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A Pakistan Perspective

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Preface

Groundwater is used for drinking water, irrigation lands, or general industrial processes. The quality of groundwater determines if it is suitable for consumption. At present (2014), arsenic and fluoride contamination of groundwater resources has been identified in many parts of the world, although recognition of the widespread nature of the problem has been advanced only relatively recently. Despite localized inputs of As from human activities, much of the contamination of groundwater with As is shown to arise from geogenic sources and affected groundwater has been found in countries on nearly every continent or major land mass. To date, little is known about arsenic and fluoride and its health effects in Pakistan.

Arsenic and fluoride Pollution: A Pakistan Perspective aims to provide a comprehensive background for students and researchers interested in simultaneous presence of arsenic and fluoride in groundwater, its consequences on human health, and to find the protection and sustainable management of the groundwater for the future use. This book gives an overview of the arsenic and fluoride contamination of groundwater in Pakistan and focuses on a case study from Lahore, Punjab, distribution of arsenic and fluoride, its mechanism, possible contaminant sources, and health risk assessment.

Chapter 1 of the book is devoted to general aspects of arsenic and fluoride in groundwater and soil, its worldwide distribution, documented cases of As contamination in groundwater and the environment, health effects, and revisiting the mechanisms of arsenic and fluoride. Status of arsenic and fluoride groundwater pollution is discussed in Chap. 2. Population exposed and sources and causes of arsenic and fluoride in different provinces of Pakistan are presented here. This chapter shows the severity of the problem in Pakistan as this problem is less focused in Pakistan compared to other arsenic and fluoride effected countries in South Asia.

From Chap. 3 the focus is on the case study of arsenic and fluoride groundwater pollution from Lahore, Punjab. This chapter is from the author's Ph.D. thesis. This chapter is divided into two parts; Part A is concerned with study background, sampling methods, and analysis, while Part B describes the isotope analysis which was used as tracer of pollution sources in the area.

Results of the case study are extended in Chap. 4 while Chap. 5 is about the sources of pollution which could be anthropogenic or natural. Sources of nitrogen and sulfur are discussed with reference to isotopes used in this study. Factors affecting the arsenic and fluoride mobility and the natural mechanism of arsenic in case study is discussed in this chapter. Chapter 6 is about the health risk assessment of arsenic in the area. Carcinogenic and non-carcinogenic risk is discussed in the chapter. Chapter 7 is about the remedies used in the arsenic affected areas of Pakistan and the environmental legislations regarding arsenic and fluoride in the area. This book can serve as a good reference for the student and researcher populations exposed to arsenic and its level of risk.

This book is written to give an overview of the arsenic and fluoride pollution in Pakistan and it will serve as a reference book for students and researchers in the field of Geochemistry and dealing with arsenic contamination and its remediation. This book also provides beginning graduate students in environmental geochemistry sciences with an overview of contaminant behavior of arsenic in groundwater; on the basis of these studies further research can be framed. I hope that I have succeeded in presenting the reader with a comprehensive—but not exhaustive—overview of the current knowledge of arsenic and fluoride pollution in Pakistan.

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About the Author

Abida Farooqi received her Ph.D. from the Earth Sciences Department of Osaka City University in 2007 on the Geochemistry of Arsenic and Fluoride and its mechanism. Currently, she is Assistant Professor in Environmental Sciences at Quaid-i-Azam University, Islamabad. Previously she was a faculty at the Environmental Sciences Department, Fatima Jinnah Women University and COMSATS Institute of Information Technology. She teaches courses in Ground and Surface Water Chemistry, Environmental Geology, Environmental Analytical Techniques and Environmental Chemistry. Abida Farooqi is Environmental Geochemist, focusing on arsenic and fluoride pollution and its remedial measures in Pakistan. She is involved in several research projects related to arsenic and fluoride pollution at the National and International levels.

1 Arsenic and Fluoride Pollution in Water and Soils

Water is an essential natural source for sustaining life and environment which we have always thought to be available in abundance and free gift of nature. Natural and anthropogenic pollutants threaten the quality of life through environmental pollution. Rainwater recharged from surface into the underground becomes groundwater. In many parts of the world, groundwater is pumped out of the ground so it can be used as a source of water for drinking, bathing, other household uses, agriculture, and industry. If rain water or surface water comes into contact with contaminated soil while seeping into the ground, it can become polluted and can carry the pollution from the soil to the groundwater.

The groundwater can be contaminated by various processes through air, soil, and surface water contamination. Contaminated groundwater can affect the health of animals and humans when they drink or bath in water contaminated by the groundwater or when they eat organisms that have themselves been affected by groundwater contamination. Due to the long residence time and complicated processes of pollution mechanism, it takes long time to recover from the groundwater contamination if once it happens. However, once the contaminated groundwater occurred, we have to understand whole process of its formation including sources, migration paths and geochemical evolution of the groundwater chemistry.

Arsenic and fluoride contamination in drinking water is a great challenge for various nations of the world and both of these elements are recognized worldwide as the most dangerous inorganic pollutants in drinking water (Smedley and Kinniburgh 2002; Kim et al. 2010).

1.1 World-Wide Occurrences of Arsenic and Fluoride Contaminated Groundwater

Arsenic (As) is a metalloid element, with atomic number 33, one naturally occurring isotope of atomic mass 75, and four oxidation states (−3, 0, +3, and +5) (Smedley and Kinniburgh 2002). In the aqueous environment, the +3 and +5 oxidation states are most prevalent, as the oxyanions arsenite (H_3AsO_3 or H_2AsO^{3-} at pH ~ 9−11) and arsenate ($H_2AsO_4^{-}$ and $HAsO_4^{2-}$ at pH ~ 4–10) (Smedley and Kinniburgh 2002). In soils, arsine gases (containing As^{3-}) may be generated by fungi and other organisms (Woolson 1977). The different forms of As have different toxicities, with arsine gas being the most toxic form. Of the inorganic oxyanions, arsenite is considered more

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toxic than arsenate, and the organic (methylated) arsenic forms are considered least toxic.

Arsenic is a global health concern due to its toxicity and the fact that it occurs at harmful levels in water supplies, particularly groundwater. There are more than 70 arsenic affected countries in the world and majority of these nations belong to South Asia and South East Asia. About 150 million people are affected via consumption of As contaminated water worldwide (Ravenscroft et al. 2009).

Release of soluble As species into groundwater is a serious problem in many areas of the world (Varsanyi et al. 1991; Lepkowski 1998; Welch et al. 2000; Tian et al. 2001; Bhattacharya et al. 2002; Nickson et al. 2005; Farooqi et al. 2006, 2007; Guo et al. 2011; Brahman et al. 2013). A number of large aquifers in the various parts of the world have been reported with As >50 µg/L. The most noteworthy As occurrences are in parts of Argentina, Bangladesh, Chile, China, Hungry, India, Mexico, Romania, Taiwan, Vietnam, and many parts of the USA (Smedley and Kinniburgh 2002). Recent reconnaissance surveys of groundwater quality in other areas such as of Nepal, Myanmar and Cambodia have been revealed presence of contaminated aquifer with >50 µg/L of As, although documentation of the affected aquifers is so far limited (Food and agricultural organization 2006).

Public concerns over As pollution in both soils and waters have substantially increased in recent years. Arsenic, a toxic ubiquitous element with metalloid properties is almost often present in environment i.e. soil, sediment, water, aerosol, rain, aquatics, vegetation, milk, etc. (Abernathy et al. 1997). The ecosystem is contaminated via both natural and anthropogenic sources i.e. industries, mining, farming, rock weathering, atmospheric depositions, etc. (Patel et al. 2005). The major transport mechanism for As in the environment is via water and uses of contaminated drinking water represent so far the greatest health hazard. The main sources of As in soils is from which the soil is derived, although atmospheric deposition contributes significantly to the geochemical cycle of As (Smith et al. 1998).

Distribution of documented cases of As contamination in groundwater and the environment are found all over the world. Many of these cases are related to areas of mineralization and mining activity and a few are associated with geothermal sources. Arsenic associates with geothermal waters has also been reported in several areas, including hot springs from parts of Argentina, Japan, New Zealand, Chile, Iceland, France, Dominica and the USA (Smedley and Kinniburgh 2002).

The As contamination is a result of either natural geological process or the release of As waste by man, from farming, industrial, and agricultural activities (Patel et al. 2005).

The world health organization (WHO) guideline of As concentration in drinking water was reduced from 50 to 10 µg/L in 1993 (WHO 1993; http://www.who.int/media). According to the WHO recommendation many developed countries changed the maximum admissible concentrations to 10 µg/L, however the developing countries, in which the arsenicosis appears among the people, are still using the previous guideline values (50 µg/L) due to the lack of facilities to analyze such a small concentrations precisely (Nickson et al. 2005).

Fluoride in most groundwaters occurs as the anion F^-. Waters with high F^-content are found mostly in calcium-deficient groundwaters hosted by granite and gneiss, geothermal waters and those in sedimentary basins (Hurtado and Torresdey 2004). Groundwaters with high F^- concentrations occur in many areas of the world including large parts of Africa, China, the Middle East and southern Asia (India, Sri Lanka). One of the best known high F^- belts on land extends along the East African Rift from Eritrea to Malawi. There is another belt from Turkey through Iraq, Iran, Afghanistan, India, northern

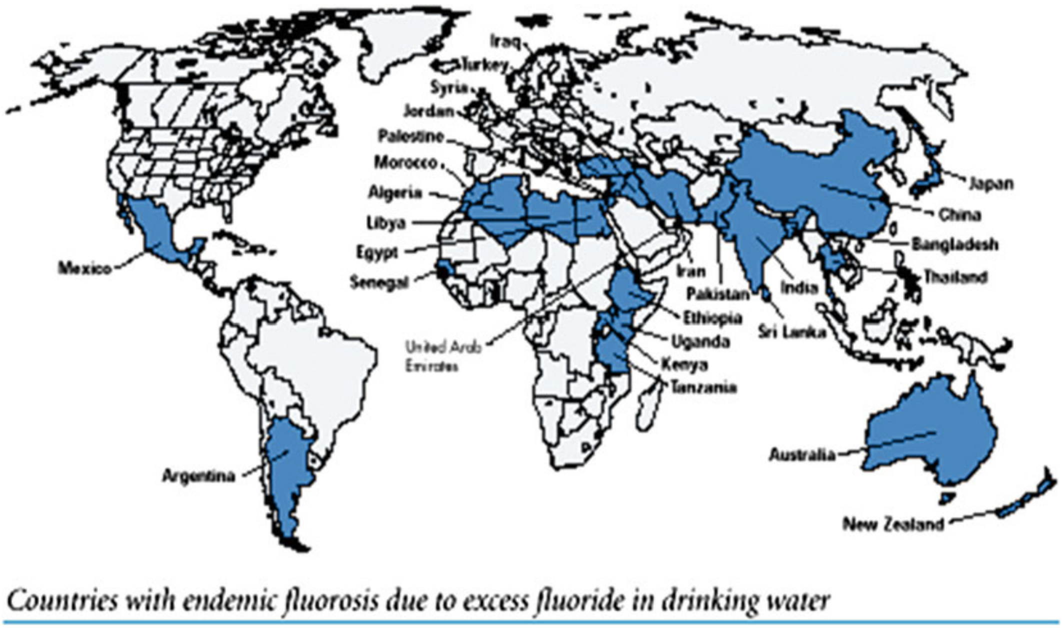

Fig. 1.1 Documented fluoride areas in the world www.iabot.icspana.es

Thailand and China. The Americas and Japan have similar belts (WHO 1993).

Fluoride is a common constituent in rocks and soils. Fluoride belongs to halogen family represented as ‘F’ with atomic weight 18.998 and atomic number 9. It occurs as a diatomic gas in its elemental form and has a valence number 1. It is the most electronegative and the most reactive when compared to all chemical elements in the periodic table (Greenwood and Earnshaw 1984; Gillespie et al. 1989). It has an oxidation state of −1 and occurs as both organic and inorganic compounds. It is the 13th most abundant element in the earth’s crust (Weinstein and Davison 2003). Its natural abundance in the earth’s crust is 0.06–0.09 % (Fawell et al. 2006) and the average crustal abundance is 300 mg/kg (Tebutt 1983).

The latest information shows that fluorosis is endemic in at least 25 countries across the globe (UNICEF) (Fig. 1.1). The total number of people affected is not known, but a conservative estimate would number in the tens of millions. In Mexico, 5 million people (about 6 % of the population) are affected by F^- through groundwater use.

The drinking water limit (DWL) for F^- is 1.5 mg/L (WHO 1994). Fluoride in drinking water has a narrow optimum concentration range in relation to human health. It prevents dental caries in the range of 0.7–1.2 mg/L, but is responsible for dental and skeletal fluorosis, if it is higher than 1.5 mg/L (CDCP 1999). In areas of high As and F^- concentrations, drinking water provides a potentially major source of As and F^- in diet so its early detection is of considerable importance.

Groundwater with fluoride concentration above the permissible limit set by WHO i.e. 1.5 mg/L have been recorded in several parts of the world. In 1984, WHO estimated that more than 260 million people living all over the world consume water with fluoride concentration above 1 mg/L (WHO 1984). The problem of high fluoride in groundwater has been reported by several researchers in India, China, Japan, Sri Lanka, Iran, Pakistan, Turkey, Southern Algeria,

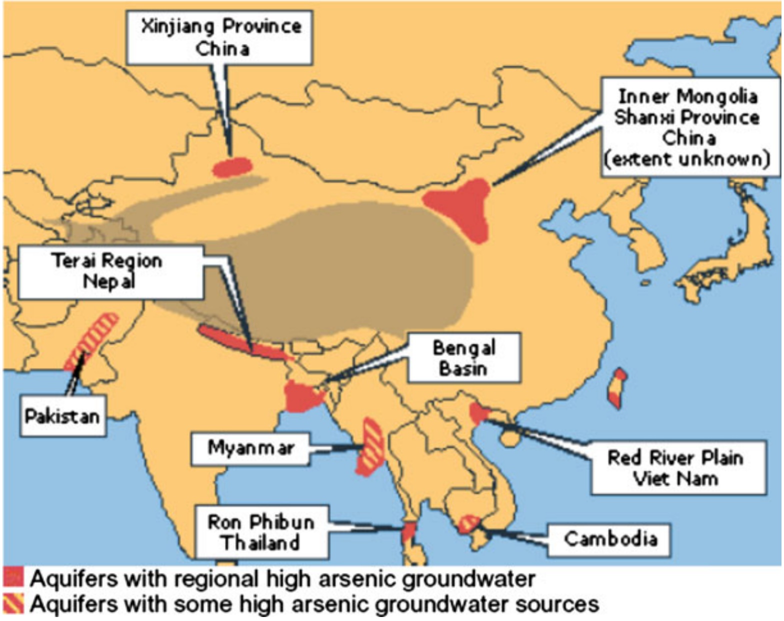

Fig. 1.2 Recognized As polluted aquifers in South and East Asia. *Source* Smedley et al. (2001)

Mexico, Korea, Italy, Brazil, Malawi, North Jordan, Ethiopia, Canada, Norway, Ghana, Kenya, South Carolina, Wisconsin and Ohio (Dissanayake 1991; Gaciri and Davies 1993; Srinivasa Rao 1997; Banks et al. 1998; Oruc 2003; Kim and Jeong 2005; Tekle Haimanot et al. 2006; Valenzuela-Vásquez et al. 2006; Zheng et al. 2006; Chae et al. 2007; Farooqi et al. 2007; Mirlean and Roisenberg 2007; Msonda et al. 2007; Vivona et al. 2007; Davraz et al. 2008; Messaïtfa 2008; Moghaddam and Fijani 2008; Oruc 2008; Desbarats 2009; Li et al. 2009; Karthikeyan et al. 2010; Keshavarzi et al. 2010; Kim et al. 2010; Looie and Moore 2010; Naseem et al. 2010; Reddy et al. 2010a; Yidana et al. 2010; Young et al. 2010; Sultana et al. 2014). The other possible sources of intake of fluoride apart from drinking water are through food, beverages and dental products like tooth paste.

The major cause of higher F^- concentrations in soils is weathering of F^- rich minerals in the country rocks (Tripathy et al. 2005). Various anthropogenic sources also do contribute to high F^- concentrations. The F^- sources of greatest magnitude include manufacturing of bricks, iron, fertilizers and glass, coal fired power stations and aluminum smelters (Israel 1974; Polomiski et al. 1982a; Pickering 1985; Gritsan et al. 1995).

Simultaneous air and groundwater pollution by F^- and As, due to coal combustion, causes serious health diseases over large areas of southern China (Zheng et al. 1996; An et al. 1997; Robert et al. 2002) and Inner Mongolia (Wang et al. 1999; Smedley et al. 2003; Farooqi et al. 2007), although F^- does not coexist with As in polluted groundwater in most other areas.

1.2 Arsenic and F^- Pollution in South and South East Asia

Many aquifers with recognized As and F^- problems are located in Asia as shown in Fig. 1.2 where large alluvial and deltaic plains occur, particularly around the perimeter of the Himalayan Mountain range (World bank technical report 2004). Some countries have taken As problem to the national level of attention, including Bangladesh, Nepal, and Cambodia. Others, such as India, Pakistan, and China, have only started to address the issue of As and F^-, while in other international organizations such as UNICEF and local NGOs and universities are the focal points for As related activities (World bank technical report 2004).

This section gives an account of the occurrence and scale of groundwater As and F^- problems in countries where such problems have been identified. There may be other Quaternary aquifers with high groundwater As concentration; 2s that have not yet been identified, but since awareness of the As and F^- problem has grown substantially over the last few years, these are likely to be on a smaller scale than those already identified. A summary of the recognized occurrences, aquifers involved, and populations potentially at risk (that is, using drinking water with As concentrations >50 μg L^{-1}) is given in Table 1.1.

In some As affected regions of Asia, low-As groundwater has been found in deeper aquifers underlying the young sediments. Groundwater with low As concentrations (<10 μg L^{-1}) has been found in, for example, deep aquifers in the Bengal basin (Bangladesh, India) and the Nepal Terai (World Bank technical report 2004). The depth at which these aquifers occurs varies considerably (tens to hundreds of meters) and so considerable confusion has arisen over the descriptions of these aquifers. The stratigraphy of the aquifers is poorly defined in most countries (World Bank technical report 2004).

More investigation has been carried out in Bangladesh than elsewhere. Here, the deep aquifers with low As groundwater are mineralogically distinct from the younger overlying sediments and are relatively oxic. They are likely to be of Pleistocene age (Quaternary; greater than 10,000 years old) and are considered to have undergone more flushing by groundwater over their geological history than the sediments bearing high-arsenic groundwater that overlie them (Smedley et al. 2003). Although older, deeper Quaternary aquifers in the Bengal basin and

Table 1.1 Summary of the distribution, nature, and scale of documented As problems (>50 μg L^{-1}) in aquifers in South and East Asia

Location	Areal extent (km^2)	Population at risk	Arsenic range (μg/L)
Alluvial/deltaic/lacustrine plains			
Bangladesh	150,000	35,000,000	<1–2,300
China (Inner Mongolia, Xinjiang, Shanxi)	68,000	5,600,000	40–4,400
India (West Bengal)	23,000	5,000,000	<10–3,200
Nepal	30,000	550,000	<10–200
Taiwan (China)	6,000	(?) 10,000	10–1,800
Vietnam	1,000	10,000,000	1–3,100
Myanmar	(?) 3,000	3,400,000	–
Cambodia	(?) <1,000	320,000	–
Pakistan	–	–	–

– Not available
Source World Bank Regional Operational Responses to Arsenic Workshop in Nepal, 26–27 April 2004

Nepal have been found to contain low groundwater As concentrations; this has been found not to be the case in some other regions.

Some groundwaters in Pleistocene aquifers of Vietnam also appear to have high As concentrations. Aquifer depth is therefore not an indicator of susceptibility to As mobilization. Rather, dissolved As concentrations are determined by a combination of geochemical conditions suitable for mobilizing it and hydrogeological conditions which prevent its removal (World bank technical report 2004).

In 1993, 15 of India's 32 states were identified as endemic for fluorosis (Rajiv Gandhi report 1993). In parts of northern China, high As concentrations have been found in groundwater from both shallow (young Quaternary) and deeper (older Quaternary) aquifers. Fluorosis is prevalent in some parts of central and western China and caused not only by drinking F^{-} in groundwater but also by breathing airborne fluoride released from the burning of fluoride-laden coal (Zheng et al. 1996).

1.3 Sources of As and F^{-}

1.3.1 Anthropogenic Sources of As

Anthropogenic sources of As include mining and processing of ores and manufacturing using As-bearing sulfides. Smelters in numerous countries, including Canada, Chile, Italy, South Africa, the USA have processed metal ores, mainly copper and inc, gold, and tin that contain As. The smelting process, both recent and ancient, has released As to the air and soils both locally and globally (Matschullat 2000). Soils surrounding smelters have frequently been documented with Elevated As levels in e.g., Ball et al. (1983); Beaulieu and Savage (2005). As contamination of groundwater in numerous places, including in Thailand, Ghana, and Turkey is caused by the disposal of mining wastes (Smedley and Kinniburgh 2002; Smedley 2008; Gunduz et al. 2010). In southwestern England, mineral deposits and mineral processing (tin, copper, with accessory As minerals) are recognized sources of As to soils and groundwater (Brunt et al. 2004; Camm et al. 2004; Palumbo-Roe et al. 2007). In southeastern Europe (Serbia, Bosnia, Poland), and in Spain, mining activities are responsible for contaminated soils and waters (Gomez et al. 2006; Dangic 2007; Karczewska et al. 2007). Groundwater contamination in mined areas is also found in parts of the western USA and Canada (Welch et al. 2003; Moncur et al. 2005).

Numerous products contained arsenic compounds e.g. arsenic has been used in glass production and by the wood-preservation industry (Welch et al. 2000), and contamination of soils and surface-water bodies has resulted from use of chromated copper arsenate (CCA) treated wood (Rice et al. 2002; Khan et al. 2006). The use of inorganic arsenical pesticides has declined in recent years owing to bans in the 1980s and 90s (Welch et al. 2000), but, in the past, production and use of arsenical pesticides were important contributors of As to the environment (e.g., Barringer et al. 1998; USEPA 2011).

Inorganic arsenicals have been used on a variety of crops (citrus, cotton, tobacco, and potatoes) and on fruit trees; (Walsh and Keeney 1975; Welch et al. 2000). Production of pesticides has been responsible for As contamination of soil, surface water, and groundwater. Examples of contamination caused by these former pesticide manufacture are found in India and in the USA (Barringer et al. 1998; Mukherjee et al. 2006; USEPA 2011). Soil contamination by As may also occur in areas where soils are amended with chicken and swine manure (Hileman 2007).

Arsenic was used in chemical warfare agents, most recently in the first half of the 20th century (Krüger et al. 2007). Arsenic presently is used in various electronic devices, and wrong disposal and lack of recycling these materials also can add As to the environment (Brooks 2008). Anthropogenic sources of As can affect the quality of surface water through groundwater discharge and runoff (Hemond 1995; Martin and Pederson 2002; Durant et al. 2004). Anthropogenic sources of As originated from mineral processing, glass manufacturing, wood preserving, pesticide production and application, landfill/waste pile leaching, and coal/oil production and processing, industrial waste, and coal combustion etc. (Peter et al. 2008; Farooqi et al. 2006, 2007) are the typical sources of As that result in regional increases in As concentration in the environment.

1.3.2 Anthropogenic Sources of Fluoride

The anthropogenic F^- is released in the environment by coal combustion via air pollution, and waste production by various industries, such as steel, aluminum, copper and nickel smelting; and the production of glass, phosphate fertilizers, brick and tile (Pickering 1985). Fluoride due to coal combustion is a big source in China that causes serious health diseases over large areas of southern China (Zheng et al. 1996; An et al. 1997; Robert et al. 2002) and Inner Mongolia (Wang et al. 1999; Smedley et al. 2003).

Many industrial applications, most notably brick making (Debackere and Delbeke 1978), glass, china and steel works (Kabata-Pendias 2001), sewage, production and application of phosphate fertilizer and pesticides (Kabata-Pendias 2001) are among the anthropogenic sources of F^-. Phosphate containing fertilisers add up to the fluoride content in soil and groundwater (Motalane and Strydom 2004; Farooqi et al. 2007). It is evident that superphosphate (2,750 mg of F/kg), potash (10 mg of F/kg) and NPK (Nitrogen Phosphorous Potassium) (1,675 mg of F/kg) which are phosphatic fertilisers contain remarkable amount of fluoride (Srinivasa Rao 1997). Also, fluoride concentration in irrigation water accounts to be 0.34 mg/L. In agricultural areas successive irrigation had led to the increase in fluoride concentration in groundwater (Young et al. 2010). The amount of water soluble fluoride in the soil near a phosphate fertilizer plant in Brazil was 10 mg/kg. Datta et al. (1996) put forth that if an agriculture field of 1 ha receives 10 cm of irrigation water containing 10 mg/L of fluoride, then the soil can obtain 10 kg of fluoride. This is considered as a potential threat for increase in fluoride concentration in soil and groundwater. The source of the problem lies in the fact that raw phosphate ore contains high concentrations of fluoride, usually between 20,000–40,000 parts per million (equivalent to 2–4 % of the ore). When this ore is processed into water-soluble phosphate (via the addition of sulfuric acid), the fluoride content of the ore is vaporized into the air, forming highly toxic gaseous compounds (hydrogen fluoride and silicon tetrafluoride). The continuing accumulation of F^- in soil from distributed P fertilizers in New Zealand and Australia (Cronin et al. 2000) has raised concern over future risk.

1.4 Natural Source of Arsenic

1.4.1 Minerals Having Arsenic

Arsenic occurs naturally in rocks and minerals, although its distribution varies widely. Arsenic occurs as a major constituent in more than 500 minerals, including elemental arsenic, arsenides, sulfides, oxides, arsenates, and arsenites. Most are ore minerals or their alteration products. The most abundant arsenic ore mineral is arsenopyrite (FeAsS). This is often present in ore deposits. Other arsenic sulfides found in mineralized areas are realgar (AsS) and orpiment (As_2S_3). Though not a major component, arsenic is also present in varying concentrations in common rock-forming minerals (Smedley and Kinniburgh 2002). There are about 24 As-bearing minerals that are commonly found in hydrothermal veins, ore deposits, and rocks. Most primary As minerals are sulfides, of which arsenopyrite is the most common (Ehrlich and Newman 2009) (Table 1.2).

1.4.2 Volcanic Rocks, Geothermal Activity

Arsenic being an incompatible element, it accumulates in differentiated magmas, and is commonly found at higher concentrations in volcanic rocks of intermediate (andesites) to felsic (rhyolites) composition than in mafic (basaltic) rocks (Welch et al. 1988, 2000). Geothermal waters on Dominica in the Lesser Antilles also contain concentrations of As >50 µg/L (McCarthy et al. 2005). In Maine and New Hampshire, USA, pegmatites, granites and metamorphic rocks (granofels) were found to have substantial As contents up to 60, 46 and 39 mg/kg, respectively (Peters et al. 1999; Peters 2008). Fractured ultramafic rocks in Vermont, USA, contribute up to 327 µg/L of As to groundwater although mafic rocks contain much lower As (Ryan et al. 2011). As in hot springs from geothermal fields in New Zealand is found at concentrations that range to 4,800 µg/L and Acidic (pH 1.2) geothermal springs in Japan contained As at 2,600 µg/L (Noguchi and Nakagawa 1969).

Arsenic concentrations in the geothermal springs along the coastal volcanic areas of Central and South American countries where rocks are mainly andesitic or rhyolitic in composition. Arsenic concentrations in the geothermal springs throughout these areas vary widely. Concentrations of several thousand micrograms per liter are reported in these areas. In Bolivian Altiplano, As concentrations in the lake water are reported as high as 4,600,000 µg/L, the As apparently being contributed by oxidation of sulfide deposits (Lopez et al. 2012). In the Chaco- Pampean plain of Argentina dissolution of volcanic glasses in ash layers and leaching of loess-type deposits have resulted in groundwater As concentrations that range from <10 to 5,300 µg/L (Nicolli et al. 2012). Mining of various metals (gold, copper, silver) in Latin America has played an important role in mobilizing As from the geologic materials and exacerbating contamination of groundwater resources (McClintock et al. 2012).

1.4.3 Sedimentary Bedrock

Arsenic is found in coals, highest from China 826 to 2,578 mg/kg is reported (Nriagu et al. 2007) and up to 32,000 mg/kg is listed by Wang and Mulligan (2006). In Germany As content of bituminous shales ranges from 100 to 900 mg/kg (Smedley and Kinniburgh 2002) and in American colas the As content of is high as 2,200 mg/kg (Wang and Mulligan 2006) with the mean concentration for more than 7,000 samples is about 24 mg/kg (Kolker et al. 2006). Pyrite is the main source of As in coals with high As content, whereas in lower As coals, the As tends to be associated with the organic material (Yudovich and Ketris 2005). In Australia due to drought and increased water withdrawals caused oxidation of pyrite in sedimentary aquifers, resulting in As contamination of

Table 1.2 Typical Arsenic concentrations in rock-forming minerals

Mineral	Arsenic (mg kg^{-1})
Sulfide minerals	
Pyrite	100–77,000
Pyrrhotite	5–100
Marcasite	20–126,000
Galena	5–10,000
Sphalerite	5–17,000
Chalcopyrite	10–5,000
Oxide minerals	
Hematite	up to 160
Fe oxide (undifferentiated)	up to 2,000
Fe(III) oxyhydroxide	up to 76,000
Magnetite	2.7–41
Ilmenite	<1
Silicate minerals	
Quartz	0.4–1.3
Feldspar	<0.1–2.1
Biotite	1.4
Amphibole	1.1–2.3
Olivine	0.08–0.17
Pyroxene	0.05–0.8
Carbonate minerals	
Calcite	1–8
Dolomite	<3
Siderite	<3
Sulfate minerals	
Gypsum/anhydrite	<1–6
Barite	<1–12
Jarosite	34–1,000
Other minerals	
Apatite	<1–1,000
Halite	<3–30
Fluorite	<2

well water (Appleyard et al. 2006). Groundwater from a sandstone aquifer contained As at concentrations that crossed 10–50 µg/L; the As content of the sandstone ranged from 5 to 15 mg/kg. Desorption at pH of about 8 appeared to be the mechanism for As release to groundwater (Kinniburgh et al. 2006). Water from wells completed in a Mesozoic Era sandstone in northern Bavaria also contained As at concentrations from 10 to 150 µg/L (Heinrichs and Udluft 1999). Typical As-bearing minerals include arsenopyrite (FeAsS), cobaltite ((Ni, Co, Fe) AsS), alloclasite ((Co, Fe)AsS), gersdorffite (NiAsS), erythrite ($Co_3(AsO_4)_2 \cdot 8H_2O$), and safflorite (Co, Fe, Ni) As_2) (Senior and Sloto 2006).

In Taiwan black shales, muds and fine sands is contaminated with As while in northern Bavaria, Phosphorite deposits can contain substantial amounts of As up to about 400 mg/kg (Smedley and Kinniburgh 2002) because arsenate can substitute for phosphate in minerals.

1.4.4 Alluvial Sediments

The extensive alluvial plain and delta are formed by the sediments shed from the Himalayas through which the Ganges, Brahmaputra and Meghna and Indus Rivers flow and which form aquifers in India (West Bengal Delta Region) and adjacent Bangladesh and Pakistan. Arsenic released from these sediments has caused the most well-known contamination in the world, with populations of many millions affected by drinking As contaminated water (Nordstrom 2002). The As contents of these young sediments are not extremely high about 1–15 mg/kg, but vary with depth (Smedley 2008). The concentrations of As in groundwater range, however, from undetectable to several thousand µg/L (Smedley 2008; van Geen et al. 2003).

In the shallow aquifer in West Bengal, organic carbon is present as petroleum-related compounds (Rowland et al. 2006). In Cambodia, Vietnam, and Laos, As in young deltaic sediments of the Mekong and Red River basins has also contaminated groundwater (>1,000 µg/L in some cases) in drinking water (Berg et al. 2001; Agusa et al. 2006; Luu et al. 2009; Hoang et al. 2010; Chanpiwat et al. 2011).

Quaternary sediments of fluvial and eolian origin in the Pannonian Basin of Hungary and Romania have contributed As to groundwater; the sediments are composed of sands and loess. Quartz, feldspar, carbonates (Varsányi and Kovács 2006). Other Fe-bearing minerals, from which As may be released, are reported to include goethite, limonite, pyrite, and siderite.

