C.2 for Site B. The following order was observed for iron i.e., Site A < Site B which was due to the wide spread industrial activities in that region, as the water samples were located near the industrial area of Site B (Figure 3.31a). Fe showed positive correlation with Pb (r = 0.388).

In Pakistan, iron is one of the major pollutants of both ground and surface water. A country-wide study conducted by PCRWR reported an overload of iron in 28% of ground and 40% of surface water samples (PCRWR 2005). The iron concentration was higher than the previous study conducted in Muzaffargarh and Multan District (Nickson, McArthur et al. 2005). In the study area, drinking water was also contaminated with Fe and ingestion of high level of Fe can cause hemochromatosis with symptoms such as chronic fatigue, arthritis, heart disease, cirrhosis, diabetes, thyroid disease, impotence and sterility. Fe, which facilitates persistent hepatitis B or C infection, also induced malignant tumors, colorectal, liver, lung, stomach and kidney cancers (Huang 2003). The possible sources of iron in drinking water in the current study area could be attributed to enrichment of soil with iron bearing minerals, industrial waste, construction material, paints and pigments.

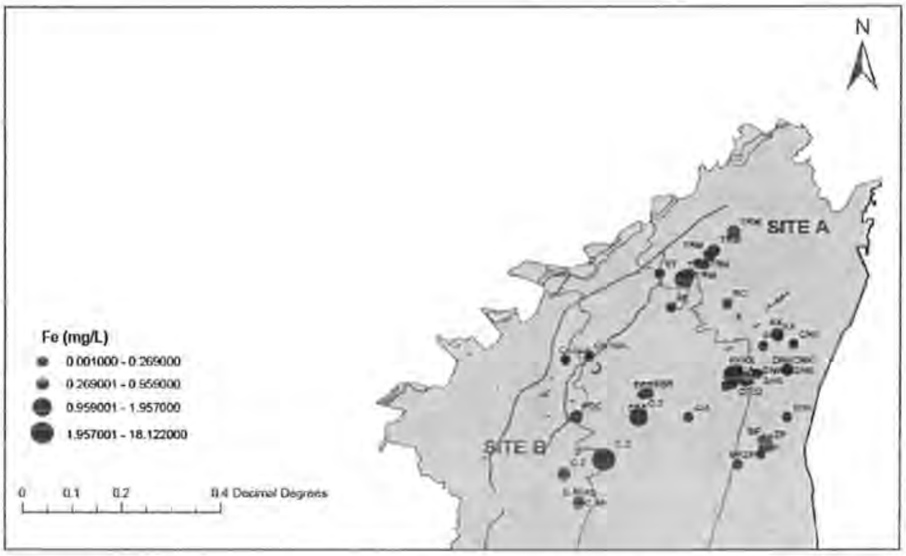


Figure 3.31a: Spatial distribution of Fe in groundwater of District Rahim Yar Khan

d) Lead

The results of Pb were very alarming, as the Pb values crossed the safe limits of WHO (0.01ppm) in all of the water samples. Similarly, the HQ >1 in all of the water samples, thus posing significant health risks for the population consuming the drinking water of the study area. Site A had a mean and range of 1.7ppm and 0.9-3.6ppm. The highest and lowest value was reported in the samples of KK (tube well i.e., 200ft) and CK104L (tube well i.e., 70ft). The deep groundwater samples were more contaminated than shallow groundwater samples. The samples were arranged in this order i.e., CK104L < SHK < DNK < CNK < BS < JJA < BP < TRM < KK < ZP < BBR < KDW. The Site B had a mean and range value of 4.8ppm and 4.1-5.6ppm. The highest and lowest value was recorded in the samples of C.2 (motor pump i.e., 70ft) and PS (hand pump i.e., 70ft). The samples of Site B were arranged in this order i.e., PSC < CK86 <

C.2.The following order was observed for various sites i.e., Site A < Site B which was due to the wide spread industrial activities in that region, as the water samples were located near the industrial area of Site B (Figure 3.32a).

Positive correlation was observed between Pb-Fe (r = 0.318) and Pb-Cd (r = 0.745) and negative correlation was found between Pb-Mg^{+2} (r = -0.462). The results were in agreement with previous studies reported in our country, as elevated levels of Pb were also reported in 100% samples of drinking water in Sialkot (Ullah, Malik et al. 2009). There are various anthropogenic sources of Pb responsible for contamination of drinking water which include household paints, vehicular exhaust and industrial wastes (Nadeem-ul-Haq, Haque et al. 2009). Pb accumulates in the skeleton and cause adverse impacts on health including subencephalopathic, neurological and behavioral effects (Lehloesa and Muyima 2000) (WHO 2006). The high Pb concentration could be due to paints, vehicular exhausts and industrial wastes in the present study.

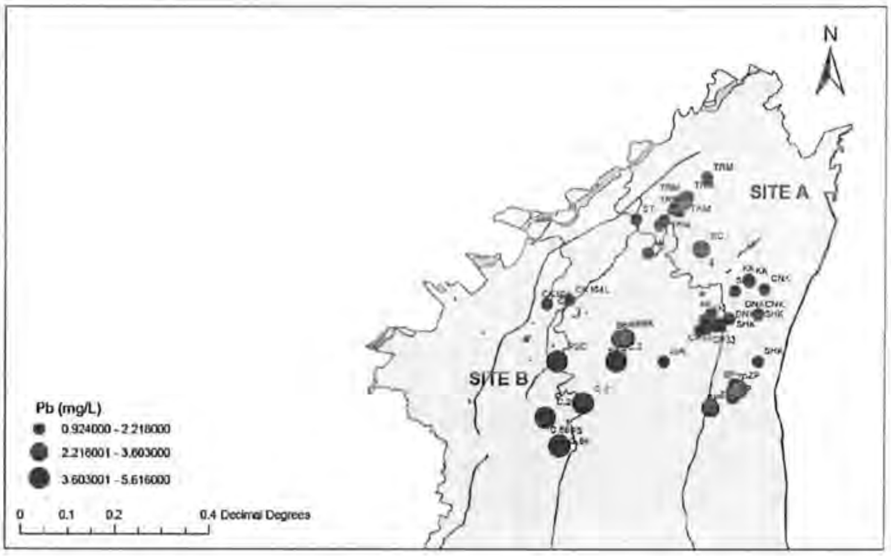


Figure 3.32a: Spatial distribution of Pb in groundwater of District Rahim Yar Khan

e) Cadmium

Similarly, the results of Cd were also very critical and revealed higher values crossing the safe of WHO (0.003ppm) limits in all of the water samples. Moreover, the HQ values were extremely higher than the permissible limits in all water samples. Thus, Cd posed significant health risk for the local people consuming this drinking water. The Site B was more contaminated with Cd than

Site B due to the industrial activities in that region. The Site A had a mean and range value of 0.5ppm and 0.3-0.7ppm. The highest and lowest value was observed in the samples of ZP (rotor pump i.e., 55ft) and CK104L (tube well i.e., 30ft). The order of sampling sites for Site A was CK104L < CP33 < SHK < BS < CNK < DNK < KK < BP < JJA < TRM < ZP < BBR < KDW. The Site B had a mean and range value of 0.7ppm and 0.6-0.8ppm. The highest and lowest value was observed in CK86 (rotor pump i.e., 70ft) and PS (hand pump i.e., 70ft). The Site B showed this order for the sampling sites i.e., PSC < CK86 < C.2. The following order was observed for the sampling sites i.e., Site A < Site B as shown in Figure 3.33a.

Cd showed positive correlation with Pb (r = 0.745) which shows both pollutants that possibly both pollutants are originated from the same source. The Cd exposure can cause the health problems such as nausea, vomiting, diarrhea, muscle cramps, salvation, sensory disturbances, liver injury convulsions, shocks and renal failure. Long term exposure can cause certain effects such as kidney, liver, bone and blood damages (US-EPA 2003). In literature, it has also been reported that the groundwater of KPK and Sindh is more contaminated with Pb than Punjab's groundwater (Azizullah, Khattak et al. 2011). There are source of Cd including phosphate fertilizers, sewage sludge and corrosion of some galvanized plumbing and water pipe materials (Azizullah, Khattak et al. 2011). The possible sources of Cd were attributed to phosphate fertilizers, leakage from plumbing system and sewage sludge in the current study.

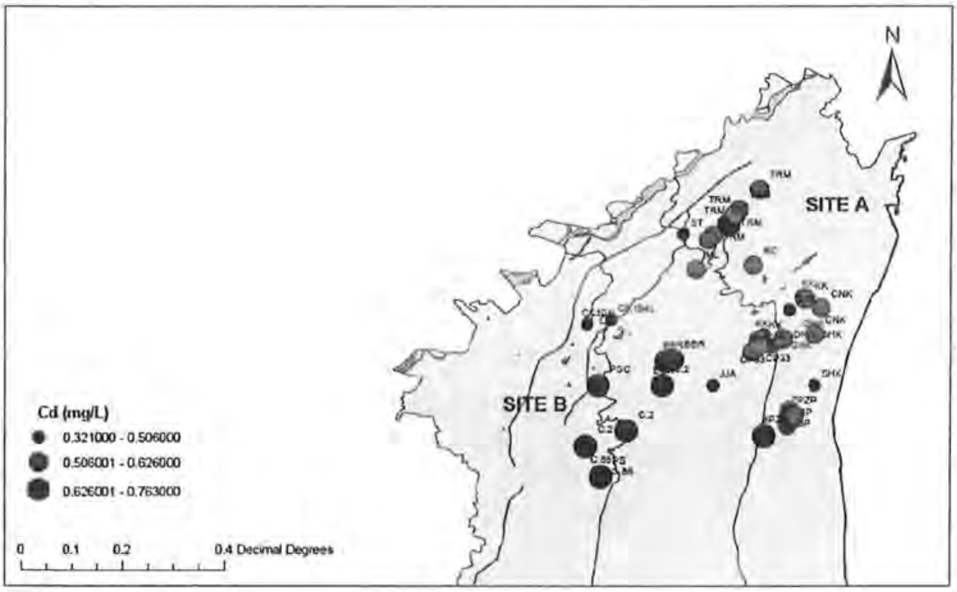


Figure 3.33a: Spatial distribution of Cd in groundwater in District Rahim Yar Khan

Table 3.5a: Health Risk Assessment of trace metals in ground water

Site	Site's code	Ni (mg/L)	ADD	HQ	Mn (mg/L)	ADD	HQ	Pb (mg/L)	ADD	HQ	Cd (mg/L)	ADD	HQ
SITE A	CK104L	0.07	0.002	0.1	0.01	0.00025	0.0001	1.06	0.02	1.4	0.3	0.009	20.2
		0.06-0.08	0.001-0.002	0.08-0.1	0.01-0.002	0.0002-0.0003	0.0001-0.0002	0.9-1.2	0.02-0.03	1.2-1.6	0.3-0.4	0.008-0.1	17.8-22.7
	CP33	0.058	0.001	0.08	0.004	0.0001	0.0007	1.2	0.03	1.7	0.4	0.01	23.6
		0.02-0.07	0.0006-0.002	0.03-0.01	0.002-0.008	5.5E-5-0.0002	0.0003-0.001	1.1-1.3	0.02-0.03	1.5-1.8	0.3-0.4	0.009-0.01	19.4-27.2
	SHK	0.039	0.001	0.05	0.008	0.0002	0.001	1.2E+00	3.0E-02	1.6E+00	4.0E-01	1.0E-02	2.5E+01
		0.03-0.04	0.0008-0.001	0.04-0.06	0.001-0.01	2.7E-05-0.0004	0.0001-0.003	1.09-1.4	0.03-0.04	1.5-2.08	0.43-0.46	0.01-0.1	24.1-25.6
	DNK	0.009	0.0002	0.01	0.01	0.0003	0.002	1.3	0.03	1.9	0.5	0.01	28.9
		0.008-0.01	0.0002-0.0003	0.011-0.014	0.007-0.02	0.0001-0.0005	0.001-0.003	1.2-1.5	0.03-0.04	1.7-2.09	0.4-0.5	0.01-0.1	26.3-31.5
	CNK	0.06	0.001	0.09	0.006	0.0001	0.001	1.4	0.03	2.06	0.5	0.01	28.8
		0.05-0.08	0.001-0.002	0.07-0.1	0.003-0.009	8.3E-05-0.0002	0.0005-0.001	1.2-1.7	0.03-0.04	1.6-2.4	0.50-0.53	0.01-0.1	28.1-29.5
	KK	0.04	0.001	0.05	0.005	0.0001	0.001	1.5	0.03	2.1	0.5	0.01	28.8
		0.007-0.05	0.0001-0.001	0.009-0.08	0.001-0.01	2.7E-05-0.0002	0.0001-0.001	1.3-1.7	0.03-0.04	1.8-2.4	0.50-0.52	0.01-0.1	27.8-30.7
	JJA	0.06	0.001	0.08	0.012	0.0003	0.002	1.6	0.04	2.2	0.5	0.01	31.9
		0.02-0.1	0.0005-0.003	0.02-0.1	0.002-0.02	5.5E-05-0.0006	0.0003-0.004	1.5-1.6	0.03-0.04	2.1-2.4	0.54-0.60	0.01-0.1	30.4-33.7
	BS	0.04	0.001	0.05	0.009	0.0002	0.001	1.4	0.04	2.06	0.5	0.01	27.9
		0.1-0.007	0.0001-0.002	0.1-0.009	0.006-0.01	0.0001-0.0003	0.001-0.002	1.4-1.5	0.03-0.04	2.02-2.1	0.4-0.5	0.01-0.1	27.05-28.8
	BP	0.06	0.001	0.09	0.007	0.0002	0.001	1.6	0.04	2.3	0.5	0.01	30.7
		0.04-0.08	0.001-0.002	0.05-0.1	0.05-0.1	0.0001-0.0003	0.0009-0.002	1.4-1.7	0.0-0.04	2.02-2.4	0.48-0.59	0.01-0.1	27.05-32.8
	TRM	0.05	0.001	0.08	0.005	0.0001	0.001	1.7	0.04	2.4	0.5	0.01	33.2
		0.01-0.1	0.0004-0.004	0.2-0.2	0.002-0.01	5.5E-05-0.0003	0.0003-0.02	1.6-1.7	0.04-0.05	2.3-2.6	0.53-0.65	0.01-0.1	29.9-36.3
	ZP	0.08	0.002	0.1	0.005	0.0001	0.001	2.1	0.05	2.8	0.6	0.01	35.6
		0.05-0.09	0.001-0.002	0.07-0.1	0.001-0.01	2.7E-05-0.0002	0.001-0.0001	1.9-2.2	0.05-0.06	2.7-3.08	0.60-0.69	0.01-0.1	33.5-34.7
	BBR	0.05	0.001	0.07	0.025	0.0007	0.005	2.5	0.06	3.5	0.01	0.6	36.9
		0.02-0.09	0.006-0.002	0.03-0.1	0.004-0.05	0.0001-0.001	0.0007-0.01	2.4-2.6	0.06-0.07	3.3-3.7	0.5-0.7	0.01-0.02	32.5-39.9
	KDW	0.03	0.0009	0.04	0.005	0.0001	0.001	3.5	0.09	4.9	0.6	0.01	37.2
		0.01-0.04	0.0004-0.001	0.02-0.06	0.01-0.001	2.7E-05-0.0002	0.0001-0.001	3.01-4.1	0.08-0.1	4.1-5.7	0.6-0.7	0.01-0.02	34.1-41.5
SITE B	PSC	0.02	0.0007	0.03	0.006	0.0002	0.01	4.1	0.1	3.2	0.7	0.02	36.9
		0.01-0.03	0.0003-0.0009	0.02-0.05	0.002-0.009	5.5E-05-0.0002	0.003-0.01	4.09-4.1	0.1-0.2	3.1-3.2	0.64-0.69	0.01-0.02	35.5-38.5
	CK86	0.04	0.0005	0.03	0.004	0.0001	0.007	4.7	0.13	3.7	0.7	0.01	39.4
		0.03-0.05	0-0.001	0-0.05	0.003-0.005	8.3E-05-0.0001	0.0001-0.009	4.5-4.8	0.12-0.13	3.5-3.7	0.6-0.7	0.01-0.02	36.8-41.8
	C.2	0.06	0.002	0.08	0.04	0.001	0.1	5.3	0.1	4.1	0.7	0.01	38.9
		0.006-0.09	0.0001-0.002	0.008-0.1	0.002-0.1	5.5E-05-0.002	0.003-0.1	5.02-5.6	0.13-0.15	3.8-4.3	0.7-0.8	0.01-0.02	37-42.3

Table 3.4a: Trace metals in groundwater of Site A and Site B

Site	SAMPLE ID	Ni (ppm)			Cu (ppm)			Cr (ppm)			Mn (ppm)			Fe (ppm)			Pb (ppm)			Cd (ppm)		
		Mean	Max	Min	Mean	Max	Min	Mean	Max	Min	Mean	Max	Min	Max	Max	Min	Mean	Max	Min	Mean	Max	Min
SITE A	CK104L (n=2)	0.08	0.09	0.06	BDL*	BDL	BDL	BDL	BDL	BDL	0.01	0.02	0.01	0.07	0.1	0.04	1.1	1.2	0.9	0.4	0.4	0.3
	CP33 (n=3)	0.06	0.08	0.02	BDL	BDL	BDL	BDL	BDL	BDL	0.004	0.008	0.002	0.2	0.4	0.006	1.3	1.3	1.1	0.4	0.5	0.4
	SHK (n=4)	0.04	0.05	0.03	BDL	BDL	BDL	0.002	0.004	0	0.009	0.02	0.001	0.1	0.4	0.02	1.2	1.5	1.1	0.4	0.5	0.4
	DNK (n=2)	0.009	0.01	0.008	BDL	BDL	BDL	BDL	BDL	BDL	0.01	0.02	0.007	0.04	0.07	0.005	1.4	1.5	1.3	0.5	0.6	0.5
	CNK (n=2)	0.07	0.08	0.05	BDL	BDL	BDL	BDL	BDL	BDL	0.006	0.009	0.003	0.2	0.3	0.1	1.4	1.6	1.2	0.52	0.53	0.5
	KK (n=4)	0.04	0.06	0.01	BDL	BDL	BDL	BDL	BDL	BDL	0.006	0.01	0.001	0.1	0.4	0.03	2	3.6	1.3	0.6	0.6	0.5
	JJA (n=4)	0.06	0.1	0.02	BDL	BDL	BDL	BDL	BDL	BDL	0.01	0.02	0.002	0.5	1.4	0.09	1.6	1.7	1.5	0.6	0.6	0.5
	BS (n=3)	0.04	0.1	0.007	BDL	BDL	BDL	BDL	BDL	BDL	0.009	0.01	0.006	0.03	0.05	0.001	1.6	1.7	1.5	0.5	0.5	0.5
	BP (n=3)	0.07	0.08	0.04	BDL	BDL	BDL	BDL	BDL	BDL	0.007	0.01	0.005	0.3	0.7	0.004	1.7	1.7	1.6	0.6	0.6	0.5
	TRM (n=7)	0.06	0.1	0.02	BDL	BDL	BDL	BDL	BDL	BDL	0.006	0.011	0.002	0.2	1	0.002	1.8	1.9	1.6	0.6	0.7	0.5
	ZP (n=3)	0.08	0.09	0.05	BDL	BDL	BDL	BDL	BDL	BDL	0.006	0.01	0.001	1.04	2	0.3	2.1	2.2	2	0.6	0.7	0.6
	BBR (n=3)	0.05	0.09	0.02	BDL	BDL	BDL	BDL	BDL	BDL	0.03	0.05	0.004	0.03	0.04	0.02	2.6	2.7	2.4	0.7	0.7	0.6
	KDW (n=4)	0.03	0.05	0.02	BDL	BDL	BDL	BDL	BDL	BDL	0.005	0.01	0.001	0.1	0.3	0.002	2.8	3.4	1.7	0.7	0.7	0.6
SITE B	PSC (n=2)	0.02	0.03	0.01	BDL	BDL	BDL	BDL	BDL	BDL	0.006	0.009	0.002	0.4	0.5	0.2	4.1	4.2	4.1	0.7	0.7	0.6
	CK.86 (n=2)	0.04	0.05	0.04	0.004	0.007	0	BDL	BDL	BDL	0.004	0.005	0.003	0.3	0.6	0.05	4.7	4.9	4.6	0.7	0.8	0.7
	C.2 (n=3)	0.06	0.09	0.006	0.002	0.005	0	BDL	BDL	BDL	0.04	0.1	0.002	6.8	18.1	0.4	5.3	5.6	5	0.7	0.8	0.7

3.6: Field Survey

A questionnaire based field survey was conducted in district Rahim Yar Khan. The questionnaire comprised of various demographic and human healths related questions. All of these questions were asked in their native language of Saraiki from the selected villages of the Tehsil Khanpur and Tehsil Rahim Yar Khan of the district Rahim Yar Khan. In the current study data regarding common disease was also collected from the Sheikh Zayed Hospital in the present study. The results of this field survey can be summarized as follows:-

- The major source of drinking water in most of the areas of the district is ground water and the major source of irrigation water is canal water.
- It was observed that the desert area had brackish and saline water and in this region the major source of drinking water is canal water. In this region, the canal water is collected in pools or ponds known as tubas. Both, animals and human beings use this water of tubas for drinking purpose.
- The desert area has less population than the riverain and canal irrigated area. In this region, very few crops are grown and irrigated.
- The major crops of Tehsil Khanpur include 90% sugar and 10% comprise of cotton, wheat, rice and vegetables. However, the major crops of Tehsil Rahim Yar Khan include 50% wheat and 50% cotton and rice.
- The problem of water logging and salinity is prevalent in only Tehsil Liaquat pur and this problem is not found in the rest of the Tehsils of district.
- The major fertilizers used in this area are urea, DAP and animal dung.