1.5 Natural Sources of Fluoride

Some of the minerals where fluorides can be found in significant fractions are fluorite (CaF_2), which occurs in both igneous and sedimentary rocks, apatite $Ca_5 [PO_4]_3(Cl, F, OH)$, villiaumite (NaF), cryolite ($NaAlF_6$), topaz $[Al_2SiO_4 (F, OH)_3]$, and rock phosphate. Fluorine is a lithophile element with atmophile affinities, and occurs in many common rock-forming minerals, topaz $Al_2F_2 [SiO_4]$, simple halides such as carobbite KF, silicates such as muscovite $KAl_2 (OH, F)_2 [AlSi_3O_{10}]$ and a range of amphibole and mica minerals (Wedepohl 1978).

Felsic igneous rocks tend to have higher concentrations of fluorine than mafic rocks. The average F^- content of rocks is 1,000 mg/kg in Felsic rocks, 400 mg/kg in intermediate rocks, dropping to 100 mg/kg^{-1} in ultramafic rocks deficient in SiO_2 (Wedepohl 1978). In general, mica minerals tend to be the major source of F^- in igneous rocks e.g., the mica phlogopite $KMg_3 (OH, F)_2 [AlSi_3O_{10}]$ is main source of fluorine in ultramafic rock types (Rimsaite 1970).

Fluoride minerals such as fluorite and cryolite are not readily soluble in water under normal pressure and temperature. But under alkaline conditions and range of specific conductivity between 750 and 1,750 µs/cm, dissolution rate of fluorite minerals increase. Granitic rocks which are a typical source of fluoride rich rocks contain fluoride ranging between 500 and 1,400 mg/kg (Koritnig 1978; Krauskopf and Bird 1995), which is much higher than any other rock type. The world average content of fluoride in granitic rocks is 810 mg/kg (Wedepohl 1969). The weathering of these rocks results in increased fluoride content in groundwater. Longer residence time in aquifers with fractured fluoride rich rocks enhance fluoride levels in the groundwater. Naseem et al. (2010) put forth that granitic rock and clay in Pakistan contained average fluoride of 1939 and 710 mg/kg respectively. Granite and granitic gneisses in Nalgonda, India contain fluoride rich minerals such as fluorite (0–3.3 %), biotite (0.1–1.7 %) and hornblende (0.1–1.1 %) (Rao et al. 1993). Mondal et al. (2009) reported from the same area that the rocks contain 460–1,706 mg/kg of fluoride.

1.6 Health Effects of As and F$^-$

1.6.1 Health Effects of As

- Blackfoot Disease

  Arsenic is a major risk factor for what is known as blackfoot disease, that is, peripheral atherosclerosis resulting in dry gangrene and spontaneous amputation of affected extremities. The disease was endemic to the south-eastern coastal region in Taiwan, where residents have used arsenic-contaminated water for more than 50 years (Tseng et al. 1968; Chen et al. 1985).

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- Skin and Other effects

  The carcinogenic properties of As were suspected as early as the late 19th Century. Arsenic is now widely recognized and regulated as a carcinogen (USEPA 2001). Chronic ingestion of inorganic As causes characteristic skin lesions, such as keratosis and hyperpigmentation and hypopigmentation, as observed in populations in Bangladesh, Chile, China, India, and Taiwan (Ma et al. 1999).

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- Skin Cancer

  In 1887, Hutchinson first described skin cancer in patients treated with arsenic containing medication for psoriasis and other skin conditions. A characteristic sequence of skin effects caused by chronic arsenic exposure seems to involve initial hyper pigmentation, followed by the precancerous condition keratosis, and finally, in some cases, skin cancer (Roth 1957).

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- Kidney and Bladder Cancer
  Dose-response relationships between mortality from kidney and bladder cancer and levels of arsenic in drinking water have been described extensively in a population in Taiwan, and the relative risk of mortality due to bladder cancer was estimated to be extremely high (28.3 for men; 65.4 for women (Chen et al. 1985, 1988)).
- Lung Cancer
  Reports from Argentina and Taiwan have mentioned elevated rates of lung cancer and Bowen's disease in relation to arsenic in drinking water (Pershagen 1985).

1.6.2 Health Effects of Fluoride

- Osteoporosis and Arthritis
  On July 9, 1998 the Manchester Guardian reported news of fluoride poisoned water in Central India, from untested wells drilled in the 1980s, causing severe arthritic damage to tens of millions of people a national disaster (Datta et al. 1996).
- Hip fractures
  Drinking fluoridated water will double the number of hip fractures for both older men and women. Some studies have indicated 87 % higher risk of hip fractures to the elderly in areas where water fluoridation was even below 1.5 ppm.
- Cancer
  Fluoride was found to be an equivocal carcinogen by the National Cancer Institute Toxicological Program (Maurer et al. 1990). Further studies by the New Jersey Department of Health have now confirmed a 6.9 fold increase in bone cancer in young males (Cohn et al. 1992).
- Infertility
  Infertility in women was found to increase with water fluoridation. Food and Drug Administration (FDA) scientists reported a close correlation between decreasing total fertility rates in women between ages of 10 and 49, and increasing fluoride levels.
- Brain damage
  Fluorides lower the intelligence capacity of humans, with children, again, especially susceptible to early fluoride toxicity.
- Alzheimer Disease
  There are also several studies linking aluminum with fluoride, showing that the bioavailability of aluminum is increased in the presence of fluorides, causing aluminum in the brain to double in treated animals. In the US every 2nd person over 70 will develop Alzheimer's (National Research Council 1993).

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1.7 Geochemical Processes Controlling As and F^- Mobility

1.7.1 Geochemical Processes Controlling As Mobility

Two processes largely control As mobility in aquifers:

(1) adsorption and desorption reactions and
(2) solid-phase precipitation and dissolution reactions.

Fixation of As an iron oxide surface is an example of an adsorption reaction. The reverse of this reaction, As becoming detached from surface, is an example of desorption. Solid-phase precipitation is the formation of mineral(s) from dissolved components in aqueous solution (Langmuir 1997).

Arsenic adsorption and desorption reactions are influenced by changes in pH, occurrence of redox (reduction/oxidation) reactions, presence of competing anions, (Smedley and Kinniburgh 2002). Solid-phase precipitation and dissolution reactions are controlled by solution chemistry, including pH, redox state, and chemical composition (Smedley and Kinniburgh 2002). The detail of these two processes and the factors affecting is described below.

- Adsorption and desorption processes

Arsenic is a redox-sensitive element. Arsenate and arsenite are the two forms of As commonly found in groundwater (Masscheleyn et al. 1991). Arsenate generally predominates under oxidizing conditions, while arsenite predominates under reducing one. Under the pH conditions of most groundwater, arsenate As^{V} is present as the negatively charged oxyanions $H_2AsO_4^-$ or $HAsO_4^{2-}$, whereas arsenite As^{III} is present as the neutral species $H_3AsO_3^0$. Arsenate and arsenite are adsorbed to surfaces of a variety of particles in aquifer such as, aluminum oxides, and clay minerals. Arsenate is adsorbed strongly on iron-oxide surfaces in acidic and near-neutral-pH water (Dzombak and Morel 1990). However, it is favorably desorbed from iron-oxide surfaces as pH becomes alkaline (Dzombak and Morel 1990). The pH-dependence of As^{V} adsorption onto iron-oxide surface appears to be related to the change in net surface charge of iron-oxide from positive to negative in association with increasing pH increases above the zero-point-of-charge (pH at which the net surface charge is equal to zero), which varies with mineral species e.g., it is about 7.7 for goethite (crystalline iron oxide) or 8.0 for ferrihydrite (amorphous iron oxide) (Dzombak and Morel 1990). When pH is above about 8, iron oxide can repel negatively charged ions such as As^{V}. As is the case for adsorption of As^{V} to iron-oxide surfaces, adsorption of As^{III} to iron-oxide surfaces tends to decrease as pH increases, at least between the range from pH 6 to 9 (Dzombak and Morel 1990). As a result of the pH dependence of As adsorption, changes in ground-water pH can promote adsorption or desorption of As. Because solid-phase digenesis (water-rock interaction) typically consumes H^+, the pH of groundwater tends to increase with residence time, which, in turn, increases along ground-water flow paths. Because iron-oxide surfaces can hold large amounts of adsorbed As^{V}, geochemical evolution of groundwater to high (alkaline) pH can induce desorption of As^{V} sufficient to result in exceeding the USEPA current MCL in some environments (Robertson 1989). Redox reactions involving either aqueous or adsorbed As can affect As mobility (Manning and Goldberg 1997).

Arsenic adsorption also can be affected by the presence of competing ions. In particular, phosphate and As^{V} have similar geochemical behavior, thus, both compete for sorption sites (Manning and Goldberg 1996). Oxyanions in addition to phosphate also may compete for sorption sites. For example, Robertson (1989) suggested that correlation of As^{V} with oxyanions of molybdenum, selenium, and vanadium in groundwater of the Southwestern United States may be evidence for competitive adsorption among those oxyanions.

- Precipitation and dissolution processes

Various solid phases (minerals, amorphous oxides, volcanic glass, and organic carbon) in aquifers exist in a variety of thermodynamic states. At any given time, some solid phases are undergoing dissolution in the aquifer, whereas the others are precipitated from the groundwater solution. Arsenic contained within solid phases, either as a primary structural component of or an impurity in any of a variety of solid phases is released into groundwater when those solid phases are dissolved. Similarly, arsenic is removed from groundwater when As bearing solid phases is precipitated. Since As is often coprecipitated with iron oxide, iron oxide may act as an arsenic source (case of dissolution) or a sink (case of precipitation) in the aquifer. The release of adsorbed As associating with solid-phase dissolution is distinct from desorption from stable solid phases.

1.7.2 Geochemical Processes Controlling F^- Mobility

Fluorine occurs in almost all waters from trace to concentrations as high as 2,800 mg/L (e.g. Soda Lakes of East African Rift System; Gaciri and Davies 1993). Its concentration in natural waters depends on such factors as temperature, pH, presence or absence of complexing or precipitating ions and colloids, solubility of fluorine-bearing minerals, anion exchange capacity of aquifer materials (OH^- for F^-), the size and type of geological formations traversed by water, and the amount of time that water is in contact with a particular formation.

Minerals which have the greatest effect on the hydro-geochemistry of fluoride are fluorite, apatite, micas, amphiboles, certain clays, and villiaumite. Fluorite is the main mineral controlling aqueous fluoride geochemistry in most environments; there are however some notable exceptions in sedimentary basin environments (Foster 1950; Boyle 1992) and certain igneous terranes (Krainov and others 1969). Apatite, micas, and amphiboles have much lower solubilities than fluorite; the dissolution of fluoride from these minerals is most pronounced at low pH values. Certain clay minerals (illite, chlorite, smectites) represent excellent anion exchange media from which large aqueous concentrations of F^- can be generated (Boyle 1992). Villiamite (NaF) is an almost infinitely soluble mineral which may contribute considerably to F^- concentrations in groundwaters associated with certain per alkaline intrusive bodies, such as the Lovozero Massif of Russia (Krainov et al. 1969). The amount of F^- released by the dissolution of fluorite in water with low ionic strength is of the order 8–10 ppm (Boyle 1976). However, the concentrations of Ca, Na, hydroxyl ion, and certain complexing ions, such as Fe, Al, B, Si, Mg, and H, can alter this concentration range of fluoride.

Due to the common ion effect, the dissolution of fluorite is suppressed when the concentration of calcium is above the limit for fluorite solubility. Various research studies (Voroshelov 1966; Boyle 1976, 1992) have indicated a strong negative correlation between Ca and F^- in groundwaters that contain Ca in excess of that required for the solubility of fluorite. Voroshelov (1966) has shown that Ca in excess of that contributed by fluorite seriously affects the concentration of fluoride at levels of 0.5–3.0 ppm. This concentration range is well below the levels of fluoride (8–10 ppm) produced by the dissolution of fluorite in water of low ionic strength. Because of this, the majority of groundwaters are greatly under saturated with respect to fluorite.

Sodium may exhibit a positive correlation with F^- in many types of groundwater, especially those having low concentrations of calcium (waters undergoing base exchange). High concentrations of Na will increase the solubility of fluorite in waters. A process that can lead to very high concentrations of F^- in waters (values up to 30 mg/L). This process invariably follows base exchange softening (Ca and Mg for Na) where the pH is progressively driven to quite high alkaline values (pH 9.0–10.5). Anion exchange can occur in sedimentary basins (Boyle 1992) or igneous terranes, but is most dominant in the former environment.

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Status of As and F^{-} Groundwater and Soil Pollution in Pakistan

2

Arsenic and F^{-} testing of groundwater is considered as an important activity because As and F^{-} are now recognized as the most serious inorganic contaminants in drinking water on a worldwide basis and due to its serious effects on human health (Smedley et al. 2002). Considering the adverse effects of As and F^{-} on human health and increasing incidences of As and F^{-} pollution in the world, Pakistan Council of Research in Water Resources (PCRWR) and United Nations Children's Fund (UNICEF) has jointly carried out preliminary investigative studies for initial detection which led to detailed monitoring. Major programs in this regard are as following:

1. Northern Punjab phase-I and II (1999–2000)
2. National survey for As (2001)
- effort of UNICEF, LG&RD, PCSIR and
3. National Water Quality Monitoring Program (NWQMP 2001–2006)
4. Arsenic mitigation program (2002–2004)
- Southern Punjab (2002–2003)-Phase-I and II
- Central Sindh (2003–2004)-Phase-I

The data collected from the Phase-I (2001–2002) of NWQMP program revealed the presence of As above 50 ppb in some cities of Punjab particularly in Multan, Sheikhupura, Lahore, Kasur, Gujranwala and Bahawalpur. The situation of presence of As in groundwater of Southern Punjab has become clearer as the result of detailed testing by UNICEF and PCRWR. According to field data, 22.63 % samples had As concentration above the WHO guidelines of 10 ppb (Ahmad et al. 2004).

It was reported that As contamination exceeded 200 ppb in some districts of Sindh (Ahmad et al. 2004). The province of Sindh forms the Lower Indus basin with an area of 1, 40,915 km^2. The population of the province stands around the 40 million souls. In 2001, the Public Health Engineering Department (PHED), Government of Sindh in collaboration with the UNICEF, Sindh Karachi conducted drinking water quality survey in nine districts of Sindh in order to determine presence of As in drinking water. For this evaluation study five samples were taken from each Union Council of these districts. The survey found that out of nine (09) districts, five districts namely Khairpur, Dadu, Nawabshah, Naushero-feroz, and Thatta contained As in drinking water. Thirtyfive districts from all the four provinces monitored through an inter-organizational program.

Under the arid conditions in Pakistan, high F^{-} concentrations and high salinity appear to be more widespread water-related problems. Fluoride has also been reported from some areas of Pakistan; F^{-} is contained in most groundwater, however, concentrations are commonly <1 mg/L, with the highest concentration at 2.8 mg/L (www.pcrwr.gov.pk/Arsenic), but F^{-} testing is not done in detail as compared to the As testing, while on soil and sediment pollution no data is available (Fig. 2.1; Tables 2.1 and 2.2).

The main sources of drinking water in Pakistan come from ground or surface water which is being highly polluted by freeway disposal of agricultural,

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industrial and domestic wastes into natural water bodies (Arain et al. 2009a, b). Studies by Farooqi et al. (2007a, b), Arain et al. (2009a, b), revealed high levels of As in different regions of the country. Government of Pakistan along with collaboration of UNICEF, conducted a study in 2004 in order to assess arsenic level in different parts of the country. From total of 144 districts, 35 were selected and 8,712 drinking water samples were collected. Most of the samples were found contaminated with As in a range of 0–500 μg/L and 9 % samples were found contaminated with >10 μg/L and 0.7 % with >50 μg/L (Fatmi et al. 2009).

2.1 Spatial Extent of Arsenic Contamination

For the very first time, Ashraf et al. (1991) conducted a study in 1990 for identification of different trace metals in three large water reservoirs of the country including Tarbela, Chashma and Lloyd. The order of elevated concentrations of As were Chashma > Tarbela, Lloyd with values of 750, 620 and 620 μg/L respectively. After that no published study was reported till 1997 on As contamination in water. Aziz (2005) in his review highlighted the results of unpublished report that groundwater sampling from

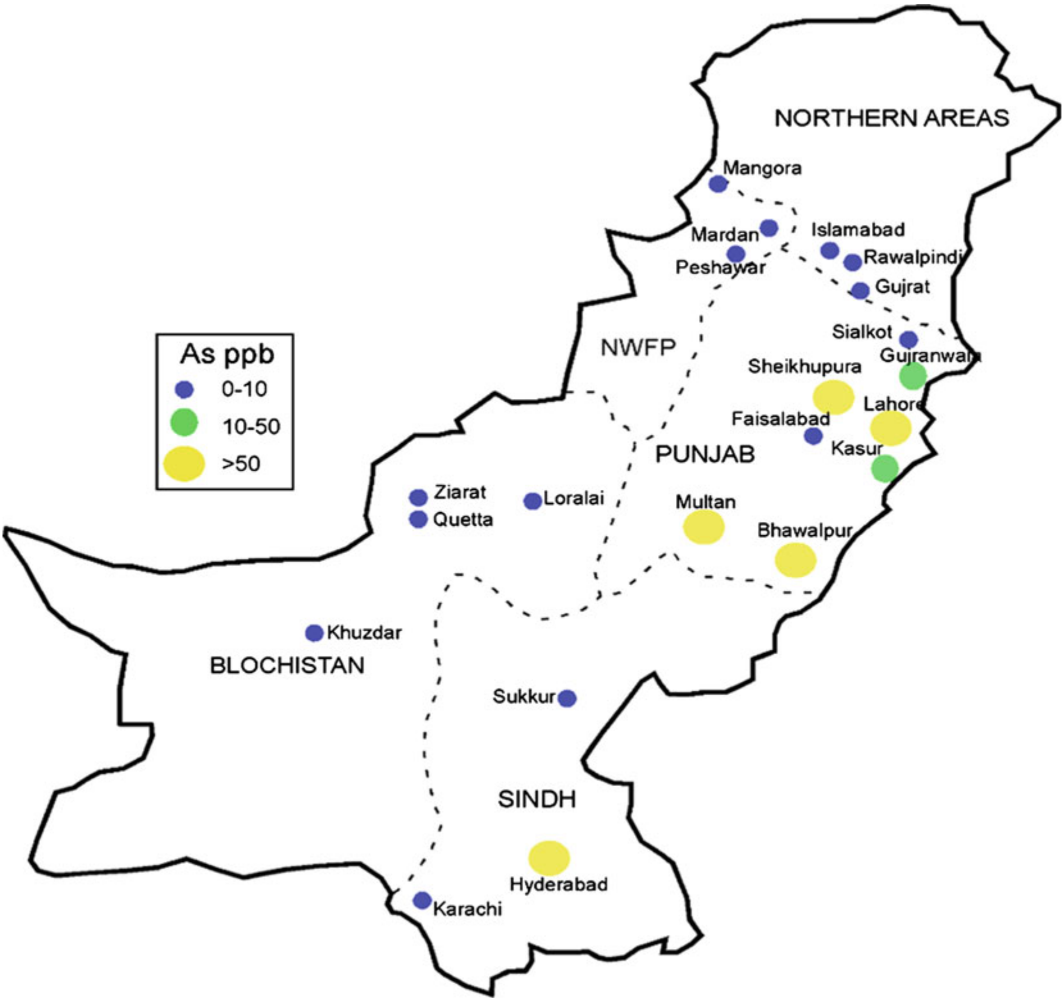

Fig. 2.1 Documented arsenic areas in Pakistan

Table 2.1 Results of the initial screening done by PCRWR and UNICEF

Province	Total area (km^2)[a]	Population[a]	Total districts[a]	Number of districts having wells contaminated with As[b]			
				<10	10–50	>50	Unknown
Punjab	205,345	73,621,000	36	6	13	14	3
Sindh	140,914	30,440,000	23	2	1	10	13
[c]Balochistan	347,190	6,566,000	30	NS	NS	NS	NS
[c]Khyber Pakhtunkhwa	74,521	17,744,000	24	NS	NS	NS	NS

[a] *Source* Pakistan Bureau of Statistics, Government of Pakistan, 1998

[b] *Source* Pakistan Council of Research in Water Resources, 2001

[c] According to PCRWR, In Khyber Pakhtunkhwa, 156 samples were analyzed, out of which 0.3 % were found exceeded the WHO limits. Samples taken from Peshawar, Mangora and Mardan were found with As concentration less than 10 mg/L. In Balochistan, 71 samples were analyzed out of which 1.4 % exceeded the WHO limits and Ziarat, Quetta, Loralai and Khuzdar were the areas where As concentration were found less than 10 mg/L (PCRWR 2001)

NS No study conducted

Table 2.2 Arsenic and fluoride analysis of groundwater samples in selected cities of Pakistan from 2002 to 2006 by PCRWR

Province	City	Parameter	2002	2003	2004	2005	2006	Number of samples
			Percentage exceeding the WHO limit As (10 ppb) and F (1.5 mg/L)					
Punjab Province	Bahawalpur	As	72	68	76	80	88	767
		F	4	4	4	4	4	
		No. of samples	25	25	25	25	25	
	Faisal abad	As	–	–	–	–	–	
		F	7	8	8	15	15	
		No. of samples	14	13	13	13	13	
	Gujranwala	As	7	43	43	43	64	
		F	–	–	–	–	–	
		No. of samples	14	14	14	14	14	
	Gujrat	As	–	–	–	–	–	
		F	–	–	–	–	–	
		No. of samples	9	9	9	9	9	
	Kasur	As	30	40	80	90	100	
		F	30	20	20	20	20	
		No. of samples	10	10	10	10	10	
	Lahore	As	31	100	100	100	100	
		F	–	–	–	–	–	
		No. of samples	16	16	16	16	16	

(continued)

Table 2.2 (continued)

Province	City	Parameter	2002	2003	2004	2005	2006	Number of samples
			Percentage exceeding the WHO limit As (10 ppb) and F (1.5 mg/L)					
	Multan	As	75	94	88	94	94	
		F	–	–	–	–	–	
		No. of samples	16	16	16	16	16	
	Rawalpindi	As	–	–	–	–	–	
		F	–	–	–	–	–	
		No. of samples	15	14	15	15	15	
	Sarghodha	As			13	13	13	
		F			8	4	4	
		No. of samples			24	24	24	
	Shekupura	As	45	64	45	64	73	
		F						
		No. of samples	11	11	11	11	11	
	Sialkot	As		10	20	20	20	
		F	–	–	–	–	–	
		No. of samples	10	10	10	10	10	
KPK Province	Abbottabad	As	–	–	–	–	–	196
		F	–	–	–	–	–	
		No. of samples				11	11	
	Mangora	As	–	–	–	–	–	
		F	–	–	–	–	–	
		No. of samples	10	9	10	10	10	
	Mardan	As						
		F						
		No. of samples	12	12	12	12	12	
	Peshawar	As	–	–	–	–	–	
		F	–	–	–	–	–	
		No. of samples	13	13	13	13	13	

(continued)

Jhelum, Gujrat and Sargodha districts has shown exceeded As concentrations in some samples above the WHO guidelines. A study conducted by Rahman et al. (1997) reported relatively less concentrations (80 μg/L) of As in ground water samples from Karachi but this concentration was still very high when compared to permissible limits (10 and 50 μg/L) of WHO. In 2000, a joint study by the Pakistan Council of Research in Water Resources (PCRWR) and United Nations Children Fund (UNICEF) was conducted and the issue of As was raised as a threat to drinking

Table 2.2 (continued)

Province	City	Parameter	2002	2003	2004	2005	2006	Number of samples
			Percentage exceeding the WHO limit As (10 ppb) and F (1.5 mg/L)					
Balochistan Province	Khuzdar	As	–	–	–	–	–	319
		F	–	–	–	–	–	
		No. of samples	8	8	11	9	11	
	Loralai	As	–	–	–	–	–	
		F	55	10	9	9	9	
		No. of samples	11	10	11	11	11	
	Quetta	As	–	–	–	–	–	
		F	42	31	24	22	24	
		No. of samples	38	35	34	32	34	
	Ziarat	As	–	–	–	–	–	
		F	–	–	–	–	–	
		No. of samples	8	7	10	10	10	
Sindh Province	Hyderabad	As	–	–	–	–	–	275
		F	–	–	–	–	–	
		No. of samples	15	15	15	15	15	
	Karachi	As	–	–	–	–	–	
		F	7	14	4	4	4	
		No. of samples	28	28	28	28	28	
	Sukkur	As	–	–	8	–	8	
		F	–	8	–	8	8	
		No. of samples	12	12	12	12	12	
								1,557

water in Pakistan. The results of monitoring program showed As contamination in many areas of Punjab and Sindh province (PCRWR 2004). Ahmad et al. (2004) reported that 16–36 % of population of Sindh is exposed to As contaminated water with over 10–50 µg/L.

A total of 49 groundwater samples were collected by Nickson et al. (2005) from Muzaffargarh, a district of southern Punjab, reported As contamination in 58 % samples with exceeded limits above 10 µg/L. Samples from 21 wells had As contamination level >50 µg/L and these wells were all found in urban areas while rest of wells containing less than 50 µg/L were found in outside the urban areas. A study conducted by Farooqi et al. (2007a, b) in eastern part of the Punjab province reported high As concentrations in water. In first attempt, Kalalanwala and Kot Asadullah, two small villages of the area, were selected for assessment of As contamination in water. The results reported arsenic concentrations range from 32 to 1,900 µg/L in the analyzed groundwater samples. These values are alarming are far more than permissible limits of WHO. Higher As concentration was found in shallow groundwater samples. Another finding of this study was presence of As in rain water samples with a maximum value of 90 µg/L which indicates the possible contribution of atmospheric pollutants to groundwater contamination (Farooqi et al. 2007a). Another study by the same author (Farooqi et al. 2007b) in the same area with sampling from different wells revealed high As contamination of groundwater. It was reported that from a total of 149 groundwater samples, 91 % were found contaminated with As concentration more than 10 μg/L. A positive correlation between As and pH was also observed. Overall, groundwater samples were found contaminated with arsenic in a range from 1 to 2,400 μg/L (Farooqi et al. 2007b).

Apart from groundwater, lake water is also heavily contaminated by As in Pakistan. Manchar lake is one of the major shallow water natural lake of Pakistan whose water is used for agriculture, fishing, drinking and domestic purposes. A study by Arain et al. (2008) reported high levels of As in this lake water ranged from 60.4 to 101.8 μg/L which is 6–10 times more than permissible limits of WHO. Another study by Arain et al. (2009a, b) conducted at the same site by taking 5 sampling sites of lake and 18 sampling sites of groundwater from the adjacent areas of Manchar lake showed high concentration of As levels. The As concentration in 1944 groundwater samples ranged between 23.3 and 96.3 μg/L which is unable for drinking purposes. The lake water was also found heavily polluted and ranged between 35 and 157 μg/L. A study at Jamshoro district which is located in southwest edge of the Sindh province reported varied As concentrations ranged between 13.0 and 106 μg/L in groundwater and 3.00–50.0 μg/L in surface waters (Baig et al. 2009). The As concentration in river water from Lahore was reported to be 2,400 μg/L (Farooqi et al. 2009) which is then used for irrigation and drinking purposes and may highly contaminate the adjacent soils where this water is used for agricultural purposes. Muhammad et al. (2010) analyzed surface and groundwater of Jijal-Dubair, Besham and Alpuri of northern kohistan areas for As concentration. The highest As concentration was reported in Dubair (16.69 μg/L) in surface waters. Overall, the As concentration in ground and surface waters of Dubair, Besham and Alpuri in μg/L were <0.03 to 0.48 and 0.13 to 16.69, 0.05 to 1.11 and <0.03 to 0.45, 0.98 to 2.02 and <0.03 to 0.02 respectively. Except one value of Dubair in surface water, all other As concentrations were in the ranges allowed by WHO for safe drinking water.

2.2 Depth Dependent Contamination of Arsenic

Hydro geochemical investigation regarding As is very important in order to understand the release of As into groundwater aquifers. According to Farooqi et al. (2007a, b) flowing rate and direction of groundwater deeply affect the chemistry of groundwater and these are further dependent upon the geological profile of the area under consideration. In Pakistan, very rare work has done in order to understand the relationship of deep aquifers and geological profile due to which As contamination of ground water has done. These studies were carried out in east Punjab by Farooqi et al. (2007a, b) but still the complete understanding of the geochemical behavior of As in geological profiles and underground water aquifers is unclear and demands further investigations. Farooqi et al. (2007a, b geo) describes the physic-chemical behavior of As in the area and reported high As concentrations in shallow depths. It is because that As mobilizes at high pH and EC which means that under alkaline conditions, As mobilizes from bound forms under oxidizing conditions (Smedley and Kinniburgh 2002). Furthermore, As releases to underground aquifers through oxidation of arsenic-bearing sulfide minerals or desorption of FeOOH adsorbing As at high pH and decrease of redox potential of the groundwater (Farooqi et al. 2007a, b geo). In east Punjab, As (V) was found to be the dominant As species and it mobilizes in alkaline conditions, otherwise it is adsorbed on Fe-oxyhydroxide/oxide at weakly acidic to neutral pH conditions. The study of Farooqi et al. (2007a, b geo) showed a negative correlation between As and Fe which indicates that FeOOH controls the As concentration in the studied groundwater. The deep aquifers >40 m depth was found most polluted with As which is the indication of high pH and Na–HCO_3^- dominant type of As, indicating typical characteristics of groundwater chemistry in stagnant aquifers. Another study by Farooqi et al. (2009) in the same area indicated that wet and dry deposition of atmospheric pollutants cause As pollution in the local soil. It was reported that soil of east Punjab has low pH but it increases owing to extensive fertilizer application in the area which mobilizes the As adsorbed onto the soil particles. After mobilization, As is released into the water and infiltrate into the shallowest groundwater. Furthermore Farooqi et al. (2007a, b) reported that As contaminated groundwater contain NO_3^- as dominant species as compared to NH_4^+, indicating the oxidizing condition for As (V) to become a dominant species form of As in the area (Table 2.3).