3.6.1: Data having the record of diseases:

This is the data having the record of diseases in District Rahim Yar Khan of the year 2012 and till May 2013. The data is categorized into two different types:-

- Outdoor patients
- Indoor patients

Table 3.6a: Cases attending indoor patients from indoor register of the year 2012

Name of diseases	No. of admissions	No. of deaths	% Percentage
Diarrhea/dysentery in <5 years	2374	1	7.08
Pneumonia in < 5 years	277		0.82
Malaria	291		0.56
Pulmonary tuberculosis	156	1	0.45
Obstretic maternal complications	2937		8.76
Other cases	2784	6	3.80
Total	33519	8	0.30

Table 3.7a: Cases attending outdoor patients OPD (from OPD abstract) of the year 2012

Name of diseases	Total number of patients
Acute (upper) respiratory infections	453607
Pneumonia < 5 years	9255
Pneumonia > 5 years	6142
TB suspects	12471
Asthma	48511
Diarrhea/dysentery < 5 years	70083
Diarrhea/dysentery > 5 years	66969
Entric/typhoid fever	9974
Worm infestations	29503
Peptic ulcer	51319
Cirrhosis of lever	721
Suspected malaria	45658
Suspected meningitis	1
Nephrosis/ nephritis	1490
Suspected measles	2
Suspected viral hepatitis	935
Hepatitis B +ve	111
Hepatitis C +ve	115
Heart diseases	1544
Hypertension	36492
Dermatitis	31138
Diabetes mellitus	29213
Depression	13169
Dental caries	42838
Epilepsy	223
Cataract	4195
Trachoma	2276
Glaucoma	774

Table 3.8a: Cases attending outdoor patients OPD (from OPD abstract) of the year 2013

Name of diseases	Total number of patients
Acute (upper) respiratory infections	173940
Pneumonia < 5 years	2740
Pneumonia > 5 years	1623
TB suspects	5369
Asthma	15617
Diarrhea/dysentery < 5 years	22154
Diarrhea/dysentery > 5 years	20434
Entric/typhoid fever	2364
Worm infestations	10149
Peptic ulcer	20584
Cirrhosis of lever	282
Suspected malaria	12728
Suspected meningitis	11
Nephrosis/ nephritis	426
Suspected measles	121
Suspected viral hepatitis	293
Hepatitis B +ve	27
Hepatitis C +ve	29
Heart diseases	403
Hypertension	11437
Dermatitis	7982
Diabetes mellitus	10417
Depression	3439
Dental caries	16763
Epilepsy	136
Cataract	1098
Trachoma	646
Glaucoma	346

Table 3.9a: Cases attending indoor patients from indoor register of the year January-May 2013

Name of diseases	No. of admissions	% Percentage
Diarrhea/dysentery in <5 years	919	7
Pneumonia in < 5 years	202	1.5
Malaria	97	0.7
Pulmonary tuberculosis	91	0.7
Obsteritic maternal complications	1379	10.87
Other cases	9683	76.5
Total	12648	

3.7: Identification of pollution sources via Cluster Analysis (CA) and Principal Component Analysis (PCA)

3.7.1: Cluster Analysis of sampling sites

Cluster Analysis is a multivariate analysis technique used for the grouping or clustering of similar objects in the same class (Danielsson, Cato et al. 1999). Levels of similarity at which observations are merged, used to construct a dendogram (Chen, Jiao et al. 2007). Cluster analysis was used to identify spatial variability between the sites based on physicochemical parameters. The resulted dendogram (Fig.3.34a) grouped all the 16 sampling sites into two statistically significant clusters.

The group 1 explained 40% of total variation in the data set and group 2 explained 60% variation in the data set. The group 1 comprised of SHK, ZP, BBR, BS, BP, JJA and KK. The group 2 comprised of CK104L, CP33, KDW, CNK, DNK, TRM, PSC, CK86 and C.2. Both of the clusters comprised of sampling sites with comparable characteristics and natural background that are affected by sources of similar strength/type. The CA technique is helpful in offering consistent classification of underground waters in the whole region and may serve as good in spatial assessment of the water quality as the whole network. The same aspect is also reported by other researchers (Kim, Kim et al. 2005).

3.7.2: Principle Component Analysis

PCA is also a multivariate technique used for the source identification of various physio-chemical parameters. Principal component analysis (PCA) transforms large data sets into fewer significant dimensions and evaluates the degree of contribution for pollutant sources. PCA results are summarized in Table 3.10a, which shows the variable loadings characterizing the main contamination patterns and their explained variance. High positive and negative loadings indicate the significance of variables. Different variables have varying association in each of the principal component (PC).

PCA resulted in the reduction of entire data set into 4 statistically significant Axes. All of these Axes explained about 99.5% of variation in the whole data set. Among all of the Axes, the first Axis 1 was the most important which accounted for about 99.2% of total variation in data set. The Axis 1 had a significant positive loading of pH, thus suggesting its anthropogenic and geogenic origin. The pH of all water samples was alkaline in nature and it resulted from the presence of all pollutants in groundwater, as pH plays an important role in the solubility of various pollutants like heavy metals (Ho et al., 2003). The Axis 2 accounted for about 0.1% variation to the data set. The Axis 3 contributed 0.1% to total variation with higher loadings of EC and TDS. Both of these variables accounted for their natural and anthropogenic origin of Axis 3. The Axis 4 contributed 0.06% of total variation with high loadings of As and SO_4^{-2} thus indicating its anthropogenic origin.

Table 3.10a: PCA loadings for selected physio-chemical parameters in groundwater

	Axis 1	Axis 2	Axis 3	Axis 4
Depth (ft)	0.052	-0.028	-0.081	0.136
Ph	**0.911**	0.058	-0.07	-0.052
EC (uS/cm)	0.062	-0.125	**0.502**	0.098
TDS (mg/L)	0.062	-0.125	**0.502**	0.098
DO (mg/L)	0.298	0.013	-0.002	-0.01
Cl^- (ppm)	0.044	-0.127	0	0.034
HCO_3^- (ppm)	0.061	-0.118	0.472	0.092
NO_3^- (ppm)	0.148	0.004	0.003	-0.003
SO_4^{-2} (ppm)	0.03	0.202	0.001	**0.604**
$P0_4^{-3}$ (ppm)	0.113	-0.398	0.003	-0.039
Na^+ (ppm)	0.043	0.427	0.009	0.026
K^+ (ppm)	0.023	0.264	0.239	-0.429
Ca^{+2} (ppm)	0.043	0.13	0.001	-0.037
Mg^{+2} (ppm)	0.016	0.214	0.347	-0.06
Ni (ppm)	0.053	0.01	-0.187	-0.004
Pb (ppm)	0.036	-0.296	0.001	0.082
Cd (ppm)	0.113	-0.203	-0.222	0.055
Fe (ppm)	0.008	-0.336	0	0.093
Mn (ppm)	0.023	-0.31	0	0.086
As (ppb)	0.017	0.202	0	**0.607**
F^- (ppm)	0.085	0.206	0	0
Percentage	99.242	0.144	0.142	0.065
Cum. Percentage	99.242	99.386	99.528	99.593

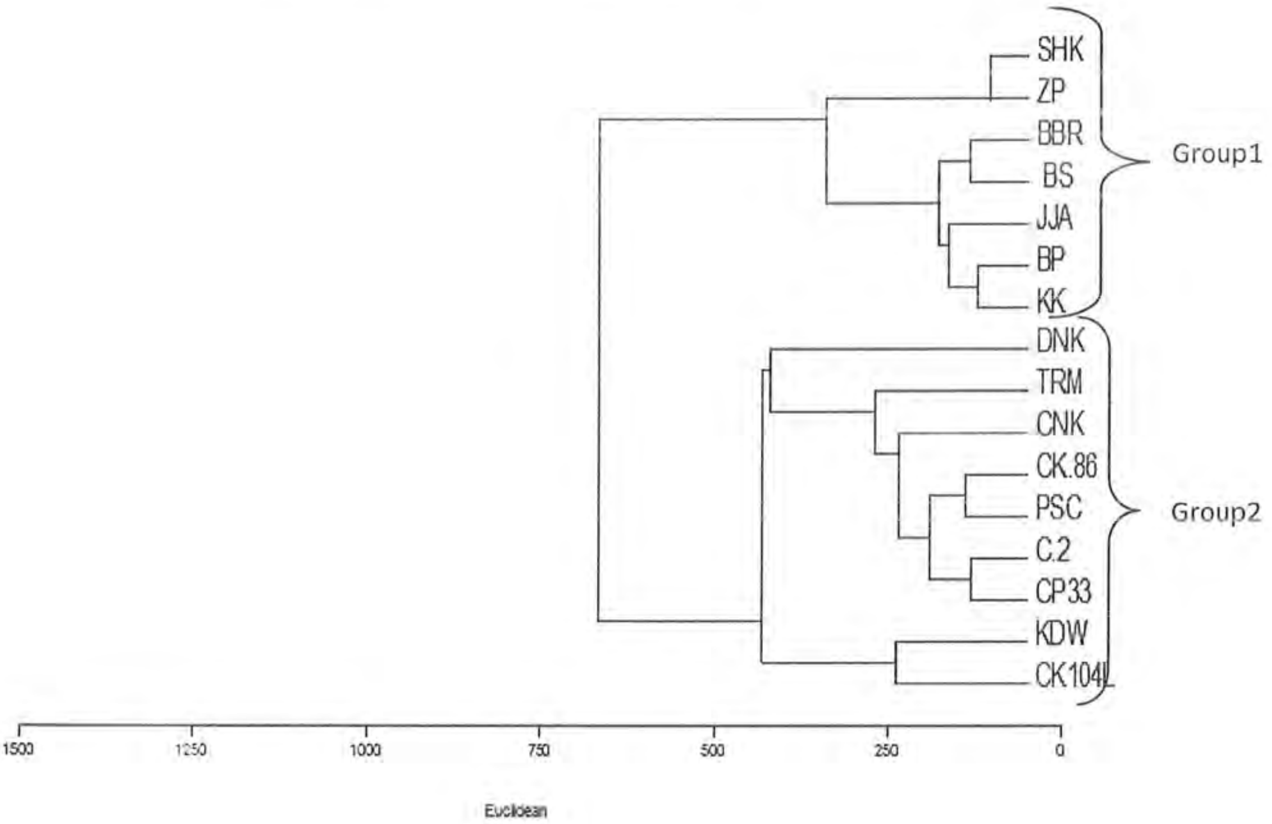


Figure 3.34a: Dendogram showing clusters of various groups in water samples

Section- B: Soil and Sediments

All of the soil and sediment samples were also categorized into 2 major sites i.e., Site A and Site B. The Site A comprised all of the agricultural soil samples and sediment samples of Tehsil Khan pur. However, the Site B included all of the industrial soil samples of Tehsil Rahim Yar Khan. All samples were collected from 0-30 cm depth.

3.1: Physio-chemical parameters

The results of the physio-chemical parameters of all soil and sediment samples are shown in Table C.1 (Annexure C); while the results of each sampling site are summarized in Table 3.1b and Figure 3.1b. The overall results demonstrated that all of the soil and sediment samples were alkaline in nature similar to the water samples. The following order was observed for pH, EC, TDS in both sites i.e., Site B < Site A.

Soil and sediment texture was sandy loam and loamy sand in most of the samples. All of the samples comprised fine grain particles, as sand formed the major proportion followed by silt and clay in all samples. The percentage of silt and clay varied in all of the samples (Table 3.1b). All of the soil and sediment samples were rich in organic matter. However, the ascending order for soil texture (%sand + % silt+ % clay) and organic matter (%OC and %TOC) was observed i.e., Site A < Site B.

3.1.1: Site A

a) pH, EC and TDS of Soil Samples

The pH of Site A for agricultural soil samples ranged between 8.2-11.4 with a mean value of 10.3. Highest value of pH was recorded in the sample of CK104L and smallest value of pH was found in DNK. The sampling points were arranged in the following ascending order in terms of pH i.e.

DNK < CNK < SHK < CP33 < BP < JJA < KK < BS < TRM < ZP < CK104L

The mean and range value for EC was 74.3 μS/cm and 38.1-95.1 μS/cm. The sample TRM had the largest value of EC and the sample CK104L had the smallest value of EC. The mean and range value of TDS was 36.9ppm and 19-48ppm. The largest and smallest value of TDS was recorded in the samples of TRM and CK104L. The sampling points were arranged in this ascending order for EC and TDS values i.e.

CK104L < CP33 < SHK < DNK < CNK < KK < JJA < BS < BP < ZP < TRM

b) *pH, EC and TDS of Sediment samples*

The pH values of sediment samples had a mean and range value of 10.09 and 8.9-12.2. The ascending order for pH values was i.e.,

PC < RI < AC

The mean and range value of EC was 1081.3 μS/cm and 593-1396 μS/cm. the TDS had a mean and range value of 540.6ppm and 296.5-698ppm. The ascending order of EC and TDS for sediment samples was i.e.,

RI < PC < AI

c) *Soil texture, OC, TOC and OM for soil samples*

The composition of sand ranged between 74.6-93% with a mean value of 83.6%. Largest and smallest proportion of sand was present in the sample of ZP and JJA. The sampling points showed this order for composition of sand i.e.

JJA < BP < KK < SHK < CNK < DNK < CP33 < BS < TRM < CK104L < ZP

The composition of silt had a mean and range value of 6.5% and 1-13.6%. The highest and lowest proportion of silt was found in the samples BP and BS. Silt showed the following ascending order in all of the sampling points i.e.,

BS < CK104L < DNK < TRM < ZP < KK < CNK < CP33 < SHK < JJA < BP

The component of clay had a mean and range value of 1.4% and 0.1-2.4%. The highest and smallest portion of clay was found in the samples ZP and KK. However, the following order was observed for clay i.e.,

ZP < CP33 < CK104L < SHK < TRM < BP < BS < CNK < JJA < DNK < KK

The findings of the present study were in agreement with the District Census Report, (1998) as it it is stated that sand is major component of soil in District Rahim Yar Khan.

The mean and range value of % OC was 1.4 and 0.1-2.4. The highest and lowest value of % OC was found in the samples CK104L and BP. The mean and range value of % TOC was 1.9 and 0.2-3.2. The highest and lowest value was recorded in CK104L and ZP. The % OM had a mean and range value of 3.5 and 1.3-5.5. The highest and lowest value was found in the samples

CK104L and BS. The sampling points showed the following order for % OC, % TOC and % OM i.e.

BP < CP33 < CK104L < SHK < TRM < ZP < BS < CNK < JJA < DNK < KK

According to Agronomy Fact Sheet Series of Cornell University, the OM of productive agricultural soils is between 3-6% (M Fenton. 2008). The results of the current study showed that the %OM of all agriculture soil samples were within the safe limits set by Fenton et al., 2008.

d) Soil texture, OC, TOC and OM for soil samples

The composition of sand in all of the sediment samples had a mean and range value of 89.3% and 88-90%. The highest and lowest portion of sand was found in the sample of RI and AC. The following order was observed for composition of sand in the sediment samples i.e.,

RI < PC < AC

The composition of silt had a mean and range value for the sediment samples was 3.3% and 2.1-5%. Highest and lowest value of % silt was found in the samples PC and AC. The sampling points showed the following order i.e.,

PC < AC < RI

The composition of clay had a mean and range value of 7.5% and 7-8%. Highest and lowest value was recorded in the samples in AC and RI. The sampling points of sediment samples showed the following order i.e.,

PC < RI < AC

The findings of the present study were in agreement with the District Census Report, (1998).

3.1.2: Site B

a) *pH, EC and TDS*

The pH values of Site B had a mean value and range value of 9.8 and 8.7-11.07. Highest and lowest value of pH was recorded in the samples MI and TI. The sampling points were arranged in the following ascending order in terms of pH i.e.

TI < AI < SI (2) < RCI < CI < SI (1) < MI

The mean and range value for EC was 151.7 μS/cm and 113.8-239 μS/cm. The sample CI had the largest value of EC and the sample AI had the smallest value of EC. The mean and range value of TDS was 76.3ppm and 58-119.5ppm. The largest and smallest value of TDS was recorded in the samples of CI and AI. The sampling points were arranged in this ascending order for EC and TDS values i.e.

AI < MI < SI (1) < RCI < TI < SI (2) < CI

b) Soil texture, OC, TOC and OM

The composition of sand ranged between 72-95.5% with a mean value of 85.9% for Site A. Largest and smallest proportion of sand was present in the sample of RCI and TI. The sampling points showed this order for composition of sand i.e.

RCI < MI < SI (1) < SI (2) < AI < CI < TI

The composition of silt had a mean and range value of 7.1% and 2-16.5%. The highest and lowest proportion of silt was found in the samples MI and AI. Silt showed the following ascending order in all of the sampling points i.e.

AI < TI < CI < SI (2) < RCI < SI (1) < MI

The component of clay had a mean and range value of 6.8% and 1-19.7%. The highest and smallest portion of clay was found in the samples RCI and TI. However, the following order was observed for clay i.e.

TI < CI < SI (1) < SI (2) < MI < AI < RCI

The findings of the current study were in agreement with the District Census Report (1998).

b) OC, TOC and OM

The mean and range value of % OC was 2 and 0.3-3.4. The highest and lowest value of % OC was found in the samples AI and TI. The mean and range value of % TOC was 2.6 and 0.5-4.6. The highest and lowest value was recorded in AI and TI. The % OM had a mean and range value of 3.5 and 0.3-7.9. The highest and lowest value was found in the samples AI and TI. The sampling points showed the following order for % OC, % TOC and % OM i.e.,

TI < SI (2) < MI < RCI < CI < SI (1) < AI

The results demonstrated that the %OM values of all samples were within the safe limits set by Fenton et al., 2008 and in only 1 sample the value was above the permissible limits i.e., TI (Textile industry).

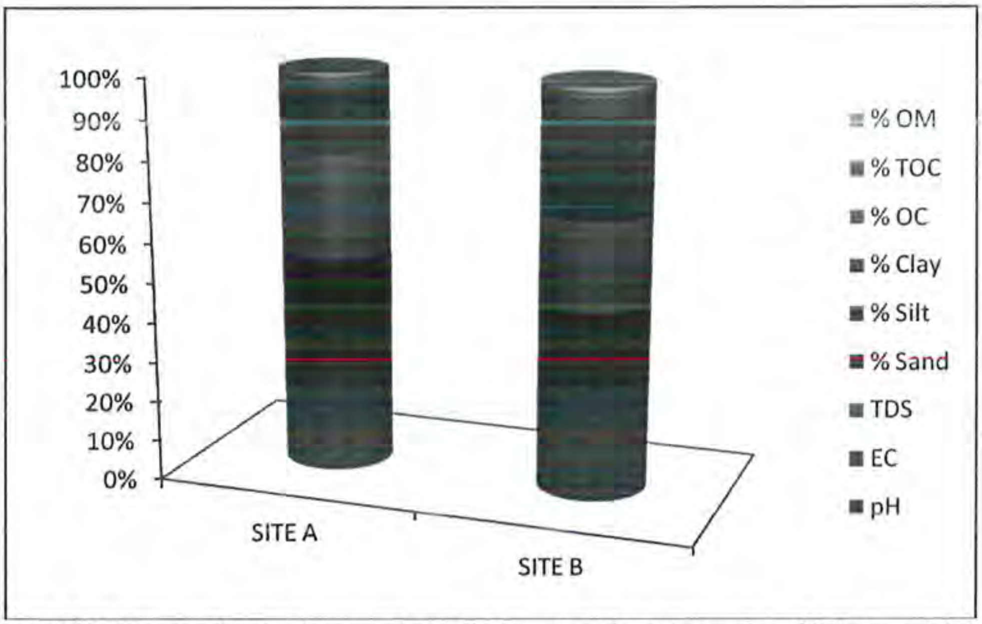


Figure 3.1b: Physio-chemical parameters of soil and sediment samples of Site A and Site B

Table 3.1b: Mean values of all physio-chemical properties for all sampling sites of soil and sediment samples

Site	Sapling code	Depth of soil (cm)	pH	EC (uS/cm)	TDS (mg/L)	% Sand	% Silt	% Clay	Textural Class	% OC (w/w)	% TOC (w/w)	% 0M (w/w)
SITE A	CK104L	0-30	11.4	38.1	19	91.5	2.5	6	Sand	2.4	3.2	5.51
	CP33	0-30	10.6	38.5	19	87	8	5	Loamy sand	1.57	2.09	4.13
	SHK	0-30	10.3	65.9	33	80	12	8	Loamy sand	1.5	2	5.17
	DNK	0-30	8.2	72.2	36.1	84	3	13	Loamy sand	0.6	0.8	3.44
	CNK	0-30	8.9	75.6	38	81	7	12	Loamy sand	1.2	1.6	2.75
	JJA	0-30	10.7	80.04	36.4	74.6	13.4	12	Sandy loam	1.95	2.6	3.37
	KK	0-30	10.8	76.9	38.45	79	5	16	Sandy loam	2.25	3	3.44
	BS	0-30	11	90	45	87	1	12	Loamy sand	1.57	2.1	1.37
	BP	0-30	10.6	91.7	46.1	75	13.6	11.4	Sandy loam	0.15	0.2	3.3
	ZP	0-30	11.4	93.6	47	93	3	4	Sand	1.8	2.4	3.61
	TRM	0-30	11.2	95.1	48	88	3	9	Loamy sand	1.5	2	3.44
	AC	0-30	12.2	1396	698	89.9	2.1	8	Sand	1.44	1.92	5.51
	PC	0-30	8.9	1255	627.5	88	5	7	Loamy sand	1.47	1.96	4.81
	RI	0-30	9.06	593	296.5	90	3	7	Sand	1.45	1.94	5.51
		Mean	10.3	290.1	144.8	84.8	5.8	9.3		1.49	1.98	3.95
		Maximum	12.2	1396	698	93	13.6	16		2.4	3.2	5.51
		Minimum	8.2	38.1	19	74.6	1	4		0.15	0.2	1.37
SITE B	AI	0-30	9.1	113.8	58	90	2	8	Sand	3.45	4.6	4.48
	MI	0-30	11.	120.2	61	77	16.5	6.5	Loamy sand	1.8	2.4	3.62
	SI (1)	0-30	10.5	127	64	85	9	6	Loamy sand	2.4	3.2	0.34
	RCI	0-30	10	130	65	72	8.3	19.7	Sandy clay loam	2.1	2.8	3.79
	TI	0-30	8.7	152	77	95.5	3.5	1	Sand	0.37	0.5	7.93
	SI(2)	0-30	9.3	180	90	88	6	6	Loamy sand	1.5	2	4.13
	CI	0-30	10.5	239	119.5	94	5	1	Sand	2.4	3.2	0.86
		Mean	9.8	151.7	76.3	85.9	7.1	6.8		2	2.67	3.59
		Maximum	11	239	119.5	95.5	16.5	19.7		3.45	4.6	7.93
		Minimum	8.7	113.8	58	72	2	1		0.37	0.5	0.34

3.2: Trace Metals in soil and sediments

The concentrations of all the trace metals in soil and sediment samples are summarized in Table C.2 (Annexure C) and Table.3.2b. All of these metals had the following order i.e.,

Cr > Cu > Cd > Ni > Pb > Mn > Fe

The spatial distribution of all these trace metals was determined via various concentration maps. The results of all these metals were compared with the permissible limits set by the State Environmental Protection Administration, China (SEPA) (1995) and European Union, (2000) (Khan, Rehman et al. 2010). Positive correlation was observed between Fe-Cu ($r = 0.98$), Pb-Cd ($r = 0.88$), Pb-Cr ($r = 0.46$), Cd-Cr ($r = 0.51$), Pb-Mn ($r = 0.47$), Cd-Mn ($r = 0.49$), Ni-Mn ($r = 0.69$), Cr-Ni ($r = 0.48$) and Cr-Mn ($r = 0.67$) indicating that all of these metals might have originated from the common source as shown in Table D.2 (Annexure D).

a) Copper

The concentration of Cu crossed the permissible limit of SEPA (i.e., 100 mg/kg) in only 1 sample i.e., CNK. This sample was taken from the agriculture land.