2.3 Population Exposed to Arsenic Contamination

Ground and surface water contamination of heavy metals through anthropogenic activities like large scale use of chemicals in agriculture and improper discharge industrial and municipal waste is attributed to major public health concern specially in developing countries like Pakistan where no proper waste management and treatment system is present (Haque et al. 2007). Arsenic is one of the most toxic heavy metal in context of human health globally and in the countries like India, Bangladesh, China and Nepal it has been reported as a major threat to health (Azizullah et al. 2011; Haque et al. 2007). Similar situation is present in Pakistan and according to a study conducted by Rahman et al. (1997) a large number of population in the

Table 2.3 Concentration of As in Pakistan coming from different sources (μg/L)

Location	Source	No. of samples (*n*)	As (μg/L)	Mean value	References
Groundwater					
Various spots in Karachi	Groundwater	–	–	80	Rahman et al. (1997)
Multan	Well water	3	60–1000	–	Nickson et al. (2005)
Muzaffargarh	Well water	46	0.0–400	–	Nickson et al. (2005)
Kalanwala, Punjab	Well water from residential area	24	32–1900	–	Farooqi et al. (2007a)
Manchar lake, Sindh	Hand pump water	1,944	23.3–96.3	60.2	Arain et al. (2009b)
Jijal-Dubair	Groundwater	10	0.13–16.69	6.07 ± 6.23	Muhammad et al. (2010)
Besham	Groundwater	15	<0.03–0.45	0.14 ± 0.18	
Alpuri	Groundwater	12	<0.03–0.02	0.01 ± 0.01	
Manchar lake adjacent areas	Groundwater	–	–	60.2 ± 12.5	
Jamshoro, Sindh	Groundwater	–	13–106	–	Baig et al. (2009)
Dera Ghazi Khan	Groundwater	–	0.37–29.30	–	Malana and Khosa (2011)
Lahore and Kasur districts, Punjab	Shallow groundwater	32		235	Farooqi et al. (2007a)
Lahore and Kasur districts, Punjab	Middle groundwater	17		45	Farooqi et al. (2007a)

(continued)

Table 2.3 (continued)

Location	Source	No. of samples (*n*)	As (µg/L)	Mean value	References
Lahore and Kasur districts, Punjab	Deep groundwater	3		60	Farooqi et al. (2007a)
Surface water					
Manchar Lake	Lake water	150	35–157	97.5 ± 28.5	Arain et al. (2009b)
Tarbela Reservoir	River water	–	–	0.620 ± 0.040	Ashraf et al. (1991)
Chashma Reservoir	River water	–	–	0.750 ± 0.146	Ashraf et al. (1991)
Lloyd	River water	–	–	0.620 ± 0.051	Ashraf et al. (1991)
River Ravi, Lahore	River water	5	0.32–1.8	–	Tariq et al. (1994)
River Chanab	River water	1	–	7	Nickson et al. (2005)
Manchar lake	Lake water	–	–	97.5 ± 28.5	Arain et al. (2009a)
Manchar lake		2,160	76.5–86.1	–	Kazi et al. (2009)
Besham	Surface water	9	0.05–1.11	0.71 ± 0.35	Muhammad et al. (2010)
Jamshoro, Sindh	Surface water	–	3.0–50.0	–	Baig et al. (2009)
Jijal-Dubair	Surface water	8	<0.03–0.48	0.24 ± 0.34	Muhammad et al. (2010)
Alpuri	Surface water	8	0.98–2.02	1.50 ± 0.73	Muhammad et al. (2010)
Industrial wastewater					
Peshawar Industrial Estate No. 1 Peshawar	Industrial discharge water	–	–	643	Rehman et al. (2008)
Gujranwala Industrial Estate No. 2	Industrial discharge water	–	–	475	
Hattar Industrial Estate Haripur	Industrial discharge water	–	–	942	

country is exposed to high doses of Arsenic and are under risk of various health problems and overexposure may cause a decrease in the production of red and white blood cells, gastrointestinal irritation, disruption of heart rhythm, blood vessels damage and may cause “pins and needles” sensation in hands and feet (Abernathy et al. 2003). Arsenic concentration of 80 µg/L was found in groundwater samples of Karachi (Rahman et al. 1997). Recently a study conducted in eastern Punjab reaching have reported a high concentration in groundwater reaching 1,900 and 2,400 µg/L and 91 % of samples have exceeded the WHO standard limits of 10 µg/L (Farooqi et al. 2007a, b). population living close to large water channels like river, streams and canals have a higher risk of health related problems and in Pakistan and it has been reported that, the health burden in the skin lesions alongside the river Indus suggests that there is a strong link present between proximity of river and Arsenic contamination in ground water

(Fatmi et al. 2009; Shafiq et al. 2011). Nafees et al. (2011) reported that decrement in lung function is significantly related with chronic exposure to arsenic in drinking groundwater among population living around indus river in district kahirpur, Sindh. A study conducted by Masuda et al. (2010) reported a high concentration of Arsenic in the sediments of village of Kalalanwala, Punjab, Pakistan and this high concentration was attributed to various anthropogenic sources like industrial waste, or detrital chlorite. Arsenic concentration in drinking water and tobacco smoking was correlated with human health in the population living in the vicinity of Manchar lake, southern Sindh and it was revealed that high concentration of Arsenic in lake water (35.2–158 µg/L) and in local cigarette tobacco was attributed to respiratory effects among the population (Arain et al. 2009a, b). Industries play a major role in the increase in heavy metal contamination of groundwater and these heavy metals when enter into the food chain through agriculture or groundwater seepage, have potential to cause some serious health issue (Rehman et al. 2008). Pathway of arsenic may also be related to occupational exposure especially those people working in various industries and a study in the industrial estates of Gujranwala, Peshawar and Hattar have shown a significant increase in the arsenic concentration (0.942 mg/L) in the groundwater and ultimately affecting the health of the population exposed to it (Rehman et al. 2008). Southern Punjab has also been reported under the influence of arsenic contamination and a study conducted by Nickson et al. (2005) reported a high concentration of arsenic in the urban areas of District Muzaffargarh however, the concentration in the rural areas was found within permissible limits and this low arsenic level was attributed less pollution level in the rural areas. In conclusion, ground and surface water of most areas especially urban and industrial areas are under the high influence of Arsenic contamination and population exposed to this contamination has serious threats to their health. Therefore mitigation measures must be taken to minimize the burden of arsenic exposure and must be considered a priority and included in the water policies. Millions of people that reside along the banks of river Indus, principally in Punjab and Sindh provinces in Pakistan are exposed to high level of arsenic and should be a major target for mitigation.

2.4 Epidemiological Investigation of Arsenic in Pakistan

Arsenic concentration is found to be high in different areas of Pakistan in ground and surface water which is used for drinking and irrigation purposes. By the use of As contaminated water, public health is severely affected in the country (Shah et al. 2009). Rare epidemiological investigations have been carried out regarding arsenic in the country. Although exposure to even low quantities of arsenic is dangerous and can cause severe diseases and need epidemiological investigations by public health officials and professionals but unfortunately there is less awareness regarding this serious issue. Kazi et al. (2009) conducted epidemiological investigation in Sindh to reveal the health effects of arsenic. Their findings showed that 61–73 % population suffered from chronic arsenic toxicity residing on the bank of Manchar lake. Melanosis and keratosis were the commonly found diseases owing to arsenic toxicity. A strong correlation was also observed in drinking water and patients samples (hair and blood samples of exposed skin) in terms of arsenic concentration which indicated that As contaminated drinking water is the source of such diseases. Other health problems like anemia, respiratory effects, muscles cramps and gastrointestinal effects were also observed in the patients. All these diseases were found in those effected persons who had high As intake in their diet or drinking water. The people consuming less As contaminated water were found free from such problems discussed above. At the same area, but with different sampling location, Arain et al. (2009a, b) conducted a study in Bobak village near Manchar lake and found that

Table 2.4 Diseases reported in Pakistan due to high As contamination

Water source	Disease	City/area	References
Ground water	Skin lesions	District Khairpur	Fatmi et al. (2009)
Drinking water	Respiratory diseases	Southern Sindh	Arain et al. (2009a, b)
Drinking water	Lungs function decrement	District Khairpur	Nafees et al. (2011)
Ground and surface water	Cancer risk	Kohistan region	Muhammad et al. (2010)

30–40 % of people were suffering from skin lesions and rough skin with black dots possibly due to exposure of high arsenic concentrations. Malik et al. (2009) recognized drinking water as one of the major source of arsenic intake by humans. The authors also describes that detection of arsenic in drinking water is a difficult process because of involvement of complex analytical techniques and without its proper detection, one cannot find its presence in water because even at high As concentrations in drinking water, it does not accompanied any change in taste, odor or visible appearance of drinking water (Table 2.4).

2.5 Sources and Causes of As Contamination in Pakistan

Natural and anthropogenic are the main sources of water contamination (Arain et al. 2009a, b) including industrial, municipal and domestic disposal in water systems (Ahmad et al. 2004). Intensive agricultural system also causes arsenic pollution through runoff containing organic and inorganic arsenic fertilizers. Similarly industrial activities contribute a lot in arsenic pollution. According to Sial et al. (2006), there are total 6,634 registered industries in Pakistan, out of which, 1,228 are considered highly polluting. The waste effluent of these industries contains high organic loads and toxic metals including arsenic (Rehman et al. 2008) conducted a study to assess arsenic concentrations in industrial discharges. Their results clearly indicated high arsenic containing discharge from major industries of the country. The maximum concentration of As was found in Hattar Industrial Estate samples with a mean concentration of 942 µg/L. Among agricultural sources, Arain et al. (2009a, b) pointed out that extensive application of inorganic As herbicides, insecticides, and fungicides would be the source of As pollution. Farooqi et al. (2007a, b) also pointed out that pesticides in the form of calcium arsenate, arsenic acid, lead arsenate and sodium arsenate are the major contributor of As in local water bodies. Another source from agriculture is the use of arsenic fertilizers such as di ammonium phosphate (DAP) which contains water soluble As (Farooqi et al. 2007a, b). It is estimated that DAP contains 5–10 mg/kg with an average of 7.4 mg/kg which may seep down to underground waters and cause contamination (Baig et al. 2009). Furthermore, the problem is extended when As containing fertilizers are not properly utilized by crops and agricultural runoff of As during flooding and monsoon season also increases. Another main route of water pollution is from air deposition of As mainly from coal burning and brick kilns (Baig et al. 2009; Farooqi et al. 2009). It is supported by the study of Farooqi et al. (2007a, b) who reported high As concentration in rain water which clearly indicates the atmospheric pollution of As. According to Shah et al. (2009) ore mining and processing, dye manufacturing, tanneries, thermal power plants, pesticides, herbicides and insecticides are the major As pollution sources in the country. Domestic and municipal wastes also contain high arsenic levels which are directly discharged into drains or thrown openly in fields in many areas of the country. These drains when discharge into the lake or river bodies cause high As pollution such as reported by (Shah et al. 2009), according to whom As pollution in Manchar lake is possibly due to local drains receiving high domestic and municipal wastes.

Table 2.5 Arsenic polluted countries in South Asia with affected population and the reason/mechanism of pollution

Country	Year of discovery	Population affected by As	Max. range of Pollution	Mechanism/reason of pollution
Bangladesh	1993	35,000,000	0.052–4.727	Over-exploitation of groundwater (pyrite oxidation) or arsenic released under reducing condition
India	1978	11,000,000	0.05–3.7	Over-exploitation of groundwater (pyrite oxidation)
China	1953	5,600,000	[a]	Use of coal as fuel
Pakistan	2000	2, 000,000[b]	0.05–2.4	Oxidation of arsenic bearing minerals[c]

[a] *Not exactly known*
[b] *Not exactly known*
[c] *Probable source not exactly known*
*Source*Akram (1997), BGS (1999), SOES-DCH (2000) and Farooqi et al. (2007b)

2.6 Co-occurrence of F with As

Fluoride occurs naturally in soil, water, plants, animals and humans in trace quantities. It is an essential element for human health and both its deficiency and overexposure lead to different severities like bone deformities and dental fluorosis. In Pakistan, a large variation in fluoride concentration has been observed in drinking water (Azizullah et al. 2011). The high concentrations of fluoride that are observed in various studies is due to leaching from fluoride-bearing minerals (Naseem et al. 2010; Shah and Danishwar 2003), industrial wastes (Siddique et al. 2006), agricultural fertilizers and combustion of coal which release fluoride into the air which later reaches the soil with rain (Farooqi et al. 2007a, b).

Previous researches suggest that some areas are characterized by high levels of As along with F. Highly F^- and As contaminated groundwaters appear in Waran Pira Wara, Kalalanwala, and Kot Asad Ullah (Masuda et al. 2010), and surrounding areas (Farooqi et al. 2009). There seems no appreciable trend of Arsenic concentration with respect to concentration of other physicochemical parameters except for small correlation between arsenic concentration and pH, EC, nitrate, chloride, total hardness and sodium does exist (Malana and Khosa 2011). In some areas the distribution of areas with high F^- concentrations is characterized by sites having high levels of As, however, As and F fail to show any positive correlation suggesting that the two may have different sources but similar polluting paths (Farooqi et al. 2009) (Table 2.5).

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3

Mechanism of Arsenic and Fluoride Release: A Case Study from Lahore and Kasur, Punjab Pakistan

A. Study Background and Sampling for Water and Soil Samples

B. Environmental Isotopes

3.1 Study Background

Groundwater pollution in Pakistan, Kasur district, was first officially noted in July 2000, when a newspaper reported that residents of Kalalanwala village suffered from a mysterious bone disease (22nd July, 2000 Dawn, Jang, The News). The serious nature of the problem attracted the attention of domestic and international media (The Nation, July 2000). Around 8 years ago the world media including BBC rushed to highlight the cases of bone deformation among children. Some severe cases were brought to hospitals in Lahore city. Some were operated and some treated in the outdoor. The government agencies provided alternate source of water supply.

More than 400 residents were diagnosed with bone disease, which included common complaints of joint and back pain. Bone deformation and spinal defects were also observed. Children were especially affected; 72 patients were under 15 years of age (Table 3.1). Many local Government organizations like PCSIR, PCRWR and GSP collected and analyzed the water samples from Kalalanwala.

The initial reports showed very high level of F^- (>20 mg/L) along with high concentrations of As 960 µg/L (Naseem et al. 2010). A reconnaissance survey of groundwater at Kalalanwala and Kot Asadullah was undertaken during November 2002 to investigate the level of F^- and As contamination and to identify the formation mechanism of the contaminated groundwater. I have collected 24 groundwater samples from the Kalalanwala area in November 2002 and analyzed for major and As and F^- concentrations. Very high concentrations of As (2,100 µg/L) and F^- (21.1 mg/L) were detected from the study area. In order to know the extent of contamination and the possible migration paths of these contaminants, the study area was extended from a single village to surrounding 17 villages (Fig. 3.1).

Increasing incidence and awareness of As in many alluvial aquifers of South-east Asia has raised concern over possible As and F^- in the alluvial plains of Pakistan. Pakistan Council for Research and Water Resources (PCRWR) and UNICEF have undertook assessing drinking water quality since 1999 following the As crisis in Bangladesh and other neighboring countries. Consequently, the presence of As contaminated groundwaters (10–200 µg/L) has been recognized in many areas of Pakistan (www.pcrwr.gov.pk/Arsenic). According to the report, F^- is contained in most groundwater, however, concentrations are commonly <1 mg/L, with the highest concentration at 2.8 mg/L (www.pcrwr.gov.pk/Arsenic). Also, no specific correlation

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Table 3.1 Characteristics of children affected with bone deformity disease in Kalalanwala, Kasur

Parameter	Characteristics	Number of patients
Age	1–5 years	24
	6–10 years	31
	11–15 years	16
	>15 years	1
Gender	Male	42
	Female	30
Total number of households in Kalalanwala village	381	
Total population of Kalalanwala village	3,042	
Number of cases reported with bone deformity disease	72	
Typical clinical presentation main bones and joints involved	Femur, tibia, fibula knee joints, humerus radius, ulna, small joints of hands	
Dental problems	Dental caries, teeth molting, brown discoloration of teeth	
Typical radiological findings in various bones	Coarsening trabeculae Osteosclerosis Growth arrestation Calcification at the site of tendon insertions	

Source Jahangir and Nabeel, University of Lahore, 2001

between As and F^- content was observed in the monitored groundwater.

The Public Health Engineering Department of Pakistan, in collaboration with UNICEF, recently revealed that As-enriched groundwater occurs in the Indus alluvial basin and that the highest As concentration was 906 µg/L in the Muzaffargarh district, southwest Punjab (Nickson et al. 2005). Many non-profit organizations like UDERC (http://www.uderc.org/) are also working on the As groundwater pollution in Pakistan.

Although arsenic's acute toxicity has been described by these organizations, UNICEF, LG&RD, PCSIR & PHED, but the possible sources and the factors controlling the As and F^- solubility in groundwater and those in soil along with the geochemistry of As and F^- was not discussed before, moreover there was lack of any scientifically published data from Pakistan.

The main objectives of the study are:

- To know the extent of contamination and the spatial distribution of As and F^- in groundwaters and soils from Punjab Pakistan.
- To know the contribution of anthropogenic sources.
- To understand the geochemistry of As and F^- and the factors which control the mobilization of As and F^- into the soil, and ultimately into the groundwater.
- To formulate a mechanism that explain the As and F^-mobilization into the soil and groundwater.

Around 400 children were reported with bone deformation

Dental fluorosis among children in Kalalanwala

Fig. 3.1 Pictures of patients from the study area; district Kasur, Punjab, Pakistan. *Source* www.uderc.org

3.2 Geological and Geographical Settings of Study Area

The study area is a part of Indus Plain, which represents a vast geosynclines lying between the Himalayan foothills and central core of the Indian subcontinent. This depression, which once may well have been an offshoot of the sea, had been filled with tremendous quantities of sediments brought down by rivers from Himalayans, and has consequently turned into an alluvial plain. In few places this plain, has been estimated to be several thousand feet thick (Greenman et al. 1967).

Quaternary sediments, mainly of alluvial and deltaic origins, occur over large parts of the Indus Plain of Pakistan, predominantly in Punjab Province. These sediments have some similarities to those of the As affected aquifers in Bangladesh and West Bengal, being Quaternary sediments derived from Himalayan source rocks. However, the Indus basin is in arid climate comprising greater prevalence of older Pleistocene deposits including eolian sediments and is dominated by aerobic conditions of unconfined groundwater aquifers (Mahmood et al. 1998; Tasneem 1999; Cook 1987).

The Punjab Province is an alluvial plain underlain by >350 m of Quaternary sediments derived from the Ravi and Satluj rivers, and the sediments are mostly coarse, containing high percentage of fine to very fine sand and silt and low organic matter (Greenman et al. 1967).

The soils of the area have formed by the sediments laid down by the Ravi, Bias and Satluj rivers. In many respects the soils show a high degree of similarity throughout the area. The soils are reddish brown to grayish brown, mostly moderately coarse and medium-textured soils, containing high percentage of fine to very fine sand and silt. The clay part consists of non-swelling materials, which may account for the generally favorable permeability characteristics of the soil. Most soils in the Punjab are moderately to highly permeable; only some have low permeability. The lime content of the soils is high. The soils are depleted in phosphorus and organic contents, pH 8.5 or more to at least 75 cm depth (Greenman et al. 1967) (Fig. 3.2).

The main soil in most of the study area comprises of silty clay loam. The entire area is underline by sand at various depths, below the soil.

The Lahore district is drained by the Ravi and Satluj rivers, which enter into Pakistan from India. The area is mainly recharged by those two rivers during monsoon season; however, the recharge from the rivers has diminished, since canal irrigation started in the 17th century (Greenman et al. 1967). Canal water seeps into the surrounding aquifer to cause dangerously high concentration of dissolved salts in the surface and shallow soils and water. Groundwater

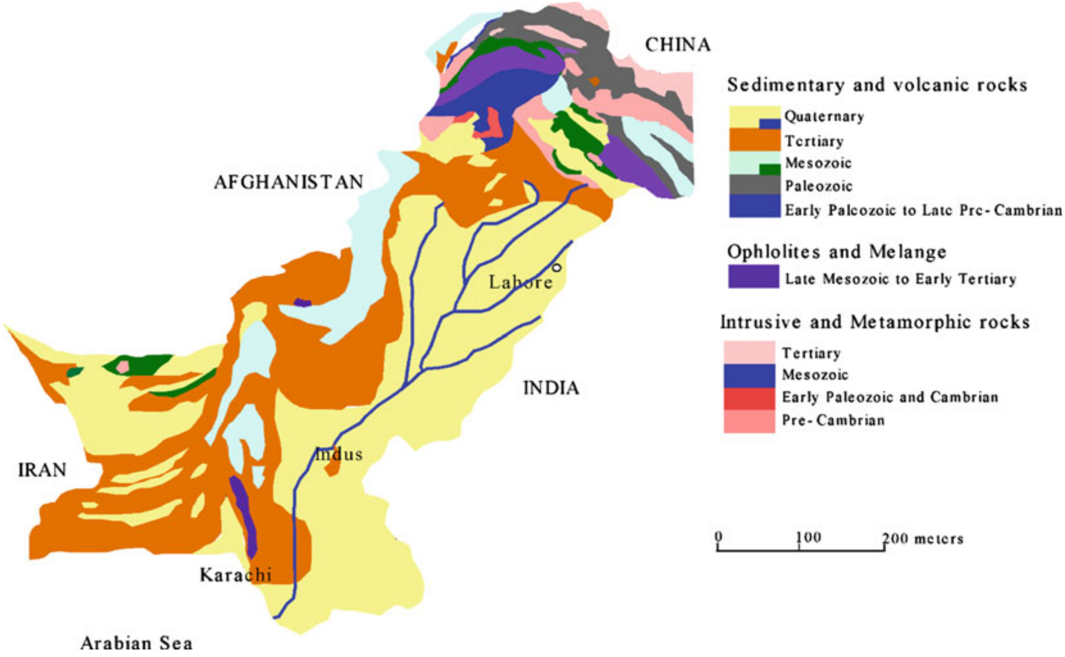

Fig. 3.2 Geological map of Pakistan. *Source* Geological survey of Pakistan 1991

containing sodium bicarbonate, with the passage of time, has given rise to soils with very high exchangeable sodium percentages which are very unsuitable against mechanical disturbance. This more far reaching process is due to the fact that much of the exchangeable calcium is displaced from the soils by sodium and is precipitated as calcium carbonate (Ali et al. 1968) (Fig. 3.3).

As a result the shallow groundwaters are badly affected by the canals and contain very high salts >2,000 ppm, while less affected deeper water, has salt contents <1,000 ppm (Ali et al. 1968). Most urban and rural water is supplied from groundwater. Over 50 % of the village water supply is obtained through hand pumps installed by private households. In saline groundwater areas, irrigation canals are the main source of domestic water (Food and Agriculture Organization 2004) (Fig. 3.4).

Climate

The Punjab province has semiarid and subtropical continental climate characterized by sultry summers and cold winters. The mean annual maximum temperature recorded from May to June is 41 °C and the mean annual minimum temperature is 4 °C from December to January (Greenman et al. 1967).

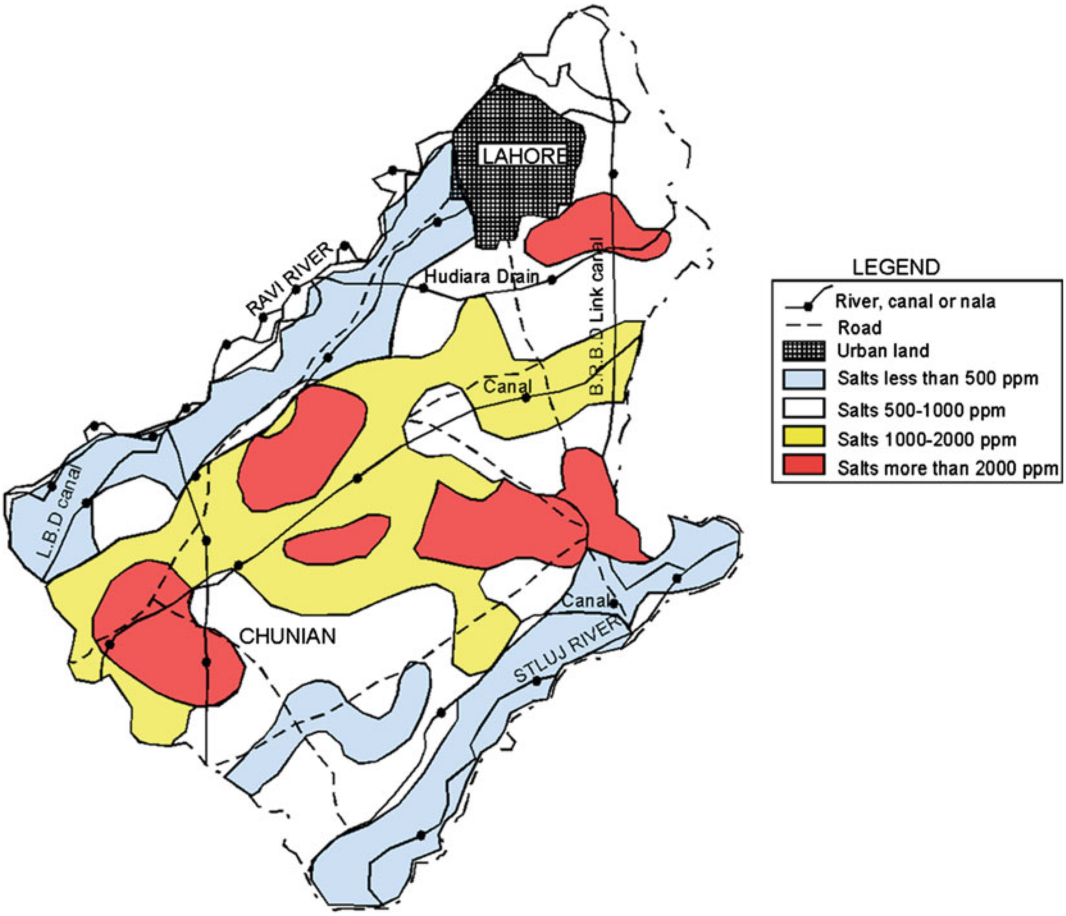

Fig. 3.3 Map showing the dissolved salts in groundwaters from Punjab district. *Source* Soil survey of Pakistan

Fig. 3.4 Agricultural lands with increased salts in Punjab (saline soils)

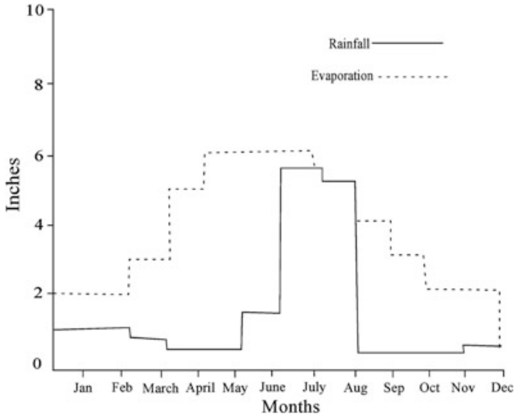

Fig. 3.5 Rainfall and evaporation (soil survey of Pakistan 1968)

The annual rainfall ranges from 125 mm in the extreme southern plains to 500–900 mm in the sub-mountainous and northern plains. About 70 % of the total rainfall occurs as heavy downpours in summer from July to September (Fig. 3.5) originating from the summer monsoons, and 30 % in winter. Summers, except in the mountainous areas, are very hot with a maximum temperature of more than 40 °C, while the minimum temperature in winter is a few degrees above the freezing point.

3.3 Brief Description of the Study Area

Pakistan is situated between the latitudes of 24° and 37° north and longitudes of 61° to 75° east, stretching over 1,600 km from north to south and 885 km from east to west. The Punjab province, southeast Pakistan, is located between 24–37°N and 62–75°E within an alluvial plain of the south-flowing Indus River and its five major tributaries. The districts Lahore and Kasur are located in the central Pakistan at the eastern edge of the Punjab province occupying an area of 3,995 and 1,772 km^2 and total population of 2.31 and 6.31 million, respectively.

The present study area covers 1/5th of the Kasur and 1/6th of the Lahore districts. The area is located along the eastern bank of River Ravi (Fig. 3.6) and includes 17 villages between Chung, 15–20 km south from main Lahore and Zahirabad near to the district Chunian (Fig. 2.4). For daily water use, including drinking water, most of the residents use groundwater extracted from tube wells drilled up to 30 m in depth from the ground surface within individual dwellings.

In the studied areas, there is also no sewer system, thus household wastewater is widely stored in cesspools or directly disposed in the environment. In the study region, pit latrines, unlined sewage discharge channels, and open ponds are used for disposal of human and animal sewage, are in hydraulic continuity with the underlying unconfined shallow aquifer which is tapped by the majority of shallow wells sampled in the study area (20–27 m total depth). As most of the wells used for local people are shallow, those are easily affected by contaminants from human activities. The present study area consist of agricultural lands, Kalalanwala and Kot Asad Ullah are the two villages located adjacent to an industrial state. District Chunain is famous

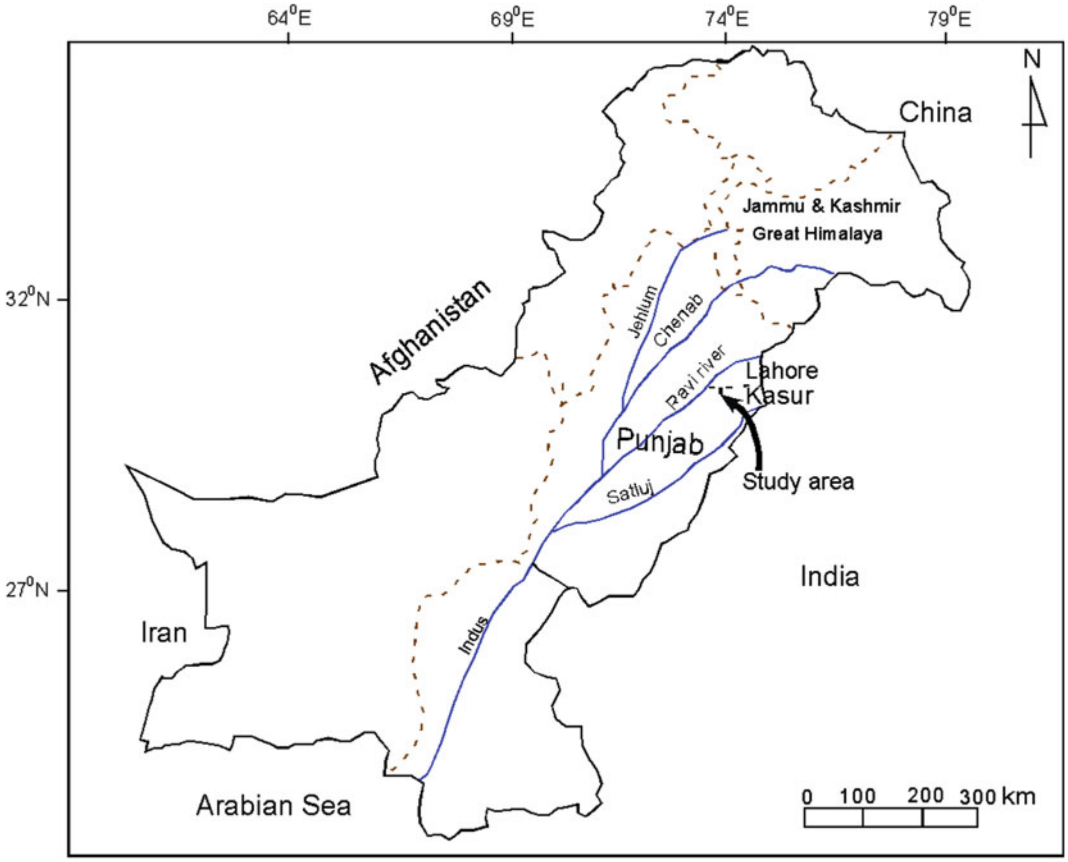

Fig. 3.6 Index map showing the study area

industrial state for leather and tanneries, while in Raiwind near Kasur many chemical and fertilizer industries are present. These industries also do not have any proper waste treatment plants and they are dumping their waste into the river and canals.

Pakistan is an agricultural country. Agriculture contributes about 24 % of Gross Domestic Product (GDP) and accounts for half of employed labor force and is the largest source of foreign exchange earnings. Agriculture feeds whole rural and urban population (Food and agriculture organization 2004). Although there is agricultural activity in all areas of Pakistan, most crops are grown in the Indus River plain in Punjab and Sindh. The present study area is also an agriculture area, where fertilizers like DAP, urea and much kind of pesticides are extensively used for high production of crops. The annual consumption of fertilizers in 1999 was 2,824 thousands metric tons with 129 kg/ha cropland in Pakistan and mostly in Punjab (http://earthtrends.wri.org) (Fig. 3.7).

One of the major concerns in today's world is the pollution and contamination of soil and groundwater by the use of fertilizers. The use of

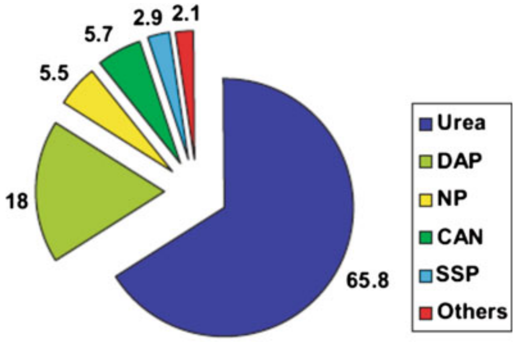

Fig. 3.7 Fertilizer's consumption by product (FAO 2004)

chemical fertilizers and pesticides has caused tremendous harm to the environment. Fertilization practice is far from the recommendations, farmers use the fertilizers more than the recommended values that results in consequent loss of yield, financial waste and environmental contamination (Food and agricultural Organization (FAO) 2004).

3.4 Sampling

Based on the sampling the study can be divided into four parts

1. Groundwaters sampled from Kalalanwala in 2002.
2. Groundwaters sampled from 17 villages of Punjab Pakistan.
    - April-2004 (Dry season)
    - October-2004 (Rainy season)
3. Soil sampling April-2005
4. Core drilling March-2006

The location points of the groundwater samples from a single village Kalalanwala area are given in Fig. 3.8. The sampling locations for groundwater samples from 17 villages are given in Fig. 3.9, and soil sampling locations are given in Fig. 3.10. Drilling locations are given in Fig. 3.11. The summary of the locations and sample numbers of groundwaters is given in Table 3.2 while, the summary of the locations and type of samples for soil sampling is given in Table 3.3 and summary of the locations of core drilling in the study area is given in Table 3.4. The groundwaters and field observations from the extended study area (17 villages from Punjab Pakistan) is given in Table 3.5.

- ***Water sampling***

  From Kalalanwala 24 groundwater samples were collected in Nov 2002 at three different depths, 17 samples from shallow 27–30 m, 3 from middle 40–80 m and 4 from deep wells of 80–200 m depth. For the extended study area of about 800 km^2, 147 groundwater samples were collected from those different depths; 123 samples from the shallow hand tube wells installed at 27–30 m depth, 14 from 40–80 m depth and 8 from deep wells 80–200 m depth. Two samples were collected from a canal drawn from Chenab River which originates from Indian Territory. Sampling was done once at the end of the dry season (March 2004) and second time after rainy season (September 2004). Five rainwater samples were also collected from the study area. Samples of locally consumed coal, and fertilizers (DAP, and urea) were also collected. After filtering the sample water using a 0.45 µm membrane filter, the water was stored into two polyethylene bottles; one was acidified to be 0.06 N HCl solution for the quantitative analysis of cations (Na^+, K^+, Ca^{2+}, and Mg^{2+}), total As, and sulfur isotopes. The other aliquot was kept non-acidified for anions (Br^-, Cl^-, F^-, $PO_4{}^{3-}$, and $SO_4{}^{2-}$) and hydrogen and oxygen isotope analyses. For As^{III} and nitrogen isotope analysis 50 mL of water acidified to be 0.09 N H_2SO_4 solutions was tightly sealed in a glass bottle. An additional aliquot of 1–2 L of water was sampled, to which

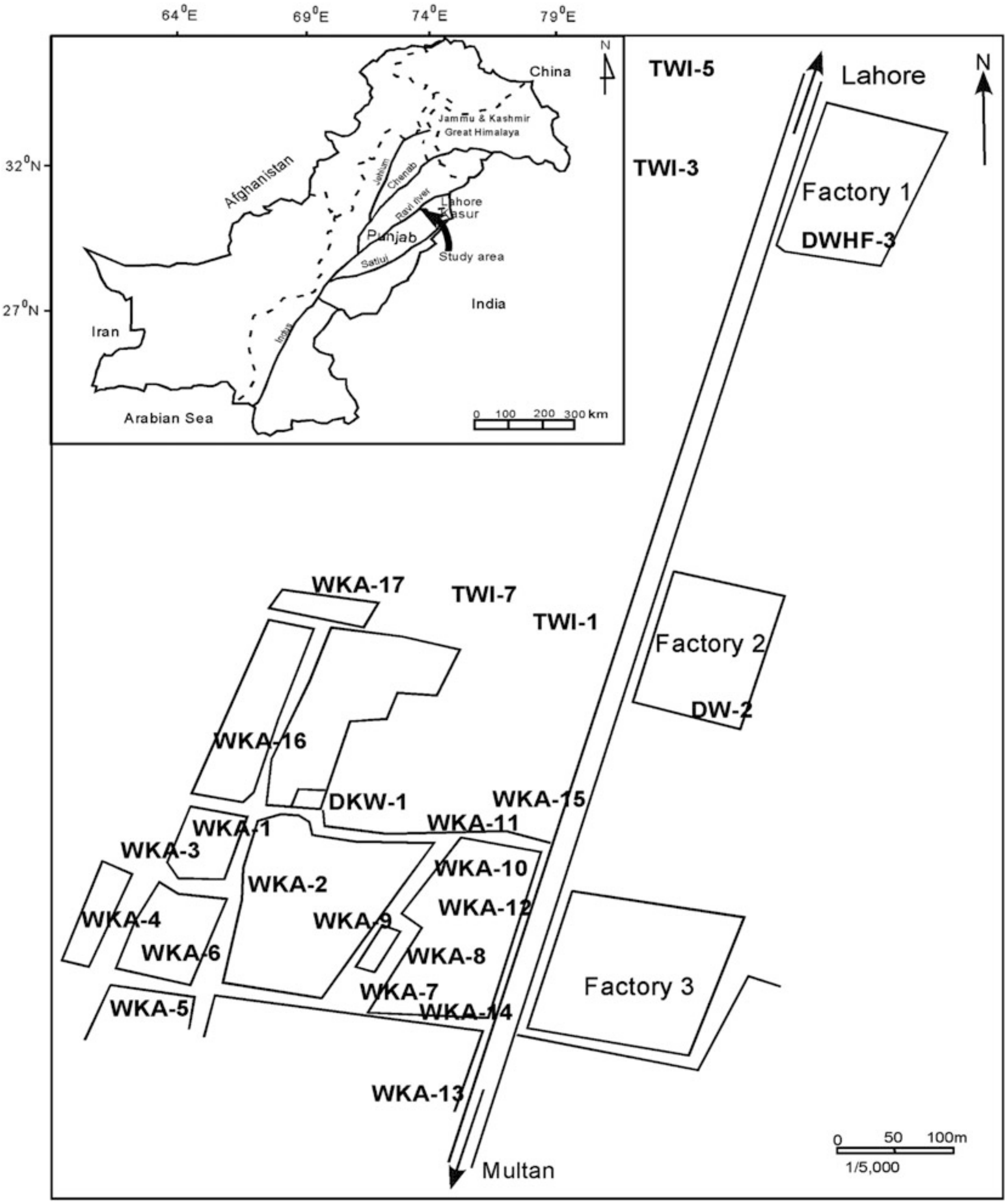

Fig. 3.8 Groundwater sample locations in Kalalanwala village

10–20 mL of 1:1 HCl was added for preparation of sulfur isotope analysis; the samples were filtered later in the laboratory.

- ***Soil sampling***
  Forty two (42) surface soils, 41 eolian layers at 30 cm depth were collected from the same

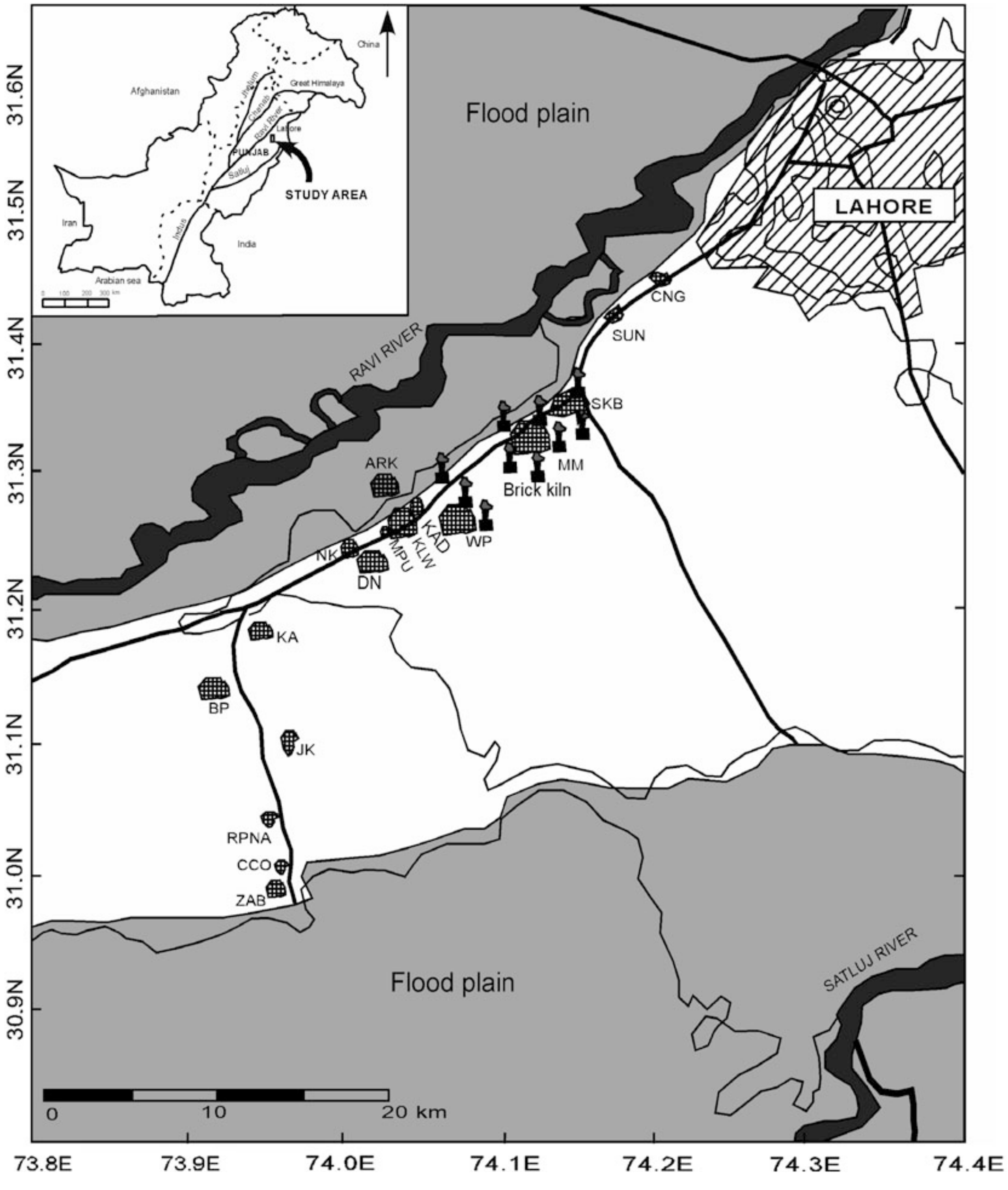

Fig. 3.9 Groundwater sample locations/villages from extended study area

locations, along with 3 sediments from alluvial plain of river bank. Sediments were also collected from outcrops up to 500 cm from the surface of alluvial plain. After coming back to

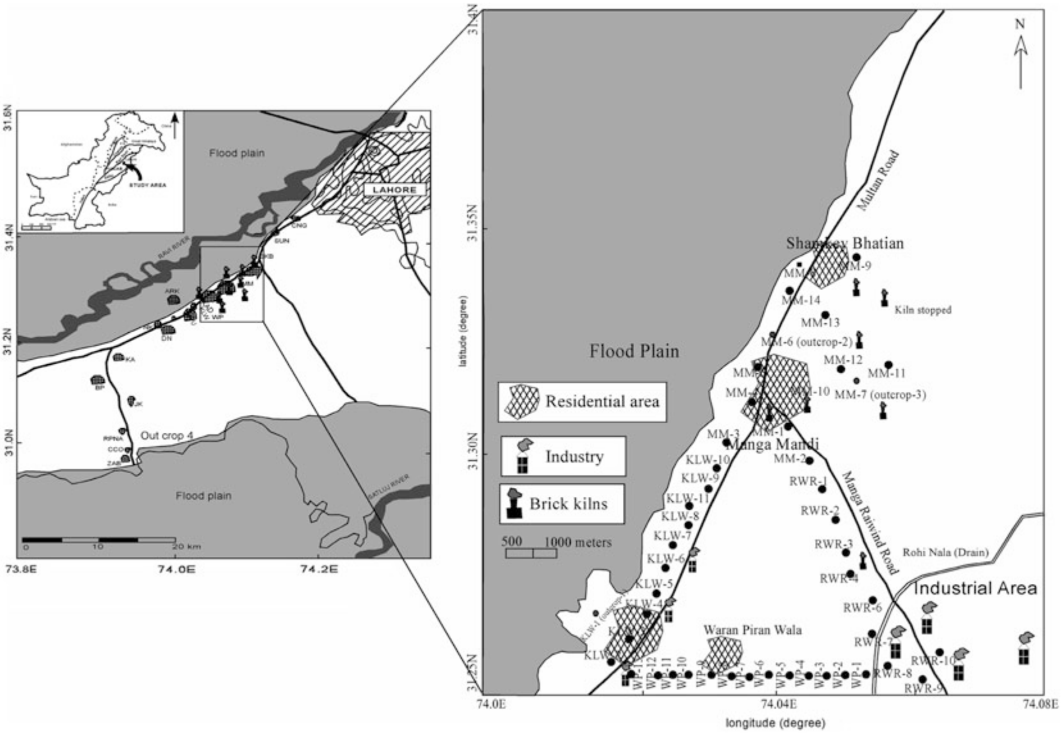

Fig. 3.10 Soil sampling locations

the laboratory the samples were oven dried, crushed and sieved to remove the materials >2 mm.

- ***Sediment cores***

  Based on the results of groundwaters, six sites were selected for drilling to observe the aquifer structure in the study area. A rotary drill rig method was used for the drilling only at one site KL-ES to obtain undisturbed sediment cores, while at other five sites the local conventional method was used just for observing the sediments. At three sites the drilling was continued up to 60 m i.e. KL-ES (Kalalanwala Elementary School), WPW (Waran Piran Wala) and CHA (Chah Arain, or Arain Da Khu) while, at three sites the drilling was done up to 36.6 m i.e. KL-S (Kalalanwala Truck Parking at South), KT-S (Kot Asad Ullah from South) and KT-N (Kot Asad Ullah from North).

3.5 Analytical Methods and Chemical Analysis

Water temperature, pH, Eh, and Electric Conductivity (EC) were measured in field using 6066-10C, 9300-10D, 9382-10D (HORIBA) electrodes, respectively. Groundwater temperature was measured with each electrode. Alkalinity (quoted as HCO_3^-) was determined in situ by titration with hydrochloric acid (0.02 N).

3.5.1 Major Ion Chemistry

Cations

Calcium and Mg^{2+} were analyzed by volumetric titration with ethylenediaminetetraacetic acid (EDTA 0.05 N) with an analytical error $<\pm 2$ %. Sodium and K^+ were determined by atomic absorption spectrometry (SAS 7500, Seiko).

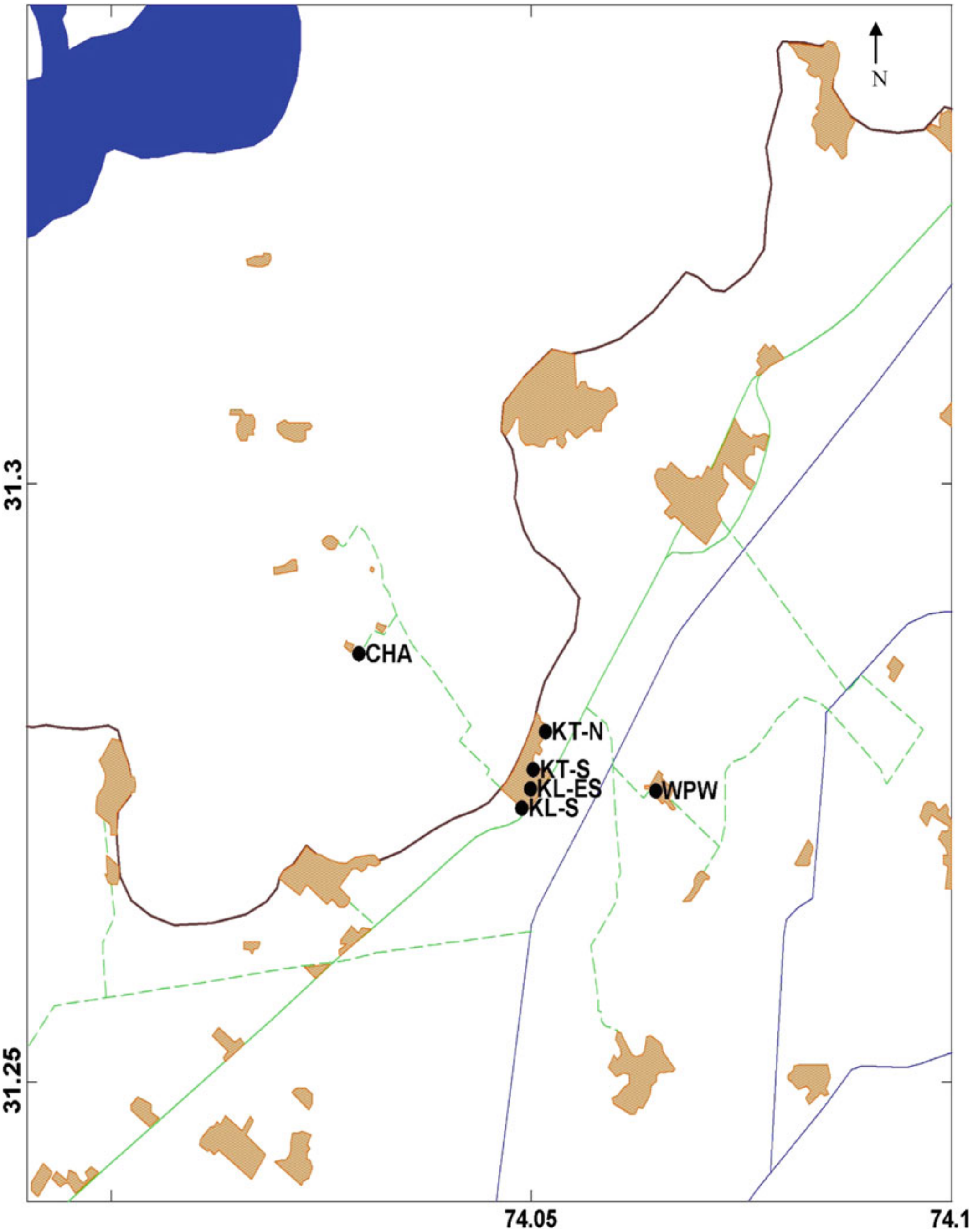

Fig. 3.11 Drilling locations from the study area

Anions

Chloride, Br^-, PO_4^{3-}, SO_4^{2-} and F^- were determined by Ion chromatograph (DX-120, Dionex) with an analytical precision <±2 %, estimated using duplicated standard solutions. SiO_2 and Fe were determined with ICP-AES.

Sample location marked after sampling

Rotary drilling

Local method

Sampler

Drilled sample

Table 3.2 Summary of the locations of groundwaters in study area

Sample location	Sample numbers	Shallow 27–30 m	Middle 40–80 m	Deep 80–200 m	Sampling time
Kalalanwala	24	17	3	4	2002–11
Extended study area	147	123	14	8	2004–04
Extended study area	138	118	13	7	2004–10

Table 3.3 Summary of the locations of soil samples in the study area

Sample location	Surface 0 cm	Eoline 30–40 cm	Alluvial 0–40 cm	Out crops Up to 500 cm	Sampling time
Kalalanwala	10	10			2004–05
Waran Piran Wala	12	12			2004–05
Manga Mandi	12	11			2004–05
Raiwind road	9	9			2004–05
Biyas River bed			2		2004–05
Manga Mandi			1		2004–05
Kalalanwala				1 × 9	2004–05
Manga Mandi				1 × 6	2004–05
Manga Mandi				1 × 5	2004–05
Biyas River bed				1 × 6	2004–05

Table 3.4 Drilling locations and number of samples

Abbr.	Location	Number of samples	Depth (m)
KL-ES	Kalalanwala Elementry School	60 at intervals of 1 m	60.0
KL-S	Kalalanwala Parking (South)	24 at intervals of about 1.5 m	36.6
KT-S	Kotasad Ullah South	24 at intervals of about 1.5 m	36.6
KT-N	Kotasad Ullah North	24 at intervals of about 1.5 m	36.6
WPW	Waran Piran Wala	60 at intervals of 1 m	60.0
CHA	Chah Araian	40 at intervals of at least 1.2 m	60.0

3.5.2 Arsenic in Groundwater and Rainwaters

Total arsenic

For total As analysis 2 mL of 12 M HCl was added into 15 mL sample water together with 0.25 mL of a solution containing 10 % KI and 10 % ascorbic acid. Hydride generation atomic absorption spectrometry (HGAAS, SAS 7500, Seiko Instruments) was employed to measure total As produced as the gaseous form (AsH_3) by reduction using sodium borohydride as reductant. Reproducibility of the analytical data was within 5 %, and the analytical error estimated to be <10 %, based on the analytical results of standard stock solutions independently prepared from the commercially distributed standard solution using a standard calibration line. The lower limit of quantification of As was 1 ppb.

Arsenite

Arsenite (As^{III}) concentrations were determined by the Voltammetry. Arsenic concentration cannot be determined accurately for the samples containing certain materials causing large interference when the calibration line made with simple standard solution is applied. In order to reduce such a matrix effect, the standard addition method was introduced. As^{III} working standard solution was added to rise the (As^{III}) concentration. The addition of working standard was

Table 3.5 Summary of the locations of groundwater samples and field measurements

Sample ID	Village name	Depth (m)	Temp. (°C)	EC (mS/cm)	pH	Eh (mV)	Latitude		Longitude		Purpose	Well type
CNG-1	Chung	20–27	27	1.95	7.3	65	31	25.799	74	10.491	Community	HP
CNG-2	Chung	20–27	27	1.36	8.1	105	31	25.849	74	10.407	Household	HP
CNG-4	Chung	20–27	26	1.70	7.7	102	31	25.834	74	10.365	Household	HP
CNG-5	Chung	20–27	27	1.25	7.3	128	31	25.803	74	10.371	Household	HP
SUN1	Sundar	20–27	29	1.30	8.1	95	31	21.127	74	7.696	Household	HP
SUN2	Sundar	20–27	29	1.61	8.0	111	31	21.132	74	7.685	Household	HP
SUN3	Sundar	20–27	27	2.56	8.0	171	31	21.112	74	7.643	Household	HP
SUN4	Sundar	20–27	27	2.26	7.4	141	31	21.345	74	7.519	Household	HP
SUN5	Sundar	20–27	28	2.60	7.2	152	31	21.337	74	7.446	Household	HP
SKB-2	Shamkey Bhatain	20–27	30	1.23	8.3	118	31	19.782	74	5.913	Household	HP
SKB-3	Shamkey Bhatain	20–27	28	1.25	8.4	94	31	19.895	74	5.945	Household	HP
SKB-4	Shamkey Bhatain	20–27	28	1.49	8.5	125	31	19..851	74	5.953	Household	HP
SKB-5	Shamkey Bhatain	20–27	29	1.13	8.5	134	31	19.766	74	6.042	Household	HP
SKB-6	Shamkey Bhatain	20–27	28	1.22	8.4	139	31	19.739	74	6.010	Household	HP
SKB-8	Shamkey Bhatain	20–27	28	1.21	8.6	129	31	19.738	74	6.113	Household	HP
SKB-9	Shamkey Bhatain	20–27	27	1.06	8.6	133	31	19.680	74	6.211	Household	HP
SKB-10	Shamkey Bhatain	20–27	30	0.66	7.2	163	31	19.726	74	6.257	Household	HP
SKB-12	Shamkey Bhatain	20–27	30	0.84	8.0	47	31	19.804	74	6.163	Household	HP
SKB-13	Shamkey Bhatain	20–27	27	0.93	8.0	114	31	19.822	74	6.127	Household	HP
SKB-14	Shamkey Bhatain	20–27	27	1.44	7.2	117	31	19.846	74	6.153	Household	HP
SKB-15	Shamkey Bhatain	20–27	28	1.14	7.8	86	31	19.880	74	6.147	Household	HP
SKB-16	Shamkey Bhatain	20–27	27	0.85	7.2	157	31	19.829	74	6.216	Household	HP
SKB-17	Shamkey Bhatain	20–27	26	0.83	7.8	139	31	19.857	74	6.214	Household	HP
SKB-18	Shamkey Bhatain	20–27	26	1.67	8.2	144	31	19.902	74	6.229	Household	HP
SKB-19	Shamkey Bhatain	20–27	27	1.13	8.2	101	31	19.948	74	6.257	Household	HP
SKB-20	Shamkey Bhatain	20–27	26	1.04	7.8	101	31	19.934	74	6.301	Household	HP
SKB-21	Shamkey Bhatain	20–27	26	1.31	7.3	117	31	19.852	74	6.326	Household	HP
SKB-22	Shamkey Bhatain	20–27	27	1.13	7.4	160	31	19.881	74	6.393	Community	HP

(continued)

Table 3.5 (continued)

Sample ID	Village name	Depth (m)	Temp. (°C)	EC (mS/cm)	pH	Eh (mV)	Latitude		Longitude		Purpose	Well type
SKB-23	Shamkey Bhatain	20–27	27	0.86	7.6	87	31	19.907	74	6.439	Household	HP
SKB24	Shamkey Bhatain	20–27	27	0.70	7.7	98	31	19.835	74	6.477	Community	HP
MM-2	Manga Mandi	20–27	28	1.37	7.5	166	31	18.213	74	3.256	Irrigation	IW
MM-3	Manga Mandi	20–27	28	1.44	7.3	129	31	18.350	74	3.132	Household	HP
MM-4	Manga Mandi	20–27	29	1.01	7.2	87	31	18.298	74	3.044	Community	HP
MM-5	Manga Mandi	20–27	28	1.43	7.3	179	31	18.283	74	2.993	Household	HP
MM-6	Manga Mandi	20–27	29	1.82	8.3	138	31	18.205	74	2.965	Household	HP
MM-7	Manga Mandi	20–27	28	1.16	8.0	128	31	18.238	74	2.926	Household	HP
MM-8	Manga Mandi	20–27	27	1.40	7.7	155	31	18.310	74	3.002	Household	HP
MM-9	Manga Mandi	20–27	27	1.57	7.4	158	31	18.411	74	3.052	Household	HP
MM-11	Manga Mandi	20–27	27	1.17	8.3	141	31	18.427	74	3.008	Household	HP
MM-12	Manga Mandi	20–27	28	0.55	8.3	177	31	18.440	74	2.964	Community	HP
MM-14	Manga Mandi	20–27	27	0.58	8.6	136	31	17.732	74	4.479	Household	HP
MM-15	Manga Mandi	20–27	26	1.90	8.5	133	31	17.702	74	4.519	Household	HP
MM-16	Manga Mandi	20–27	27	1.83	8.7	132	31	17.711	74	4.533	Household	HP
MM-17	Manga Mandi	20–27	26	1.18	8.4	104	31	17.649	74	4.331	Household	HP
WP-1	Waran Piran Wala	20–27	29	0.82	8.3	113	31	16.422	74	3.939	Household	HP
WP-3	Waran Piran Wala	20–27	26	1.90	8.5	121	31	16.432	74	3.949	Household	HP
WP-4	Waran Piran Wala	20–27	27	1.30	8.2	116	31	16.448	74	3.992	Household	HP
WP-5	Waran Piran Wala	20–27	29	2.02	7.8	120	31	16.474	74	3.949	Household	HP
WP-7	Waran Piran Wala	20–27	27	1.86	8.0	132	31	16.516	74	3.862	Household	HP
WP-8	Waran Piran Wala	20–27	28	1.90	8.0	122	31	16.435	74	3.922	Household	HP
WP-9	Waran Piran Wala	20–27	27	1.77	8.1	141	31	16.429	74	3.937	Household	HP
WP-10	Waran Piran Wala	20–27	28	1.80	8.6	130	31	16.481	74	3.878	Household	HP
WP-11	Waran Piran Wala	20–27	27	1.02	8.4	168	31	16.602	74	3.623	Household	HP
KAD-1	Kot Asad Ullah	20–27	27	2.82	8.2	98	31	16.633	74	2.978	Household	HP
KAD-2	Kot Asad Ullah	20–27	26	0.81	8.1	112	31	16.653	74	2.988	Household	HP
KAD-6	Kot Asad Ullah	20–27	27	2.74	7.8	30	31	16.619	74	2.969	Household	HP
KAD-7	Kot Asad Ullah	20–27	27	3.18	7.3	40	31	16.626	74	2.941	Household	HP
KAD-8	Kot Asad Ullah	20–27	27	2.04	8.0	66	31	16.632	74	3.039	Household	HP

(continued)

Table 3.5 (continued)

Sample ID	Village name	Depth (m)	Temp. (°C)	EC (mS/cm)	pH	Eh (mV)	Latitude		Longitude		Purpose	Well type
KAD-10	Kot Asad Ullah	20–27	26	2.55	7.7	68	31	16.578	74	2.939	Household	HP
KAD-11	Kot Asad Ullah	20–27	26	3.7	7.6	117	31	16.561	74	2.961	Household	HP
KAD-12	Kot Asad Ullah	20–27	27	2.50	8.3	89	31	16.563	74	2.926	Household	HP
KLW1	Kalalanwala	20–27	27	3.38	8.0	54	31	16.659	74	2.982	Household	HP
KLW3	Kalalanwala	20–27	28	1.60	8.5	116	31	16.528	74	2.892	Household	HP
KLW4	Kalalanwala	20–27	27	1.70	8.0	106	31	16.546	74	2.898	Household	HP
KLW5	Kalalanwala	20–27	27	1.63	8.2	107	31	16.511	74	2.882	Household	HP
KLW6	Kalalanwala	20–27	28	2.21	8.4	110	31	16.520	74	2.942	Household	HP
KLW7	Kalalanwala	20–27	28	1.60	8.4	72	31	16.508	74	2.912	Household	HP
KLW8	Kalalanwala	20–27	28	3.25	8.5	117	31	16.561	74	3.034	Household	HP
KLW9	Kalalanwala	20–27	26	2.61	8.5	130	31	16.548	74	2.945	Household	HP
KLW10	Kalalanwala	20–27	28	1.86	8.6	110	31	16.514	74	2.964	Household	HP
KLW11	Kalalanwala	20–27	27	2.66	8.4	84	31	16.530	74	2.988	Household	HP
KLW12	Kalalanwala	20–27	26	3.01	8.2	127	31	16.513	74	3.032	Household	HP
KLW13	Kalalanwala	20–27	26	4.38	8.3	81	31	16.532	74	3.059	Household	HP
KLW14	Kalalanwala	20–27	29	3.17	8.0	77	31	16.544	74	3.078	Household	HP
KLW15	Kalalanwala	20–27	28	4.60	8.3	62	31	16.537	74	3.102	Household	HP
KLW16	Kalalanwala	20–27	27	2.22	8.4	104	31	16.583	74	2.997	Household	HP
KLW17	Kalalanwala	20–27	29	3.27	8.2	83	31	16.555	74	3.134	Household	HP
KLW18	Kalalanwala	20–27	28	1.22	8.8	102	31	16.410	74	2.957	Household	HP
KLW19	Kalalanwala	20–27	29	2.26	8.3	95	31	16.393	74	2.935	Household	HP
KLW20	Kalalanwala	20–27	28	1.72	8.5	79	31	16.411	74	2.892	Community	HP
KLW21	Kalalanwala	20–27	29	1.13	7.8	135	31	16.432	74	2.918	Household	HP
KLW22	Kalalanwala	20–27	29	1.28	8.5	118	31	16.459	74	2.868	Household	HP
KLW23	Kalalanwala	20–27	28	1.58	8.0	65	31	16.463	74	2.829	Household	HP
KLW24	Kalalanwala	20–27	29	1.25	8.6	89	31	16.482	74	2.797	Household	HP
KLW26	Kalalanwala	20–27	28	1.06	8.0	40	31	16.452	74	2.771	Household	HP
KLW27	Kalalanwala	20–27	29	1.51	8.5	106	31	16.443	74	2.953	Household	HP
MPU-1	Muffat Pura	20–27	27	3.12	8.0	132	31	16.341	74	2.569	Household	HP
MPU-2	Muffat Pura	20–27	27	1.34	7.9	125	31	16.353	74	2.606	Household	HP

(continued)

Table 3.5 (continued)

Sample ID	Village name	Depth (m)	Temp. (°C)	EC (mS/cm)	pH	Eh (mV)	Latitude		Longitude		Purpose	Well type
MPU-3	Muffat Pura	20–27	26	4.10	7.9	138	31	16.351	74	2.559	Household	HP
ARK-2	Arain Da Khu	20–27	28	0.60	7.2	104	31	17.561	74	1.867	Household	HP
ARK-3	Arain Da Khu	20–27	29	0.40	7.3	118	31	17.261	74	1.909	Community	TW
ARK-4	Arain Da Khu	20–27	28	0.53	7.2	108	31	17.282	74	1.929	Household	HP
ARK-5	Arain Da Khu	20–27	29	1.04	7.2	112	31	17.180	74	1.726	Household	HP
ARK-6	Arain Da Khu	20–27	29	0.49	7.4	95	31	17.203	74	1.684	Household	HP
ARK-7	Arain Da Khu	20–27	28	0.68	7.6	107	31	17.183	74	1.650	Household	HP
DN-1	Deena Nath	20–27	28	1.22	8.0	130	31	14.663	74	00.870	Household	HP
DN-2	Deena Nath	20–27	28	1.50	7.4	109	31	14.606	74	00.906	Household	HP
DN-3	Deena Nath	20–27	26	2.10	7.5	576	31	14.616	74	1.103	Household	HP
DN-4	Deena Nath	20–27	28	1.10	7.3	118	31	14.539	74	1.307	Household	HP
DN-5	Deena Nath	20–27	27	1.60	7.5	28	31	14.598	74	1.283	Household	HP
DN-6	Deena Nath	20–27	26	1.35	8.0	57	31	14.703	74	1.296	Household	HP
NK-1	Nathy Khalsa	20–27	29	1.24	7.7	98	31	16.062	74	01.453	Household	HP
NK-2	Nathy Khalsa	20–27	29	1.70	7.3	113	31	16.113	74	01.432	Household	HP
NK-3	Nathy Khalsa	20–27	29	1.40	7.5	135	31	16.061	74	01.425	Household	HP
NK-4	Nathy Khalsa	20–27	27	1.41	7.4	142	31	16.003	74	01.420	Community	HP
NK-5	Nathy Khalsa	20–27	27	1.33	7.4	154	31	15.996	74	01.522	Household	HP
NK-6	Nathy Khalsa	20–27	28	1.42	7.9	132	31	15.984	74	1.587	Household	HP
KA-1	Kot Ashraf	20–27	28	1.38	8.2	103	31	14.880	74	00.149	Household	HP
KA-2	Kot Ashraf	20–27	29	1.38	8.6	135	31	14.883	74	00.219	Household	HP
KA-3	Kot Ashraf	20–27	28	1.2	8.6	135	31	14.825	74	00.203	Household	HP
BP-1	Bhai Pheru	20–27	29	1.48	8.1	132	31	8.173	73	54.924	Household	HP
BP-2	Bhai Pheru	20–27	28	1.23	7.8	152	31	8.173	73	54.924	Household	HP
BP-3	Bhai Pheru	20–27	29	0.64	7.5	140	31	8.173	73	54.924	Household	HP
JK-1	Jamber Kalan	20–27	26	3.40	8.3	123	31	5.373	73	57.798	Household	HP
JK-2	Jamber Kalan	20–27	27	3.60	8.1	137	31	8.173	73	54.927	Household	HP
RPNA1	Rehman Pura	20–27	26	2.10	7.5	65	31	05.374	73	57.786	Household	HP
RPNA2	Rehman Pura	20–27	27	1.82	7.8	66	31	05.379	73	57.838	Household	HP
CCO1	Central Colony	20–27	28	0.73	7.2	66	31	4.904	73	58.071	Household	HP