The agricultural soil samples of Site A had a mean and range value of 29.2mg/kg and 3.9-225.8mg/kg. Highest value was recorded in the sample CNK and the lowest value was found in the sample CP33. The sampling points of agricultural soil samples of Site A showed the following ascending order i.e.,

CP33 < BP < DNK < TRM < JJA < CK104L < SHK < ZP < KK < BS < CNK

The mean concentration of Cu in sediment samples for Site A was 12.6mg/kg and it ranged between 7.2-17.3mg/kg. The highest and lowest value was recorded in the samples RI and PC. The sampling points of sediment samples showed the following order i.e.,

PC < AC < RI

The Site B had a mean and range value of 10.5mg/kg and 3.9-31.7mg/kg. The highest and lowest value of Cu was observed in the samples of TI and SI (1). The sampling points showed the following order i.e., SI (1) < SI (2) < CI < RCI < MI < AI < TI. In Site B, the sample of textile industry comprised the largest proportion of Cu indicating the major source of Cu in the industrial area. However, the soap industry made the least contribution in this regard. However, for Cu the following order was observed i.e., Site B < Site A. The agricultural soil samples had higher values than the industrial soil samples as shown in Figure 3.2b.

Cu showed positive correlation with Fe (r = 0.97). This positive correlation shows the common source of these pollutants in the area. The results of the present study were in agreement with the previous study conducted in Faisalabad (Parveen, Ghaffar et al. 2012). However, the Cu concentration was less than the previous study conducted in China (Khan, Cao et al. 2008). Copper is both an essential and toxic element. The major anthropogenic sources of Cu include phosphate fertilizers, vehicular exhaust, sewage sludge, wood production, metal production, forest fires, decomposition of organic matter and industrial practices. It is retained in the soil via exchange and specific adsorption mechanism (Merain 1991). The possible sources for Cu in sample CNK could be the extensive use of fertilizers in the area.

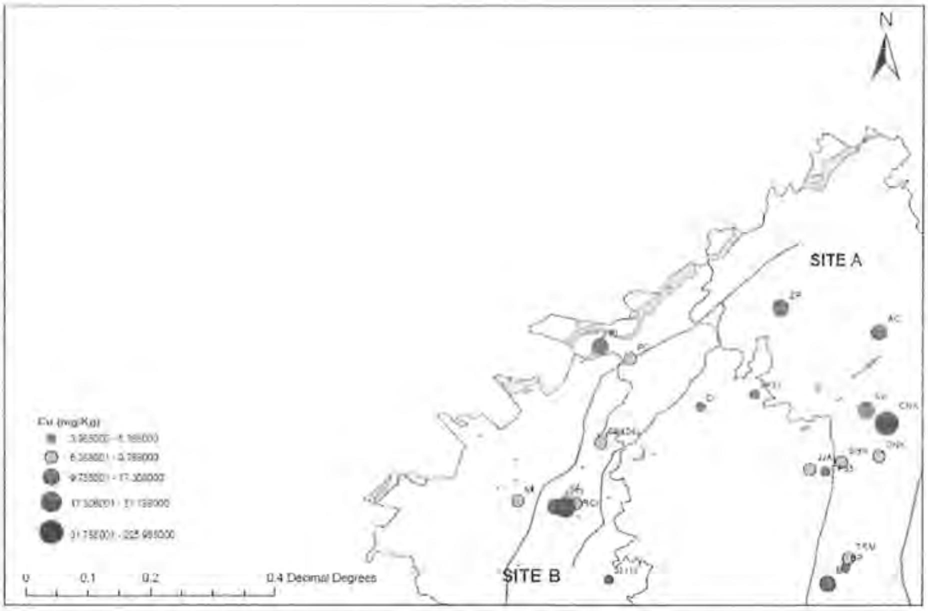


Figure 3.2b: Spatial distribution of Cu in soil and sediments of District Rahim Yar Khan

b) Chromium

The value of Cr was within the safe limits set by SEPA (250mg/kg) in all of the samples. The agricultural soil samples of Site A had a mean and range value of 8.4mg/kg and 3.6-20mg/kg. The highest and lowest value was recorded in the samples KK and CP33. The ascending order of all agricultural soil samples for Cr was i.e.,

CP33 < ZP < BP < CK104L < JJA < BS < SHK < CNK < DNK < TRM < KK

The sediment samples of Site A had a mean and range value of 13.2mg/kg and 8.6-21.2 mg/kg. The highest and lowest value was recorded in the samples of AC and RI. The sampling points showed the following order for sediments of Site A i.e.,

PC < RI < AC

The Site B had a mean and range value of 36.2mg/kg and 6.2-143.4mg/kg. Highest and lowest value was recorded in the samples in TI and CI. The textile industry made the major contribution and CI made the least contribution for Cr in Site B. The sampling point showed the following order i.e.,

CI< SI (2) < SI (1) < RCI< MI < AI < TI

The following order was found for Cr i.e., Site A < Site B. The industrial soil samples had higher values of Cr than the agricultural soil and sediment samples as shown in Figure 3.4b.
Positive correlation was observed between Cr-OM (r = 0.62), Cr-sand (r = 0.45), Cr-Pb (r = 0.46), Cr-Cd (r = 0.51), Cr-Ni (r = 0.48) and Cr-Mn (r = 0.67) as shown in Figure.3.3b. The Cr concentration was higher than those reported in China (Khan, Cao et al. 2008) and sediments of Rawal Lake (Zahra, Hashmi et al. 2014).

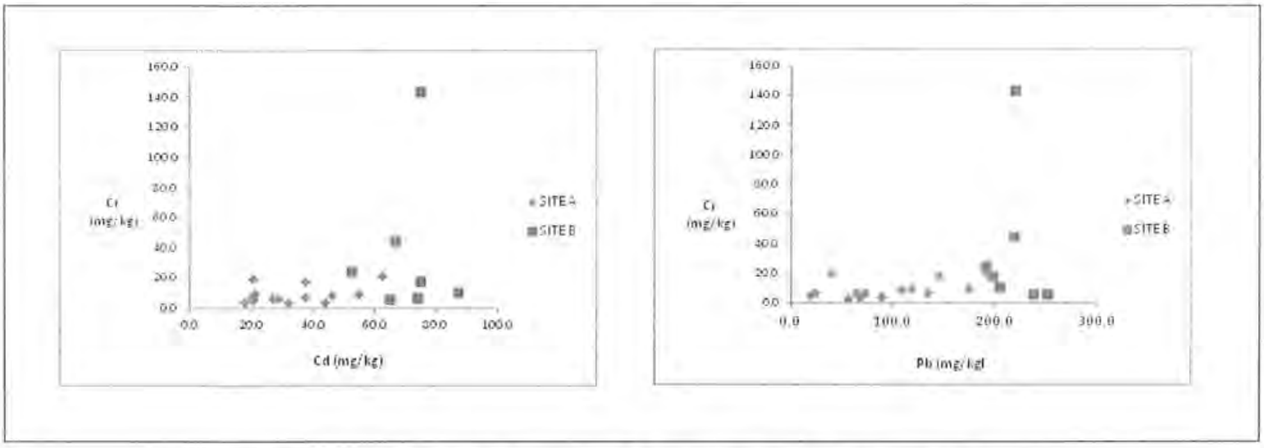


Figure 3.3b: Relationship of (a) Cr vs. Cd (b) Cr vs. Pb

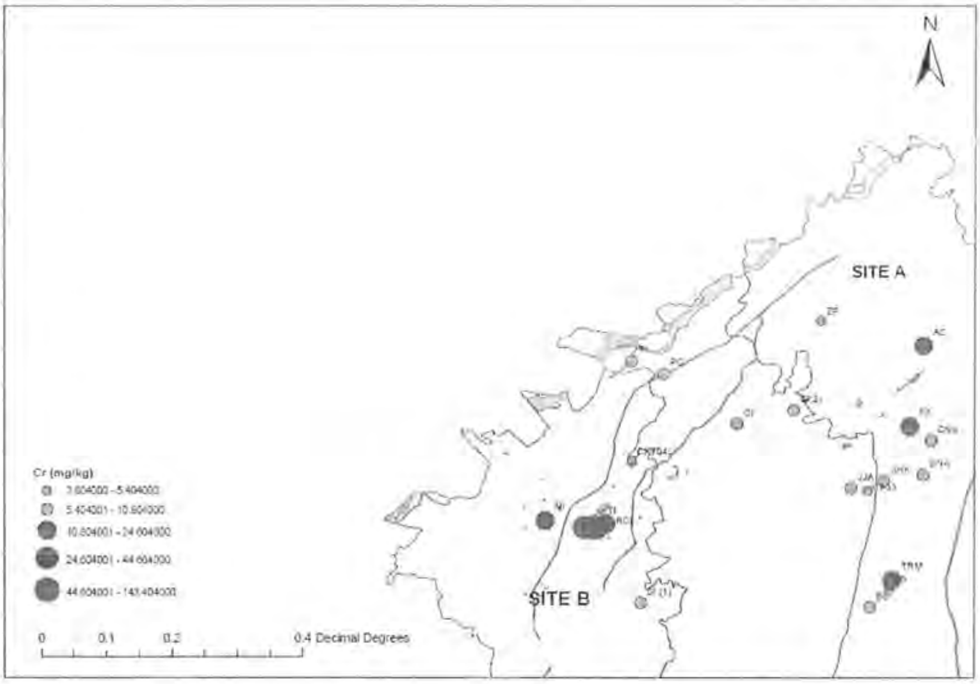


Figure 3.4b: Spatial distribution of Cr in soil and sediments of District Rahim Yar Khan

c) Nickel

The value of Ni surpassed the safe limits set by SEPA (60 mg/kg) in about 90% of samples and only 10% samples were free from Ni. The agricultural soils of Site A had a mean value of 112.5mg/kg and ranged between 81.147.2mg/kg respectively. The highest and lowest value was observed in CNK and CK104L. The sampling points showed the following ascending order i.e.,

CK104L < CP33 < DNK < JJA < SHK < BP < ZP < KK < TRM < BS < CNK

The sediment samples of Site A had a mean and range value of 202.8mg/kg and 169.5-234.5mg/kg. The highest and lowest value was observed in the samples of AC and PC. The sampling points of sediment samples of Site A showed the following order i.e.,

PC < RI < AC

The Site B had a mean and range value of 97.7mg/kg and 7.8-358.4mg/kg. Highest and lowest value was found in AI and CI. The ascending for Ni concentration of all sampling points was CI < SI (2) < SI (1) < RCI < MI < TI < AI. The following order was observed for the sites i.e., Site B < Site A. Thus, the agricultural soil samples were more contaminated than the industrial soil samples as shown in Figure 3.5b.

Ni showed positive correlation with Ni-Mn (r = 0.69), Ni-Cr (r = 0.48), Ni-clay (r =0.40), Ni-TOC (r = 0.52) and Ni-OM (r = 0.52) as shown in Figure 3.6b. The Ni level was much lower than those found in sediments of Rawal Lake (Zahra, Hashmi et al. 2014) and its concentration was much higher than the agricultural soils of China (Khan, Cao et al. 2008) Faisalabad (Parveen, Ghaffar et al. 2012) and Bangladesh (Rahman, Khanam et al. 2012).

About 95% of Ni emitted to the environment is associated with human activity (Abrahim and Parker 2008). There are various sources of Ni which include wear of bearings, bushings and other moving parts in engines, petroleum products, leakage from septic tanks and leaded gasoline (Priju and Narayana 2006). In soils, Ni is usually present in the organically bound form, which increases its bioavailability and mobility (Mukherjee 2007). The higher levels of Ni in the study area may be associated with various anthropogenic and natural sources. The natural source might be its presence with organic compounds, as all of the soil and sediment samples were enriched with organic matter in the current study which will be discussed further. While, the anthropogenic sources might be the petroleum products, leaded gasoline and leakage from septic tanks. Higher levels of Ni in the human body can cause allergy, hand eczema, lung and nasal injury (Filon, D'Agostin et al. 2009).

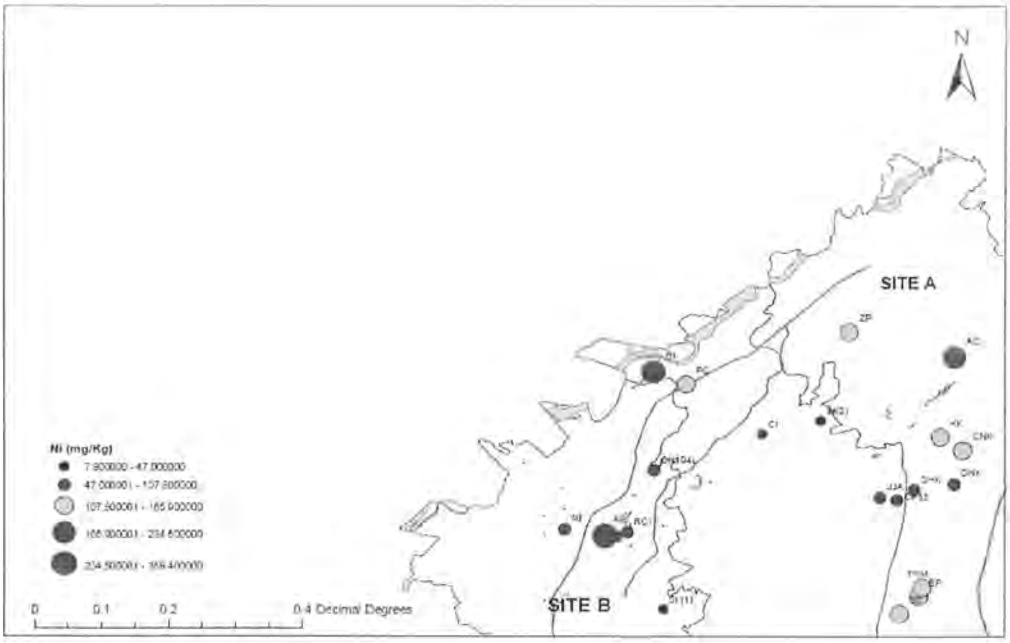


Figure 3.5b: Spatial distribution of Ni in soil and sediments District Rahim Yar Khan

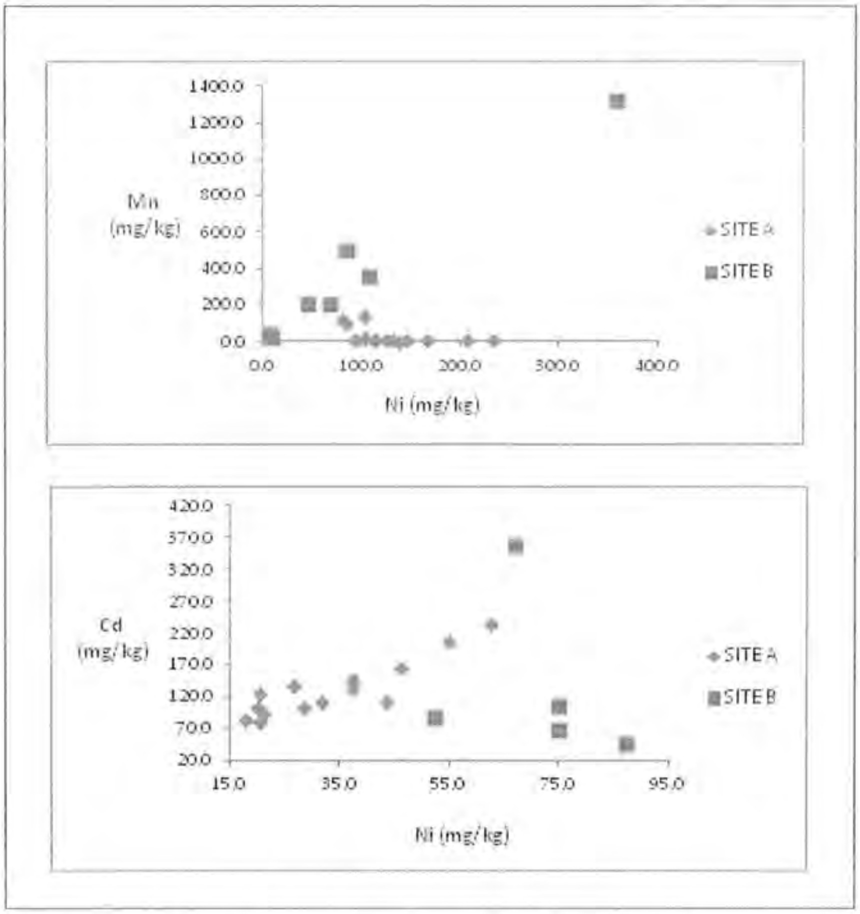


Figure 3.6b: Relationship of (a) Ni vs. Mn and (b) Ni vs. Cd

d) Mangenese

The concentration of Mn in all the samples was less than its background values i.e., 720mg/kg (Taylor 1964) and only 1 sample had the value greater than the background values i.e., AI (Industry of agricultural instruments).

The agricultural soil samples of Site A had a mean and range value of 37.6mg/kg and 2.6-134.6mg/kg. The highest and lowest value was recorded in the samples of SHK and BS. The sampling points showed the following order i.e.,

BS < CNK < BP < KK < ZP < DNK < TRM < JJA < CP33 < CK104L < SHK

The sediment samples of Site A had a mean and range value of 8mg/kg and 5.5-10.8mg/kg.

The sample AC had the smallest value and the sample RI had the largest value. The sediments of Site A had the following order i.e., AC < PC < RI

The Site B had a mean and range value of 377.7mg/kg and 7.8-358.4mg/kg. The highest and lowest concentration was found in the samples of AI and SI (2). The industry of agricultural instruments produced largest amount of Mn and the sugar industry produced the smallest amount of Mn in the current study. The sampling points showed the following order i.e., SI (2) < CI < SI (1) < RCI < TI < MI <AI. The following order was observed for the sites i.e., Site A < Site B, as the industrial soil samples were more contaminated than the agricultural soil samples as shown in Figure 3.7b.

The Mn level was much higher than the previous study conducted in sediments of Rawal Lake (Zahra, Hashmi et al. 2014). However, the Mn level was much lower than those reported in the sediments of Langcang River, China (Khan, Cao et al. 2008) and agricultural soils of Bangladesh (Rahman, Khanam et al. 2012). Mn showed positive correlation with OC (r = 0.51), TOC (r = 0.64), OM (r = 0.38), Cr (r = 0.67), Ni (r = 0.69), Pb (r = 0.47) and Cd (r = 0.49) as shown in Figure 3.8b.