(continued)

Table 3.5 (continued)

Sample ID	Village name	Depth (m)	Temp. (°C)	EC (mS/cm)	pH	Eh (mV)	Latitude		Longitude		Purpose	Well type
CCO2	Central Colony	20–27	29	0.52	7.3	65	31	4.884	73	58.086	Household	HP
ZAB-1	Zahir Abad	20–27	26	2.17	8.1	19	30	58.437	73	58.437	Household	HP
ZAB-2	Zahir Abad	20–27	29	2.80	8.0	88	30	58.456	73	58.405	Household	HP
ZAB-3	Zahir Abad	20–27	28	2.78	8.1	92	30	58.363	73	58.472	Household	HP
ZAB-4	Zahir Abad	20–27	27	3.80	8.0	151	30	58.361	73	58.607	Household	HP
ZAB-5	Zahir Abad	20–27	29	4.40	7.4	134	30	58.214	73	58.389	Community	HP
KLW25	Kalalanwala	40–80	25	1.18	8.5	165	31	16.452	74	2.771	Community	TW
ARK-1	Arain Da Khu	40–80	24	0.20	8.1	167	31	17.551	74	1.854	Household	HP
ARK-8	Arain Da Khu	40–80	24	0.34	8.6	172	31	17.092	74	1.715	Community	TW
WP-6	Waran Piran Wala	40–80	24	0.94	8.1	108	31	16.498	74	3.928	Household	HP
SKB-1	Shamkey Bhatian	40–80	26	1.70	8.3	74	31	19.781	74	5.834	Community	TW
SKB-11	Shamkey Bhatian	40–80	26	1.01	7.7	22	31	19.811	74	6.224	Household	HP
MM-10	Manga Mandi	40–80	24	0.41	8.4	126	31	18.439	74	3.059	Household	HP
KAD-3	Kot Asad Ullah	40–80	26	0.81	7.5	102	31	16.653	74	3.159	Household	HP
KAD-4	Kot Asad Ullah	40–80	27	0.34	7.4	157	31	16.783	74	3.132	Community	TW
KAD-5	Kot Asad Ullah	40–80	24	1.10	7.3	73	31	16.752	74	3.072	Household	HP
KAD-9	Kot Asad Ullah	40–80	25	2.19	8.3	35	31	16.600	74	3.010	Community	TW
KLW-29	Kalalanwala	40–80	25	2.50	8.7	203	31	16.612	74	3.023	Community	TW
CNG-3	Chung	40–80	24	0.38	8.3	80	31	25.856	74	10.403	Community	TW
SKB-7	Shamkey Bhatian	40–80	25	1.01	8.1	144	31	19.750	74	6.069	Household	HP
WP-2	Waran Piran Wala	80–200	23	1.84	8.3	116	31	16.350	74	3.860	Community	Turbine
SKB25	Shamkey Bhatian	80–200	24	1.07	8.6	145	31	19.730	74	7.569	Irrigation	IW
MM-1	Manga Mandi	80–200	21	1.07	8.4	130	31	17.833	74	3.268	Irrigation	IW
MM-13	Manga Mandi	80–200	23	0.89	8.7	147	31	18.113	74	3.619	Community	HP
KLW2	Kalalanwala	80–200	22	1.94	8.0	116	31	16.540	74	2.856	Irrigation	IW
KLW-28	Kalalanwala	80–200	20	0.45	7.6	102	31	16.530	74	2.836	Irrigation	TW
ARK-9	Araian Da Khu	80–200	24	0.74	7.5	105	31	19.680	74	6.211	Household	HP
ARK-10	Araian Da Khu	80–200	23	0.56	7.5	145	31	19.726	74	6.257	Household	HP

Note *HP*, *IW* and *TW* stands for hand pump, irrigation water and tubewell waters, respectively repeated at least three times after the quantification of raw sample solution. Obtained a linear relationship between the redox potential and As^{III} concentrations, which is expressed by the equation X + 5 * n (X: true conc. of As^{III}, n = number of addition of standard solution rising 5 ppb by one aliquot), As^{III} concentrations can be calculated as the interception on the X-axis.

The lower detection limit of arsenite was 5 ppb, and the relative standard deviation was 8.5 % for 20 ppb of the solution. As^{V} is calculated from the concentration difference between the total As and As^{III}. The detection limit was determined from the lowest concentration of the standard solution giving the optical peak.

3.5.3 Arsenic in Soil Samples

Arsenic was analyzed by hydrogen-generated atomic absorption photometry (SAS7000, Seiko Instruments). For the analysis of total As, the bulk sample was fused with sodium carbonate, and digested in dilute hydrochloric acid. Standard solutions were prepared using standard sediment samples (Sedimentary rock series, JSd-1, JSd-2, JSd-3, JLK-1, JSI-1, and JLs-1; Geological Survey of Japan (http://www.aist.go.jp/RIODB/geostand/semiment.html), and then treated by the same procedure as for the other samples for AAS. The lower limit for quantification of As was 1 ppb. The reproducibility of analytical values for duplicate samples was within 5 %, and the analytical error for total As was less than 10 % (estimated using the standard rock samples).

3.5.4 Water Soluble F^- in Soil and Fertilizers

Water soluble fluoride in soils and fertilizers determine by shaking 5 g of soil or fertilizer sample and 25 mL distilled water in polyethylene bottles for 0.5 h. The solution was centrifuged and the resultant water was used for the analysis by ion selective electrode (Orion) and ion meter (Metro Ohm).

3.5.5 Water Soluble As in Fertilizers

Same solution as for water extractable F for fertilizers was used for As determination.

3.5.6 As and Total F^- in Coals

Total F^- concentration of coals was analyzed by an ion chromatography method after the alkaline fused coal was dissolved in water (Crossley 1944). Powdered sample was weighed accurately, mixed well with anhydrous sodium carbonate and Zinc oxide at a mixing ratio of 1:3:1 by weight in a Pt crucible. The mixture was heated in an electric furnace starting from 500 °C and fused at 900 °C for 30–40 min. After cooling 1–2 mL of distilled water was added into Pt crucible and the fused cake in the Pt crucible was transferred to a 10 mL polycarbonate centrifuged tube completely by scrubbing the wall of the Pt crucible several times using a plastic spatula. Collected fused sample was fragmented with a glass rod and mixed well with demonized water in an ultrasonic bath. Then the solution was centrifuged and the supernatant fluid was transferred to a 20 mL volumetric flask. About 3 mL distilled water was added to the centrifuged tube. The residue was again well mixed with distilled water using a glass rod in the ultrasonic bath and the solution was removed into the volumetric flask after centrifugation. This washing procedure was repeated three times, total amount of solution was finally adjusted to 20 mL with distilled water. At least 4 mL of the solution was then filtered (Millipore, USA, Millex, pore size: 0.22 μm) and injected into an IC (DX-120, Dionex). The reproducibility of analytical data was <10 % for the duplicated samples.

For total As in coal samples acid digestion method was used (USGS), 0.1 g sample was taken into a 125 mL Erlenmeyer flask with 20 mL HNO_3, 2 mL H_2SO_4, and let for overnight. Then 3 mL of $HCLO_4$ was added and the flask was heated at 175 °C for 30 min with refluxers. After heating at 30 min the refluxers were removed and continued to heat till dense fumes of $HCLO_4$, was produced. Then, it was cooled and 25 mL 6 N HCL was added and finally, the obtained solution was analyzed by hydride generation atomic absorption spectrometry (HGAAS, SAS 7500, Seiko Instruments).

3.5.7 pH of Soil Samples

The pH of the soil was measured by using an ion selective electrode (HORIBA) after shaking with water. Soil and water were used in the ratio of 1:5 for pH determination.

3.5.8 Major Chemical Composition of Soil Samples

The major chemical composition of bulk samples were quantitatively determined by X-ray fluorescence photometry (VXQ-160S, Shimadzu) using glass bead samples formed by the fusion with lithium borate. LOI done samples were used for making the bead. LOI (Loss on ignition) was done by keeping 2 g of samples in furnace at 700 °C for 30 min in porcelain crucible (pre-weighed), after 30 min the temperature was raised to 900 °C and the heating was continued at this temperature 50 min. The samples were cooled, taken out in a desiccator and cooled. The samples were weighed and LOI was calculated by the weight difference. Flux (Lithium borate) was pre-heated at 450 °C for 12 h, while $LiNO_3$ was dried at 115 °C for 2 h. Calibration lines were obtained using glass beads made by using standard rock samples (Sedimentary rock series, JSd-1, JSd-2, JSd-3, JLK-1, JSI-1, and JLs-1; Geological Survey of Japan (http://www.aist.go.jp/RIODB/geostand/semiment.html). The analytical error for major elements was estimated using duplicate standard samples to be within 10 %.

3.5.9 Grain Size Distribution

The grain size distribution was analyzed by a laser diffraction spectroscopy (SLAD-3000S, Shimadzu) after dispersion of the samples in sodium hexametaphosphate. The reproducibility of analytical results for the duplicate samples was within ±3 %.

3.5.10 Mineralogy

Bulk mineralogy of the powdered samples was determination of by XRD (RAD-1A, Rigaku).

B. Stable Isotopes

The application of environmental isotopes is a powerful tool to estimate the transport pathways of pollutants and identify those sources in a certain hydrological cycle. From the point of views of environmental groundwater pollution, the stable isotopes are used for (1) isotopes comprising the water molecule itself $^2H/^1H$ and $^{18}O/^{16}O$ are applied as natural tracers to identify origins of the water, recharge areas, hydraulic connections between aquifers including surface water, modern and fossil groundwater and mixing processes of those acquirers; (2) The stable isotope compositions of dissolved constituents in water is used to explain their origin, dynamic process of the hydrological system including the migration and transformation of the targeted constituents and biogeochemical processes.

The variation in the naturally occurring isotopes is quite small; the stable isotope ratios are expressed by the permil deviation from standard materials. Isotope ratio is defined by the δ (delta) notation as:

$$\delta X' = (X'/X)_{\text{sample}}/(X'/X)_{\text{std}} - 1) \times 1{,}000\,(\text{permil})$$

where X′ is a heavier isotope, X is the light most one, Sample means sample water, and STD denotes the standard water.

3.6 Hydrogen and Oxygen Isotopes

Most of the groundwaters are mainly meteoric in origin. There is a strong relationship between δD and $\delta^{18}O$ values of precipitation and its originating waters, known as global Meteoric Water Line (GML, $\delta D = 8 \times \delta^{18}O + 10$). Isotope analysis combined with hydrogeochemical analysis can be used to distinguish multiple origins of groundwaters and often to calculate mixing ratios of those. An example of two components groundwater mixing was reported by Gat et al. (1969): two mineral springs, the Hamei Zohar and Hamei Yesha springs, were lain on the fresh water Dead Sea water mixing line, indicating these springs were formed by intermixing of Dead Sea water (brine) brought to surface with the emerging local fresh water.

Among numerous studies, stable isotopes are occasionally applied for planning the environmental managements. For example, in the southern California, Orange country wants to supplement its water supplies with treated wastewater and must respond to regulations requiring that such waters remain in the aquifer for a year before being withdrawn for drinking. After the treated wastewater was recharged to the subsurface from spreading ponds, the distinctive δD and $\delta^{18}O$ of water samples taken at monitor wells down gradient of those ponds should follow the migration of this water in the subsurface (Davisson et al. 1997).

3.7 Sulfur Isotopes

There are three major natural reservoirs of sulfur in the shallower part of the earth's crust and hydrosphere: evaporite sulfate (with $\delta^{34}S$ values of +10 to 30 ‰, mean +17 ‰), dissolved sulfate in modern ocean water ($\delta^{34}S$ values of +20 ‰), sedimentary sulfides (with very wide range of $\delta^{34}S$ values of −50 to +23 ‰, with mean value of −12 ‰) (Strauss 1997).

Concentration of dissolved sulfate in the groundwater ranges from few mg/L in shallow subsurface waters to tenths of g/L in fossil brines. This sulfate-sulfur is originated from minerals, biomass and atmospheric wet and dry depositions including aerosol comprising volcanic gas, marine salts, biological emissions and anthropogenic emissions. Anthropogenic activity also directly supplies the pollutants into the local groundwater. Those sulfur isotopic compositions are important to characterize the origins of sulfates.

A simple mixing with negligible fractionation could explain the sulfate sources of groundwater in the Zechstein sediments, the Harz Mountain in Germany. Four spring waters contained the sulfate ions originated from gypsum and anhydrite in the evaporites, which showed a very narrow range of $\delta^{34}S$ from +9.9 to +12.4 ‰. Sulfate sulfur isotope ratios of three of those spring waters (+10.6 to +11.6 ‰) are close to those of the evaporite minerals, indicating that the dissolved sulfate originates from the rock. On the other hand, $\delta^{34}S$ of the rest one is less positive (+8.3 ‰), indicating a mixing with sulfate from an isotopically lighter source, which must be the local precipitation, in which $\delta^{34}S$ is equal to +4.5 ‰. The mixing proportions of the atmospheric and evaporite components of the sulfates in this spring water are estimated using $\delta^{34}S$ to be 46 and 54 ‰, respectively.

The sulfur isotopic composition is also a useful indicator of anthropogenic pollution of groundwater. When the sulfate-sulfur isotope composition was determined for the groundwaters in the vicinity of a settling pond of ash produced at the power plants at Sulkov, Czech Republic (Smejkal and Jetel 1990), three sources of sulfate were specified: (1) highly concentrated sulfate along with high sulfur isotopes is derived from the ash; (2) much concentrated sulfate with low sulfur isotopes is from oxidized pyrite in the local host rocks; (3) less concentrated sulfate with low sulfur isotopes is from atmospheric sulfate. Many of the studied include mixtures of those three different sulfates.

Moncaster et al. (2000) was successful using sulfur isotopes to specify the different sources of sulfate and that relative importance in the aquifer in the Lincolnshire Limestone aquifer of eastern England. The principal source depleted in δ^{34}S, and would be derived through the pyrite (−15 ‰) oxidation within the host sediment and the overlying mudstone. Another source enriched in δ^{34}S, suggesting anthropogenic inputs derived from acid rain (+2.4 ‰) or agrochemicals (Triplesuperphosphate TSP and NPK fertilizers, +1 to +10 ‰).

3.8 Nitrogen Isotopes

Although nitrogen in groundwaters comes from natural sources such as atmospheric nitrogen and biological emissions, large part of this element comes from the anthropogenic pollutants; wet and dry depositions of air pollutants, chemical fertilizers, and living and dead matters including animal waste and domestic sewage. Analytical data of nitrogen isotopes and major dissolved species leave fingerprints of natural and anthropogenic sources of this element in the groundwater (Heaton 1986). The isotopic compositions of nitrates in the groundwater us also the result of complex processes such as nitrification and denitrification to cause isotopic fractionation.

Rivers et al. (1996) used nitrogen isotopes to identify nitrogen contaminants of unconfined Sherwood Sandstone aquifer beneath the city of Nottingham, United Kingdom. Two thirds of the groundwater samples have δ^{15}N ranging from +4 to +8 ‰, indicative of predominately presented oil organic nitrogen for the dissolved nitrate source. Most remaining (one-third) groundwater samples (δ^{15}N < 5 ‰) would be derived from nitrogen containing fertilizers, possibly passing through a contaminated river water. Some samples have δ^{15}N > 8 ‰, suggestive of local inflow of the nitrogen contaminants from sewer leakage. The δ^{15}N values (+8.1 to +12.5 ‰) of the most of the contaminated groundwaters (NO_3^- > 200 mg/L) suggested that the major source of NO_3^- was derived from the animal manure (Widory et al. 2005).

3.9 Isotope Measurements

Isotope analyses of hydrogen, oxygen and sulfur were performed at the Institute for Study of the Earth's Interior, Okayama University, and that of nitrogen was conducted at the Centre for Ecological Research, Kyoto University.

3.9.1 Hydrogen and Oxygen Isotope Analyses of Water

Oxygen isotope ratio ($^{18}O/^{16}O$) was measured by H_2O–CO_2 equilibration method originally developed by Epstein and Mayeda (1953), using online vacuum system attached to a mass spectrometer (VG-PRISM, Micromass). The analytical error was within 0.1 ‰. Hydrogen isotope ratio (D/H) was determined by the online Cr reduction method (Itai and Kusakabe 2004) attached with the mass spectrometer (VG-SIRA10, Micromass). The analytical error was within 0.5 ‰.

3.9.2 Sulfur Extraction

(a) ***Sulfate-sulfur of water***

Sulfate was extracted as $BaSO_4$ by adding 10 % $BaCl_2$ solution in water samples for

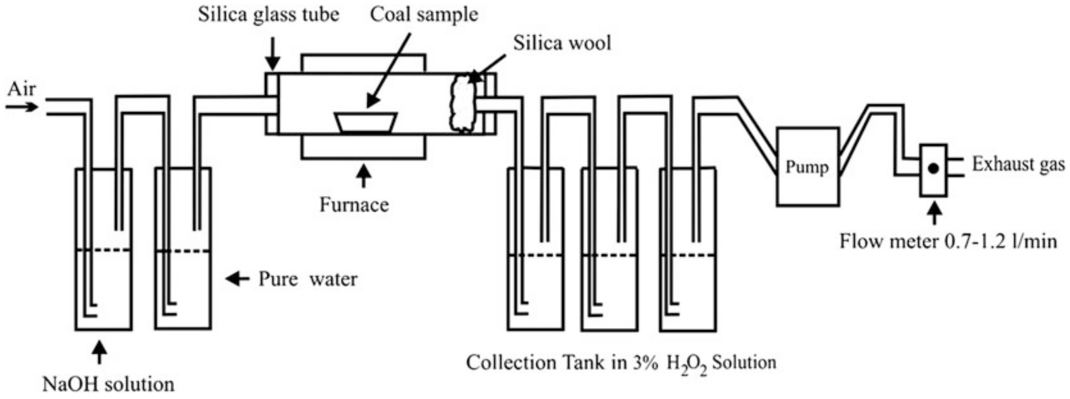

Fig. 3.12 Apparatus for coal combustion

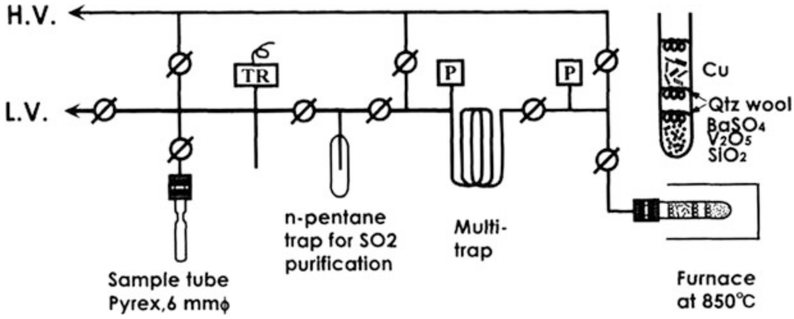

Fig. 3.13 Preparation line for SO_2 gas

sulfur isotope analysis. The precipitated $BaSO_4$ was collected on a 0.45 µm membrane filter paper, dried, and ground together with SiO_2 and V_2O_5.

(b) ***Sulfur in fertilizer***
Twenty grams of fertilizer was dissolved in 500 mL distilled water and acidified with 5 mL HCl. Sulfate was precipitated as $BaSO_4$ using the same procedure as that for groundwater.

(c) ***Sulfur in coal***
Coal samples were combusted using the apparatus shown in Fig. 3.9. To analyze the sulfur isotopes of coal, the sample was processed according to the procedure modified from Nakai and Jensen (1967), and Ohizumi et al. (1997). Two grams of coal was accurately weighed and combusted at 900 °C in a vacuum line. The resulting gases were oxidized in 3 % H_2O_2 solution to produce sulfate ions. The obtained solution was passed through a membrane filter (ADVENTEC, A045A047A) and the dissolved sulfates were recovered via $BaSO_4$ precipitation using the same procedure as that for groundwater (Fig. 3.12).

3.9.3 Sulfur Isotope Analysis

The precipitated $BaSO_4$ were dried and 10 mg of sample was ground together with 100 mg SiO_2 and 100 mg of V_2O_5. The sample powder was reduced to produce SO_2 gas by heating at 850 °C following the method by Yanagisawa and Sakai (1983) (Fig. 3.10). The producing water vapor and CO_2 gas was removed by dry-ice + acetone and n-Pentalene respectively. The pure SO_2 gas collected in sample tube and used to analyze the sulfur isotope ratio by a mass spectrometer VG SIRA 10. The analytical precision for $\delta^{34}S$ was <±0.2 ‰.

The obtained isotope ratios are expressed in the familiar delta notation $\delta^{34}S$, referring to the CDT (Canyon Diablo Troilite) scale and defined by the Eq. 3.1 (Fig. 3.13):

$$\delta^{34}\mathrm{S} = \left[\frac{(^{34}\mathrm{S\ sample}/^{32}\mathrm{S\ sample})}{(^{34}\mathrm{S\ standard}/^{32}\mathrm{S\ standard})} - 1\right] \times 1000 \tag{3.1}$$

3.9.4 Pretreatment for Nitrogen Isotope Analysis

(a) ***Nitrate-nitrogen of water***

The Devarda's alloy/ammonia protocol, developed by Sigma et al. (1997), was used for pretreatment of NO_3^-–N isotope analysis. Using this protocol, samples were pre-incubated at 50 °C for about 7 days with a high pH approximately 12 by adding 9 N NaOH in order to create decomposition of labile dissolved organic nitrogen (DON) to NH_3 and allow it to be released. Nitrogen isotope analysis was done using an online elemental analyzer continuous flow isotope ratio mass spectrometer (EA-IRMS).

(b) ***Nitrogen in fertilizers***

Appropriate amount of fertilizer was weighed and packed in a tin boat and was analyzed by mass spectrometer (EA-IRMS).

3.9.5 Nitrogen Isotope Analysis

Nitrogen isotope analysis was performed using an online elemental analyzer-continuous flow isotope ratio mass spectrometer (EA-IRMS) at Kyoto University. The EA-IRMS consist of a Carlo Erba 1108 elemental analyzer coupled with a continuous flow interface to the Finnigan-MAT Delta SIRM. The nitrogen compounds fixed on a filter or fertilizer were transformed into N_2 by using combined oxidation and reduction tubes (Fig. 3.11). The oxidation tube was filled with

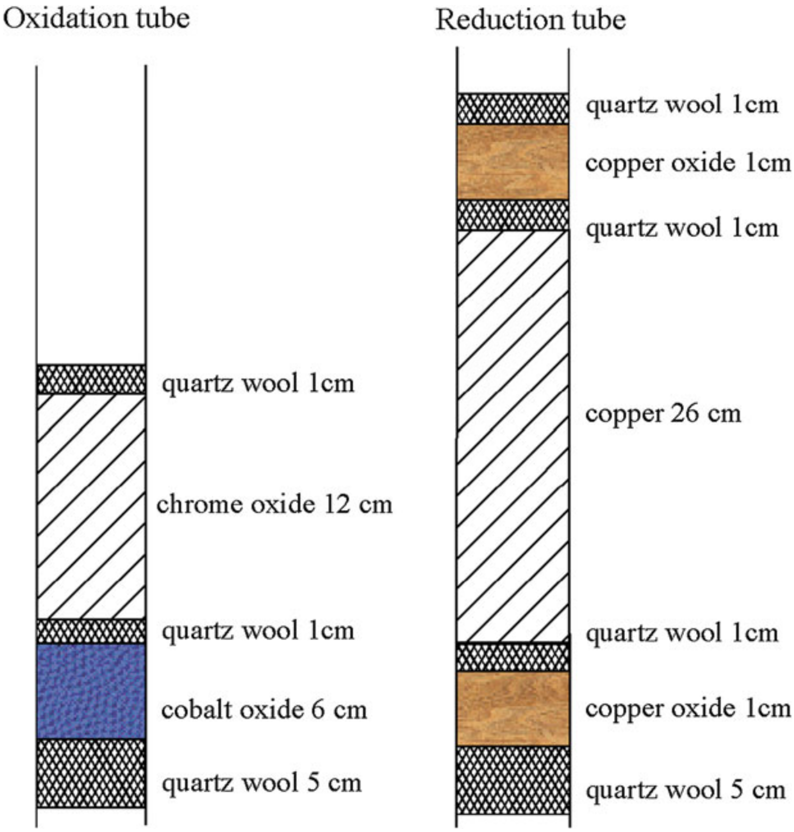

Fig. 3.14 Oxidation, reduction tubes

oxidizing reagents (Chrome oxide and Cobalt oxide) and controlled at 1,020 °C; the reduction tube was filled with copper and copper oxide and was controlled at 650 °C. After the produced water is adsorbed by anhydrous magnesium perchlorate, the remaining gas is introduced into a chromatographic column to separate N_2, which is isotopically analyzed by IRMS. Results for ^{15}N natural abundance were expressed as following:

$$\delta^{15}N = \left[\frac{\text{R sample}}{\text{R standard}} - 1\right] * 100 \qquad (2)$$

where $R = {}^{15}N/{}^{14}N$.

Atmospheric N_2 ($\delta^{15}N = 0$ ‰) is used as the standard and reference gases. Based on the multiple analyses of laboratory standards (KNO_3, $(NH_4)_2SO_4$, and DL-alanine), the precision of the analytical data was <0.20 ‰ (Fig. 3.14).

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Results: Case Study

4

4.1 Major Chemical Compositions of Groundwaters from Kalalanwala (2002)

4.1.1 Groundwater Samples

The chemistry and stable isotopic composition of sulfur from a single village Kalalanwala is given in Table 4.1. For convenience in description, groundwater samples are grouped into three categories according to well depth: groundwaters sampled from 24 to 27 m deep wells (shallow groundwater); 60–90 m (middle groundwater); and 165–183 m (deep groundwater).

All shallow groundwater ($n = 17$) is alkaline, pH 7.3–8.7. Alkalinity, expressed as HCO_3^-, ranges between 579 and 1,900 mg/L. Sulfate is one of the dominant anions, with a concentration range of 284–1,550 mg/L, Cl^- ranges from 20.4 to 299 mg/L, while Na^+, the most dominant cation, is 301–878 mg/L. Calcium concentrations are notably low, ranging from 8.4 to 44.8 mg/L. Six shallow groundwater samples (KLW-1, 3, 7, 11, 16 and 17) contain NO_3^-–N above the WHO standard for drinking water (10 mg/L). The highest concentration of NO_3^-–N is 64 mg/L in KLW-16, probably due to the use of fertilizers in the area.

Middle groundwater ($n = 3$) gives pH ranging 7.6–7.8. The alkalinity of this group ranges within 237–363 mg/L, SO_4^{2-} is up to 906 mg/L, and Na^+ up to 380 mg/L, Ca^{2+} concentrations of 59.2–129 mg/L, and Cl^- up to 224 mg/L. The groundwater temperature is notably higher (27.3–28.8 °C) than those of the other two groups of groundwater.

Deep groundwater ($n = 4$) has a pH range of 7.4–7.9. The alkalinity is up to 433 mg/L, SO_4^{2-} up to 718 mg/L, Na^+ ranges from 234 to 300 mg/L, Ca^{2+} of 65.6–89.6 mg/L, and Cl^- up to 110 mg/L. Middle and deep groundwater have NO_3^-–N of <10 mg/L. The major ion composition of this water group is similar to that of the middle groundwater, while the water temperature is low (25.2–26.9 °C). Since water temperature is one of the conservative properties in the water cycle, the difference in temperature ranges between the middle and deep groundwater is suggestive of the presence of two separate confined aquifers.

Sulfate concentrations of the studied groundwater show a positive correlation ($r^2 = 0.95$, $n = 24$) with Cl^- (Fig. 4.1), indicating that most groundwater is a mixture of at least two independently recharged waters. Rainwater is considered to be one of the recharging sources in the area, and Ravi River water is another possible source, although it cannot be specified at present.

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Table 4.1 Major element chemistry, arsenic concentrations and sulfur isotope ratios of groundwaters from Kalalanwala, Pakistan

Sample I.D.	Depth (m)	pH	T (°C)	EC (mS/cm)	Alkalinity (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	Na^{+} (mg/L)	K^{+} (mg/L)	NH_4^{+} (mg/L)	Tct meq/L	F^{-} (mg/L)	Cl^{-} (mg/L)	Br^{-} (mg/L)	$NO_3^{-}N$ (mg/L)	PO_4^{3-} (mg/L)	SO_4^{2-} (mg/L)	Tan (meq/L)	As (µg/L)	$\delta8^{34}S$ (‰)
WKA-1	24–27	7	26	2.92	788	44.8	31.4	696	6.30	0.03	32.8	8.55	264	0.56	24.3	bdl	1,213	33.8	68	4.8
WKA-2	24–27	8.0	26	2.42	859	28.0	26.5	644	5.50	0.02	29.9	7.03	175	0.48	bdl	bdl	939	29.1	227	6.5
WKA-3	24–27	8.0	26	2.62	686	32.0	15.3	679	5.50	0.03	31.1	10.00	232	0.56	20.2	bdl	1,111	30.2	110	5.5
WKA-4	24–27	8	25	2.36	1,895	35.0	21.0	629	5.90	0.04	29.2	0.95	141	0.32	bdl	bdl	926	28.3	111	6.3
WKA-5	24–27	8.0	25	1.18	610	22.0	13.1	301	4.30	0.18	14.3	2.47	38.2	bdl	2.10	bdl	284	14.2	62	5.6
WKA-6	24–27	8.0	26	1.28	718	8.8	16.3	352	3.50	0.13	16.3	5.89	20.4	bdl	bdl	bdl	299	15.7	153	6.2
WKA-7	24–27	8	24	1.92	866	14.4	10.7	526	3.90	0.21	23.8	21.10	84.4	0.16	10.6	0.09	573	23.8	60	5.7
WKA-8	24–27	8.0	26	2.78	1,031	24.4	11.4	771	4.70	0.03	34.7	21.10	171	0.48	0.30	0.38	1,082	34.1	130	5.5
WKA-9	24–27	8	25	2.41	816	21.6	12.4	656	4.70	0.04	29.7	19.80	173	0.48	bdl	0.19	960	29.3	132	5.6
WKA-10	24–27	8.0	25	2.65	735	27.2	12.4	700	5.50	0.04	31.7	16.40	194	0.48	2.2	0.28	1,170	30.6	135	5.7
WKA-11	24–27	8	25	2.47	854	8.4	5.6	701	4.70	0.07	31.0	10.80	158	0.01	11.0	0.57	1,009	29.7	530	5.5
WKA-12	24–27	8	25	2.78	1,003	16.0	22.1	661	5.90	0.04	30.2	14.30	120	0.40	5.6	0.19	850	29.5	192	5.6
WKA-13	24–27	9	24	1.45	835	10.4	8.0	411	3.50	0.07	18.5	3.80	56.3	0.08	0.1	0.28	321	18.8	66.2	7.0
WKA-14	24–27	8.0	26	2.34	829	15.6	9.0	646	5.10	0.74	29.0	19.80	134	0.40	5.6	0.47	867	27.5	84.1	5.5
WKA-15	24–27	8.0	25	3.10	860	22.8	18.7	878	5.80	0.03	39.6	7.80	253	0.64	bdl	bdl	1,551	37.8	68.3	4.7
WKA-16	24–27	8.0	25	3.06	610	19.6	16.1	826	5.50	0.21	37.2	15.60	299	1.12	64.0	0.57	1,497	35.8	144	4.8
WKA-17	24–27	9	24	2.19	579	13.2	3.6	638	4.70	0.07	28.3	3.42	192	0.48	10.0	2.18	1,112	26.8	1,900	5.5
DKW-1	60–90	8	28	1.86	363	129	73.0	380	5.10	0.07	22.8	0.57	224	0.40	bdl	bdl	906	21.7	53	5.6
DW-2	60–90	8	29	0.37	237	59.2	28.5	68	2.74	0.15	5.71	0.57	13.1	bdl	bdl	bdl	112	5.44	47	5.6
DWHF-3	60–90	8	27	0.36	274	71.2	32.6	102	3.13	0.24	7.63	0.38	29.3	0.08	1.0	bdl	193	7.37	32.2	5.7
TWI-1	165–183	8	25	1.42	431	89.6	63.7	283	4.70	0.34	17.3	1.52	110	0.24	0.1	bdl	597	16.4	68	5.5
TWI-3	165–183	7	26	1.61	410	89.6	78.0	300	5.50	0.07	18.6	1.15	130	0.32	bdl	bdl	718	17.9	72	5.6
TWI-5	165–183	7	27	1.37	433	65.6	31.0	276	4.70	0.18	15.0	0.38	100	0.24	bdl	bdl	562	15.8	61	5.7
TWI-7	165–183	8	26	0.47	365	52.4	26.3	234	3.50	0.08	12.6	2.85	74.2	0.16	bdl	bdl	396	12.3	50	5.6

1. The abbreviations gives the different types of water samples as follows; *RAIN* rainwater; *WKA* shallow groundwater from Kalalanwala; *DKW*, *DW*, and *DWHF* groundwater from the middle depth; *TWI* deepest groundwaters among the studied samples

2. *bdl* stands for below detection limit

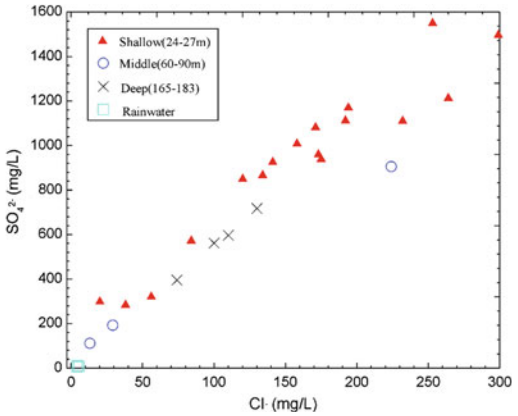


Fig. 4.1 Relationship between Cl$^-$ and SO$_4^{2-}$ of water samples from Kalalanwala area

Another source contributing high Cl$^-$ and SO$_4^{2-}$ concentrations would be anthropogenic, and will be discussed in detail later in the text.