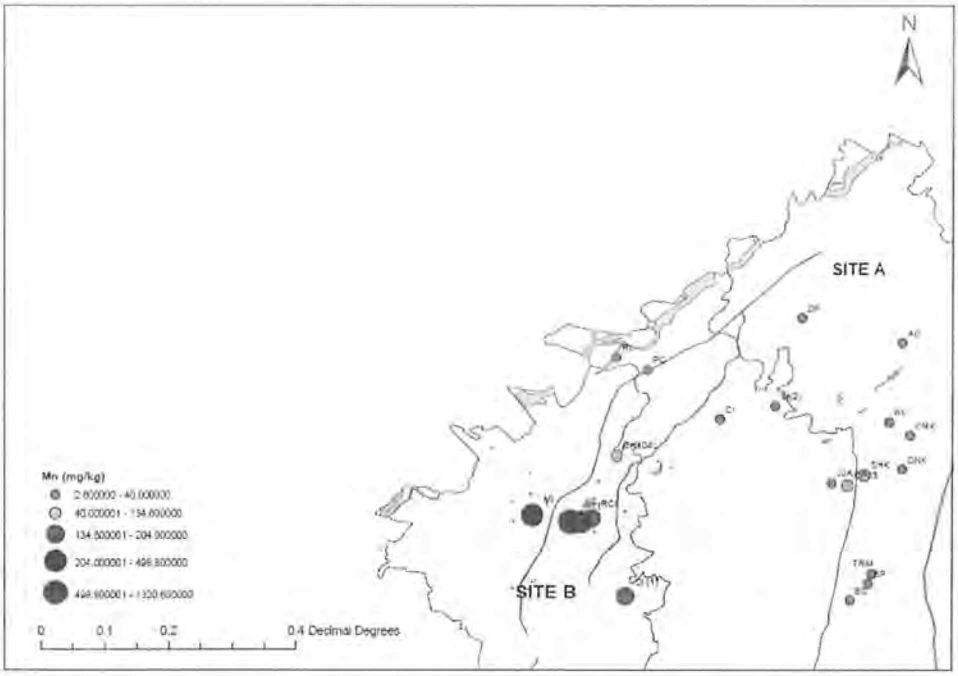


Figure 3.7b: Spatial distribution of Mn in soil and sediments of District Rahim Yar Khan

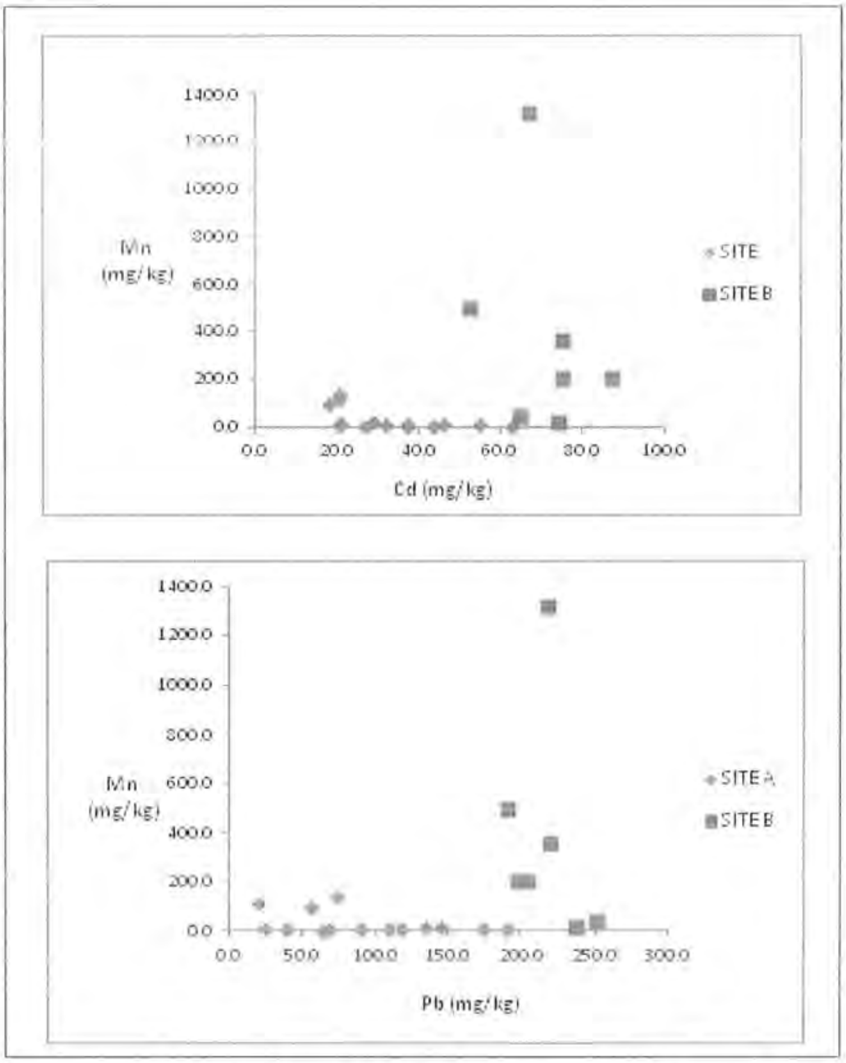


Figure 3.8b: Relationship of Mn vs. Pb and b) Mn vs. Cd

e) Iron

The concentration of iron was less than the background values in earth i.e., 35900mg/kg (Taylor 1964). The mean and range of Fe for agricultural soil samples of Site A was 18523.9mg/kg and ranged between 2990.6-94440.4mg/kg. The largest and smallest concentration of Fe was recorded in the samples of CNK and JJA respectively. The sampling points of Site A showed the following order i.e.,

JJA < CK104L < CP33 < DNK < BP < SHK < BS < KK < ZP < TRM < CNK

However, the sediment samples of Site A had a mean and range value of 11598.3mg/kg and 6448.4-15623.6mg/kg. The highest and lowest value was found in the samples of AC and RI. The sediments showed the following order i.e., RI < PC < AC

The Site B had a mean and range value of 11898.4mg/kg and 8891.6-16999.6mg/kg. The smallest and highest value was recorded in the samples of SI (1) and AI. The industry of agricultural instruments made the highest contribution and the soap industry made the least contribution for iron in the current study. The sampling points of Site B showed the following order i.e.,

SI (1) < SI (2) < RCI < TI < CI < MI < AI

Fe showed the following order Site B < Site A as shown in (Figure 3.9b). Fe showed significant positive correlation with Cu (r = 0.97). The Fe concentration was much higher than the previous studies reported in sediments of Rawal Lake (Zahra, Hashmi et al. 2014). However, the findings of the current study were in agreement with the previous studies conducted in Bangladesh (Rahman, Khanam et al. 2012) and China (Wang, Liu et al. 2012), as in the present and previous studies, very high levels of iron were found in the samples.

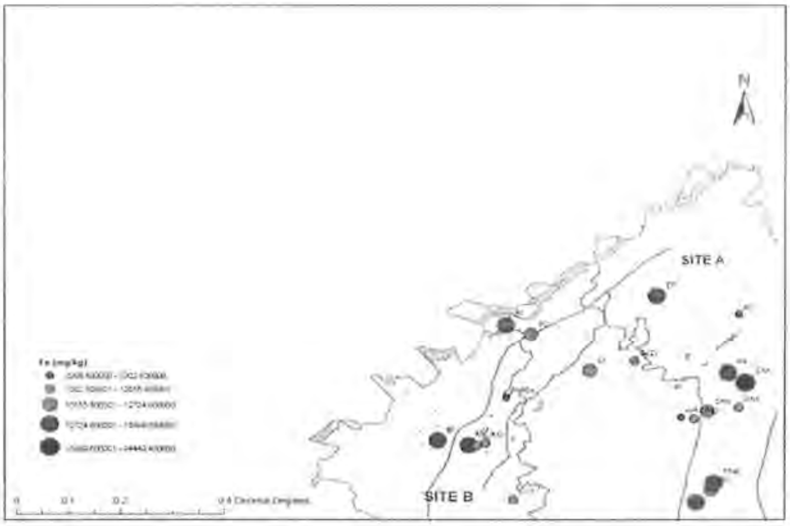


Figure 3.9b: Spatial distribution of Fe in soil and sediments of District Rahim Yar Khan

f) Lead

The concentration of Pb in all of the samples was within the permissible limits set by SEPA (350mg/kg). The mean and range value of agricultural soil samples of Site A was 75.5mg/kg and 19.7-145.7mg/kg. The highest and lowest value was observed in the samples of TRM and CK104L. The sampling points showed the following order i.e.,

CK104L < CNK < KK < CP33 < BS < ZP < SHK < BP < DNK < JJA < TRM

The sediment samples of Site B had a mean and range value of 158mg/kg and 108.7-190.7mg/kg. Highest and lowest of Pb was recorded in the samples of AC and PC. The sediment samples of Site A showed the following order i.e.,

AC < RI < PC

The Site B had a mean and range value of 216.9mg/kg and 190.1-250.7mg/kg. The highest and lowest value was observed in CI and MI. The sampling points showed the following order i.e., MI < RCI < SI (1) < AI < TI < SI (2) < CI. The following order was observed i.e., Site A < Site B, as the Site B was the industrial area making the major contribution as shown in Figure 3.10b. The Pb concentration was much higher than those found in the sediments of Rawal Lake (Zahra, Hashmi et al. 2014), urban soils of Faisalabad (Parveen, Ghaffar et al. 2012), agricultural soils of Bangladesh (Rahman, Khanam et al. 2012) and sediments of China (Wang, Liu et al. 2012). Positive correlation was observed between Pb-Cr (r = 0.46), Pb-Mn (r = 0.47) and Pb-Cd (r = 0.88).

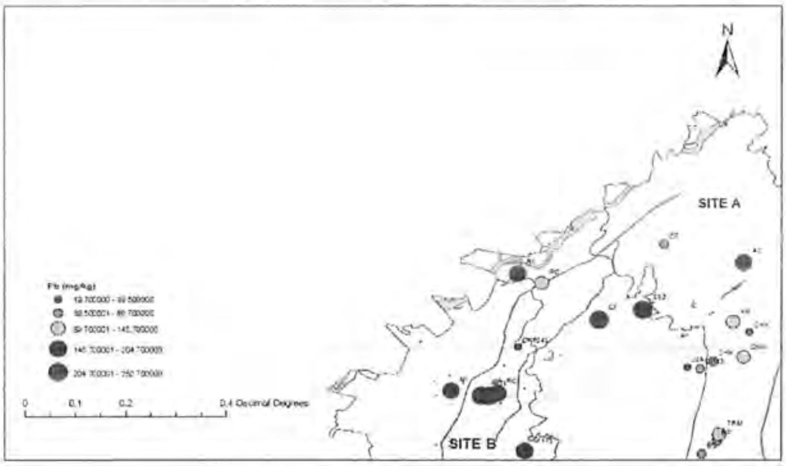


Figure 3.10b: Spatial distribution of Pb in soil and sediments of District Rahim Yar Khan

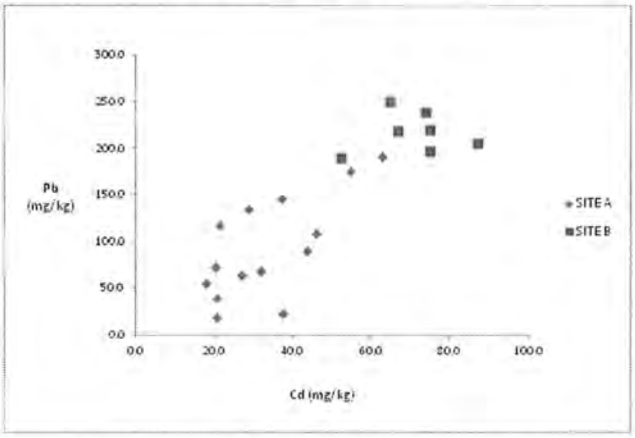


Figure 3.11b: Relationship of Pb vs. Cd

g) Cadmium

The concentration of Cd crossed the safe limits of SEPA (0.6mg/kg) in all of the samples. The agricultural soil samples of Site A had a mean and range value of 27.7mg/kg and 17.8043.6mg/kg. BP and CP33 had the largest and lowest value of Cd. The sampling points of agricultural soils showed the following order i.e.,

CP33 < SHK < KK< CK104L < CNK < JJA < CNK < ZP < TRM < DNK < BP

The sediment samples of Site had a mean and range value of 54.4mg/kg and 46.03-62.7mg/kg. The highest and lowest value was recorded in the samples of AC and RI. The following order was observed for the sediment samples i.e.,

RI < PC < AC

The Site B had a mean and range value of 70.7mg/kg and 52.4-87.03mg/kg. Highest and smallest value was recorded in the samples of MI and SI (1). The marble industry made the largest contribution and the soap industry made the smallest contribution for Cd metal in the industrial area of Site B. the sampling points showed the following order for industrial soil samples of Site B i.e.,

MI < CI < AI < SI (2) < RCI < TI < SI (2) < SI (1)

Cd observed the following order i.e., Site A < Site B. The industrial soil samples were more contaminated than the agricultural soil samples as shown in (Figure 3.12b).

Positive correlation was observed between Cd-Pb ($r = 0.88$), Cd-Cr ($r = 0.51$) and Cd-Mn ($r = 0.49$). The Cd levels were much higher than the agricultural soils of Bangladesh (Rahman, Khanam et al. 2012) and sediments of Rawal Lake (Zahra, Hashmi et al. 2014). There are various sources of Cd including batteries, pigments, paints, plastics, ceramics, glasses, enamels, construction material and sewage sludge applications. The possible sources of higher Cd levels in the current study might be sewage sludge applications, construction and developmental activities and industrial applications (US-EPA 2003). The Cd exposure can cause the health problems such as nausea, vomiting, diarrhea, muscle cramps, salvation, sensory disturbances, liver injury convulsions, shocks and renal failure. Long term exposure can cause certain effects such as kidney, liver, bone and blood damages (US-EPA 2003).

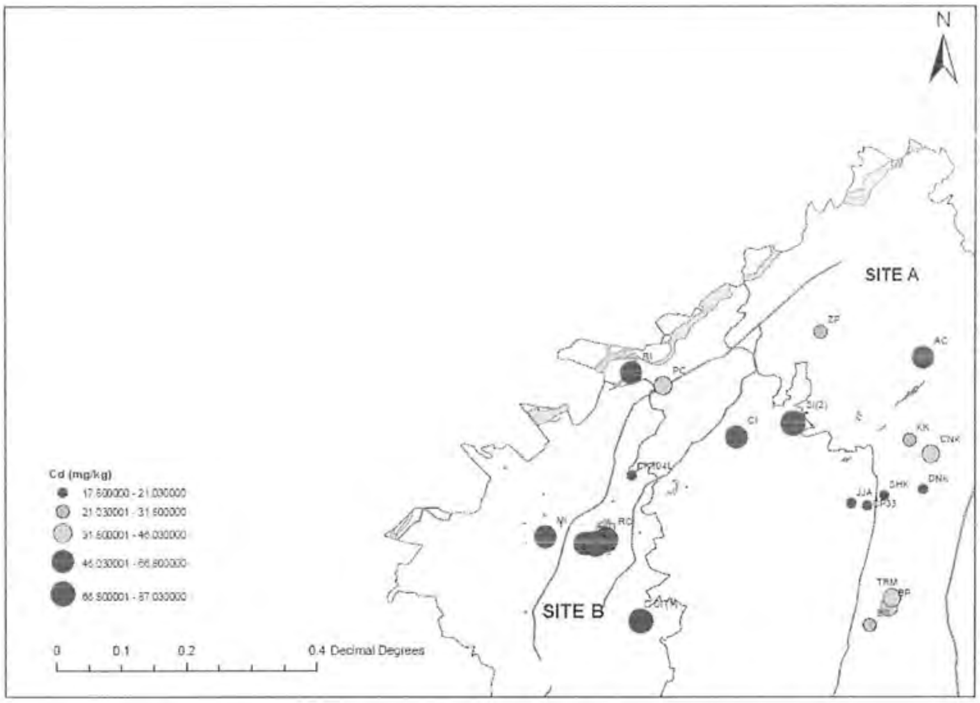


Figure 3.12b: Spatial distribution of Cd in soil and sediments of District Rahim Yar Khan

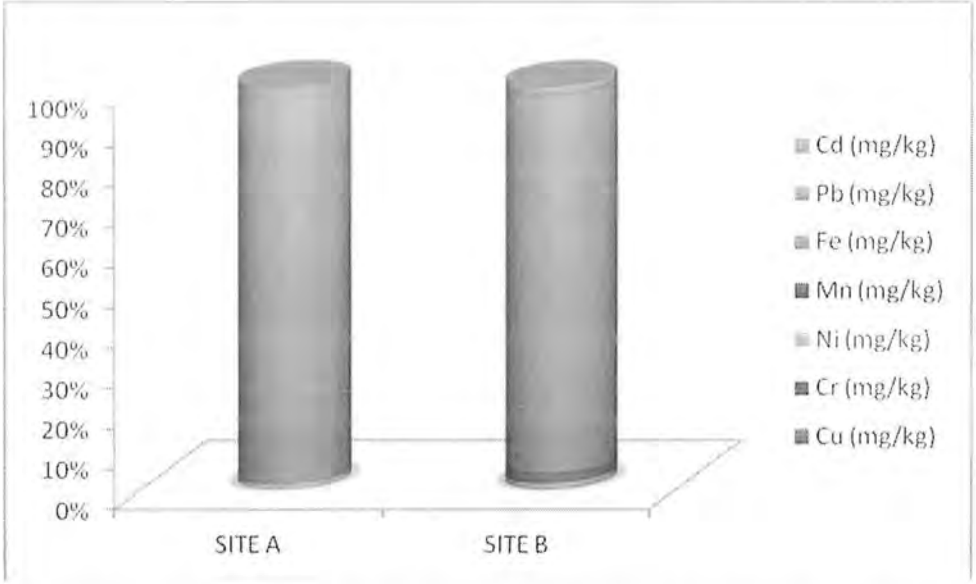


Figure.3.13b: Trace metals in soil and sediment samples of Site A and Site B

3.3: Role of pH, organic matter and soil texture in retention of trace metals

There are various factors controlling the concentration of various trace and heavy metals in water and sediments. These include pH, organic matter and soil texture and all of these factors play a significant role in this regard. At low pH competition between metals and hydrogen ions for binding sites increases which may dissolve metal complexes releasing free metal ions into the water column (Praveena, Ahmed et al. 2007), while heavy metals at alkaline pH generally precipitate (Jain et al., 2007). The findings of the current study showed opposite trend, as all of the samples were alkaline in nature and highly enriched with trace metals. The results of the current study suggested that the metals concentration was higher at high pH but they were not mobile, as the metals are mobile at low pH.

Soil texture plays an important role in bioavailability and toxicity of heavy metals in sediments, as metals are not homogeneously distributed over various grain size fractions. Grain size and OM have greater surface area for metal adsorptions (Yan and Tang 2009) and influence their distribution (Rodríguez-Barroso, García-Morales et al. 2010). Fine grain sediments and more organic matter facilitate the accumulation of more heavy metal contents. It means that sediments having greater proportion of fine grain size particles i.e., sand and higher proportion of organic matter are highly enriched with trace metals (Lin, He et al. 2008). Similar, trend was observed in the results of the present study, as all of the samples were highly enriched with organic matter and had the greatest proportion sand. According to the findings of the present study, OM and soil texture resulted in the increase of Cu, Ni and Mn concentration, as positive correlation existed between Cr-OM ($r = 0.62$) and Cr-sand ($r = 0.45$), Ni-OM ($r = 0.52$) and Ni-clay ($r = 0.40$) and Mn-OM ($r = 0.38$). Thus, the results of the present study showed that the trace metals were present at higher levels in the alkaline soil and sediment samples having greater proportion of sand and organic matter. Similar pattern was observed in the previous studies conducted in Rawal Lake (Zahra, Hashmi et al. 2014) and China (Khan, Cao et al. 2008).

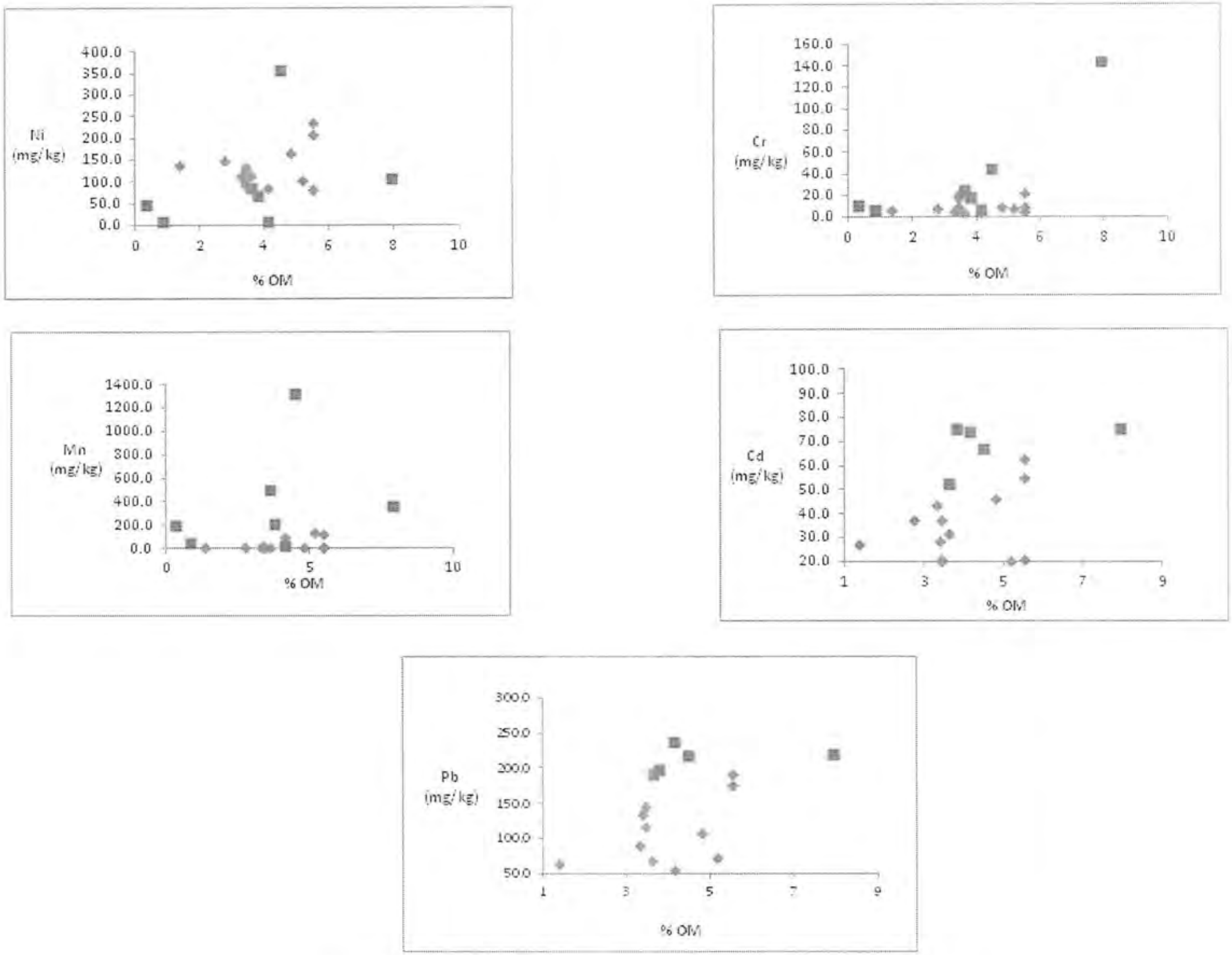


Figure 3.14b: Relationship of OM with various metals

Table 3.2b: The concentration of trace metals in soils and sediments of District Rahim Yar Khan

	Sample ID	Depth (cm)	Cu (mg/Kg)	Cr (mg/kg)	Ni (mg/Kg)	Mn (mg/kg)	Fe (mg/kg)	Pb (mg/kg)	Cd (mg/kg)
SITE A	CK104L	0-30	8.6	5.4	81.3	117.6	7002.8	19.7	20.6
	CP33	0-30	4	3.6	84.7	95.2	9418.6	55.7	17.8
	SHK	0-30	9.8	7.2	104.3	134.6	11452.6	73.1	20.2
	DNK	0-30	6.8	9.8	93.7	8.8	10555.8	117.7	21.03
	CNK	0-30	226	7.2	147.2	4.6	94440.4	23.5	37.4
	KK	0-30	15.6	20.0	125.8	6.2	14314.8	134.5	28.6
	JJA	0-30	7.4	6.6	102.6	15	2990.6	39.5	20.4
	BS	0-30	16.2	6.8	137.8	2.6	13565.6	64.1	26.8
	BP	0-30	5.4	4.4	113.4	5.2	10958.4	89.7	43.6
	ZP	0-30	14.8	4.2	114.1	6.2	14348.6	67.7	31.8
	TRM	0-30	7.2	18.2	133	12.2	14715	145.7	37.2
	RI	0-30	17.3	9.9	208.1	10.8	15623.6	190.7	62.7
	PC	0-30	7.3	8.7	165.9	7.7	12724.8	108.7	46.03
	AC	0-30	13.3	21.2	234.5	5.5	6448.4	174.7	54.7
	Mean		25.6	9.5	131.8	8	17040	93.2	33.4
	Maximum		225.9	21.2	234.5	134.6	94440.4	190.7	62.7
	Minimum		3.9	3.6	81.2	2.6	2990.6	19.7	17.8
SITE B	AI	0-30	14.4	44.6	358.4	1320.6	16999.6	217.9	66.8
	MI	0-30	7.6	24.6	86	498.8	15863.6	190.1	52.4
	SI (1)	0-30	4	10.8	47	200	8891.6	204.7	87.03
	RCI	0-30	7.4	17.8	68.2	204	10159.6	196.9	75.03
	TI	0-30	31.8	143.4	107.8	361	10455.6	220.1	75.03
	SI(2)	0-30	4.2	6.4	8.8	20	9999.6	237.9	74.03
	CI	0-30	4.6	6.2	7.8	40	10919.6	250.7	64.8
	Mean		10.6	36.3	97.7	377.8	11898.5	216.9	70.7
	Maximum		31.8	143.4	358.4	1320.6	16999.6	250.7	87.03
	Minimum		4	6.2	7.8	20	8891.6	190.1	52.4

3.4: Higher levels of trace metals in soil causing groundwater pollution

The 2 matrices including water and soil are interlinked with other. There are various processes which play an important role in the release of various pollutants from soil into water. Infact, soil is the major cause for the pollution of drinking water whether it is in the form of surface or groundwater. Soil is the most environmental component because it is not only a geochemical sink for pollutants but also a natural buffer for the pollutants by controlling the transport of chemical elements and substances to the atmosphere, hydrosphere and biosphere (Khan, Rehman et al. 2010). It has the capacity to accumulate heavy metals resulting from the deposition of particles emitted by urban and industrial activities, vehicular exhausts and industrial practices. The heavy metals may be leached from soil into water and their availability to the plants and other organisms depends upon the soluble/exchangeable fraction of these metals (Rodríguez-Barroso, García-Morales et al. 2010).

In the current study, there were 11 similar sampling points for water and soil. All of these samples were collected from the Site A (agricultural area). Correlation was also carried out between the similar sampling points of both matrices in order to determine the relationship of between soil and water. In the current study, it was observed that significant positive correlation existed between Cd water-Cd soil (r =0.644) and Pb water- Pb soil (r =0.874). Thus, the results showed that the trace metals present in soil are the possible source for groundwater pollution. Trace metals including Pb and Cd might be the possible source of groundwater pollution in the study area, as positive correlation existed between Cd water-Cd soil (r =0.644) and Pb water- Pb soil (r =0.874) as shown in Table 3.3b and Figure 3.15b.

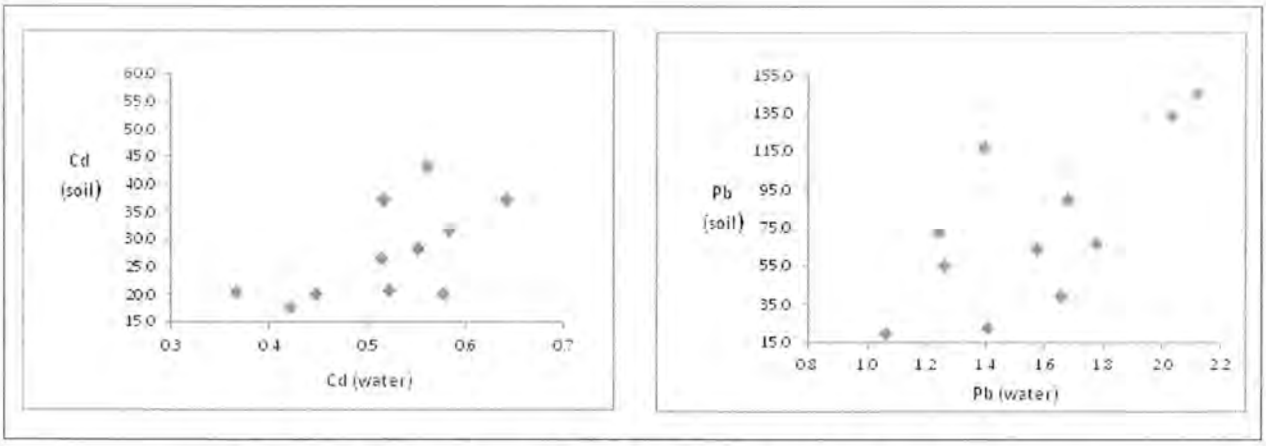


Figure 3.15b: Relationship of Cd and Pb levels in both soil and water samples

		pH (water)	pH (soil)	EC (water)	EC (soil)	TDS (water)	TDS (soil)	Fe (water)	Fe (soil)	Cd (water)	Cd (soil)	Pb (water)	Pb (soil)
pH (water)	Pearson Correlation	1											
	Sig. (2-tailed)												
pH (soil)	Pearson Correlation	-.381	1										
	Sig. (2-tailed)	.247											
EC (water)	Pearson Correlation	-.519	.546	1									
	Sig. (2-tailed)	.102	.082										
EC (soil)	Pearson Correlation	**.645***	-.339	-.443	1								
	Sig. (2-tailed)	.032	.307	.173									
TDS (water)	Pearson Correlation	-.520	.546	**1.000****	-.443	1							
	Sig. (2-tailed)	.101	.082	.000	.172								
TDS (soil)	Pearson Correlation	.572	.043	-.246	.222	-.246	1						
	Sig. (2-tailed)	.066	.899	.466	.512	.466							
Fe (water)	Pearson Correlation	.469	**-.683***	-.408	.337	-.408	-.141	1					
	Sig. (2-tailed)	.146	.021	.213	.311	.213	.678						
Fe (soil)	Pearson Correlation	-.171	-.375	-.004	.100	-.003	-.129	-.050	1				
	Sig. (2-tailed)	.614	.256	.991	.770	.992	.706	.885					
Cd (water)	Pearson Correlation	.545	-.494	**-.682***	**.833****	**-.683***	.076	.306	.021	1			
	Sig. (2-tailed)	.083	.123	.021	.001	.021	.824	.361	.952				
Cd (soil)	Pearson Correlation	.408	-.330	-.502	**.702***	-.502	.053	.350	.416	**.644***	1		
	Sig. (2-tailed)	.213	.322	.116	.016	.116	.877	.292	.203	.032			
Pb (water)	Pearson Correlation	.569	-.503	**-.720***	**.774****	-.720*	-.025	.546	-.092	**.874****	.588	1	
	Sig. (2-tailed)	.068	.115	.012	.005	.012	.941	.082	.788	.000	.057		
Pb (soil)	Pearson Correlation	**.676***	-.203	-.292	.487	-.292	.041	.550	-.314	.459	.287	**.705***	1
	Sig. (2-tailed)	.022	.550	.384	.129	.383	.906	.080	.347	.156	.392	.015	

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

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

*Correlation for depth of soil, Cu, Mn and Ni was not computed due to constant value

Table 3.3b: Correlation matrix between similar parameters of water and soil of similar sampling points

3.5: Health Risk Assessment of Trace Metals in soil and sediments

The health risk assessment of trace metals in soil and sediment samples was determined via various methods including Geo-Accumulation index, Enrichment Factor, Contamination Factor and Degree of Contamination. The results of all these factors are summarized in Table 3.6b. The results of all significant results were also plotted via boxplots.

a) Geo-Accumulation Index (I_{geo})

The Geo-Accumulation index is the quantitative measure of pollution index by comparing the current and pre-industrial concentrations in soil and sediments. Any increase in the current level is an indication of anthropogenic pollution. The natural fluctuations in metal contents of soil and sediments are countered by a constant factor 1.5 (Iqbal and Shah 2011). The I_{geo} values are categorized into various classes for the determination of soil and sediment throughout the world (Table 3.4b).

The mean and range of I_{geo} values for Cu was 0.06 and 0-0.8, respectively. The I_{geo} value for Cu showed very little pollution in all samples, as all of the values were less than 1. The samples were free from Cr pollution. The mean and range value for Cr was 0.01 and 0-0.3. The I_{geo} values for Ni indicated moderate contamination, as all of the values were slightly greater than 0. Similarly, all of the I_{geo} values for Fe indicted un-polluted sites. Ni had a mean and range value of 0.3 and 0.02-0.95. Majority of the samples were unpolluted in terms of Mn and only few of samples showed very slight contamination. The mean and range of I_{geo} values for Pb was 2.1and 0.3-4 respectively. 19.03% samples had I_{geo} values indicated low to moderate contamination, 28.5% samples exhibited moderate contamination, 14.2% samples exhibited moderate-heavy contamination and 38.1% samples were heavily contaminated for Pb. The results of Cd were very much alarming and demonstrated that all the values even crossed the International classes of I_{geo}. The mean and range value was 46.01 and17.8-87.3, respectively. Thus, all of the samples were severely polluted with Cd thus indicating the role of various anthropogenic activities in the study area. The following order of I_{geo} values for all of the metals was observed i.e., Cr > Mn > Cu > Fe > Ni > Pb > Cd. Thus, in can be concluded the anthropogenic sources are the major cause for Ni, Cd and Pb pollution in soil and sediments samples.

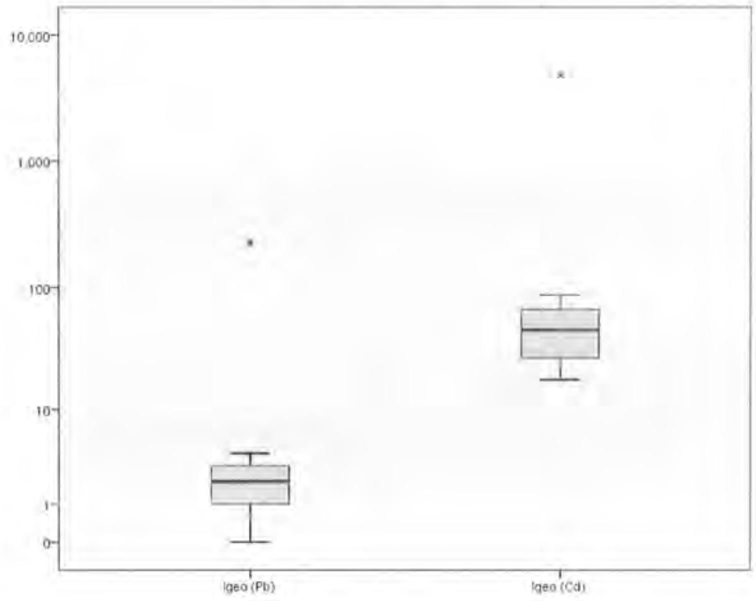


Figure 3.16b: Igeo values for Pb and Cd

b) Enrichment Factor

Enrichment factor is also used for the determination of anthropogenic sources of pollution in soil and sediments. It is based on the standardization of a measured metal against a reference metal. In the current study, Fe was used as a reference metal because of its uniform distribution in earth's crust. Moreover, it is characterized by fine solid surfaces and its geochemistry is similar with many metals (Iqbal and Shah 2011). The EF values are divided into various classes throughout the world as described in Table 3.4b. The EF values of all measured metals except Fe showed deficient to minimal enrichment. The mean and range of EF value for Fe was 3.4 and 0.3-12. The EF value for only 1 sample was less than 1. About 8 sites were characterized with minor enrichment, 6 sites were characterized with moderate enrichment, 2 sites had moderately severe enrichment and only 1 site had severe enrichment. The trace metals were arranged in the following ascending order in terms of their EF values i.e., Cu > Mn > Cr > Ni > Pb > Cd > Fe.

Table 3.4b: Description of Enrichment factor and Igeo classes in relation to soil/sediment quality

EF classes	Soil/Sediment quality	Igeo	Igeo class	Soil/Sediment quality
EF < 1	No Enrichment	0-0		Unpolluted
EF < 3	Minor Enrichment	0-1	0	Unpolluted to moderately polluted
			1	
EF 3-5	Moderately Enrichment	1-2		Moderately polluted
EF 5-10	Moderately Severe Enrichment	2-3	2	Moderately to highly polluted
			3	
EF 10-25	Severe Enrichment	3-4	4	Highly polluted
EF 25-30	Extremely Severe Enrichment	4-5	5	Highly to very highly polluted
		5-6	6	Very highly polluted

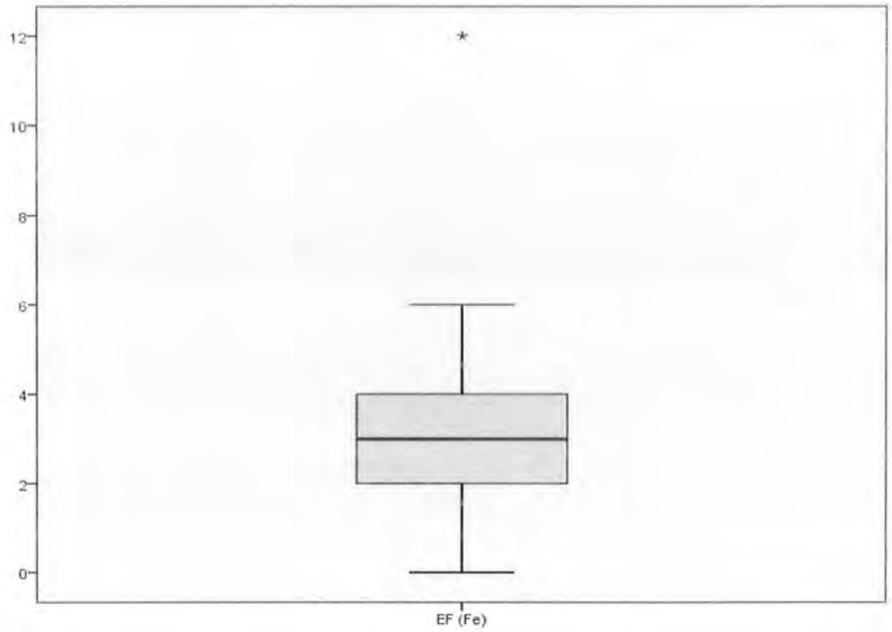


Figure 3.17b: EF value for Fe

c) Contamination Factor and Degree of Contamination

The degree of contamination is a cumulative index used for the determination of overall contamination caused by each metal. It is basically the aggregate sum of all contamination factors of each site of a particular metal. It is considered as more appropriate parameter to assess overall contamination by all measured elements in soil and sediments, hence act as a cumulative index (Iqbal and Shah 2011). Different classes of contamination factor and degree of contamination are summarized in Table 3.5b. The Cu metal had low degree of contamination in all of the sites except 1 site exhibited considerable contamination. Cr showed the C_{deg} and C_f values within the safe limits in all of the sites. All of the C_f values for Ni indicated very low to moderate contamination factor. However, the C_{deg} of Ni showed very high degree of contamination in all of its sites. Only 1 site had moderate contamination factor and rest of the sites were characterized with low degree of contamination for Mn. Mn had very low degree of contamination in all of the sites. All of the C_f values of Fe showed low contamination factor and it also exhibited very low degree of contamination for all of the sites. Both, Pb and Cd showed quite alarming results and their degree of contamination even crossed all of its classes. Both, of these metals exhibited the highest degree of contamination and their C_f values crossed the safe limits in all of the sites. The metals exhibited this order for their C_f and C_{deg} values i.e., Cr > Mn > Ni > Cu > Fe > Pb > Cd.

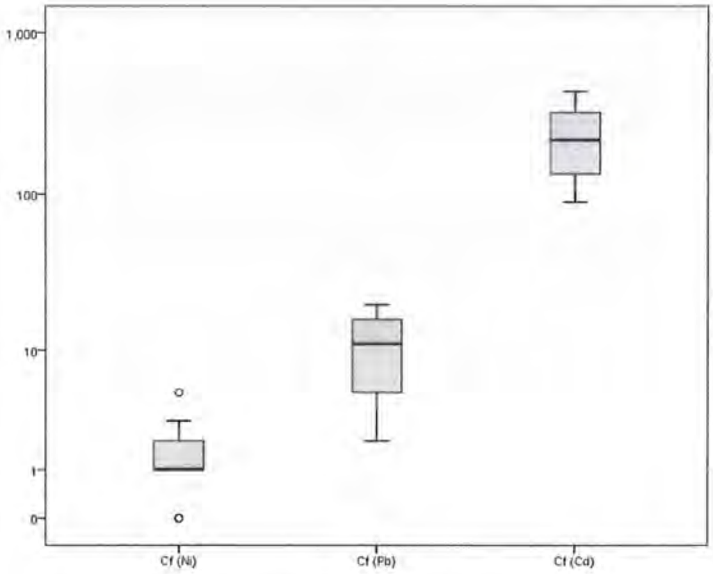


Figure 3.18b: Cf values of Pb, Cd and Ni

Table.3.5b: Description of Contamination factor and Degree of Contamination

C_f classes	Soil/Sediment quality	C_{deg} classes	Soil/Sediment quality
$C_f < 1$	Low contamination factor indicating low contamination	$C_{deg} < 8$	Low degree of contamination
$1 \leq C_f < 3$	Moderate contamination factor	$8 \leq C_{deg} < 16$	Moderate degree of contamination
$1 \leq C_f < 6$	Considerable contamination factor	$16 \leq C_{deg} < 32$	Considerable degree of contamination
$6 \leq C_f$	Very high contamination factor	$32 \leq C_{deg}$	Very high degree of contamination

Table 3.6b: Igeo, EF and Cf values of all trace metals in the study area

Sample code	Cu			Cr			Pb			Cd			Ni			Fe			Mn		
	I_{geo}	EF	C_f	I_{geo}	EF	C_f	I_{geo}	EF	C_f	I_{geo}	EF	C_f	I_{geo}	EF	C_f	I_{geo}	EF	C_f	I_{geo}	EF	C_f
CK104L	0	0	0.2	0	0.0008	0.05	0.3	0.0008	1.5	20.6	0.0007	103	0.21	8E-04	1.08	0.03	5.1	0.1	0	0	0.2
CP33	0	0	0.1	0	0.0005	0.03	0.9	0.0006	4.4	17.8	0.0005	89	0.22	5E-04	1.1	0.05	3.8	0.2	0	0	0.1
SHK	0	0	0.2	0	0.0004	0.07	1.2	0.0005	5.8	20.2	0.004	101	0.27	4E-04	1.3	0.06	3.1	0.3	0	0	0.2
DNK	0	0	0.1	0	0.0005	0.09	1.9	0.0005	9.4	21.1	0.0005	105.1	0.25	5E-04	1.2	0.05	3.4	0.2	0	0	0
CNK	0.8	0	4.1	0	5.90E-05	0.07	0.4	0.0001	1.8	37.5	5.9	187	0.39	5E-04	1.9	0.2	0.3	2.6	0	0	0
KK	0.1	0	0.3	0	0.0003	0.2	2.2	0.0004	10.7	28.6	0.0003	143	0.33	3E-04	1.6	0.08	2.5	0.3	0	0	0
JJA	0	0	0.1	0	0.001	0.06	0.6	0.0019	3.1	20.4	0.001	102	0.27	0.001	1.3	0.01	12	0.08	0	0	0
BS	0.1	0	0.3	0	0.0004	0.06	1	0.0004	5.1	26.8	0.0004	134	0.36	4E-04	1.8	0.07	2.6	0.3	0	0	0
BP	0	0	0.1	0	0.0005	0.04	1.4	0.0005	7.1	43.7	0.0005	218	0.3	5E-04	1.5	0.06	3.2	0.3	0	0	0
ZP	0.1	0	0.3	0	0.0003	0.04	1.1	0.0004	5.4	31.9	0.0003	159	0.3	3E-04	1.5	0.08	2.5	0.3	0	0	0
TRM	0	0	0.1	0	0.0003	0.1	2.3	0.0004	11.6	37.3	0.0003	186	0.35	3E-04	1.7	0.08	2.4	0.4	0	0	0
AI	0.1	0	0.3	0.1	0.0003	0.4	3.5	0.0003	17.4	67.02	0.0003	334	0.95	3E-04	4.7	0.09	2.1	0.4	0.4	0	1.8
MI	0	0	0.1	0	0.0003	0.2	3.1	0.0004	15.2	52.5	0.0003	262	0.23	3E-04	1.1	0.08	2.2	0.4	0.1	0	0.7
SI (1)	0	0	0.1	0	0.0006	0.1	3.3	0.0006	16.3	87.3	0.0006	435.1	0.12	6E-04	0.6	0.04	4	0.2	0.1	0	0.3
RCI	0	0	0.1	0	0.0005	0.1	3.2	0.0006	15.7	75.2	0.0005	375.1	0.18	5E-04	0.9	0.05	3.5	0.2	0.1	0	0.3
TI	0.1	0	0.6	0.3	0.0005	1.43	3.5	0.0005	17.6	75.2	0.0005	375.1	0.28	5E-04	1.4	0.05	3.4	0.2	0.1	0	0.5
SI(2)	0	0	0.1	0	0.0005	0.06	3.8	0.0006	19.03	74.2	0.0005	370.1	0.02	5E-04	0.1	0.05	3.5	0.2	0	0	0
CI	0	0	0.1	0	0.0005	0.06	4	0.0005	20	65.01	0.0005	324	0.02	5E-04	0.1	0.06	3.2	0.3	0	0	0.1
RI	0.1	0	0.3	0	0.0003	0.09	3.1	0.0004	15.2	62.9	0.0003	313.5	0.55	3E-04	2.7	0.08	2.2	0.4	0	0	0
PC	0	0	0.1	0	0.0004	0.08	1.7	0.0004	8.6	46.1	0.0004	230.1	0.44	4E-04	2.2	0.07	2.8	0.3	0	0	0
AC	0	0	0.2	0	0.0008	0.2	2.8	0.0009	13.9		0.0008	273.5	0.62	8E-04	3.1	0.03	5.5	0.1	0	0	0
C_{deg}	7.9			0.009			225.8			4819.9			32.8			7.7			4.2		

3.6: Identification of pollution sources via Cluster Analysis (CA) and Principal Component Analysis (PCA)

3.6.1: Cluster Analysis of sampling sites

Cluster Analysis is a multivariate analysis technique used for the grouping or clustering of similar objects in the same class (Danielsson, Cato et al. 1999). Levels of similarity at which observations are merged, used to construct a dendogram (Chen, Wang et al. 2005). Cluster analysis was used to identify spatial variability between the sites based on physicochemical parameters. The resulted dendogram (Fig.3.19b) grouped all the 21 sampling sites into three statistically significant clusters.