4.1.2 Rainwater Samples

Major ion chemistry and As concentrations of rainwater from study area is given in Table 4.2. The rainwater has a pH range of 6.9–7.1, alkalinity up to 12 mg/L, SO$_4^{2-}$ ranging from 5 to 14 mg/L, Na$^+$ 2.62–6.7 mg/L and Ca^{2+} 6.4–10 mg/L.

4.1.3 Arsenic and F$^-$ Concentrations

All shallow groundwater samples except KLW-4 (Table 4.1) contain F$^-$ > 1.5 mg/L, which is the WHO drinking water standard. The highest concentration is 21.1 mg/L. In contrast, F$^-$ concentrations in groundwater from the middle and deep wells are below WHO standards, except for TWI-7, which contains 2.85 mg/L of F$^-$. Samples with high F$^-$ concentrations invariably have low concentrations of Ca^{2+} (Fig. 4.2) and high concentrations of Na$^+$. Rainwater samples (n = 5) contain F$^-$ in the range of 0.16–0.28 mg/L, indicating that F$^-$ in the groundwater originates in part from dissolved air pollutants.

Arsenic concentrations range from 32 to 1,900 μg/L in the analyzed groundwater samples. All the samples, irrespective of the depth, contain As in excess of the WHO guideline (10 μg/L), however, As concentrations tend to be higher in the shallow groundwater samples, which give high pH ranging 7.3–8.7. Sample KLW-17 has a pH of 8.5 and the highest concentration of As at 1,900 μg/L. An important finding of this study is that 4 of 5 rainwater samples contain As >10 μg/L, with a maximum value of 90 μg/L; this indicates a clear contribution of atmospheric pollutants to the contamination of groundwater.

Figure 4.3a, b show distribution maps of F$^-$ and As in the study area. The concentrations of these elements are poorly correlated with each other; however, both elements are enriched in shallow groundwater, suggesting the contribution of a common source, factors or pathway for both elements.

4.1.4 Sulfur Isotopes

Stable isotope ratios of sulfate-sulfur vary in a narrow range from 4.7 to 7.0 ‰ (Table 4.1). The relationship between SO$_4^{2-}$ concentration and δ^{34} S indicates at least three different sources of sulfur in the analyzed groundwater (Fig. 4.4). The δ^{34} S values of the three end members are 5.5–5.7 ‰ (A), 4.7–4.8 ‰ (B), and about 7.0 ‰ (C). End member A contains the least SO$_4^{2-}$ < 20 mg/L, while B contains >1,550 mg/L SO$_4^{2-}$, and C 320 mg/L. Most of the analyzed waters plot within a triangle connecting the three end members. All samples from the middle and deep aquifers have δ^{34} S values of 5.5–5.7 ‰ (CDT). These samples contain less soluble salts, including F$^-$ and As, than the shallow groundwater, and are therefore the least polluted waters.

Most of the middle and deep waters plot in an area close to A (Fig. 4.4), suggesting that these

Table 4.2 Chemistry of rainwater from the study area

Sample I.D	pH	T (°C)	EC (mS/cm)	Alkalinity (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	Na^{+} (mg/L)	K^{+} (mg/L)	NH_4^{+} (mg/L)	Tct (meq/L)	F^{-} (mg/L)	Cl^{-} (mg/L)	Br^{-} (mg/L)	$NO_3^{-}N$ (mg/L)	PO_4^{3-} (mg/L)	SO_4^{2-} (mg/L)	Tan (meq/L)	As (μg/L)
RAIN-1	7.1	24.1	0.05	12	10	1.02	2.62	0.64	nd	0.44	0.23	4.0	bdl	1.5	bdl	5	0.47	30
RAIN-2	6.9	25.0	0.09	12	6.4	2.03	6.70	1.75	nd	0.62	0.28	4.2	bdl	3.8	0.34	14	0.72	90
RAIN-3	7.0	24.8	0.07	11	9.0	1.02	4.20	0.52	nd	0.47	0.18	4.1	bdl	1.5	0.62	9	0.50	19
RAIN-4	7.1	24.7	0.07	10	7.5	1.04	3.50	0.43	nd	0.43	0.23	5.3	bdl	1.4	0.53	7	0.49	<10.0
RAIN-5	7.0	23.0	0.06	12	8.0	2.00	6.50	1.20	nd	0.57	0.16	5.1	bdl	1.3	0.49	9	0.53	15

Note nd stands for not detected
bdl stands for below detection limit
Detection limits for Br^{-}, NH_4 and PO_4^{3-} are 0.02, 0.02 and 0.025 respectively
Alkalinity is reported as HCO_3^{-}

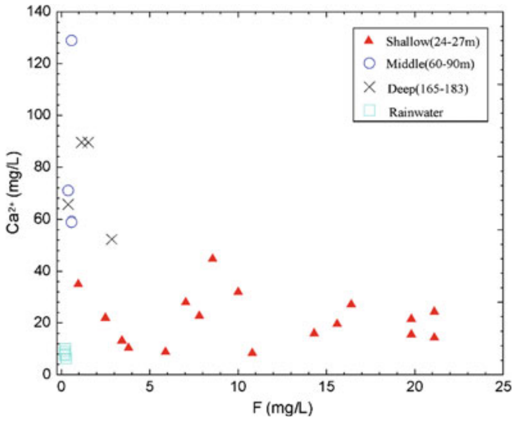


Fig. 4.2 Relationship between F^- and Ca^{2+} concentrations in analyzed water samples

waters are not seriously polluted following the recharge.

4.2 Results of Extended Study Area Punjab Pakistan (17 Villages 2004)

On the basis of the results from Kalalanwala this study was extended to 17 villages surrounding Kalalanwala, in order to reveal the extent and degree of groundwater pollution and to estimate the principal controlling geochemical factors concerned with the As and F^- pollution; based on the water chemistry including H, O, S and N isotopic ratios.

4.2.1 Major Chemical Compositions

The chemistry and stable isotopic ratios of groundwaters collected in March 2004 and October 2004 are given in Appendix. During October 2004, eleven samples could not be collected as people stopped using the hand pumps. As shown from the data in Appendix and Fig. 4.5 no significant difference in the concentrations of major component and As was detected during dry and rainy season, thus, for convince, all figures were made using the data of samples collected in March 2004 (Table 4.3).

For convenience in description, groundwater samples are grouped into three categories according to well depth, same as those from Kalalanwala described before: groundwaters sampled from 20 to 27 m deep wells (shallow groundwater); 40–80 m (middle groundwater); and, 80–200 m (deep groundwater). Two canal waters CCO-1 and 2 were also collected from the study area.

Chemistry of the groundwater showed large variation in the concentration ranges, however, many of those contained high salinity. As described below, the ranges of each ion overlapped among the groundwaters from the different depths; the highest concentration of major anions and Na^+ were almost two times as high as in the shallow groundwaters as in the middle and deep groundwaters. Ranges of analytical data of groundwaters classified by the well depth and canal water are given in Table 4.4.

Concentration ranges of major cation and anion are given in Table 4.5. The shallow groundwaters gave the widest range of EC within 0.4 and 4.6 mS/cm, and most of those have EC > 2.0 mS/cm. The alkalinity calculated as HCO_3^-, was 195–1,280 mg/L and SO_4^{2-} ranged from 38 to 960 mg/L, of which 35 % groundwaters exceeded the WHO guideline value. These two were the most abundant anions. The Cl^- ranged from 2 to 415 mg/L. Sodium, the most dominant cation, was up to 1,060 mg/L, while Ca^{2+} concentrations were low, ranging from 2 to 140 mg/L with the mean value of 32 mg/L.

Electric conductivity of the middle groundwaters was 0.2–2.2 mS/cm, SO_4^{2-} 24–480 mg/L, alkalinity (as HCO_3^-) 153–732 mg/L, Na^+ up to 322 mg/L, Ca^{2+} were 19–73 mg/L with mean value of 45 mg/L, and Cl^- up to 250 mg/L. Groundwater from the deep aquifers showed the narrow ranges of analytical data compared with those of shallow and middle groundwaters; EC 0.5–1.9 mS/cm, SO_4^{2-} 32.0–341 mg/L, alkalinity

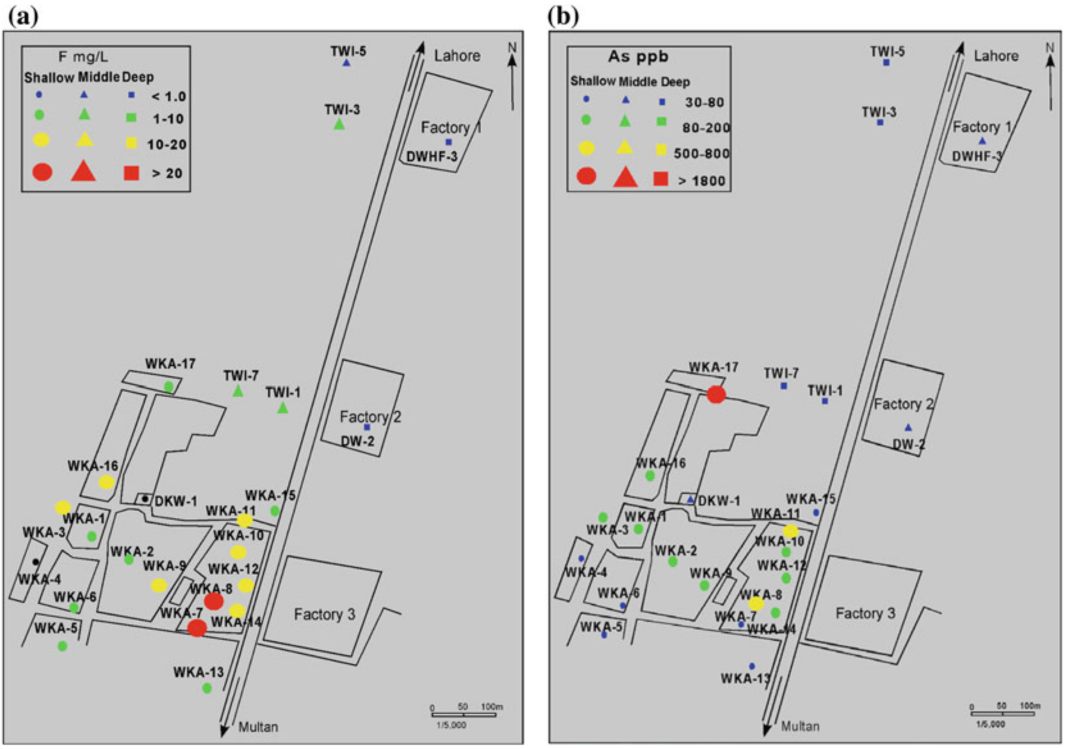


Fig. 4.3 **a**, **b** Distribution maps of fluoride and arsenic in Kalalanwala area

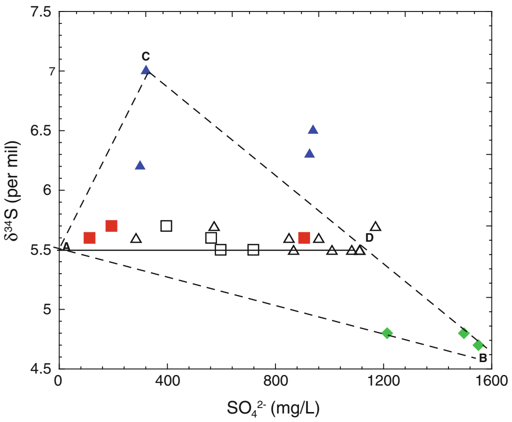


Fig. 4.4 Relationship between SO_4^{2-} and sulfur isotope ratios. *Line triangles* represent shallow groundwater with constant δ^{34} S and increasing SO_4^{2-} *solid rectangles* represents middle and *line rectangles* represents deep groundwater, *diamonds* represent shallow samples with low δ^{34} S, high SO_4 and *solid triangles* indicate shallow samples with high δ^{34} S low SO_4^{2-}. The *dashed area* of *triangle* indicates three end members, while $^{2-}$the *solid line* from A to B indicates the increase of SO_4^{2-} with input of some anthropogenic source with constant δ^{34} S values

146–671 mg/L, Na^+ up to 306 mg/L, Ca^{2+} from 6.0 to 86 mg/L, and Cl^- up to 160 mg/L. The high EC and high concentration of the above described dissolved constituents in shallow groundwater show that the shallow groundwater could be easily affected by the human activities.

More than half of the samples had $Na\text{-}HCO_3^-$ dominant type chemistry. Type of the major chemical composition was not related to the well depth. However, Ca^{2+} and Mg^{2+} tend to be slightly higher in the middle and deep groundwaters than in the shallow groundwater. Even though, the groundwaters containing high amounts of dissolved species appear mostly from the shallow wells. The trilinear diagram showing anion composition in Fig. 4.6 gives the linear relationship for the anion composition between HCO_3^- and Cl^- + SO_4^{2-}, suggesting that the latter two have common origins as major contaminants, e.g., household waste and fertilizers. The waters were in neutral to alkaline pH of 7.1–8.7.

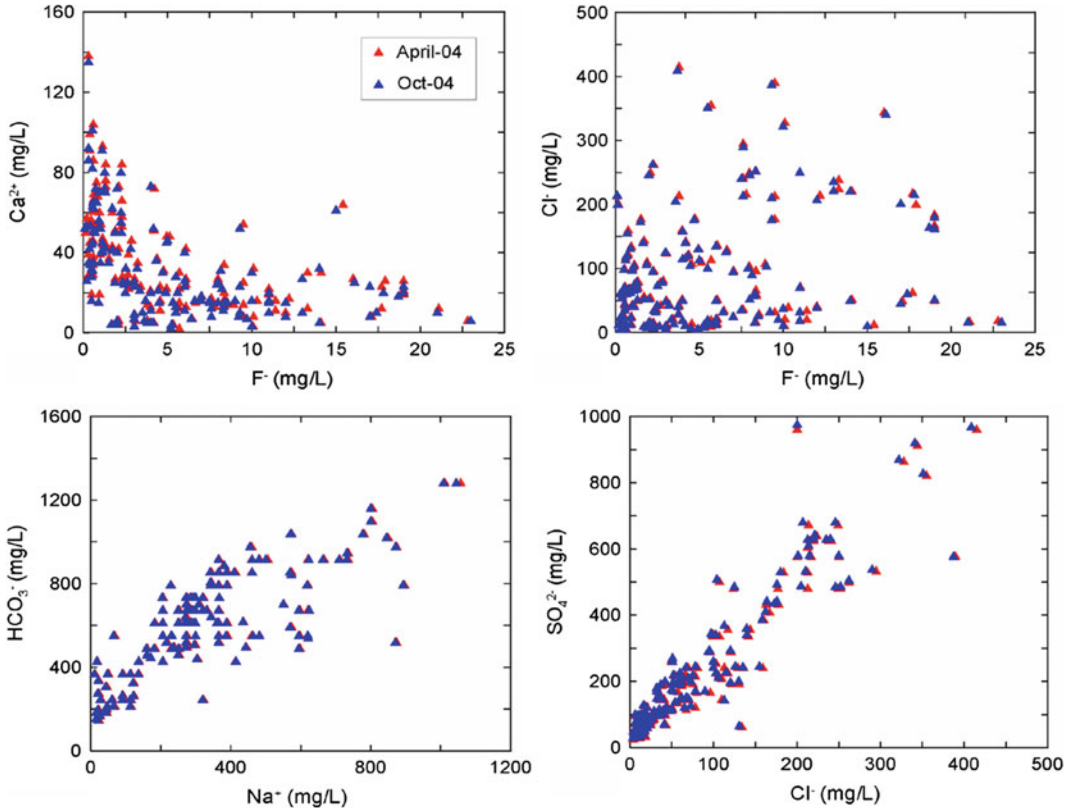


Fig. 4.5 Major concentrations difference for the groundwater samples collected in dry (April-04) and rainy (Oct-04) seasons

The two canal water samples CCO-1 and CCO-2 had EC 0.5–0.7 mS/cm, pH 7.3, and SO_4^{2-} 36.0–72.0 mg/L, alkalinity 427 mg/L, Na^+ 12.0–19.0 mg/L, Ca^{2+} 60.0–66.0 mg/L and Cl^- 10.0–15.0 mg/L.

High NO_3^-–N concentrations were observed in shallow groundwaters. Six of them contained NO_3^-–N more than the WHO standard (10 mg/L) for drinking water. The highest concentration of NO_3^-–N was 46 mg/L. Middle and deep waters had NO_3^-–N of <10 mg/L (WHO standard), with the exception of two samples from the middle depth. The absence of NO_3^-–N in the deep waters would not be related to NO_3^- reduction as the groundwaters showed Eh values, up to 860 mV. It is more likely due to the lack of nitrogen pollution at depths >30 m.

The relationships between Cl^- versus SO_4^{2-}, Na^+, NO_3^-–N, and HCO_3^-, are given in Fig. 4.7a–f. Sulfate, Na^+, HCO_3^- and NO_3^-–N concentrations show positive correlations with Cl^- (Fig. 4.7a–c, f). Thus, the pollutant source(s) would be the same or the moving paths are similar among those elements.

Concentration of Fe was low in the studied groundwaters in concordance with the highly positive Eh, indicating the oxidizing condition to prohibit high Fe dissolution. Most of the studied groundwater showed the Fe concentrations below the detection limit, 0.01 mg/L. Only twelve samples had higher Fe, i.e., more than the WHO standard of 0.3 mg/L, and the maximum concentration was 2.8 mg/L at depth of 20–27 m.

Table 4.3 Chemistry and stable isotope data of groundwaters in east Punjab, Pakistan March 2004

Sample ID	Depth (m)	T (°C)	EC (mS/cm)	pH	Eh (mV)	F^- (mg/L)	Cl^- (mg/L)	Br^- (mg/L)	NO_3^-N (mg/L)	PO_4^{3-} (mg/L)	SO_4^{2-} (mg/L)	HCO_3^- (mg/L)	Tan (meq/L)
CNG-1	20–27	27	1.95	7.3	65	4.94	131	0.33	7.00	bdl	192	976	24.79
CNG-2	20–27	27	1.36	8.1	105	2.67	78	0.23	bdl	bdl	120	549	14.06
CNG-4	20–27	26	1.70	7.7	102	8.36	96	0.30	bdl	bdl	165	671	17.88
CNG-5	20–27	27	1.25	7.3	128	6.08	51	0.14	bdl	bdl	116	610	14.33
SUN1	20–27	29	1.30	8.1	95	10.1	21	bdl	bdl	0.4	120	884	18.13
SUN2	20–27	29	1.61	8.0	111	8.36	60	0.16	0.98	bdl	192	732	18.37
SUN3	20–27	27	2.56	8.0	171	4.75	178	0.36	4.20	bdl	432	854	28.91
SUN4	20–27	27	2.26	7.4	141	4.18	142	0.34	1.68	0.7	336	915	26.69
SUN5	20–27	28	2.60	7.2	152	1.52	177	0.45	4.48	bdl	432	1,037	31.85
SKB-2	20–27	30	1.23	8.3	118	3.80	28	bdl	bdl	bdl	106	671	14.20
SKB-3	20–27	28	1.25	8.4	94	1.14	41	0.16	bdl	bdl	105	610	13.57
SKB-4	20–27	28	1.49	8.5	125	5.70	19	bdl	bdl	bdl	96	854	16.84
SKB-5	20–27	29	1.13	8.5	134	10.07	10	0.04	0.42	0.6	50	732	13.93
SKB-6	20–27	28	1.22	8.4	139	3.04	10	bdl	4.20	2.9	38	732	13.57
SKB-8	20–27	28	1.21	8.6	129	5.70	9	bdl	2.24	0.8	35	636	11.87
SKB-9	20–27	27	1.06	8.6	133	5.32	11	bdl	0.70	1.4	48	549	10.65
SKB-10	20–27	30	0.66	7.2	163	4.56	6	bdl	bdl	bdl	43	366	7.31
SKB-12	20–27	30	0.84	8.0	47	0.95	13	bdl	2.38	bdl	44	549	10.49
SKB-13	20–27	27	0.93	8.0	114	3.42	21	0.06	0.84	bdl	58	488	10.11
SKB-14	20–27	27	1.44	7.2	117	3.04	50	0.15	3.50	bdl	110	732	16.27
SKB-15	20–27	28	1.14	7.8	86	4.56	14	0.06	0.56	bdl	91	732	14.64
SKB-16	20–27	27	0.85	7.2	157	1.90	7	bdl	1.54	bdl	48	427	8.39
SKB-17	20–27	26	0.83	7.8	139	5.32	8	bdl	0.14	bdl	44	457	8.94
SKB-18	20–27	26	1.67	8.2	144	17.1	49	0.16	0.84	bdl	110	854	18.80
SKB-19	20–27	27	1.13	8.2	101	8.55	29	0.13	bdl	bdl	86	427	10.20
SKB-20	20–27	26	1.04	7.8	101	5.70	13	0.05	bdl	bdl	72	549	11.22
SKB-21	20–27	26	1.31	7.3	117	7.03	24	0.09	bdl	bdl	87	702	14.44
SKB-22	20–27	27	1.13	7.4	160	2.09	14	0.06	3.08	bdl	88	671	13.59

(continued)

Table 4.3 (continued)

Sample ID	Depth (m)	T (°C)	EC (mS/cm)	pH	Eh (mV)	F^- (mg/L)	Cl^- (mg/L)	Br^- (mg/L)	NO_3^-N (mg/L)	PO_4^{3-} (mg/L)	SO_4^{2-} (mg/L)	HCO_3^- (mg/L)	Tan (meq/L)
SKB-23	20–27	27	0.86	7.6	87	4.94	5	bdl	1.12	bdl	43	488	9.38
SKB24	20–27	27	0.70	7.7	98	3.04	5	bdl	4.20	0.2	48	549	10.61
MM-2	20–27	28	1.37	7.5	166	1.14	106	0.30	8.68	bdl	217	445	15.80
MM-3	20–27	28	1.44	7.3	129	1.33	80	0.21	7.42	bdl	165	457	14.01
MM-4	20–27	29	1.01	7.2	87	0.86	68	0.20	5.60	bdl	149	323	10.97
MM-5	20–27	28	1.43	7.3	179	2.28	262	0.76	46.00	bdl	499	549	30.97
MM-6	20–27	29	1.82	8.3	138	3.04	124	0.40	bdl	2	480	427	21.08
MM-7	20–27	28	1.16	8.0	128	1.33	50	0.20	0.84	bdl	259	610	17.13
MM-8	20–27	27	1.40	7.7	155	1.14	67	0.23	6.72	bdl	113	488	13.03
MM-9	20–27	27	1.57	7.4	158	1.90	110	0.30	7.56	bdl	207	458	15.87
MM-11	20–27	27	1.17	8.3	141	0.76	62	0.23	bdl	bdl	187	366	11.92
MM-12	20–27	28	0.55	8.3	177	0.46	28	0.10	1.26	bdl	82	213	6.22
MM-14	20–27	27	0.58	8.6	136	0.57	23	0.06	bdl	bdl	75	201	5.62
MM-15	20–27	26	1.90	8.5	133	0.57	99	0.63	bdl	bdl	336	549	19.47
MM-16	20–27	27	1.83	8.7	132	0.60	117	0.37	bdl	bdl	355	506	19.41
MM-17	20–27	26	1.18	8.4	104	4.18	11	bdl	0.84	0.6	65	610	11.94
WP-1	20–27	29	0.82	8.3	113	6.08	13	bdl	bdl	bdl	72	518	10.69
WP-3	20–27	26	1.90	8.5	121	5.70	113	0.22	5.88	bdl	241	610	19.17
WP-4	20–27	27	1.30	8.2	116	3.80	42	bdl	2.52	bdl	98	519	12.10
WP-5	20–27	29	2.02	7.8	120	6.65	129	0.66	2.38	bdl	240	616	19.93
WP-7	20–27	27	1.86	8.0	132	7.03	96	0.26	bdl	bdl	288	550	18.36
WP-8	20–27	28	1.90	8.0	122	7.98	103	0.24	bdl	bdl	254	518	17.36
WP-9	20–27	27	1.77	8.1	141	8.36	66	0.17	bdl	0.52	221	610	17.08
WP-10	20–27	28	1.80	8.6	130	11.02	71	0.18	bdl	bdl	206	610	17.06
WP-11	20–27	27	1.02	8.4	168	2.09	16	bdl	bdl	2	72	488	10.07
KAD-1	20–27	27	2.82	8.2	98	7.60	241	0.60	bdl	bdl	624	549	29.81
KAD-2	20–27	26	0.81	8.1	112	7.80	216	0.55	1.96	bdl	624	549	29.21
KAD-6	20–27	27	2.74	7.8	30	11.0	250	0.57	bdl	bdl	576	549	29.19

(continued)

Table 4.3 (continued)

Sample ID	Depth (m)	T (°C)	EC (mS/cm)	pH	Eh (mV)	F^- (mg/L)	Cl^- (mg/L)	Br^- (mg/L)	NO_3^-N (mg/L)	PO_4^{3-} (mg/L)	SO_4^{2-} (mg/L)	HCO_3^- (mg/L)	Tan (meq/L)
KAD-7	20–27	27	3.18	7.3	40	12.2	214	0.50	bdl	bdl	672	537	29.99
KAD-8	20–27	27	2.04	8.0	66	9.50	213	0.53	bdl	bdl	528	671	29.04
KAD-10	20–27	26	2.55	7.7	68	19.0	184	0.50	bdl	bdl	528	793	30.71
KAD-11	20–27	26	3.7	7.6	117	13.3	238	bdl	bdl	bdl	624	1037	37.40
KAD-12	20–27	27	2.50	8.3	89	9.50	177	0.50	bdl	bdl	480	915	31.01
KLW1	20–27	27	3.38	8.0	54	3.23	43	0.17	bdl	bdl	192	805	18.76
KLW3	20–27	28	1.60	8.5	116	9.50	32	bdl	bdl	0.5	178	854	19.12
KLW4	20–27	27	1.70	8.0	106	2.70	42	bdl	bdl	bdl	192	793	18.34
KLW5	20–27	27	1.63	8.2	107	7.60	36	bdl	0.84	bdl	144	793	17.46
KLW6	20–27	28	2.21	8.4	110	19.0	50	0.15	bdl	bdl	264	854	22.05
KLW7	20–27	28	1.60	8.4	72	11.4	34	bdl	0.7	bdl	168	671	16.11
KLW8	20–27	28	3.25	8.5	117	17.9	200	0.50	2.52	bdl	576	915	33.76
KLW9	20–27	26	2.61	8.5	130	19.0	163	0.35	bdl	bdl	432	701	26.45
KLW10	20–27	28	1.86	8.6	110	17.7	62	bdl	bdl	bdl	192	976	22.68
KLW11	20–27	27	2.66	8.4	84	19.0	167	0.40	0.14	bdl	408	841	28.42
KLW12	20–27	26	3.01	8.2	127	17.7	217	0.45	bdl	1.2	576	915	34.57
KLW13	20–27	26	4.38	8.3	81	16.0	344	0.83	1.12	bdl	912	1281	51.46
KLW14	20–27	29	3.17	8.0	77	14.1	220	0.45	bdl	bdl	624	945	35.90
KLW15	20–27	28	4.60	8.3	62	10.1	328	0.71	3.92	bdl	864	1281	49.76
KLW16	20–27	27	2.22	8.4	104	3.99	160	0.43	10.64	bdl	384	549	22.91
KLW17	20–27	29	3.27	8.2	83	7.98	249	0.53	2.38	bdl	672	1098	39.60
KLW18	20–27	28	1.22	8.8	102	3.99	18	bdl	bdl	1.2	48	732	13.72
KLW19	20–27	29	2.26	8.3	95	8.93	107	0.27	2.24	0.8	336	1037	27.91
KLW20	20–27	28	1.72	8.5	79	14.1	51	bdl	2.8	bdl	192	915	21.38
KLW21	20–27	29	1.13	7.8	135	6.46	34	bdl	bdl	bdl	96	702	14.80
KLW22	20–27	29	1.28	8.5	118	21.1	17	bdl	0.42	bdl	96	671	14.62
KLW23	20–27	28	1.58	8.0	65	10.3	39	0.12	bdl	bdl	187	793	18.66
KLW24	20–27	29	1.25	8.6	89	6.08	21	0.07	bdl	bdl	96	671	13.99

(continued)

Table 4.3 (continued)

Sample ID	Depth (m)	T (°C)	EC (mS/cm)	pH	Eh (mV)	F^- (mg/L)	Cl^- (mg/L)	Br^- (mg/L)	NO_3^-N (mg/L)	PO_4^{3-} (mg/L)	SO_4^{2-} (mg/L)	HCO_3^- (mg/L)	Tan (meq/L)
KLW26	20–27	28	1.06	8.0	40	8.36	16	bdl	bdl	bdl	82	610	12.59
KLW27	20–27	29	1.51	8.5	106	22.8	18	bdl	bdl	0.5	126	793	17.33
MPU-1	20–27	27	3.12	8.0	132	0.12	213	0.63	bdl	bdl	605	915	33.64
MPU-2	20–27	27	1.34	7.9	125	0.57	62	0.20	bdl	bdl	211	610	16.38
MPU-3	20–27	26	4.10	7.9	138	0.19	200	0.70	bdl	bdl	960	1159	39.72
ARK-2	20–27	28	0.60	7.2	104	0.38	4	bdl	bdl	bdl	48	335	6.640
ARK-3	20–27	29	0.40	7.3	118	0.65	5	0.04	0.42	bdl	38	195	4.250
ARK-4	20–27	28	0.53	7.2	108	0.61	6	0.04	0.42	bdl	72	244	5.780
ARK-5	20–27	29	1.04	7.2	112	0.31	61	0.09	7.84	bdl	144	366	11.39
ARK-6	20–27	29	0.49	7.4	95	0.38	25	0.05	0.42	bdl	67.2	274	6.71
ARK-7	20–27	28	0.68	7.6	107	0.59	39	0.09	bdl	bdl	110	305	8.52
DN-1	20–27	28	1.22	8.0	130	0.76	122	0.33	2.52	bdl	192	610	17.99
DN-2	20–27	28	1.50	7.4	109	2.85	81	1.80	1.26	bdl	240	640	19.84
DN-3	20–27	26	2.10	7.5	576	6.08	136	0.30	18.9	bdl	240	915	25.81
DN-4	20–27	28	1.10	7.3	118	2.47	36	bdl	1.40	bdl	144	671	15.23
DN-5	20–27	27	1.60	7.5	28	5.13	110	0.33	3.36	bdl	144	610	16.94
DN-6	20–27	26	1.35	8.0	57	15.4	12	bdl	bdl	bdl	96	732	15.15
NK-1	20–27	29	1.24	7.7	98	1.71	56	0.15	0.7	bdl	192	610	15.86
NK-2	20–27	29	1.70	7.3	113	0.61	14	bdl	0.42	bdl	96	793	15.46
NK-3	20–27	29	1.40	7.5	135	0.57	64	0.16	0.42	bdl	194	671	17.04
NK-4	20–27	27	1.41	7.4	142	1.33	70	0.18	bdl	bdl	240	488	15.22
NK-5	20–27	27	1.33	7.4	154	11.4	20	bdl	bdl	bdl	96	915	18.17
NK-6	20–27	28	1.42	7.9	132	8.40	57	0.14	0.70	bdl	168	854	19.74
KA-1	20–27	28	1.38	8.2	103	1.14	75	0.20	0.14	bdl	192	610	16.37
KA-2	20–27	29	1.38	8.6	135	2.09	54	0.17	1.54	0.7	216	671	17.42
KA-3	20–27	28	1.20	8.6	135	4.37	121	0.30	11.48	bdl	288	610	20.76
BP-1	20–27	29	1.48	8.1	132	3.99	52	0.14	1.96	bdl	170	549	14.50
BP-2	20–27	28	1.23	7.8	152	12.0	41	0.11	2.52	bdl	145	494	12.90