The Group 1 and 2 made the major contribution to total variance of the data set. Group 2 showed 50% variation to the data set. Group 1 and 3 together contributed about 50% variance to the data.

The group 1 comprised of AI, MI, TI, RCI, SI(1) and CI. The group 2 comprised of BS, BP, JJA, CNK, TRM, DNK, and KK. The group 3 included the sites SHK, SI (2), CP33 and CK104L. All three clusters comprise of sampling sites with comparable characteristics and natural background that are affected by sources of similar strength/type. The CA technique is helpful in offering consistent classification of Soil and sediment samples in the whole region and may serve as good in spatial assessment of the water quality as the whole network. The same aspect is also reported by other researchers (Kim, Kim et al. 2005).

3.6.2: Principle Component Analysis

PCA is also a multivariate technique used for the source identification of various physio-chemical parameters. PCA resulted in the reduction of entire data set into 4 statistically significant factors or axis (Table 3.7b). All of these Axes explained about 97.8% of data variation. Principal component analysis (PCA) transforms large data sets into fewer significant dimensions and evaluates the degree of contribution for pollutant sources. PCA results are summarized in Table 3.7b, which shows the variable loadings characterizing the main contamination patterns and their explained variance. High positive and negative loadings indicate the significance of variables. Different variables have varying association in each of the principal component (PC).

Among all of these Axes, the first 2 Axes were most important as they accounted for about 96.2% of total variation in data set. The Axes 1 was most important which contributed about 95.1% to total variance with significant positive loading of pH and % sand. Both of these variables showed the natural and geogenic origin of Axis 1. The Axis 2 and Axis 3 contributed about 1.07% and 0.8% variation to the data set. The Axis 4 accounted for 0.7% of variation to the whole data set with significant positive loading of Cu and Fe. The Axis 4 had its natural and geogenic origin, as both of these variables originated due to their natural sources in soil and sediments.

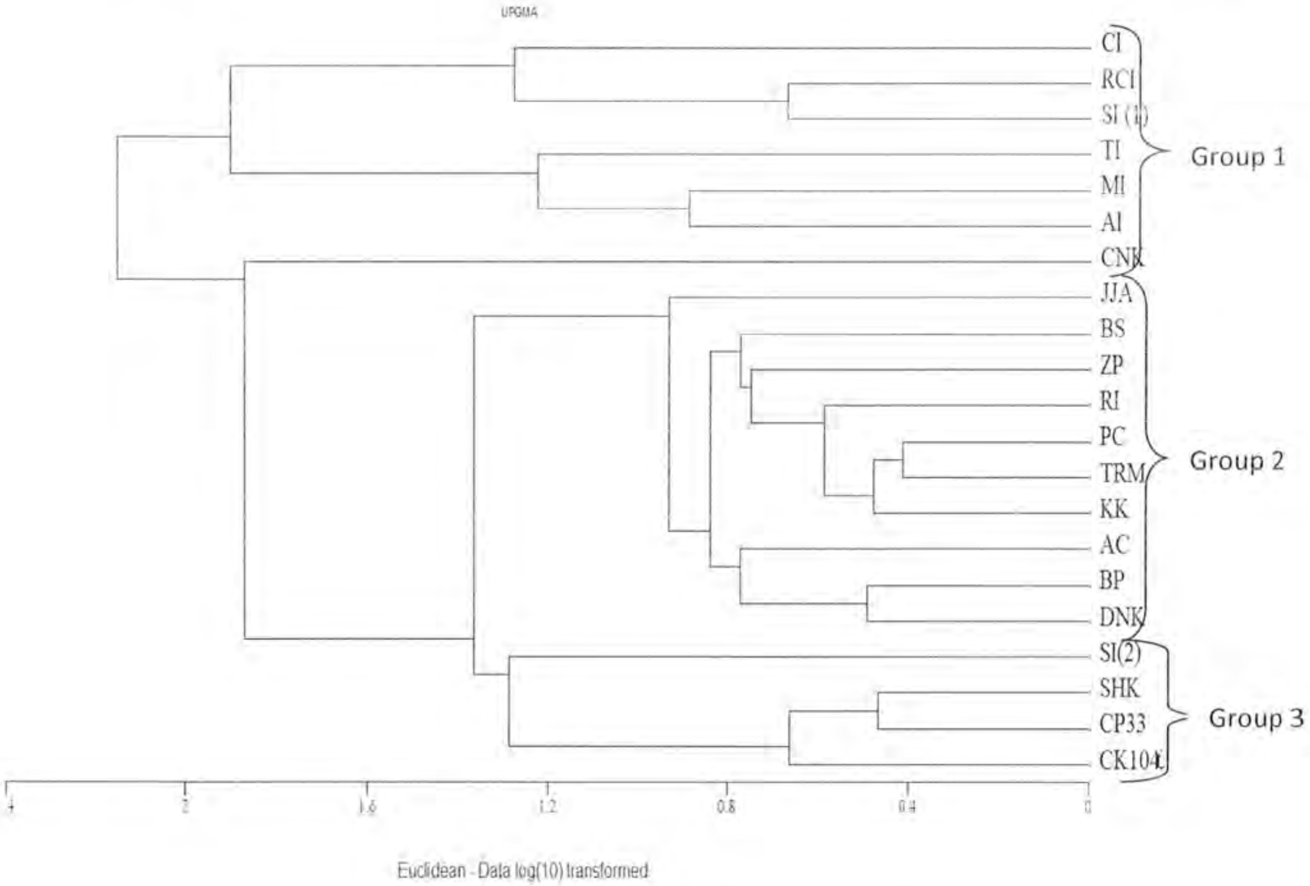


Figure.3.19b: Dendogram showing clustering of various groups of soil and sediment samples

Table 3.7b: PCA loadings of selected metals in soil and sediment samples

	Axis 1	Axis 2	Axis 3	Axis 4
pH	**0.565**	0.346	-0.011	-0.274
EC (uS/cm)	0.04	-0.3	0.198	-0.193
TDS (mg/L)	0.04	-0.3	0.198	-0.193
% Sand	**0.75**	-0.134	0.175	0.069
% Silt	0.083	0.254	-0.064	-0.121
% Clay	0.109	0.295	0.03	0.107
% OC (w/w)	0.135	0.056	-0.48	0.143
% TOC (w/w)	0.135	0.055	-0.476	0.141
% 0M (w/w)	0.135	-0.276	0.241	0.032
Cu (mg/Kg)	0.025	0.121	0.271	**0.512**
Cr (mg/kg)	0.037	-0.348	0.047	0.161
Ni (mg/Kg)	0.094	-0.205	0.012	0.308
Mn (mg/kg)	0.03	-0.216	-0.368	0.329
Fe (mg/kg)	0.049	0.15	0.239	**0.526**
Pb (mg/kg)	0.108	-0.33	-0.256	-0.104
Cd (mg/kg)	0.125	-0.305	-0.195	0.015
Percentage	95.136	1.07	0.892	0.735
Cum. Percentage	95.136	96.205	97.097	97.832

Conclusion

Section A: Water

1. The findings of water revealed that all of the groundwater samples were alkaline in nature, categorized by moderate to higher values of EC, TDS and higher DO values. Moreover, it was observed that the shallow groundwater samples had higher pH, EC and TDS except DO values than deeper groundwater samples.
2. Groundwater chemistry is $Na^+/K^+-HCO_3^-$ type.
3. The major anions in groundwater showed this order in all samples i.e., $NO_3^- < PO_4^{-3} < SO_4^{-2} < Cl^- < HCO_3^-$ and the major cations in the groundwater exhibited this order i.e., $K^+ < Ca^{+2} < Mg^{+2} < Na^+$.
4. The findings demonstrated that the groundwater samples were categorized by higher values of nitrates, phosphates, bicarbonates and potassium. However, the rest of the cations and anions were within the permissible limits in most of the samples. The findings of the current study demonstrated that Site A of agricultural area had higher values of all anions and cations except chlorides and bicarbonates than the industrial area of Site B indicating the extravagant usage of fertilizers as their major source.
5. The results of water revealed that the shallow groundwater samples were more contaminated than deep groundwater samples with all pollutants except arsenic, fluoride and sulphates as the opposite trend was observed in their case.
6. All of the groundwater sample had higher values of fluoride $\geq$ WHO limit and low levels of calcium and magnesium which shows calcite precipitation under alkaline conditions and ultimately increasing the concentration of fluoride from fluoride minerals.
7. It was observed that the industrial area of Site B was more contaminated than the agricultural area of Site A ; indicating as agricultural fertilizers, industrial wastes and soil enrichment with fluoride bearing minerals as the major source. The HQ values of fluorides revealed severe health risk for the exposed population.
8. Arsenic levels crossed the permissible levels in 32.5% samples and it was observed that higher levels of arsenic were detected in the samples located near River Indus as compared to the samples located far from it. The basic mechanism supporting the higher levels of arsenic in the current study was desorption of arsenic via PO_4^{-3} at high pH. The speciation of arsenic was not conducted in the present study. It was observed that arsenic

levels was much higher in the agricultural area of Site A than the industrial area of Site B, thus indicating as the superfluous usage of phosphatic fertilizers the major source of arsenic in groundwater.

9. The trace metals showed the following order in terms of their concentration and health risk assessment in groundwater samples i.e., Cu > Cr > Mn > Ni > Fe > Pb > Cd. Cu and Cr were below the detection limits in most of the samples and the Mn levels was within the safe limits in all of the groundwater samples. The Ni concentration crossed the WHO limits in 70.5% samples, Fe concentration exceeded the safe limits in 29.4% samples, Pb and Cd surpassed the permissible limits in 100% samples. It was observed that the shallow groundwater samples had higher levels of these metals than deep groundwater samples of Site A. It was also observed that the Site B was more contaminated with Fe, Pb and Cd than Site B, thus suggesting the industrial applications as there major source. However, the Site A had higher values of Ni and Mn,
10. Hence, on the basis of the current study, it can be concluded that the examined groundwater of both Site A (Tehsil Khan pur) and Site B (Tehsil Rahim Yar Khan) was unfit for drinking purpose, as higher levels of nitrates, phosphates, fluorides, arsenic and trace metals including iron, lead, nickel and cadmium were found in most of the samples.

Section B: Soil and Sediments

1. All of the soil and sediment samples were alkaline in nature, categorized by low EC and TDS values. The organic matter was within the limits set by Fenton et al., 2008 and exceeded the limit in only 1 sample. Most of the samples were categorized by sandy loam and loamy sand texture. All of the samples comprised fine grain particles, as sand formed the major component in all of the samples. It was observed that the agricultural soil and sediment samples of Site A had higher values of pH, EC, TDS and organic matter than the industrial soil samples of Site B.
2. The trace metals of soil and sediment samples showed the following order in all of the samples i.e., Cr > Cu > Cd > Ni > Pb > Mn > Fe.
3. The results of soil and sediments revealed that the Cu crossed the SEPA limits in only 1 sample; Cr and Pb levels were within the safe limits of SEPA in all of the samples. However, the Ni levels crossed the SEPA limits in 90% samples and Cd levels surpassed

the SEPA limits in 100% samples. The Mn and Fe concentration was less than the background values set by Taylor (1964).Moreover, the results also demonstrated that the industrial soil samples had had higher values of all trace metals except Cu than agricultural soil and sediment samples of Site A.

4. The geo-accumulation index (I_{geo} values) of the soil and sediment samples demonstrated that Cu, Cr, Fe and Mn showed minor contamination in all of the samples. While, Ni showed moderate contamination in all samples, Pb and Cd showed moderate to severe contamination in all of the samples. Thus, in can be concluded the anthropogenic sources are the major cause for Ni, Cd and Pb pollution in soil and sediments samples. I_{geo} values showed this order for all metals i.e., Cr > Mn > Cu > Fe > Ni > Pb > Cd.
5. The significant results of enrichment factor were observed only for the metal Fe. Fe showed minor to severe enrichment in all of samples. The trace metals were arranged in the following ascending order in terms of their EF values i.e., Cu > Mn > Cr > Ni > Pb > Cd > Fe.
6. The results of degree of contamination and contamination factor showed that the metals Pb, Cd and Ni showed the highest level of contamination among other metals. The metals exhibited this order for their C_f and C_{deg} values i.e., Cr > Mn > Ni > Cu > Fe > Pb > Cd.

Recommendations for Future Study:

On the basis of the findings of the current study the following recommendations were proposed for the future study:

- With respect to arsenic well switching is the first measures to be taken by the residents, as the present study shows some wells even do not contain arsenic or it is below the permissible limit of 10ppb. By sharing the neighboring well of low arsenic people of the affected area can avoid the further health effects of arsenic poisoning.
- In most of the areas in Pakistan people do not know the concentration of arsenic and fluoride, which are among the most dangerous pollutants in terms of health risk. On priority basis monitoring of each and every well should be started in the country.
- This monitoring should be on regular basis.

- The government must install efficient water treatment plants for treating the drinking water before consumption, as the drinking water of the current study area is not fit for drinking purpose.
- Proper training must be given to farmers regarding the sustainable and efficient use of fertilizers and pesticides, as the farmers are uneducated and are aware about the problems arising from the excessive usage of fertilizers.
- Moreover, mass awareness campaigns should be launched in the area, in order to give awareness to the local people regarding the drinking water problems in the study area.
- The government and various other organizations must develop efficient solid waste management systems for the disposal of solid waste and sewage sludge.
- Moreover, the industrial effluents must be properly treated before discharge and there must regular monitoring of the application of wastewater for irrigation purpose in the study area.
- Moreover, efficient and low cost systems may be devised for the simultaneous removal of arsenic and fluoride from drinking water in the current study area. Both, of these pollutants can be removed from water simultaneously via drinking water by using various naturally occurring materials or minerals. For example, goethite can remove simultaneously remove arsenic and fluoride from drinking water (Tang, Wang et al. 2010).
- Further studies must be carried out regarding assessment of arsenic and fluoride in the study area, in order to further investigate the possible mechanisms responsible for higher levels of arsenic and fluoride in drinking water.

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Annexure A: Table A.1 Field parameters of water samples

	Sampling location	Sample ID	Source	Depth (ft)	Union council	Type of depth	Latitude	Longitude	No. of people using it
SITE A	Basti Chak 104L	CK104L	H.P	30	Chak P 45	Shallow	34.10583	73.19556	150
		CK104L	T.W	70		Shallow			
	Bsti Chak P33	CP33	T.W	60	Bagobahar	Shallow	28.67528	70.81389	500
		CP33	M.P	20		Shallow			
		CP33	H.P	20		Shallow			
	Basti Sheikhan	SHK	H.P	55	Mari	Shallow	28.69083	70.83972	1200
		SHK	H.P	55		Shallow			
		SHK	M.P	55		Shallow			
		SHK	M.P	55		Shallow			
	Basti Dharecha Nagar Khakwani	DNK	H.P	60	Sehja	Shallow	28.69176	70.83833	5000
		DNK	M.P	60		Shallow			
	Basti ChAh Nasrullah Khan	CNK	H.P	70	Deen pur Sharif	Shallow	28.69083	70.9123	1000
	Basti Khokran	KK	H.P	50	Kotla Pathan	Shallow	28.7533	70.8791	84000
		KK	M.P	50		Shallow			
		KK	R.P	50		Shallow			
	Jajah Abbasia	JJA	H.P	40	Khai Khair Shah	Shallow	29.55806	71.08056	
		JJA	H.P	40		Shallow			
		JJA	R.P	40		Shallow			
	Basti Bukhari Sharif	BS	R.P	60	Chachran	Shallow			
		BS	H.P	60		Shallow			
		BS	T.W	60		Shallow			
	Basti Pahore	BP	M.P	25	Chandia	Shallow	29.43667	70.84694	2000
		BP	H.P	25		Shallow			
		BP	R.P	25		Shallow			
	Basti Tarada Molvian	TRM	H.P	45	Jhoran	Shallow	28.93889	70.74194	10,000
		TRM	H.P	45		Shallow			

		TRM	H.P	45		Shallow			
		TRM	M.P	50		Shallow			
SITE A		TRM	M.P	50		Shallow			
		TRM	M.P	50		Shallow			
	Zahir Pir	ZP	M.P	55	Zahir pir	Shallow	28.53611	70.85213	10,000
		ZP	H.P	55		Shallow			
		ZP	R.P	55		Shallow			
	Adda Bagobahar	BBR	H.P	20	Bagobahar	Shallow	28.6475	70.6075	3000
		BBR	M.P	20		Shallow			
		BBR	R.P	20		Shallow			
	Majeed Colony	MC	H.P	50	Khan pur city	Shallow	28.83889	70.77833	5000
	Satellite Town	ST	H.P	50	Khan pur city	Shallow	28.90194	70.64111	5000
	Muhala Loharan	ML	H.P	50	Khan pur city	Shallow			1500
	Railway Colony	RC	H.P	50	Khan pur city	Shallow	28.83889	70.77833	5000
	Basti Tarand Molvian	TRM	T.W	145	Jhoran	Deep	28.93889	70.74194	10,000
	Basti Chah Nasrullah Khan	CNK	T.W	150	Deen pur Sharif	Deep	28.69083	70.9123	1000
	Jajah Abbasia	JJA	T.W	200	Khai khair Shah	Deep	29.55806	71.08056	2400
	Basti Khokran	KK	T.W	200	Kotla pathan	Deep	28.68139	71.16722	84000
SITE B	Pul Sanni Colony	PSC	H.P	70	Chak 86	Shallow	28.6	70.47361	50,000
	Punl Sanni	PS	H.P	70	Chak 86	Shallow	28.6	70.47361	50,000
	Chak 86	C.86	H.P	70	Chak 86	Shallow			10,000
		C.86	R.P	70	Chak 86	Shallow			
	Colony No.2	C.2	water supply	70	Chak 86	Shallow	28.41917	70.47944	50,000
		C.2	R.P	70		Shallow			
		C.2	R.P	70		Shallow			

Table A.2: Field parameters for soil and sediment samples

Site	Sampling location	Sample code	Union Council	Latitude	Longitude	Depth (cm)	Type
SITE A	Chak 104 L	CK104L	Chak 45 P	34.10583	73.19556	0-30	Agricultural soil
	Chak P33	CP33	Bagobahar	28.67528	70.81389	0-30	Agricultural soil
	Basti Sheikhan	SHK	Mari	28.69083	70.83972	0-30	Agricultural soil
	Basti Dhareja Nagar	DNK	Sehja	28.69176	70.83833	0-30	Agricultural soil
	Basti Chah Nasrullah Khakwani	CNK	Deen pur Sharif	28.69083	70.9123	0-30	Agricultural soil
	Basti Khokharan	KK	Kotla Pathan	28.7533	70.8791	0-30	Agricultural soil
	Jajah Abbasia	JJA	Khai Khair Shah	29.55806	71.08056	0-30	Agricultural soil
	Basti Bukhari Sharif	BS	Chachran	29.43667	70.84694	0-30	Agricultural soil
	Basti Pahore	BP	Chandia	28.93889	70.74194	0-30	Agricultural soil
	Zahir pir	ZP	Zahir pir	28.53611	70.85213	0-30	Agricultural soil
	Basti Taranda Molvian	TRM	Jhoran	29.43611	70.84639	0-30	Agricultural soil
	River Indus	RI (1)	Chachran	28.8764	70.4510	0-30	Sediment
	River Indus	RI (2)	Chachran	28.8764	70.4510	0-30	Sediment
	River Indus	RI (3)	Chachran	28.8764	70.4510	0-30	Sediment
	River Indus	RI (4)	Chachran	28.8764	70.4510	0-30	Sediment
	River Indus	RI (5)	Chachran	28.8764	70.4510	0-30	Sediment
	River Indus	PC (1)	Chachran	28.8764	70.4510	0-30	Sediment
	Pajnad Canal	PC (2)	Chachran	28.8572	70.4993	0-30	Sediment
	Pajnad Canal	PC (3)	Chachran	28.8572	70.4993	0-30	Sediment
	Pajnad Canal	PC (4)	Chachran	28.8572	70.4993	0-30	Sediment
	Pajnad Canal	PC (5)	Chachran	28.8572	70.4993	0-30	Sediment
	Abbasia Canal	AC (1)	Khan pur city	28.9000	70.9000	0-30	Sediment
	Abbasia Canal	AC (2)	Khan pur city	28.9000	70.9000	0-30	Sediment
	Abbasia Canal	AC (3)	Khan pur city	28.9000	70.9000	0-30	Sediment
	Abbasia Canal	AC (4)	Khan pur city	28.9000	70.9000	0-30	Sediment
	Abbasia Canal	AC (5)	Khan pur city	28.9000	70.9000	0-30	Sediment
SITE B SITE B	Agriculrural Instruments Industry	AI	Rahim Yar Khan city	28.61806	70.37833	0-30	Industrial soil
	Marble Industry	MI	Rahim Yar Khan city	28.62806	70.3176	0-30	Industrial soil
	Soap Industry	SI (1)	Rahim Yar Khan city	28.50056	70.46583	0-30	Industrial soil
	Textile Industry	TI	Rahim Yar Khan city	28.61806	70.37833	0-30	Industrial soil
	RCC piped Industry	RCI	Rahim Yar Khan city	28.61806	70.37833	0-30	Industrial soil
	Sugar Industry	SI(2)	Rahim Yar Khan city	28.87667	73.77611	0-30	Industrial soil
	Cotton Industry	CI	Rahim Yar Khan city	29.06056	73.61306	0-30	Industrial soil

Annexure B: Table B.1 Physio-chemical parameters of all water samples

Site	Sample ID	Source	Depth (ft)	Type of depth	pH	EC (uS/cm)	TDS (mg/L)	DO (mg/L)
SITE A	CK104L	H.P	30	Shallow	8.7	1343	671.5	6.6
	CK104L	T.W	70	Shallow	8.5	1300	650	6.6
	CP33	T.W	60	Shallow	7.9	1050	525	7.6
	CP33	M.P	20	Shallow	8.5	1075	537.5	7.2
	CP33	H.P	20	Shallow	8.4	1100	550	7.1
	SHK	H.P	55	Shallow	8.4	1950	975	7.6
	SHK	H.P	55	Shallow	8.4	1945	972.5	7.6
	SHK	M.P	55	Shallow	8.3	1870	935	7.1
	SHK	M.P	55	Shallow	8.2	1940	970	7.6
	DNK	H.P	60	Shallow	8.3	1350	675	7.1
	DNK	M.P	60	Shallow	8.8	1500	750	7.5
	CNK	H.P	70	Shallow	8.2	1200	600	6.3
	KK	H.P	50	Shallow	8.3	675	337.5	6.5
	KK	H.P	50	Shallow	8.5	602	301	6.5
	KK	R.P	50	Shallow	8.6	700	350	7
	JJA	H.P	40	Shallow	8.5	720	360	8
	JJA	H.P	40	Shallow	8.6	604	302	8.1
	JJA	R.P	40	Shallow	8.4	800	400	8.2
	BS	R.P	60	Shallow	8.7	939	469.5	7.5
	BS	H.P	60	Shallow	8.7	890	445	7.8
	BS	T.W	60	Shallow	8.7	631	315.5	7.7
	BP	H.P	60	Shallow	8.4	700	350	7.8
	BP	H.P	25	Shallow	8.6	600	300	7.8
	BP	R.P	25	Shallow	9.2	928	464	7.8
	TRM	H.P	45	Shallow	8.6	1500	750	7.6
	TRM	H.P	45	Shallow	8.2	1620	810	7.6

	TRM	H.P	45	Shallow	8.3	1050	525	7.5
SITE A	TRM	M.P	50	Shallow	8.6	1200	600	7.5
	TRM	M.P	50	Shallow	8.6	1150	575	7.5
	TRM	M.P	50	Shallow	8.8	1020	510	7.5
	ZP	M.P	55	Shallow	8.6	550	275	6.4
	ZP	H.P	55	Shallow	8.8	620	310	6.5
	ZP	R.P	55	Shallow	9.1	550	275	6.3
	BBR	H.P	20	Shallow	8.7	670	335	7.7
	BBR	M.P	20	Shallow	8.8	900	450	6.4
	BBR	R.P	20	Shallow	8.9	800	400	7
	MC	H.P	50	Shallow	8.6	1400	700	7.5
	ST	H.P	50	Shallow	8.5	1380	690	7.3
	ML	H.P	50	Shallow	8.6	1720	860	8.2
	RC	H.P	50	Shallow	8.6	1420	710	7.6
	TRM	T.W	145	Deep	8.5	1400	700	7.5
	CNK	T.W	150	Deep	8.1	950	475	7
	JJA	T.W	200	Deep	8.6	915	457.5	8.1
	KK	T.W	200	Deep	8.4	900	450	6.5
SITE B	PSC	H.P	70	Shallow	8.8	1150	575	7.4
	PS	H.P	70	Shallow	8.8	1180	590	7.4
	C.86	H.P	70	Shallow	8.8	1050	525	7.5
	C.86	R.P	70	Shallow	8.5	1380	690	6.4
	C.2	Water supply	70	Shallow	8.3	1362	681	6.4
	C.2	R.P	70	Shallow	8.7	950	475	8
	C.2	R.P	70	Shallow	8.5	980	490	6.5

Table B.2: Major Ionic Composition of all water samples

Site	Sample ID	Source	Cl^- (ppm)	HCO_3^- (ppm)	$N0_3^-$ (ppm)	SO_4^- (ppm)	PO_4^{-3} (ppm)	Na^+ (mg/L)	K^+ (mg/L)	Ca^{+2} (mg/L)	Mg^{+2} (mg/L)
SITE A	CK104L	H.P	65	800	31.2	19.8	59.9	62.6	13.8	26.6	53.2
	CK104L	T.W	25	785	14.2	44.14	38	1.7	0.1	3.4	0.7
	CP33	T.W	25	550	20.1	55	36.5	11.3	1.3	9.0	5.5
	CP33	M.P	115	580	27.5	39.7	62	25.3	4.5	27.8	10.8
	CP33	H.P	209.9	600	28.4	43	62.4	44.7	6.4	87.3	27.6
	SHK	H.P	110	980	19.6	33	57.2	44.0	49.9	31.6	83.8
	SHK	H.P	25	900	23.2	36	56.5	45.9	51.0	39.3	79.1
	SHK	M.P	75	850	21.5	43	39	46.0	3.7	40.5	87.5
	SHK	M.P	100	930	15	45	32	80.0	55.0	29.0	16.6
	DNK	H.P	224.9	900	14.9	114.6	58.9	57.8	7.6	32.4	26.1
	DNK	M.P	344.9	600	15.5	120	57	59.7	7.4	24.2	25.4
	CNK	H.P	45	550	23.8	98.13	41.1	62.0	6.1	19.1	31.5
	KK	H.P	40	370	16.8	30	48	60.2	5.6	24.8	31.6
	KK	H.P	95	300	27.8	23.3	55.6	63.5	7.4	23.4	24.1
	KK	R.P	5	400	16.1	25.7	44.8	28.9	11.1	20.9	4.2
	JJA	H.P	174.9	420	25.2	33	56.9	58.7	8.1	14.6	16.7
	JJA	H.P	110	300	30	25.5	37.5	15.4	2.5	21.4	4.9
	JJA	R.P	25	500	21.3	28.7	52	23.5	3.8	61.4	10.0
	BS	R.P	25	495	22	28	24.4	66.6	13.9	20.6	44.2
	BS	H.P	135	450	19.7	29.9	26.4	39.3	8.7	33.5	7.2
	BS	T.W	50	335	31.9	32.01	46.4	61.7	10.3	21.5	25.7
	BP	H.P	60	395	28.9	33.12	28.8	58.7	38.7	24.4	30.5
	BP	H.P	10	300	29.5	30.1	30	70.2	24.6	14.8	7.7
	BP	R.P	15	425	33	31.2	35	58.5	30.0	38.8	2.3
	TRM	H.P	564.8	640	23.3	110	50.1	8.8	5.9	86.5	4.4
	TRM	H.P	40	723	30.3	113	55	20.6	3.8	45.3	2.7
	TRM	H.P	65	550	27	115	51	14.5	0.5	6.6	0.5

SITE A	TRM	M.P	160	475	25	117	50.7	70.6	4.7	27.7	1.2
	TRM	M.P	55	600	21	118	53	10.8	3.5	32.7	1.0
	TRM	M.P	115	500	25	119	52	14.1	9.7	27.5	5.0
	ZP	M.P	299.9	210	24.8	114.6	54	28.8	7.0	24.7	3.2
	ZP	H.P	50	355	28.5	99.9	52	17.7	3.7	75.2	1.0
	ZP	R.P	115	213	29.2	96.7	53.6	69.0	13.4	60.3	0.2
	BBR	H.P	65	375	24.5	43	41.9	5.4	0.3	7.4	2.1
	BBR	M.P	35	550	25.5	38.6	40	42.2	14.8	19.7	0.3
	BBR	R.P	100	490	26.7	28.7	49.5	49.8	32.7	25.4	0.2
	MC	H.P	25	800	30.9	40	45	70.0	10.1	16.2	1.2
	ST	H.P	100	570	28	58	40.2	19.5	2.3	5.2	1.3
	ML	H.P	85	915	28.7	60	41	67.7	35.9	8.2	0.1
	RC	H.P	125	854	33.6	69.4	43	13.0	3.4	6.2	0.3
	TRM	T.W	25	805	40.7	168.6	56	59.6	8.4	22.4	10.5
	CNK	T.W	50	400	13.7	108.13	25	67.4	6.3	19.3	31.3
	JJA	T.W	229.9	350	13.2	28.9	40.1	39.5	6.7	68.5	14.0
	KK	T.W	50	380	25	30	28	7.4	0.3	6.8	1.9
SITE B	PSC	H.P	95	585	27	29.8	57.0	57.3	7.9	15.091	0.2643
	PS	H.P	10	600	25	27.7	55.6	40.8	36	57.229	0.2013
	C.86	H.P	179.9	550	21	24	44.8	36.7	8.0	15.201	0.1429
	C.86	R.P	40	671	25	26	50.0	7.0	3.4	20.317	0.3359
	C.2	water supply	45	650	24.8	28	56.9	20.3	9.6	17.57	0.431
	C.2	R.P	95	470	23	25	60.0	3.3	3.0	7.004	0.2118
	C.2	R.P	100	490	27	26	58.0	8.1	3.1	7.615	0.1993

Table B.3: Health Risk Assessment of Arsenic and Fluoride in all water samples

Site	SAMPLE ID	Source	Depth (ft)	Type of depth	F^- (ppm)	ADD/CDI	HQ	As (ppb)	As (mg/L)	ADD	HQ=ADD/RfD	CR
SITE A	CK104L	H.P	30	Shallow	6.1	0.2	2.8	8.09	0.008	0.0002	0.7	0.0003
	CK104L	T.W	70	Shallow	8.3	0.2	3.8	9.6	0.01	0.0003	0.9	0.0004
	CP33	T.W	60	Shallow	9.0	0.2	4.1	24.9	0.02	0.0007	2.3	0.001
	CP33	M.P	20	Shallow	7.8	0.2	3.6	11.9	0.01	0.0003	1.1	0.0005
	CP33	H.P	20	Shallow	8.3	0.2	3.8	1.2	0.001	0.0000	0.1	0.0001
	SHK	H.P	55	Shallow	6.2	0.2	2.8	4.3	0.004	0.0001	0.4	0.0002
	SHK	H.P	55	Shallow	5.7	0.2	2.6	BDL	BDL	BDL	BDL	BDL
	SHK	M.P	55	Shallow	6.0	0.2	2.7	BDL	BDL	BDL	BDL	BDL
	SHK	M.P	55	Shallow	6.4	0.2	2.9	BDL	BDL	BDL	BDL	BDL
	DNK	H.P	60	Shallow	8.6	0.2	3.9	4.9	0.005	0.0001	0.5	0.0002
	DNK	M.P	60	Shallow	7.0	0.2	3.2	BDL	BDL	BDL	BDL	BDL
	CNK	H.P	70	Shallow	8.5	0.2	3.9	23.9	0.02	0.0007	2.2	0.001
	KK	H.P	50	Shallow	8.6	0.2	3.9	BDL	BDL	BDL	BDL	BDL
	KK	H.P	50	Shallow	7.5	0.2	3.4	15.2	0.02	0.0004	1.4	0.0006
	KK	R.P	50	Shallow	8.0	0.2	3.7	17.3	0.02	0.0005	1.6	0.0007
	JJA	H.P	40	Shallow	6.9	0.2	3.0	BDL	BDL	BDL	BDL	BDL
	JJA	H.P	40	Shallow	8.4	0.2	3.8	3.3	0.003	9.0E-05	0.3	0.0001
	JJA	R.P	40	Shallow	6.5	0.2	3.0	5.8	0.01	1.6E-04	0.5	0.0002
	BS	R.P	60	Shallow	5.2	0.1	2.4	30.7	0.03	0.001	2.8	0.001
	BS	H.P	60	Shallow	6.1	0.2	2.8	35.5	0.04	0.001	3.3	0.001
	BS	T.W	60	Shallow	9.2	0.3	4.2	60.9	0.06	0.002	5.6	0.003
	BP	H.P	60	Shallow	14.3	0.4	6.5	1.7	0.002	4.9E-05	0.2	0.0001
	BP	H.P	25	Shallow	7.2	0.2	3.3	BDL	BDL	BDL	BDL	BDL
	BP	R.P	25	Shallow	6.1	0.2	2.8	BDL	BDL	BDL	BDL	BDL
	TRM	H.P	45	Shallow	9.0	0.2	4.1	9.3	0.009	0.0003	0.9	0.0004
	TRM	H.P	45	Shallow	8.7	0.2	4.0	10.2	0.01	0.0003	0.9	0.0004

SITE A	TRM	H.P	45	Shallow	8.0	0.2	3.7	4.5	0.00452	0.0001	0.4	0.0002
	TRM	M.P	50	Shallow	7.0	0.2	3.2	20.2	0.02023	0.0006	1.9	0.0008
	TRM	M.P	50	Shallow	7.5	0.2	3.4	6.1	0.006103	0.0002	0.6	0.0003
	TRM	M.P	50	Shallow	7.7	0.2	3.5	5.7	0.005712	0.0002	0.5	0.0002
	ZP	M.P	55	Shallow	6.5	0.2	3.0	29.2	0.02922	0.0008	2.7	0.001
	ZP	H.P	55	Shallow	6.8	0.2	3.1	30.5	0.03053	0.0008	2.8	0.001
	ZP	R.P	55	Shallow	6.8	0.2	3.1	19.0	0.01895	0.0005	1.8	0.0008
	BBR	H.P	20	Shallow	5.5	0.2	2.5	5.3	0.0053	0.0001	0.5	0.0002
	BBR	M.P	20	Shallow	6.3	0.2	2.9	9.3	0.00925	0.0003	0.9	0.0004
	BBR	R.P	20	Shallow	8.8	0.2	4.0	8.2	0.0082	0.0002	0.8	0.0003
	MC	H.P	50	Shallow	6.0	0.2	2.7	10.7	0.01068	0.0003	1.0	0.0004
	ST	H.P	50	Shallow	5.9	0.2	2.7	14.4	0.01439	0.0004	1.3	0.0006
	ML	H.P	50	Shallow	5.5	0.2	2.5	BDL	BDL	BDL	BDL	BDL
	RC	H.P	50	Shallow	6.5	0.2	3.0	5.6	0.005624	0.0002	0.5	0.0002
	TRM	T.W	145	Deep	7.3	0.2	3.3	107.2	0.107	0.003	9.9	0.004
	CNK	T.W	150	Deep	7.2	0.2	3.3	89.1	0.089	0.002	8.3	0.004
	JJA	T.W	200	Deep	7.0	0.2	3.2	BDL	BDL	BDL	BDL	BDL
	KK	T.W	200	Deep	20.4	0.6	9.3	32.5	0.03	0.001	3	0.001
SITE B	PSC	H.P	70	Shallow	9.4	0.3	4.4	4.3	0.006	0.0002	0.5472	0.0002
	PS	H.P	70	Shallow	8.1	0.2	3.8	3.7	BDL	BDL	BDL	BDL
	C.86	H.P	70	Shallow	8.5	0.2	3.9	3.9	0.00227	6.3E-05	2.1E-01	9.5E-05
	C.86	R.P	70	Shallow	26.4	0.7	12.2	12.1	0.00343	9.5E-05	3.2E-01	1.4E-04
	C.2	Water supply	70	Shallow	8.5	0.2	3.9	6.07	0.00607	1.7E-04	5.6E-01	2.5E-04
	C.2	R.P	70	Shallow	7.4	0.2	3.4	4.5	0.0045	1.3E-04	4.2E-01	1.9E-04
	C.2	R.P	70	Shallow	5.8	0.2	2.7	3.9	0.0039	1.1E-04	3.6E-01	1.6E-04

Table B.4: Trace metals concentration in all water samples

	Sample ID	Source	Depth (ft)	Type of depth	Ni (mg/L)	Cr (mg/L)	Cu (mg/L)	Mn (mg/L)	Fe (mg/L)	Pb (mg/L)	Cd (mg/L)
SITE A	CK104L	H.P	30	Shallow	0.062	BDL	BDL	0.011	0.10	1.2	0.41
	CK104L	T.W	70	Shallow	0.088	BDL	BDL	0.011	0.04	0.9	0.32
	CP33	T.W	60	Shallow	0.073	BDL	BDL	0.002	0.10	1.1	0.35
	CP33	M.P	20	Shallow	0.022	BDL	BDL	0.002	0.36	1.3	0.42
	CP33	H.P	20	Shallow	0.079	BDL	BDL	0.008	0.01	1.3	0.49
	SHK	H.P	55	Shallow	0.038	BDL	BDL	0.001	0.03	1.1	0.46
	SHK	H.P	55	Shallow	0.031	0.004	BDL	0.008	0.4	1.2	0.45
	SHK	M.P	55	Shallow	0.045	0.002	BDL	0.017	0.02	1.2	0.44
	SHK	M.P	55	Shallow	0.044	BDL	BDL	0.008	0.06	1.5	0.44
	DNK	H.P	60	Shallow	0.008	BDL	BDL	0.02	0.01	1.3	0.57
	DNK	M.P	60	Shallow	0.01	BDL	BDL	0.007	0.07	1.5	0.48
	CNK	H.P	70	Shallow	0.053	BDL	BDL	0.009	0.25	1.2	0.53
	KK	H.P	50	Shallow	0.059	BDL	BDL	0.004	0.04	1.4	0.52
	KK	H.P	50	Shallow	0.037	BDL	BDL	0.008	0.4	1.3	0.55
	KK	R.P	50	Shallow	0.042	BDL	BDL	0.01	0.03	1.7	0.50
	JJA	H.P	40	Shallow	0.047	BDL	BDL	0.011	0.09	1.7	0.58
	JJA	H.P	40	Shallow	0.127	BDL	BDL	0.022	1.38	1.7	0.57
	JJA	R.P	40	Shallow	0.02	BDL	BDL	0.002	0.36	1.7	0.55
	BS	R.P	60	Shallow	0.017	BDL	BDL	0.009	0.03	1.5	0.49
	BS	H.P	60	Shallow	0.007	BDL	BDL	0.006	0.05	1.5	0.52
	BS	T.W	60	Shallow	0.101	BDL	BDL	0.012	0.001	1.7	0.54
	BP	H.P	60	Shallow	0.081	BDL	BDL	0.012	0.71	1.6	0.59
	BP	H.P	25	Shallow	0.076	BDL	BDL	0.005	0.18	1.7	0.53
	BP	R.P	25	Shallow	0.041	BDL	BDL	0.005	0.004	1.7	0.56
	TRM	H.P	45	Shallow	0.058	BDL	BDL	0.004	0.04	1.8	0.59
	TRM	H.P	45	Shallow	0.045	BDL	BDL	0.003	0.004	1.8	0.66

SITE A	TRM	H.P	45	Shallow	0.034	BDL	BDL	0.005	0.02	1.8	0.60
	TRM	M.P	50	Shallow	0.015	BDL	BDL	0.002	0.03	1.6	0.57
	TRM	M.P	50	Shallow	0.069	BDL	BDL	0.011	0.54	1.8	0.62
	TRM	M.P	50	Shallow	0.149	BDL	BDL	0.003	0.96	1.9	0.54
	ZP	M.P	55	Shallow	0.086	BDL	BDL	0.006	0.91	2.1	0.60
	ZP	H.P	55	Shallow	0.097	BDL	BDL	0.001	1.96	2.0	0.63
	ZP	R.P	55	Shallow	0.054	BDL	BDL	0.01	0.27	2.2	0.70
	BBR	H.P	20	Shallow	0.042	BDL	BDL	0.004	0.02	2.4	0.59
	BBR	M.P	20	Shallow	0.095	BDL	BDL	0.018	0.03	2.6	0.72
	BBR	R.P	20	Shallow	0.024	BDL	BDL	0.054	0.04	2.7	0.69
	MC	H.P	50	Shallow	0.033	BDL	BDL	0.005	0.33	3.0	0.62
	ST	H.P	50	Shallow	0.037	BDL	BDL	0.004	0.08	3.2	0.75
	ML	H.P	50	Shallow	0.015	BDL	BDL	0.01	0.02	3.4	0.71
	RC	H.P	50	Shallow	0.045	BDL	BDL	0.001	0.002	1.7	0.59
	TRM	T.W	145	Deep	0.034	BDL	BDL	0.011	0.002	1.8	0.51
	CNK	T.W	150	Deep	0.084	BDL	BDL	0.003	0.12	1.6	0.50
	JJA	T.W	200	Deep	0.052	BDL	BDL	0.013	0.11	1.5	0.61
	KK	T.W	200	Deep	0.007	BDL	BDL	0.001	0.07	3.6	0.63
SITE B	PSC	H.P	70	Shallow	0.013	0.013	BDL	0.002	0.49	4.09	0.69
	PS	H.P	70	Shallow	0.034	0.034	BDL	0.009	0.24	4.16	0.64
	C.86	H.P	70	Shallow	0.038	0.038	BDL	0.003	0.57	4.57	0.66
	C.86	R.P	70	Shallow	0.05	0.05	0.007	0.005	0.05	4.89	0.75
	C.2	water supply	70	Shallow	0.093	0.093	BDL	0.1	18.12	5.03	0.67
	C.2	R.P	70	Shallow	0.006	0.006	0.005	0.01	1.72	5.62	0.76
	C.2	R.P	70	Shallow	0.083	0.083	BDL	0.002	0.43	5.23	0.68