(continued)

Table 4.3 (continued)

Sample ID	Depth (m)	T (°C)	EC (mS/cm)	pH	Eh (mV)	F^- (mg/L)	Cl^- (mg/L)	Br^- (mg/L)	NO_3^-N (mg/L)	PO_4^{3-} (mg/L)	SO_4^{2-} (mg/L)	HCO_3^- (mg/L)	Tan (meq/L)
BP-3	20–27	29	0.64	7.5	140	1.01	43	0.12	0.42	bdl	67	213	6.30
JK-1	20–27	26	3.40	8.3	123	13.3	224	bdl	10.50	bdl	638	1019	37.20
JK-2	20–27	27	3.60	8.1	137	9.50	390	1.02	10.00	bdl	576	976	41.18
RPNA1	20–27	26	2.10	7.5	65	4.56	107	0.25	2.59	bdl	500	494	22.22
RPNA2	20–27	27	1.82	7.8	66	1.71	144	0.27	10.00	bdl	355	495	20.35
CCO1	20–27	28	0.73	7.2	66	2.28	15	bdl	bdl	bdl	72	427	9.04
CCO2	20–27	29	0.52	7.3	65	1.71	10	bdl	bdl	bdl	36	366	7.11
ZAB-1	20–27	26	2.17	8.1	19	3.80	213	bdl	7.00	bdl	480	671	27.70
ZAB-2	20–27	29	2.80	8.0	88	8.36	252	bdl	7.56	bdl	480	590	27.75
ZAB-3	20–27	28	2.78	8.1	92	7.60	295	bdl	5.60	bdl	532	488	28.20
ZAB-4	20–27	27	3.80	8.0	151	3.80	415	0.64	14.00	bdl	960	518	42.05
ZAB-5	20–27	29	4.40	7.4	134	5.70	355	bdl	10.50	bdl	821	793	41.15
KLW25	40–80	25	1.18	8.5	165	2.28	7	bdl	bdl	bdl	96	732	14.33
ARK-1	40–80	24	0.20	8.1	167	0.30	4	bdl	bdl	bdl	24	153	3.125
ARK-8	40–80	24	0.34	8.6	172	0.38	4	bdl	bdl	bdl	29	183	3.74
WP-6	40–80	24	0.94	8.1	108	0.95	67	0.14	bdl	bdl	148	244	9.18
SKB-1	40–80	26	1.70	8.3	74	2.28	96	0.30	bdl	bdl	288	732	21.13
SKB-11	40–80	26	1.01	7.7	22	2.66	9	0.04	0.70	bdl	62	610	11.79
MM-10	40–80	24	0.41	8.4	126	0.57	14	0.06	0.28	bdl	48	366	7.51
KAD-3	40–80	26	0.81	7.5	102	0.44	57	0.15	0.28	bdl	134	213	8.09
KAD-4	40–80	27	0.34	7.4	157	0.44	5	bdl	0.28	bdl	30	165	3.50
KAD-5	40–80	24	1.10	7.3	73	4.20	117	0.28	0.56	bdl	225	213	12.04
KAD-9	40–80	25	2.19	8.3	35	2.09	249	0.54	bdl	bdl	480	244	21.7
KLW-29	40–80	25	2.50	8.7	203	2.32	36	bdl	bdl	bdl	96	549	12.12
CNG-3	40–80	24	0.38	8.3	80	0.25	12	0.04	bdl	bdl	29	183	3.98
SKB-7	40–80	25	1.01	8.1	144	0.95	134	bdl	bdl	bdl	62	610	15.13
WP-2	80–200	23	1.84	8.3	116	1.03	100	0.25	0.70	bdl	341	439	17.47
SKB25	80–200	24	1.07	8.6	145	3.10	10	bdl	0.84	3.3	73	671	13.05

(continued)

Table 4.3 (continued)

Sample ID	Depth (m)	T (°C)	EC (mS/cm)	pH	Eh (mV)	F^- (mg/L)	Cl^- (mg/L)	Br^- (mg/L)	NO_3^-N (mg/L)	PO_4^{3-} (mg/L)	SO_4^{2-} (mg/L)	HCO_3^- (mg/L)	Tan (meq/L)
MM-1	80–200	21	1.07	8.4	130	1.33	78	0.30	0.70	bdl	215	262	11.4
MM-13	80–200	23	0.89	8.7	147	0.57	45	0.14	0.14	bdl	120	263	8.25
KLW2	80–200	22	1.94	8.0	116	0.78	159	0.40	bdl	bdl	240	610	19.95
KLW-28	80–200	20	0.45	7.6	102	0.95	25	bdl	bdl	bdl	77	244	6.36
ARK-9	80–200	24	0.74	7.5	105	0.59	71	0.18	bdl	bdl	144	146	7.61
ARK-10	80–200	23	0.56	7.5	145	0.50	19	bdl	bdl	bdl	32	244	4.00

Sample ID	Na^+ (meq/L)	K^+ (meq/L)	Ca^{2+} (meq/L)	Mg^{2+}	Tca (meq/L)	As^V (μg/L)	As^{III} (μg/L)	Fe (mg/L)	SiO_2 (mg/L)	$\delta^{18}O^a$ (‰)	δD^a (‰)	$\delta^{15}N$ (‰)	$\delta^{34}S$ (‰)
CNG-1	460	8.97	48	13	23.65	6	nd	0.17	18.81	−8.0	−50.32	n.a	5.4
CNG-2	230	4.76	39	18	13.582	71	nd	0.05	27.00	−7.50	−46.89	n.a	n.a
CNG-4	322	5.07	34	15	17.09	23	nd	0.05	19.50	−8.20	−52.66	n.a	5.1
CNG-5	299	3.90	42	14	14.90	14	nd	<0.00	12.00	−8.37	−53.82	n.a	n.a
SUN1	380	4.68	8	4	17.32	92	nd	0.10	22.50	−8.50	−53.25	n.a	5.7
SUN2	368	3.12	20	8	18.12	57	nd	0.10	21.30	−8.00	−52.34	n.a	5.7
SUN3	575	7.80	31	18	28.28	85	nd	<0.00	24.80	−7.65	−48.61	n.a	5.7
SUN4	483	8.58	51	24	26.22	19	nd	<0.00	23.24	−7.30	−46.59	n.a	n.a
SUN5	575	11.7	37	35	30.80	1	nd	0.01	22.44	−7.30	−45.91	n.a	n.a
SKB-2	299	3.90	6	3	13.62	91	nd	0.06	17.01	−8.74	−59.11	n.a	n.a
SKB-3	207	5.46	40	23	13.08	70	nd	0.24	27.66	−8.28	−51.40	n.a	5.9
SKB-4	345	5.07	12	7	16.33	92	nd	0.01	24.00	−8.20	−51.42	n.a	n.a
SKB-5	276	3.90	3	13	13.38	443	nd	0.04	23.98	−8.89	−57.02	n.a	5.7
SKB-6	288	1.95	3	6	13.19	283	nd	0.05	16.11	−9.03	−56.43	10.0	n.a
SKB-8	276	3.90	2	3	12.46	195	nd	0.12	15.00	−9.03	−59.83	n.a	5.6
SKB-9	230	3.90	4	2	10.42	231	nd	0.05	16.10	−9.20	−61.17	n.a	n.a
SKB-10	115	4.29	16	13	6.97	223	nd	0.04	22.03	−9.06	−59.32	n.a	n.a
SKB-12	69	9.75	71	46	10.38	3	nd	<0.00	16.56	−8.26	−51.03	n.a	n.a
SKB-13	184	6.24	23	12	10.32	56	nd	0.05	25.25	−8.98	−55.25	n.a	n.a
SKB-14	322	6.78	25	11	16.17	15	nd	0.04	25.53	−8.27	−52.75	12.5	5.7

(continued)

Table 4.3 (continued)

Sample ID	Na^+ (meq/L)	K^+ (meq/L)	Ca^{2+} (meq/L)	Mg^{2+}	Tca (meq/L)	As^V (μg/L)	As^{III} (μg/L)	Fe (mg/L)	SiO_2 (mg/L)	$\delta^{18}O^a$ (‰)	δD^a (‰)	$\delta^{15}N$ (‰)	$\delta^{34}S$ (‰)
SKB-15	299	4.68	11	4	13.96	43	nd	0.05	21.10	−8.67	−52.43	n.a	5.6
SKB-16	138	6.24	27	14	8.72	12	nd	0.07	26.36	−8.64	−55.95	n.a	7.0
SKB-17	161	3.90	15	10	8.68	41	nd	0.08	20.76	−9.20	−56.13	n.a	6.2
SKB-18	368	7.80	8	3	16.88	63	nd	0.23	24.38	−8.30	−53.88	n.a	5.8
SKB-19	207	4.68	14	6	10.32	79	nd	0.13	21.84	−8.44	−55.09	n.a	5.7
SKB-20	207	5.85	22	11	11.13	30	nd	0.11	22.73	−8.52	−54.17	n.a	n.a
SKB-21	276	7.80	18	13	14.14	155	nd	0.12	16.70	−8.71	−56.03	n.a	5.6
SKB-22	207	8.19	42	24	13.25	27	nd	0.02	17.00	−7.79	−48.81	11.9	n.a
SKB-23	161	5.07	22	14	9.39	33	nd	0.20	25.25	−8.50	−54.11	n.a	5.7
SKB24	230	3.90	9	5	11.00	38	nd	0.10	18.43	−9.30	−61.91	n.a	n.a
MM-2	170	11.70	93	50	16.48	36	nd	<0.00	34.00	−7.52	−46.78	30.0	n.a
MM-3	161	15.60	84	36	14.62	10	nd	0.31	30.00	−7.50	−46.39	14.0	n.a
MM-4	124	8.97	68	26	11.23	4	nd	0.00	26.00	−7.70	−47.66	13.0	5.0
MM-5	460	39.00	84	55	29.80	8	nd	<0.00	32.00	−7.20	−42.54	25.0	n.a
MM-6	414	12.87	27	15	20.91	46	nd	0.01	30.00	−7.40	−44.98	n.a	5.6
MM-7	253	19.50	73	33	17.80	23	nd	0.06	15.10	−7.70	−46.53	n.a	n.a
MM-8	230	8.19	44	11	13.35	4	nd	<0.00	26.30	−7.50	−44.29	12.5	n.a
MM-9	253	9.36	51	26	15.98	5	nd	0.03	30.00	−7.52	−46.20	n.a	5.7
MM-11	138	9.36	68	25	11.68	68	nd	0.04	28.33	−8.09	−49.42	n.a	5.3
MM-12	46	5.85	56	19	6.53	42	nd	0.07	24.60	−8.12	−51.66	n.a	n.a
MM-14	46	5.46	36	18	5.46	134	nd	0.04	21.72	−8.47	−53.79	n.a	n.a
MM-15	368	8.97	29	12	18.67	70	nd	0.37	23.51	−8.32	−52.02	n.a	n.a
MM-16	299	7.80	38	61	20.28	75	nd	0.56	27.75	−7.80	−48.62	n.a	n.a
MM-17	276	2.73	5	2	12.45	424	nd	0.01	18.43	−8.70	−56.35	n.a	5.6
WP-1	219	3.90	13	7	10.82	33	nd	0.16	16.44	−8.30	−51.77	n.a	5.1
WP-3	391	7.80	30	16	19.98	166	nd	0.13	17.33	−7.84	−46.48	n.a	4.9
WP-4	276	3.90	5	2	12.52	242	nd	0.00	12.18	−8.13	−52.02	n.a	5.1
WP-5	437	5.07	15	7	20.45	153	nd	<0.0	20.00	−8.24	−51.55	n.a	5.6

(continued)

Table 4.3 (continued)

Sample ID	Na^+ (meq/L)	K^+ (meq/L)	Ca^{2+} (meq/L)	Mg^{2+}	Tca (meq/L)	As^V (μg/L)	As^{III} (μg/L)	Fe (mg/L)	SiO_2 (mg/L)	$\delta^{18}O^a$ (‰)	δD^a (‰)	$\delta^{15}N$ (‰)	$\delta^{34}S$ (‰)
WP-7	391	5.46	16	10	18.80	69	nd	0.02	24.50	−7.44	−45.97	n.a	5.7
WP-8	368	5.46	26	10	18.26	86	nd	0.02	21.35	−7.66	−47.45	n.a	n.a
WP-9	368	4.68	14	7	17.42	46	nd	<0.00	20.00	−7.76	−48.47	n.a	5.8
WP-10	363	5.07	19	12	17.78	70	nd	0.12	21.60	−8.07	−49.74	n.a	n.a
WP-11	230	2.73	4	2	10.41	677	nd	0.02	26.11	−8.27	−51.32	n.a	5.7
KAD-1	621	7.80	17	9	28.96	42	nd	0.04	15.02	−7.55	−47.39	n.a	5.5
KAD-2	621	7.80	13	8	28.52	142	nd	0.04	19.27	−7.85	−49.90	n.a	5.5
KAD-6	598	6.63	22	12	28.25	42	nd	0.02	19.64	−7.45	−45.32	n.a	5.4
KAD-7	621	7.80	17	10	28.90	158	nd	0.06	19.60	−7.25	−43.68	n.a	5.3
KAD-8	621	7.80	14	9	28.64	10	nd	0.00	19.27	−7.41	−45.79	n.a	5.6
KAD-10	621	6.24	26	9	29.18	62	nd	2.42	11.14	−7.60	−47.50	n.a	5.5
KAD-11	782	8.97	30	16	37.09	34	nd	2.40	7.35	−7.70	−48.45	n.a	5.3
KAD-12	621	7.80	25	14	29.58	171	nd	0.01	24.40	−8.17	−52.92	n.a	5.6
KLW1	345	7.80	35	13	18.26	38	nd	0.31	23.36	−8.45	−54.35	n.a	5.5
KLW3	414	4.29	8	3	18.91	615	nd	0.00	17.06	−8.23	−52.68	n.a	n.a
KLW4	345	4.68	22	15	17.64	90	nd	0.18	24.72	−8.40	−53.41	n.a	5.7
KLW5	345	7.80	16	6	16.70	82	nd	0.06	23.5	−8.16	−51.41	n.a	5.6
KLW6	460	5.85	21	2	21.41	131	nd	0.22	27.11	−8.53	−56.82	n.a	5.5
KLW7	334	5.85	16	6	15.93	159	nd	0.07	26.00	−8.30	−53.94	n.a	5.7
KLW8	713	7.80	26	11	33.50	217	nd	0.03	26.70	−7.69	−46.98	n.a	5.3
KLW9	552	11.70	19	2	25.42	213	nd	0.09	24.10	−8.40	−54.76	n.a	5.6
KLW10	460	3.90	12	16	22.00	234	nd	0.03	21.44	−8.70	−58.86	n.a	5.5
KLW11	575	5.85	21	14	27.11	157	nd	0.25	19.20	−8.49	−52.00	n.a	5.6
KLW12	736	5.85	23	12	33.75	103	nd	0.05	23.68	−8.48	−53.40	n.a	n.a
KLW13	1,058	12.09	27	30	49.47	111	nd	<0.00	23.92	−8.30	−53.48	n.a	5.4
KLW14	736	7.80	30	17	34.42	79	nd	0.25	22.27	−7.65	−47.73	n.a	5.7
KLW15	1,012	11.70	32	22	48.30	185	nd	<0.00	23.66	−7.80	−49.91	n.a	5.6
KLW16	483	5.46	13	9	22.50	250	nd	<0.00	20.42	−7.90	−49.32	15.0	5.7

(continued)

Table 4.3 (continued)

Sample ID	Na^+ (meq/L)	K^+ (meq/L)	Ca^{2+} (meq/L)	Mg^{2+}	Tca (meq/L)	As^V (μg/L)	As^{III} (μg/L)	Fe (mg/L)	SiO_2 (mg/L)	$\delta^{18}O^a$ (‰)	δD^a (‰)	$\delta^{15}N$ (‰)	$\delta^{34}S$ (‰)
KLW17	805	8.58	27	22	38.02	137	nd	<0.00	22.33	−8.00	−51.96	n.a	5.5
KLW18	299	3.90	5	3	13.64	2,400	nd	0.10	18.45	−8.21	−50.53	n.a	5.6
KLW19	575	6.63	14	10	26.85	460	nd	0.22	21.63	−8.01	−51.22	n.a	5.7
KLW20	460	4.68	5	3	20.60	634	nd	0.18	18.53	−8.10	−53.25	n.a	5.8
KLW21	311	3.90	7	6	14.52	23	nd	0.06	16.11	−8.40	−54.72	n.a	5.5
KLW22	288	4.68	12	9	14.00	120	nd	0.51	22.80	−8.60	−52.40	n.a	n.a
KLW23	391	5.07	16	7	18.75	30	nd	0.03	21.76	−8.20	−51.46	n.a	5.6
KLW24	276	5.46	24	8	14.02	639	nd	0.07	24.66	−8.70	−60.68	n.a	5.2
KLW26	253	3.90	13	5	12.18	52	nd	0.07	22.40	−8.50	−56.68	n.a	5.4
KLW27	368	3.90	6	2	16.58	124	nd	0.21	18.60	−8.55	−54.26	n.a	5.5
MPU-1	667	7.80	50	11	32.70	64	nd	0.14	23.28	−8.10	−50.47	n.a	5.7
MPU-2	299	6.24	34	14	16.02	59	nd	0.16	26.00	−8.05	−50.35	n.a	n.a
MPU-3	805	11.70	57	23	40.08	52	nd	0.25	18.50	−7.90	−50.98	n.a	5.6
ARK-2	23	7.80	99	10	6.96	8	nd	<0.00	14.30	−7.46	−45.71	n.a	5.1
ARK-3	23	4.68	54	7	4.37	56	23	0.07	18.80	−7.23	−48.76	n.a	5.0
ARK-4	30	4.68	69	14	6.02	2	nd	0.00	10.42	−7.70	−48.03	n.a	5.4
ARK-5	51	23.4	138	20	11.40	1	nd	0.16	16.00	−7.82	−52.59	11.0	5.5
ARK-6	23	5.85	91	14	6.88	40	12	0.51	20.00	−7.87	−54.79	n.a	5.4
ARK-7	46	27.30	104	9	8.62	73	nd	0.14	16.00	−7.22	−45.26	n.a	5.6
DN-1	299	7.80	52	28	18.22	8	nd	0.10	29.00	−7.70	−47.90	n.a	n.a
DN-2	345	7.80	46	22	19.34	31	nd	0.05	27.47	−7.88	−48.47	n.a	5.5
DN-3	506	11.70	27	18	25.16	8	nd	0.02	32.00	−7.70	−47.09	12.5	5.0
DN-4	299	7.80	27	18	15.80	33	nd	<0.00	15.00	−7.90	−47.47	n.a	n.a
DN-5	276	11.70	48	2	16.20	37	nd	0.02	17.00	−7.20	−46.00	9.40	5.4
DN-6	276	7.80	64	8	15.80	38	nd	0.23	15.00	−8.13	−51.03	n.a	n.a
NK-1	276	7.80	43	15	15.64	61	nd	0.03	24.30	−8.30	−49.91	n.a	5.8
NK-2	230	15.60	66	35	16.20	39	nd	0.02	12.22	−8.30	−51.66	n.a	n.a
NK-3	253	11.70	60	26	16.50	65	nd	2.80	25.00	−8.20	−50.59	n.a	5.8

(continued)

Table 4.3 (continued)

Sample ID	Na^+ (meq/L)	K^+ (meq/L)	Ca^{2+} (meq/L)	Mg^{2+}	Tca (meq/L)	As^V (μg/L)	As^{III} (μg/L)	Fe (mg/L)	SiO_2 (mg/L)	$\delta^{18}O^a$ (‰)	δD^a (‰)	$\delta^{15}N$ (‰)	$\delta^{34}S$ (‰)
NK-4	253	11.70	44	25	15.62	41	nd	0.14	24.50	−8.20	−49.17	n.a	6.2
NK-5	368	15.60	11	6	17.50	46	nd	<0.00	25.50	−8.30	−55.03	n.a	n.a
NK-6	391	11.70	17	8	18.90	94	nd	<0.00	18.50	−8.37	−51.17	n.a	6.3
KA-1	253	8.97	47	28	15.75	177	nd	0.03	26.6	−8.70	−53.86	n.a	5.6
KA-2	368	3.90	6	3	16.68	621	nd	0.00	23.00	−7.50	−45.81	n.a	5.7
KA-3	368	11.70	37	21	19.96	392	nd	<0.00	32.00	−7.98	−48.06	8.1	5.6
BP-1	299	5.07	21	6	14.71	109	nd	0.04	29.33	−8.37	−52.37	n.a	5.6
BP-2	276	4.29	10	4	12.97	40	nd	0.02	31.26	−8.55	−54.13	n.a	5.3
BP-3	69	4.68	39	17	6.52	54	nd	0.04	27.15	−7.91	−49.63	n.a	n.a
JK-1	851	12.87	12	11	38.89	103	nd	<0.00	21.70	−7.70	−48.14	15.0	3.7
JK-2	874	46.80	54	45	39.70	6	nd	0.60	37.00	−7.80	−49.94	14.5	3.9
RPNA1	445	11.70	23	14	21.97	23	nd	0.03	18.60	−8.28	−56.36	n.a	3.8
RPNA2	239	23.40	4	5	20.56	70	nd	0.01	25.24	−7.30	−44.28	7.2	3.7
CCO1	19	19.50	66	47	8.64	1	nd	0.22	29.30	−9.55	−60.15	n.a	5.5
CCO2	12	27.30	60	31	6.81	1	nd	0.15	26.30	−9.32	−58.05	n.a	5.6
ZAB-1	598	9.75	6	2	26.71	56	nd	0.03	25.00	−7.30	−46.26	5.7	4.5
ZAB-2	575	15.60	14	8	26.78	27	nd	0.03	30.00	−7.60	−46.56	5.0	4.3
ZAB-3	598	9.75	8	7	27.21	32	nd	0.03	23.15	−7.00	−41.08	5.0	4.6
ZAB-4	874	19.50	14	12	40.18	22	nd	0.03	30.00	−7.84	−48.75	5.0	4.4
ZAB-5	897	15.60	15	13	41.28	14	nd	0.021	26.32	−7.03	−45.83	3.5	4.7
KLW25	207	7.80	53	21	14.20	80	nd	0.18	26.20	−8.58	−56.29	n.a	5.3
ARK-1	16	3.90	39	6	3.26	53	16	<0.00	17.44	−7.48	−48.06	n.a	4.4
ARK-8	16	3.90	45	7	3.60	881	nd	0.04	23.23	−7.69	−46.18	n.a	5.4
WP-6	115	5.85	55	14	9.07	68	nd	0.10	22.70	−8.15	−51.64	n.a	5.7
SKB-1	322	8.58	58	37	20.26	91	nd	0.23	28.55	−8.39	−52.62	n.a	5.6
SKB-11	184	7.80	29	21	11.38	34	nd	0.04	25.34	−8.79	−54.88	n.a	5.7
MM-10	92	3.90	46	12	7.39	52	nd	0.10	26.62	−8.06	−49.81	n.a	5.7
KAD-3	69	5.85	55	28	8.19	24	nd	0.37	23.50	−8.01	−50.59	n.a	5.6

(continued)

Table 4.3 (continued)

Sample ID	Na^+ (meq/L)	K^+ (meq/L)	Ca^{2+} (meq/L)	Mg^{2+}	Tca (meq/L)	As^V (µg/L)	As^{III} (µg/L)	Fe (mg/L)	SiO_2 (mg/L)	$\delta^{18}O^a$ (‰)	δD^a (‰)	$\delta^{15}N$ (‰)	$\delta^{34}S$ (‰)
KAD-4	28	3.12	30	8	3.50	25	nd	0.14	23.60	−8.22	−52.67	n.a	5.6
KAD-5	115	7.80	72	40	12.10	22	nd	0.07	25.00	−8.37	−53.09	n.a	5.5
KAD-9	322	6.63	73	33	21.17	64	nd	2.18	9.86	−8.48	−53.75	n.a	5.6
KLW-29	276	3.90	28	9	13.10	672	nd	<0.00	15.03	−8.74	−57.26	n.a	n.a
CNG-3	46	1.95	28	6	3.91	45	nd	0.03	20.67	−8.10	−50.69	n.a	n.a
SKB-7	299	4.68	19	14	15.28	61	nd	0.12	24.14	−8.76	−57.08	n.a	5.7
WP-2	306	6.24	54	18	17.60	60	nd	0.06	21.00	−8.17	−52.07	n.a	n.a
SKB25	276	4.00	6	4	12.72	242	nd	0.06	17.34	−8.94	−58.90	n.a	5.6
MM-1	124	8.58	76	21	11.16	80	nd	0.30	30.00	−7.94	−48.51	n.a	6.2
MM-13	92	4.68	50	21	8.38	611	nd	0.04	26.18	−7.32	−45.22	n.a	5.6
KLW2	283	7.80	75	36	19.22	38	nd	0.41	26.71	−8.28	−51.10	n.a	5.6
KLW-28	62	4.00	60	5	6.22	43	nd	0.06	19.24	−8.25	−51.55	n.a	n.a
ARK-9	23	7.80	86	26	7.70	50	10	0.11	12.40	−7.67	−47.23	n.a	5.5
ARK-10	92	6.63	19	19	4.17	8	nd	<0.00	11.00	−8.15	−52.28	n.a	n.a

Note Abbreviations for villages are the same as in those Table 4.2

n.a represents not analyzed

bdl stands for below detection limit

Detection limits are the same as in Table 4.1

n.d stands for not detected. Detection limit for As^{III} i

[a]SMOW (Standard Mean Oceanic Water) is the standard used for determining $\delta^{18}O$ and δ^2H in water

Table 4.4 Ranges of analytical data of groundwaters classified by the well depth and canal water

	Unit	Shallow n = 123			Middle n = 14			Deep n = 8			Canal water n = 2		
		Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean
EC	mS/cm	0.4	4.6	2.6	0.2	2.2	0.8	0.5	1.9	1.10	0.5	0.7	0.6
pH		7.3	8.8	8.0	7.1	8.7	8.0	6.9	8.7	7.9	7.5	7.6	7.6
Temperature	°C	26	28	27	24	27	26	23	24	23	27	27	27
HCO_3^-	mg/L	195	1,280	652	153	732	371	146	671	360	366	430	400
SO^{42-}	mg/L	38.0	960	257	24.0	480	125	32.0	341	150	36.0	72.0	54.0
Cl^-	mg/L	2.00	415	175	4.00	250	58.0	10.0	160	63.0	10.0	15.0	12.0
PO^{43-}	mg/L	bdl[a]	2.18	0.30	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
Br^-	mg/L	bdl	1.12	0.40	bdl	0.54	0.20	0.40	0.32	0.24	bdl	bdl	bdl
NO_3–N	mg/L	bdl	46.00	9.00	bdl	0.70	0.20	bdl	0.84	0.30	bdl	bdl	bdl
F^-	mg/L	0.11	22.8	6.30	0.25	4.20	1.50	0.50	3.10	1.10	1.70	2.28	2.00
Ca^{2+}	mg/L	2.0	138	32.0	19.0	73.0	45.0	6.0	86.0	53.0	60.0	66.0	63.0
Mg^{2+}	mg/L	1.44	65.0	14.7	5.5	39.6	18.0	5.0	35.0	18.0	2.0	49.0	24.0
Na^+	mg/L	12.0	1,060	630	16.0	322	150	23.0	306	150	12.0	19.0	16.0
K^+	mg/L	2.7	46.8	5.2	2.0	8.6	5.4	4.0	8.6	6.0	20	28	24
SiO_2	mg/L	7.4	37	22.3	10	28.6	22	11	30	20.5	26	29	27
As	µg/L	1.0	2,400	123	14	392	72	8.0	611	139	1.0	1.0	1.0

[a] *bdl* means below detection limit

Detection limits for Br^-, NO_3^-–N and PO_4^{3-} are 0.02, 0.05 and 0.025, respectively

Table 4.5 Concentration ranges of major anions, cations and isotopic ratios of groundwater in east Punjab, Pakistan

Locality	Abbr.	HCO_3^- (mg/L)			Cl^- (mg/L)			SO_4^{2-} (mg/L)			NO_3^-–N (mg/L)		
		Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean
Chung	CNG	550	980	600	51	131	74	120	192	125	bdl	7.00	2.33
Sundar	SUN	732	1,040	884	21	180	117	120	432	303	bdl	4.48	2.60
Shamkey	SKB	366	854	616	5	96	26	35	290	77	bdl	4.20	1.22
Manga Mandi	MM	201	610	430	11	262	79	14	440	250	bdl	46.0	6.50
Waran	WP	440	616	520	13	129	71	72	341	200	bdl	5.90	1.20
Kot Asad Ullah	KAD	165	1,037	537	5	241	212	30	672	461	bdl	2.00	0.3
Kalalanwala	KLW	244	1,280	836	16	344	106	48	912	312	bdl	10.64	1.26
Muffat Pura	MPU	610	1,160	915	62	213	138	211	960	581	bdl	bdl	bdl
Araiyan Da Khu	ARK	147	370	244	4	71	25	24	144	77	bdl	7.84	1.30
Deena Nath	DN	610	915	702	12	140	83	96	240	144	bdl	19.00	4.60
Nathe Khalsa	NK	490	915	732	14	70	46	96	240	163	bdl	0.70	0.40
Kot Ashraf	KA	610	671	630	54	121	83	192	290	231	0.14	11.50	0.90
Bahi Pheru	BP	213	550	427	41	52	46	67	170	127	bdl	2.52	1.30
Jamber Klan	JK	980	980	980	224	390	320	580	640	600	10.90	10.50	9.80
Rehman Pura	RPNA	494	494	494	107	144	125	355	500	432	2.60	10.00	6.20
Cantt Colony	CCO	370	430	400	10	15	12	39	72	54	bdl	bdl	bdl
Zaheer Abad	ZAB	480	793	610	213	415	304	480	960	672	7.00	14.00	9.52

Locality	Abbr.	Ca^{2+} (mg/L)			Mg^{2+} (mg/L)			Na^+ (mg/L)			K^+ (mg/L)		
		Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean
Chung	CNG	28	48	36	5	18	11	46	460	276	3.90	8.97	5.70
Sundar	SUN	8	51	35	4	35	15	370	575	480	3.12	11.7	7.50
Shamkey	SKB	2	71	20	2	46	13	69	368	238	1.95	9.75	7.80
Manga Mandi	MM	5	93	54	2	61	27	46	460	210	2.73	39.00	12.00
Waran	WP	4	54	23	2	16	10	115	437	315	2.73	7.80	5.12
Kot Asad Ullah	KAD	13	80	34	8	40	17	28	782	470	6.24	9.00	8.20
Kalalanwala	KLW	5	75	21	2	36	12	207	1,060	483	3.90	12.10	7.05
Muffat Pura	MPU	34	57	47	11	23	17	300	805	600	6.24	11.70	9.08

(continued)

Table 4.5 (continued)