Table B.5: Health Risk Assessment of trace metals in all groundwater samples

Site	Sample ID	Source	Ni (mg/L)	ADD	HQ	Mn (mg/L)	ADD	HQ	Pb (mg/L)	ADD	HQ	Cd (mg/L)	ADD	HQ
SITE A	CK104L	H.P	0.062	0.002	0.09	0.011	3.1E-04	0.002	1.2	0.03	1.7	0.41	0.01	22.7
	CK104L	T.W	0.088	0.002	0.1	0.011	3.1E-04	0.002	0.9	0.03	1.3	0.32	0.01	17.8
	CP33	T.W	0.073	0.002	0.1	0.002	5.6E-05	0.0004	1.1	0.03	1.6	0.35	0.01	19.4
	CP33	M.P	0.022	0.001	0.03	0.002	5.6E-05	0.0004	1.3	0.04	1.8	0.42	0.01	23.6
	CP33	H.P	0.079	0.002	0.1	0.008	0.0002	0.002	1.3	0.04	1.8	0.49	0.01	27.2
	SHK	H.P	0.038	0.001	0.05	0.001	2.8E-05	0.0002	1.1	0.03	1.5	0.46	0.01	25.6
	SHK	H.P	0.031	0.001	0.04	0.008	0.0002	0.002	1.2	0.03	1.6	0.45	0.01	25.2
	SHK	M.P	0.045	0.001	0.06	0.017	0.0005	0.003	1.2	0.03	1.7	0.44	0.01	24.4
	SHK	M.P	0.044	0.001	0.06	0.008	0.0002	0.002	1.5	0.04	2.1	0.44	0.01	24.2
	DNK	H.P	0.008	0.000	0.01	0.02	0.0006	0.004	1.3	0.04	1.8	0.57	0.02	31.6
	DNK	M.P	0.01	0.000	0.01	0.007	0.0002	0.001	1.5	0.04	2.1	0.48	0.01	26.4
	CNK	H.P	0.053	0.001	0.07	0.009	0.0003	0.002	1.2	0.03	1.7	0.53	0.01	29.5
	KK	H.P	0.059	0.002	0.12	0.004	0.0001	0.0008	1.4	0.05	2.5	0.52	0.01	28.1
	KK	H.P	0.037	0.000	0.01	0.008	0.0002	0.002	1.3	0.04	2.2	0.55	0.01	27.8
	KK	R.P	0.042	0.002	0.08	0.01	0.0003	0.002	1.7	0.04	2.0	0.50	0.01	29.1
	JJA	H.P	0.047	0.001	0.05	0.011	0.0003	0.002	1.7	0.04	1.9	0.58	0.02	30.8
	JJA	H.P	0.127	0.001	0.06	0.022	0.0006	0.004	1.7	0.05	2.4	0.57	0.01	27.8
	JJA	R.P	0.02	0.001	0.07	0.002	5.6E-05	0.0004	1.7	0.04	2.1	0.55	0.02	33.8
	BS	R.P	0.017	0.001	0.07	0.009	0.0003	0.002	1.5	0.05	2.4	0.49	0.02	32.4
	BS	H.P	0.007	0.004	0.18	0.006	0.0002	0.001	1.5	0.05	2.3	0.52	0.02	31.4
	BS	T.W	0.101	0.001	0.03	0.012	0.0003	0.002	1.7	0.05	2.3	0.54	0.02	30.4
	BP	H.P	0.081	0.000	0.02	0.012	0.0003	0.002	1.6	0.04	2.0	0.59	0.01	27.1
	BP	H.P	0.076	0.000	0.01	0.005	0.0001	0.001	1.7	0.04	2.1	0.53	0.01	28.8
	BP	R.P	0.041	0.003	0.1	0.005	0.0001	0.001	1.7	0.05	2.4	0.56	0.01	29.7
	TRM	H.P	0.058	0.002	0.1	0.004	0.0001	0.0008	1.8	0.05	2.3	0.59	0.02	32.8
	TRM	H.P	0.045	0.002	0.1	0.003	0.00008	0.0006	1.8	0.05	2.4	0.66	0.01	29.5

SITE A	TRM	H.P	0.034	0.001	0.06	0.005	0.0001	0.001	1.8	0.05	2.3	0.60	0.02	31.1
	TRM	M.P	0.015	0.001	0.05	0.002	5.6E-05	0.0004	1.6	0.05	2.3	0.57	0.02	33
	TRM	M.P	0.069	0.002	0.08	0.011	0.0003	0.002	1.8	0.05	2.5	0.62	0.02	32.5
	TRM	M.P	0.149	0.001	0.06	0.003	8.3E-05	0.0006	1.9	0.05	2.4	0.54	0.02	36.4
	ZP	M.P	0.086	0.001	0.05	0.006	0.0002	0.001	2.1	0.05	2.5	0.60	0.02	33.2
	ZP	H.P	0.097	0.000	0.02	0.001	2.8E-05	0.0002	2.0	0.04	2.2	0.63	0.02	31.4
	ZP	R.P	0.054	0.002	0.1	0.01	0.0003	0.002	2.2	0.05	2.5	0.70	0.02	34.4
	BBR	H.P	0.042	0.004	0.2	0.004	0.0001	0.0008	2.4	0.05	2.7	0.59	0.01	29.9
	BBR	M.P	0.095	0.002	0.1	0.018	0.0005	0.004	2.6	0.06	3.0	0.72	0.02	33.5
	BBR	R.P	0.024	0.003	0.1	0.054	0.002	0.01	2.7	0.06	2.8	0.69	0.02	34.7
	MC	H.P	0.033	0.002	0.08	0.005	0.00014	0.001	3.0	0.06	3.1	0.62	0.02	38.6
	ST	H.P	0.037	0.001	0.06	0.004	0.00011	0.0008	3.2	0.07	3.3	0.75	0.02	32.5
	ML	H.P	0.015	0.003	0.13	0.01	0.00028	0.002	3.4	0.07	3.6	0.71	0.02	39.9
	RC	H.P	0.045	0.001	0.03	0.001	0.00003	0.0002	1.7	0.07	3.7	0.59	0.02	38.3
	TRM	T.W	0.034	0.001	0.05	0.011	0.00031	0.002	1.8	0.08	4.2	0.51	0.02	34.2
	CNK	T.W	0.084	0.001	0.05	0.003	0.00008	0.0006	1.6	0.09	4.5	0.50	0.02	41.5
	JJA	T.W	0.052	0.000	0.02	0.013	0.0004	0.003	1.5	0.10	4.8	0.61	0.02	39.3
	KK	T.W	0.007	0.001	0.06	0.001	2.8E-05	0.0002	3.6	0.10	5.0	0.63	0.02	34.8
SITE B	PSC	H.P	0.013	0.000	0.02	0.002	5.6E-05	0.0004	4.09	0.11	5.7	0.69	0.02	38.2
	PS	H.P	0.034	0.001	0.05	0.009	0.0003	0.0018	4.16	0.12	5.8	0.64	0.02	35.6
	C.86	H.P	0.038	0.001	0.05	0.003	8.3E-05	0.0006	4.57	0.13	6.3	0.66	0.02	36.9
	C.86	R.P	0.05	0.001	0.07	0.005	0.0001	0.001	4.89	0.14	6.8	0.75	0.02	41.8
	C.2	water supply	0.093	0.003	0.1	0.1	0.003	0.02	5.03	0.14	7.0	0.67	0.02	37
	C.2	R.P	0.006	0.000	0.01	0.01	0.0003	0.002	5.62	0.16	7.8	0.76	0.02	42.4
	C.2	R.P	0.083	0.002	0.1	0.002	5.6E-05	0.0004	5.23	0.15	7.3	0.68	0.02	37.5

Annexure C: Table C.1 Physio-chemical parameters of all soil and sediment samples

Site	Sampling code	Depth (cm)	pH	EC (uS/cm)	TDS (mg/L)	% Sand	% Silt	% Clay	% OC	% T 0C	% OM
SITE A	CK104L	0-30	11.43	38.1	19	91.5	2.5	6	2.4	3.2	5.51
	CP33	0-30	11.42	93.6	47	93	3	4	1.57	2.09	3.61
	SHK	0-30	11.2	95.1	48	88	3	9	1.5	2	3.44
	DNK	0-30	11	90	45	87	1	12	0.6	0.8	1.37
	CNK	0-30	8.91	75.6	38	81	7	12	1.2	1.6	2.75
	KK	0-30	10.32	65.9	33	80	12	8	2.25	3	5.17
	JJA	0-30	9.1	113.8	58	90	2	8	1.95	2.6	4.48
	BS	0-30	11.07	120.2	61	77	16.5	6.5	1.57	2.1	3.62
	BP	0-30	10.55	127	64	85	9	6	0.15	0.2	0.34
	ZP	0-30	10.6	38.5	19	87	8	5	1.8	2.4	4.13
	TRM	0-30	8.27	72.2	36.1	84	3	13	1.5	2	3.44
	RI (1)	0-30	10.1	135	67.5	72	8	20	1.65	2.2	3.79
	RI (2)	0-30	10.3	140	70	70	10	20	1.42	1.9	3.27
	RI (3)	0-30	9.9	125	62.5	72	7.5	19.5	1.35	1.8	3.1
	RI (4)	0-30	9.8	120	60	75	5	20	1.5	2	3.44
	RI (5)	0-30	10	130	65	71	10	19	1.35	1.8	3.1
	PC (1)	0-30	10.67	126.9	45	77	13	10	1.65	2.2	3.77
	PC (2)	0-30	10.7	130	65	75	15	10	1.5	2	3.44
	PC (3)	0-30	10.61	49.2	25	76	14	10	1.5	2	3.44
	PC (4)	0-30	10.8	47	23	72	13	15	1.35	1.8	3.1
	PC (5)	0-30	10.88	47.1	24	73	12	15	1.35	1.8	3.1
	AC (1)	0-30	10.67	89.9	45	77	13	10	1.5	2	3.44
	AC (2)	0-30	10.63	85	42.5	76	12	12	1.5	2	3.44
	AC (3)	0-30	10.69	80.4	41	75	15	10	1.35	1.8	3.1
	AC (4)	0-30	10.55	100	50	72	13	15	1.35	1.8	3.1
	AC (5)	0-30	10.53	103.5	52	75	15	10	1.5	2	3.44
SITE B	AI	0-30	8.73	152	77	95.5	3.5	1	3.45	4.6	7.93
	MI	0-30	9.3	180	90	88	6	6	1.8	2.4	4.13
	SI (1)	0-30	12.29	1396	698	89.9	2.1	8	2.4	3.2	5.51
	RCI	0-30	8.94	1255	627.5	88	5	7	2.1	2.8	4.81
	TI	0-30	10.52	239	119.5	94	5	1	0.37	0.5	0.86
SITE B	SI(2)	0-30	10.81	76.9	38.45	79	5	16	1.5	2	3.44
	CI	0-30	9.06	593	296.5	90	3	7	2.4	3.2	5.51

Table C.2: Trace metal concentration in all soil and sediment samples

Site A	Sampling code	Cu (mg/Kg)	Cr (mg/kg)	Ni (mg/Kg)	Mn (mg/kg)	Fe (mg/kg)	Pb (mg/kg)	Cd (mg/kg)
SITE A	CK104L	8.6	5.4	81.3	117.6	7002.8	19.7	20.6
	CP33	4	3.6	84.7	95.2	9418.6	55.7	17.8
	SHK	9.8	7.2	104.3	134.6	11452.6	73.1	20.2
	DNK	6.8	9.8	93.7	8.8	10555.8	117.7	21.03
	CNK	226	7.2	147.2	4.6	94440.4	23.5	37.4
	KK	7.4	6.6	102.6	15	2990.6	134.5	28.6
	JJA	15.6	20.0	125.8	6.2	14314.8	39.5	20.4
	BS	16.2	6.8	137.8	2.6	13565.6	64.1	26.8
	BP	5.4	4.4	113.4	5.2	10958.4	89.7	43.6
	ZP	14.8	4.2	114.1	6.2	14348.6	67.7	31.800
	TRM	7.2	18.2	133	12.2	14715	145.7	37.2
	RI (1)	24.8	231.3	16.6	16.628	14979.6	163.9	69.6
	RI (2)	13.2	239.3	30.2	30.228	14639.6	174.1	68.6
	RI (3)	14.8	193.3	5.2	5.228	15279.6	186.7	54.8
	RI (4)	14.2	194.3	1.0	1.028	17459.6	191.7	57.2
	RI (5)	19.6	182.9	1.2	1.228	15759.6	237.1	63.6
	PC (1)	7.2	132.2	12.2	12.228	14713.6	100.3	40.6
	PC (2)	5.0	153.0	12.6	12.628	11731.6	89.5	47.4
	PC (3)	5.6	167.8	5.6	5.628	10137.6	113.9	48.6
	PC (4)	8.0	179.2	0.6	0.628	13043.6	145.5	48.0
	PC (5)	10.6	198.0	7.4	7.428	13997.6	94.3	45.4
	AC (1)	5.2	226.6	0.6	0.628	7640.4	177.3	48.0
	AC (2)	16.0	214.6	7.4	7.428	5127.1	159.3	60.4
	AC (3)	17.4	262.6	3.8	3.828	7827	159.5	54.2
	AC (4)	12.6	244.6	7.0	7.028	6695.1	194.3	57.0
	AC (5)	15.2	224.6	9.0	9.028	4952.4	183.1	54.0
SITE B	AI	14.4	44.6	358.4	1320.6	16999.6	217.9	66.8
	MI	7.6	24.6	86	498.8	15863.6	190.1	52.4
	SI (1)	4	10.8	47	200	8891.6	204.7	87.03
	RCI	7.4	17.8	68.2	204	10159.6	196.9	75.03
	TI	31.8	143.4	107.8	361	10455.6	220.1	75.03
	SI(2)	4.2	6.4	8.8	20	9999.6	237.9	74.03
SITE B	CI	4.6	6.2	7.8	40	10919.6	250.7	64.8

		Depth	pH	EC	TDS	DO	Cl	HCO$_3$	N0$_3$	SO$_4$	PO$_4$	Na	K	Ca	Mg	F	As	Fe	Pb	Cd
Depth	Pearson Correlation	1																		
	Sig. (2-tailed)																			
pH	Pearson Correlation	-.318*	1																	
	Sig. (2-tailed)	.023																		
EC	Pearson Correlation	.025	-.415**	1																
	Sig. (2-tailed)	.861	.002																	
TDS	Pearson Correlation	.025	-.415**	1.000**	1															
	Sig. (2-tailed)	.860	.002	.000																
DO	Pearson Correlation	-.099	-.002	.241	.241	1														
	Sig. (2-tailed)	.488	.987	.088	.088															
Cl	Pearson Correlation	-.002	.175	.097	.097	.111	1													
	Sig. (2-tailed)	.990	.220	.497	.497	.438														
HCO$_3$	Pearson Correlation	-.078	-.369**	.923**	.923**	.240	-.021	1												
	Sig. (2-tailed)	.587	.008	.000	.000	.089	.883													
N0$_3$	Pearson Correlation	-.229	.151	-.106	-.106	.021	-.205	-.040	1											
	Sig. (2-tailed)	.106	.289	.459	.459	.883	.149	.779												
SO$_4$	Pearson Correlation	.126	-.178	.161	.161	.083	.317*	.096	.079	1										
	Sig. (2-tailed)	.377	.212	.260	.260	.561	.023	.504	.582											
PO$_4$	Pearson Correlation	-.260	.092	.145	.145	-.175	.248	.191	.188	.195	1									
	Sig. (2-tailed)	.066	.521	.311	.311	.221	.079	.179	.188	.171										
Na	Pearson Correlation	-.038	.069	.057	.057	.073	-.063	.055	.064	.002	-.132	1								
	Sig. (2-tailed)	.792	.632	.690	.689	.610	.659	.701	.654	.991	.357									
K	Pearson Correlation	-.155	.031	.356*	.356*	.229	-.147	.344*	-.002	-.240	-.102	.473**	1							
	Sig. (2-tailed)	.279	.827	.010	.010	.106	.303	.014	.990	.089	.478	.000								
Ca	Pearson Correlation	-.031	.121	.021	.021	-.015	.382**	-.052	-.064	.150	.251	.060	.099	1						
	Sig. (2-tailed)	.831	.398	.885	.885	.915	.006	.717	.658	.293	.076	.676	.488							
Mg	Pearson Correlation	-.005	-.340*	.405**	.405**	.070	-.039	.360**	-.197	-.135	.013	.366**	.371**	.145	1					
	Sig. (2-tailed)	.972	.015	.003	.003	.624	.785	.009	.166	.343	.927	.008	.007	.310						
F	Pearson Correlation	.321*	-.181	-.057	-.057	-.300*	-.070	-.083	.016	-.127	-.094	-.269	-.137	-.096	-.167	1				
	Sig. (2-tailed)	.022	.204	.693	.693	.032	.626	.561	.910	.373	.513	.056	.339	.501	.241					
As	Pearson Correlation	.471**	-.196	-.159	-.159	-.056	-.146	-.156	.189	.421**	-.204	.167	-.210	-.083	-.007	.005	1			
	Sig. (2-tailed)	.000	.169	.265	.265	.699	.306	.275	.183	.002	.151	.241	.139	.561	.959	.971				
Fe	Pearson Correlation	.031	-.050	.038	.038	-.242	-.077	.008	.026	-.104	.167	-.170	-.046	-.056	-.125	.012	-.063	1		
	Sig. (2-tailed)	.829	.729	.792	.792	.086	.593	.956	.855	.469	.242	.232	.748	.698	.381	.936	.662			
Pb	Pearson Correlation	.151	.205	-.018	-.018	-.264	-.086	-.046	.153	-.271	.185	-.309*	-.090	-.265	-.462**	.318*	-.146	.380**	1	
	Sig. (2-tailed)	.291	.150	.901	.901	.061	.550	.748	.283	.055	.195	.027	.531	.060	.001	.023	.308	.006		
Cd	Pearson Correlation	.055	.333*	-.151	-.151	-.227	-.014	-.184	.256	-.066	.188	-.150	.015	.043	-.496**	.210	-.177	.146	.745**	
	Sig. (2-tailed)	.700	.017	.290	.290	.109	.922	.196	.070	.647	.186	.292	.914	.765	.000	.140	.215	.308	.000	

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

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

Correlation for Cr, Cu and Mn could not be calculated because at least one of their values are constant

Annexure D: Table D.1 Correlation matrix of all parameters of water

		pH	EC	TDS	Sand	Silt	Clay	OC	TOC	0M	Cu	Cr	Ni	Mn	Fe	Pb	Cd
pH	Pearson Correlation	1															
	Sig. (2-tailed)																
EC	Pearson Correlation	.041	1														
	Sig. (2-tailed)	.849															
TDS	Pearson Correlation	.040	1.000**	1													
	Sig. (2-tailed)	.853	.000														
Sand	Pearson Correlation	.073	.249	.250	1												
	Sig. (2-tailed)	.736	.241	.238													
Silt	Pearson Correlation	.289	-.215	-.216	-.355	1											
	Sig. (2-tailed)	.170	.313	.310	.088												
Clay	Pearson Correlation	.125	-.082	-.084	-.293	.338	1										
	Sig. (2-tailed)	.561	.702	.696	.165	.106											
OC	Pearson Correlation	.360	-.245	-.245	.245	.188	.328	1									
	Sig. (2-tailed)	.084	.249	.248	.249	.380	.117										
TOC	Pearson Correlation	.271	-.029	-.029	.282	.156	.410*	.890**	1								
	Sig. (2-tailed)	.201	.895	.892	.181	.466	.047	.000									
0M	Pearson Correlation	-.036	.318	.318	.476*	.134	.141	.038	.148	1							
	Sig. (2-tailed)	.869	.130	.130	.019	.532	.510	.861	.490								
Cu	Pearson Correlation	-.234	-.082	-.082	-.032	.023	.176	-.150	-.009	.032	1						
	Sig. (2-tailed)	.272	.704	.705	.884	.915	.411	.485	.967	.883							
Cr	Pearson Correlation	-.060	-.013	-.011	.450*	.207	.143	.052	.185	.628**	.056	1					
	Sig. (2-tailed)	.781	.952	.958	.028	.332	.504	.809	.386	.001	.795						
Ni	Pearson Correlation	.042	.324	.324	.377	.032	.405*	.310	.526**	.528**	.158	.482*	1				
	Sig. (2-tailed)	.844	.123	.122	.069	.882	.049	.140	.008	.008	.460	.017					
Mn	Pearson Correlation	-.035	-.123	-.121	.293	.292	.234	.515*	.641**	.383	-.021	.675**	.691**	1			
	Sig. (2-tailed)	.871	.567	.573	.165	.166	.270	.010	.001	.065	.922	.000	.000				
Fe	Pearson Correlation	-.257	-.109	-.108	-.066	.026	.172	-.096	.014	-.049	.979**	-.032	.152	-.010	1		
	Sig. (2-tailed)	.226	.613	.615	.760	.903	.422	.654	.948	.822	.000	.881	.480	.963			
Pb	Pearson Correlation	-.133	.172	.173	.207	.120	-.145	.110	.219	.093	-.304	.463*	.101	.472*	-.311	1	
	Sig. (2-tailed)	.535	.422	.419	.332	.577	.499	.608	.304	.665	.148	.023	.638	.020	.139		
Cd	Pearson Correlation	-.087	.212	.214	.233	.154	-.036	.070	.262	.152	-.063	.517**	.173	.495*	-.083	.880**	1
	Sig. (2-tailed)	.687	.321	.316	.273	.474	.866	.744	.216	.478	.769	.010	.418	.014	.701	.000	

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

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

Table D.2: Correlation matrix of all soil and sediments parameters

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