Locality	Abbr.	Ca^{2+} (mg/L)			Mg^{2+} (mg/L)			Na^{+} (mg/L)			K^{+} (mg/L)		
		Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean
Araiyan Da Khu	ARK	19	140	80	6	26	13	16	51	28	3.90	27.30	11.00
Deena Nath	DN	27	64	50	2	28	15	276	506	334	7.80	11.70	9.01
Nathe Khalsa	NK	11	66	40	6	35	20	230	391	300	7.80	15.60	11.04
Kot Ashraf	KA	6	47	30	3	28	17	253	370	330	3.90	11.70	9.00
Bahi Pheru	BP	10	39	24	4	17	10	69	300	215	4.29	5.07	5.00
Jamber Klan	JK	12	54	8	11	45	7	851	874	863	12.87	46.80	30.00
Rehman Pura	RPNA	4	23	53	5	14	40	240	44	345	11.70	23.40	18.00
Cantt Colony	CCO	60	66	63	31	47	24	12	19	16	19.50	27.30	24.00
Zaheer Abad	ZAB	6	15	12	2	13	9	575	900	713	9.75	19.50	15.00
Locality	Abbr.	EC (mS/cm)			Eh mV			pH			SiO_2 mg/L		
		Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean
Chung	CNG	0.38	1.95	1.24	257	320	298	7.3	8.3	7.8	12	27	23
Sundar	SUN	1.30	2.60	2.10	273	363	328	7.2	8.1	7.8	21	25	23
Shamkey	SKB	0.70	1.70	1.12	218	358	312	7.2	8.8	8.0	15	29	23
Manga Mandi	MM	0.55	1.90	1.20	265	362	332	7.2	8.7	8.2	15	34	27
Waran	WP	0.82	2.00	1.61	291	360	313	7.8	8.6	8.0	12	27	21
Kot Asad Ullah	KAD	0.34	3.70	2.20	222	316	287	7.6	8.3	7.7	7	20	14
Kalalanwala	KLW	0.45	4.60	2.19	225	343	276	7.6	8.7	8.1	16	27	22
Muffat Pura	MPU	1.40	4.10	2.90	315	324	323	7.7	8.0	7.5	18	26	23
Araiyan Da Khu	ARK	0.20	1.00	0.56	273	385	306	7.2	7.6	7.5	10	20	16
Deena Nath	DN	1.10	2.10	1.50	220	775	361	7.3	8.0	7.9	15	37	26
Nathe Khalsa	NK	1.24	1.70	1.40	276	346	314	7.3	7.9	7.7	12	32	24
Kot Ashraf	KA	1.20	1.38	1.50	288	320	304	8.2	8.6	8.1	19	27	23
Bahi Pheru	BP	0.64	1.50	1.11	310	337	325	7.5	8.1	8.0	12	29	21

(continued)

Table 4.5 (continued)

Locality	Abbr.	EC			Eh			pH			SiO_2		
		(mS/cm)			mV						mg/L		
		Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean
Jamber Klan	JK	3.40	3.60	3.50	322	329	324	8.1	8.3	8.0	18	21	20
Rehman Pura	RPNA	1.82	2.10	1.90	258	264	261	7.5	7.8	7.6	19	22	21
Cantt Colony	CCO	0.50	0.70	0.60	243	258	254	7.2	7.3	7.6	25	29	27
Zaheer Abad	ZAB	2.20	4.40	3.20	218	343	283	7.4	8.5	8.2	15	30	25

Locality	Abbr.	Fe			$\delta^{18}O$			δD			$\delta^{34}S$		
		mg/L			‰			‰			‰		
		Min	Max	Mean	Min	Max	Mean	Min	Max	Mean	Min	Max	Mean
Chung	CNG	bdl[a]	0.17	0.05	−8.37	−7.5	−8.19	−53.8	−46.9	−52.4	5.1	5.4	5.3
Sundar	SUN	bdl	0.10	0.03	−8.50	−7.30	−7.68	−53.25	−45.9	−53.18	5.7	5.7	5.7
Shamkey	SKB	bdl	0.24	0.09	−9.30	7.79	−8.66	−61.91	−48.81	−55.39	5.6	7.0	5.8
Manga Mandi	MM	bdl	0.56	0.07	−8.70	−7.20	−7.80	−56.35	−42.54	−48.37	5.0	5.7	5.4
Waran	WP	bdl	0.16	0.05	−8.30	−7.44	−8.01	−52.92	−43.68	−47.91	4.9	5.8	5.4
Kot Asad Ullah	KAD	bdl	2.42	0.70	−8.17	−7.25	−7.64	−52.92	−43.68	−47.91	5.3	5.6	5.5
Kalalanwala	KLW	bdl	0.50	0.12	−8.70	−7.65	−8.27	−60.68	−47.0	−52.85	5.2	5.8	5.5
Muffat Pura	MPU	0.14	0.25	0.18	−8.10	−7.90	−8.01	−51.0	−50.35	−50.6	5.7	5.7	5.7
Araiyan Da Khu	ARK	bdl	0.50	0.13	−7.87	−7.22	−7.57	−56.0	−44.42	−48.9	5.0	5.6	5.3
Deena Nath	DN	bdl	0.23	0.07	−8.13	−7.20	−7.75	−52.0	−46.48	−49.25	5.0	5.5	5.3
Nathe Khalsa	NK	bdl	2.80	0.60	−8.37	−8.20	−8.27	−54.79	−45.29	−51.81	5.8	6.3	6.0
Kot Ashraf	KA	bdl	0.03	0.01	−8.70	−7.50	−8.10	−48.76	−45.71	−47.5	5.6	5.7	5.6
Bahi Pheru	BP	0.02	0.04	0.03	−8.55	−7.91	−8.46	−56.35	−50.47	−52.6	5.3	5.6	5.4
Jamber Klan	JK	bdl	0.60	0.30	−7.80	−7.70	−7.75	−57.0	−46.48	−49.25	3.7	3.9	3.8
Rehman Pura	RPNA	0.01	0.03	0.02	−8.28	−7.30	−7.79	−50.59	−49.91	−50.25	3.7	3.8	3.7
Cantt Colony	CCO	0.15	0.22	0.20	−9.60	−9.32	−9.18	−48.47	−47.09	−47.78	5.5	5.6	5.5
Zaheer Abad	ZAB	0.03	0.03	0.03	−7.84	−7.00	−7.58	−59.83	−52.43	−54.79	4.3	4.7	4.5

[a] *bdl* means below detection limit

Detection limits for NO_3^-–N, and Fe are 0.05 and 0.01, respectively

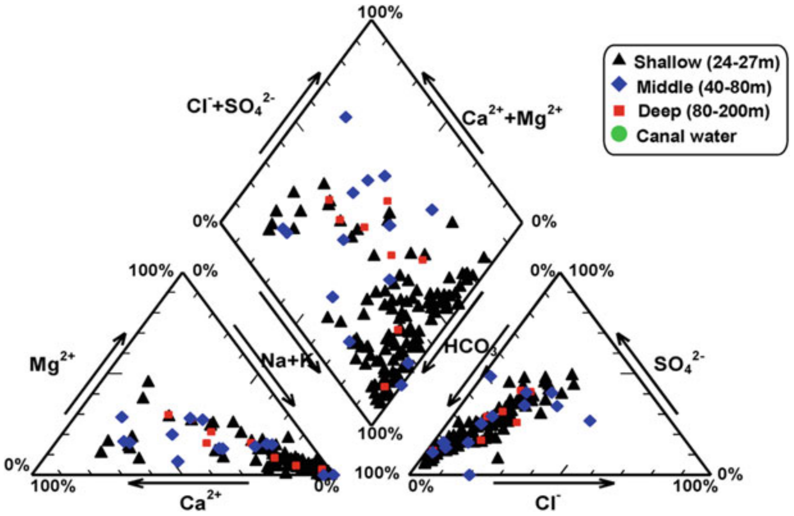


Fig. 4.6 Piper plot for major cations and anions. *Triangles* are symbol for shallow, *diamond* for middle and *square* for deep groundwaters

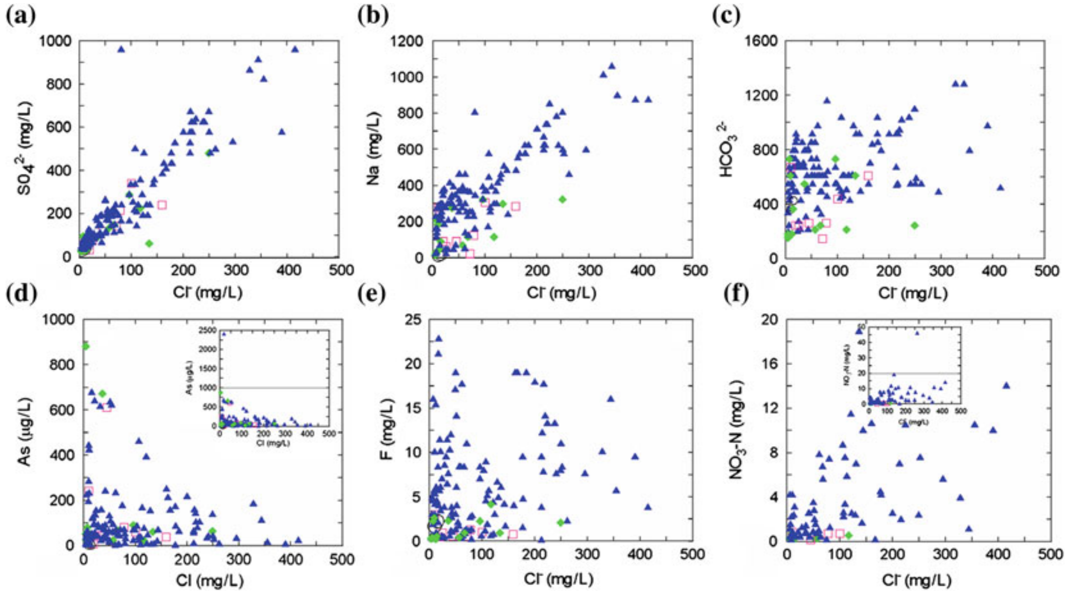


Fig. 4.7 Relationships of Cl^- versus SO_4 (**a**), Na^+ (**b**), HCO_3 (**c**), As (**d**), F^- (**e**) and NO_3–N (**f**). *Solid triangles* are symbols for shallow *diamond* for middle, and *square* for deep groundwaters, while *circles* are symbols for canal water

4.2.2 Arsenic and Fluoride Concentrations

4.2.2.1 Arsenic

Groundwater Samples

Total As

Summary of statistical data for As and F^- is given in Table 4.5. The As^V is calculated from the concentration difference between the total As and As^{III}. Arsenic concentrations in the groundwater samples widely range from 1 to 2,400 µg/L. The concentration of this element in two canal water samples was 1 µg/L. Of 123 shallow groundwaters, 11 (ARK-1, 2, MM-4, 5, 8, 9, DN-1, 3, SKB-12, JK-2, and CNG-1, Appendix) contained <10 µg/L of As. One common feature among these groundwater samples was that they contain high NO_3^-–N, e.g., MM-5 was amongst the highest containing NO_3^-–N. In the middle groundwaters, As ranged from 22 to 91 µg/L (n = 14) with the one exception ARK-8, which contains 881 µg/L As and exceptionally low SO_4^{2-} concentration 29 mg/L. The deep groundwaters (n = 8) had range of As within 8–80 µg/L except two samples, KLW-2 and MM-13, having As concentrations 242 and 611 µg/L, respectively.

Enormously high concentrations of As were found from shallow-well waters in four villages from the western and eastern part of the study area; 2,400 µg/L in Kalalanwala and Kot Asad Ullah (KLW and KAD have different names but sharing the adjacent residential areas), 883 µg/L in Shamkey Bhatian (SKB), 672 µg/L in Manga Mandi (MM), and 681 µg/L in Waran Piran Wala (WP) (Table 4.6 and Fig. 4.8a).

These four villages are located near the area where brick kilns are concentrated. The maximum As concentrations of groundwaters in the villages distributed toward west to southwest from the kiln area are between 50 and 112 µg/L except in Kot Ashraf (KA) where the maximum concentration is 625 µg/L. At Chung (CNG), 15 km away from the main Lahore City; the groundwaters had As concentrations up to 67 µg/L, while those in Sundar (SUN) had 90 µg/L As. Such a distribution of As concentrated groundwaters can support that As including wet and dry deposition derived from combusted coals in the brick kilns is one of the contributing factors to high As and F^- in the study area. On the other hand, canal waters (Cantt Colony, CCO) had As values <1 µg/L, implying that the surface running water is not seriously contaminated by As.

Arsenite

Voltammetry demonstrated that 97.3 % of the 147 samples did not contain detectable amount of As^{III}. Only 2.7 % (n = 4) groundwaters contained detectable As^{III}. Those were found in the groundwater from the village ARK (Arain Da Khu), where the maximum concentration of As^{III} was 23 µg/L in 56 µg/L total As. Two of the four samples were from the shallow wells (ARK-1, 3), while the other two were from the middle (ARK-6) and deep (ARK-9) wells. The chemical compositions of these waters were mostly similar to those of the other waters collected from this village, where the EC value is 0.2–1.0 mS/cm and pH is neutral to alkaline. This village is the only one located in the flood plain among the studied villages, thus, the geographical location would be related to the appearance of As^{III}.

As in Coal and Fertilizer Samples

The results of As in coal and fertilizer samples is given in Table 4.7. Water soluble As in fertilizers (DAP) is estimated to be 5–10 mg/kg with an average value of 7.4 mg/kg. The coal samples contain this element ranging from 4 to 12 mg/kg with an average value of 8 mg/kg. Such a high concentration of As in fertilizers would be the large pollutant source of surface soil and underlying groundwater associating with cultivation in the study area.

4.2.2.2 Fluoride

Groundwater

Among shallow groundwaters 75 % exceeded the WHO standard (1.5 mg/L), the maximum F^- content was 22.8 mg/L found in KLW. Fluoride

Table 4.6 Summary statistical data for fluoride and arsenic in study area

Locality		As^V µg/L					As^{III} µg/L					F^- mg/L				
		Min	Max	Mean	n	>10 µg/L	Min	Max	Mean	n	>10 µg/L	Min	Max	Mean	n	>1.5 mg/L
Chung	All samples	5	67	27	5	4	nd	nd	nd	5	0	0.24	8.4	4.40	5	4
	Only shallow	3	8	6	4	3	nd	nd	nd	5	0	2.67	8.4	5.50	4	4
Sundar	All samples	1	93	51	5	4	nd	nd	nd	5	0	1.52	10.1	5.80	5	5
	Only shallow	1	93	51	5	4	nd	nd	nd	5	0	1.52	10.1	5.80	5	5
Shamkey Bhatain	All samples	3	883	132	25	24	nd	nd	nd	25	0	2.00	17.1	4.70	25	25
	Only shallow	3	443	105	21	20	nd	nd	nd	25	0	0.95	17.1	5.09	21	19
Manga Mandi	All samples	3	672	121	17	13	nd	nd	nd	17	0	0.45	4.2	1.33	17	10
	Only shallow	4	424	68	14	10	nd	nd	nd	17	0	0.45	4.2	1.33	14	10
Waran Piran Wala	All samples	36	681	197	11	11	nd	nd	nd	11	0	0.95	11.0	5.50	11	10
	Only shallow	33	677	171	7	7	nd	nd	nd	11	0	2.09	11.0	6.50	7	7
Kot Asad Ullah	All samples	8	168	65	12	11	nd	nd	nd	12	0	0.40	19.0	8.10	12	9
	Only shallow	10	171	83	8	8	nd	nd	nd	12	0	7.60	19.0	11.23	8	8
Kalalnwala	All samples	23	2,400	291	29	29	nd	nd	nd	27	0	2.70	22.8	11.20	27	25
	Only shallow	23	2,400	291	25	25	nd	nd	nd	27	0	2.70	22.8	11.20	25	25
Muffat Pura	All samples	50	62	57	3	3	nd	nd	nd	3	0	0.11	0.6	0.30	3	0
	Only shallow	50	62	57	3	3	nd	nd	nd	3	0	0.11	0.6	0.30	3	0
Arian Da Khu	All samples	1	74	37	10	6	10	23	16	9	3	0.30	0.6	0.50	9	0
	Only shallow	1	74	37	6	3	12	23	11	6	2	0.30	0.6	0.50	6	0

(continued)

Table 4.6 (continued)

Locality		As^V µg/L					As^{III} µg/L					F^- mg/L				
		Min	Max	Mean	n	>10 µg/L	Min	Max	Mean	n	>10 µg/L	Min	Max	Mean	n	>1.5 mg/L
Deena Nath	All samples	7	39	25	6	4	nd	nd	nd	6	0	0.76	15.4	6.20	6	4
	Only shallow	7	39	25	6	4	nd	nd	nd	6	0	0.76	15.4	6.20	6	4
Nathy Khalsa	All samples	37	96	58	6	6	nd	nd	nd	6	0	0.50	11.4	4.10	6	4
	Only shallow	37	96	58	6	6	nd	nd	nd	6	0	0.50	11.4	4.10	6	4
Kot Ashraf	All samples	173	624	398	3	3	nd	nd	nd	3	0	1.14	4.4	2.50	3	3
	Only shallow	173	624	398	3	3	nd	nd	nd	3	0	1.14	4.4	2.50	3	3
Bhai Pheru	All samples	39	112	70	3	3	nd	nd	nd	3	0	1.00	12.0	5.70	3	3
	Only shallow	39	112	70	3	3	nd	nd	nd	3	0	1.00	12.0	5.70	3	3
Jambar Kalan	All samples	5	100	53	2	1	nd	nd	nd	2	0	9.50	13.3	11.4	2	2
	Only shallow	5	100	53	2	1	nd	nd	nd	2	0	9.50	13.3	11.4	2	2
Rehman Pura	All samples	21	69	45	2	2	nd	nd	nd	2	0	1.70	4.6	3.10	2	2
	Only shallow	21	69	45	2	2	nd	nd	nd	2	0	1.70	4.6	3.10	2	2
Cantt Colony	All samples	1	1	1	2	0	nd	nd	nd	2	0	1.71	2.28	2.00	2	2
	Only shallow	1	1	1	2	0	nd	nd	nd	2	0	1.71	2.28	2.00	2	2
Zahir Abad	All samples	13	55	29	5	5	nd	nd	nd	5	0	3.80	8.4	5.80	5	5
	Only shallow	13	55	29	5	5	nd	nd	nd	5	0	3.80	8.4	5.80	5	5

Note nd means not detected
Detection limit for As^{III} is 5 ppb

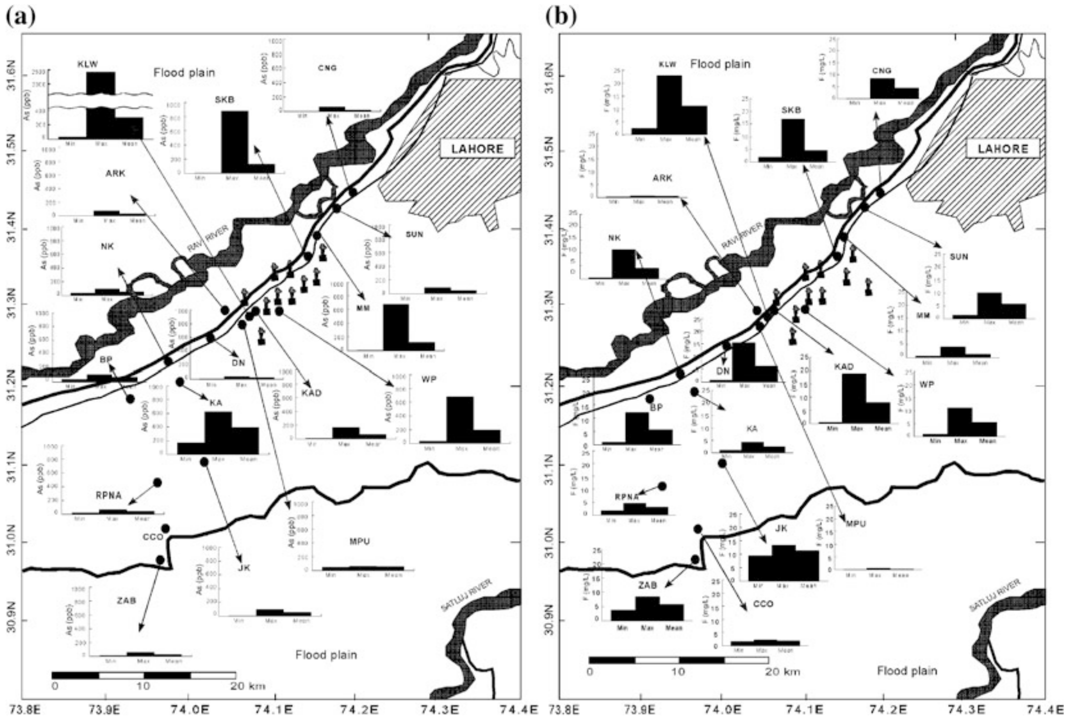


Fig. 4.8 **a**, **b** Distribution map of arsenic and fluoride from Punjab, with their minimum, maximum and mean concentrations

Table 4.7 Arsenic in coals and fertilizers

Coals		Fertilizers	
	As (Total)		As (Leachable)
Coal-1	12	DAP-1	5
Coal-2	8	DAP-2	7
Coal-3	4	DAP-3	8
Coal-4	5	DAP-4	10
Coal-5	4	DAP-5	7
Coal-6	6		
Coal-7	8		
Coal-8	9		

All values are in mg/kg

concentrations were high in the shallow-well waters that showed the high EC values >2.0 mS/cm. Twenty seven groundwater samples contained <1.5 mg/L F^- and nine of them were from MM, and six from ARK (Table 4.3), both of which are close to the kiln concentrated area. One of the F^- source(s) was presented to be air pollutant since the local rainwater contained a certain amount of F^-. However less contaminated groundwaters in Manga Mandi (MM) where also many brick kilns are located, imply that the other larger source(s) of F^- must be present in the studied area.

Of the middle groundwaters, 37 % have >1.5 mg/L of F^-. The maximum concentration was up to 4.2 mg/L found in KAD. The groundwater samples from the deep wells were <1.5 mg/L with the only exception of one sample KLW-2 that contained F^- 3.1 mg/L. The canal waters had F^- content 1.7–2.3 mg/L. Such an occurrence implies that the F^- is derived from the surface, and this ion decreases with increasing well depth.

Figure 4.8a, b shows that the highly As contaminated areas were also contaminated by high F^-, e.g., in KLW, KAD, SKB and WP, but not the same well waters. Figure 4.5 shows that F^- and As had a negative correlation. These facts suggest that not only one but rather more than two or more mechanisms and/or pollutant

Table 4.8 Fluoride in coals and fertilizers

Coal		Fertilizers	
	F^- (Total)		F^- (Leachable)
Coal-1	9.32	DAP-1	180
Coal-2	5.12	DAP-2	250
Coal-3	10.2	DAP-3	255
Coal-4	20.1	DAP-4	120
Coal-5	8.03	DAP-5	60
Coal-6	9.04		
Coal-7	8.11		
Coal-8	10.4		

All values are in mg/kg

sources are responsible for the formation of the highly As and F^- contaminated groundwaters in the study area.

Coal and Fertilizers

The results of As in coal and fertilizer samples are given in Table 4.8. The fertilizers contained soluble F^- ranging from 60 to 255 mg/kg with an average value of 175 mg/kg, while, coal samples contained total F^- ranging 5.1–20.1 mg/kg with an average value of 10.2 mg/kg.

4.2.3 Stable Isotopic Compositions

4.2.3.1 Hydrogen and Oxygen Isotopes ($\delta^{18}O$ and δD)

Groundwater

The ranges of stable isotopic ratios of hydrogen and oxygen of the groundwater samples are summarized in Table 4.9. The relationship between $\delta^{18}O$ and δD of groundwaters is plotted in Fig. 4.9, along with those values of local rainwaters. Oxygen isotopic ratios of the groundwater ranged within −9.6 and −7.0, and δD within −61.9 to −42.5 ‰. The compositions did not show any distinctive relationship to well locations or depth. The $\delta^{18}O$ of canal waters ranged from −9.6 to −9.3 and δD from −59.8 to −52.4 ‰. The $\delta^{18}O$ and δD of all studied groundwater samples fell between those of the rain and canal waters, indicating the mixing between local meteoric water and the water from the River, which is mainly recharged at the higher altitude in Indian Territory. The slope parallel to that of global meteoric water line (GMWL, $\delta D = 8 \times \delta^{18}O + 10$, Fig. 4.9) indicates that the evaporation did not seriously occur in the local groundwaters.

Rainwater

The stable isotopic ratios hydrogen and oxygen of rainwaters collected from the study area are given in Table 4.10. The rainwaters have oxygen isotopic ratios ranging from −7.5 to −7.3 ‰, and, the δD values are in the range of −48.6 to −48.2 ‰.

4.2.3.2 $\delta^{34}S$ Sulfur Isotopes

Groundwaters

Sulfur isotopic composition is an efficient tool for tracing and identifying the SO_4^{2-} pollutant sources. The $\delta^{34}S$ values of the studied groundwaters ranging from +3.7 to +7.0 ‰, and three groups can be identified from the data (Fig. 4.10); groundwaters having constant $\delta^{34}S$ values (5.5–5.7 ‰) irrespective to the SO_4^{2-} concentration (A), those with high $\delta^{34}S$ values (6.3–7.0 ‰) and low SO_4^{2-} (B), those with low $\delta^{34}S$ values (3.7–4.8 ‰) and high SO_4^{2-} (C). The $\delta^{34}S$ values of rainwater ($n = 3$) is 5.0–7.0 ‰. The $\delta^{34}S$ values of coal collected from the study area ($n = 8$) range within 3.5–10 ‰ with an average value of 6.0 ‰. The $\delta^{34}S$ values of fertilizer (DAP, $n = 5$) ranged within 3.4–7.6 ‰ with the mean value of 5.7 ‰. The sources of SO_4^{2-} will be discussed in detail in discussion.

Coals, Fertilizers and Rainwater

The sulfur isotopic values of coal and fertilizers are given in Table 4.11. In coal samples the $\delta^{34}S$ values ranged from 3.5 to 10.0 ‰, while in fertilizers the minimum value is 3.4 ‰ and maximum is 7.6 ‰. The rainwater samples have very narrow range 5–7 ‰.

Table 4.9 Stable isotope data of groundwaters

Sample ID	Depth (m)	$\delta^{18}O^a$ (‰)	δD^a (‰)	$\delta^{15}N$ (‰)	$\delta^{34}S$ (‰)
CNG-1	20–27	−8.00	−50.32	n.a	5.4
CNG-2	20–27	−7.50	−46.89	n.a	n.a
CNG-4	20–27	−8.20	−52.66	n.a	5.1
CNG-5	20–27	−8.37	−53.82	n.a	n.a
SUN1	20–27	−8.50	−53.25	n.a	5.7
SUN2	20–27	−8.00	−52.34	n.a	5.7
SUN3	20–27	−7.65	−48.61	n.a	5.7
SUN4	20–27	−7.30	−46.59	n.a	n.a
SUN5	20–27	−7.30	−45.91	n.a	n.a
SKB-2	20–27	−8.74	−59.11	n.a	n.a
SKB-3	20–27	−8.28	−51.40	n.a	5.9
SKB-4	20–27	−8.20	−51.42	n.a	n.a
SKB-5	20–27	−8.89	−57.02	n.a	5.7
SKB-6	20–27	−9.03	−56.43	10.0	n.a
SKB-8	20–27	−9.03	−59.83	n.a	5.6
SKB-9	20–27	−9.20	−61.17	n.a	n.a
SKB-10	20–27	−9.06	−59.32	n.a	n.a
SKB-12	20–27	−8.26	−51.03	n.a	n.a
SKB-13	20–27	−8.98	−55.25	n.a	n.a
SKB-14	20–27	−8.27	−52.75	12.5	5.7
SKB-15	20–27	−8.67	−52.43	n.a	5.6
SKB-16	20–27	−8.64	−55.95	n.a	7.0
SKB-17	20–27	−9.20	−56.13	n.a	6.2
SKB-18	20–27	−8.30	−53.88	n.a	5.8
SKB-19	20–27	−8.44	−55.09	n.a	5.7
SKB-20	20–27	−8.52	−54.17	n.a	n.a
SKB-21	20–27	−8.71	−56.03	n.a	5.6
SKB-22	20–27	−7.79	−48.81	11.9	n.a
SKB-23	20–27	−8.50	−54.11	n.a	5.7
SKB24	20–27	−9.30	−61.91	n.a	n.a
MM-2	20–27	−7.52	−46.78	30.0	n.a
MM-3	20–27	−7.50	−46.39	14.0	n.a
MM-4	20–27	−7.70	−47.66	13.0	5.0
MM-5	20–27	−7.20	−42.54	25.0	n.a
MM-6	20–27	−7.40	−44.98	n.a	5.6
MM-7	20–27	−7.70	−46.53	n.a	n.a
MM-8	20–27	−7.50	−44.29	12.5	n.a
MM-9	20–27	−7.52	−46.20	n.a	5.7
MM-11	20–27	−8.09	−49.42	n.a	5.3

(continued)

Table 4.9 (continued)

Sample ID	Depth (m)	$\delta^{18}O^a$ (‰)	δD^a (‰)	$\delta^{15}N$ (‰)	$\delta^{34}S$ (‰)
MM-12	20–27	−8.12	−51.66	n.a	n.a
MM-14	20–27	−8.47	−53.79	n.a	n.a
MM-15	20–27	−8.32	−52.02	n.a	n.a
MM-16	20–27	−7.80	−48.62	n.a	n.a
MM-17	20–27	−8.70	−56.35	n.a	5.6
WP-1	20–27	−8.30	−51.77	n.a	5.1
WP-3	20–27	−7.84	−46.48	n.a	4.9
WP-4	20–27	−8.13	−52.02	n.a	5.1
WP-5	20–27	−8.24	−51.55	n.a	5.6
WP-7	20–27	−7.44	−45.97	n.a	5.7
WP-8	20–27	−7.66	−47.45	n.a	n.a
WP-9	20–27	−7.76	−48.47	n.a	5.8
WP-10	20–27	−8.07	−49.74	n.a	n.a
WP-11	20–27	−8.27	−51.32	n.a	5.7
KAD-1	20–27	−7.55	−47.39	n.a	5.5
KAD-2	20–27	−7.85	−49.90	n.a	5.5
KAD-6	20–27	−7.45	−45.32	n.a	5.4
KAD-7	20–27	−7.25	−43.68	n.a	5.3
KAD-8	20–27	−7.41	−45.79	n.a	5.6
KAD-10	20–27	−7.60	−47.50	n.a	5.5
KAD-11	20–27	−7.70	−48.45	n.a	5.3
KAD-12	20–27	−8.17	−52.92	n.a	5.6
KLW1	20–27	−8.45	−54.35	n.a	5.5
KLW3	20–27	−8.23	−52.68	n.a	n.a
KLW4	20–27	−8.40	−53.41	n.a	5.7
KLW5	20–27	−8.16	−51.41	n.a	5.6
KLW6	20–27	−8.53	−56.82	n.a	5.5
KLW7	20–27	−8.30	−53.94	n.a	5.7
KLW8	20–27	−7.69	−46.98	n.a	5.3
KLW9	20–27	−8.40	−54.76	n.a	5.6
KLW10	20–27	−8.70	−58.86	n.a	5.5
KLW11	20–27	−8.49	−52.00	n.a	5.6
KLW12	20–27	−8.48	−53.40	n.a	n.a
KLW13	20–27	−8.30	−53.48	n.a	5.4
KLW14	20–27	−7.65	−47.73	n.a	5.7
KLW15	20–27	−7.80	−49.91	n.a	5.6
KLW16	20–27	−7.90	−49.32	15.0	5.7
KLW17	20–27	−8.00	−51.96	n.a	5.5
KLW18	20–27	−8.21	−50.53	n.a	5.6

(continued)

Table 4.9 (continued)

Sample ID	Depth (m)	$\delta^{18}O^a$ (‰)	δD^a (‰)	$\delta^{15}N$ (‰)	$\delta^{34}S$ (‰)
KLW19	20–27	−8.01	−51.22	n.a	5.7
KLW20	20–27	−8.10	−53.25	n.a	5.8
KLW21	20–27	−8.40	−54.72	n.a	5.5
KLW22	20–27	−8.60	−52.40	n.a	n.a
KLW23	20–27	−8.20	−51.46	n.a	5.6
KLW24	20–27	−8.70	−60.68	n.a	5.2
KLW26	20–27	−8.50	−56.68	n.a	5.4
KLW27	20–27	−8.55	−54.26	n.a	5.5
MPU-1	20–27	−8.10	−50.47	n.a	5.7
MPU-2	20–27	−8.05	−50.35	n.a	n.a
MPU-3	20–27	−7.90	−50.98	n.a	5.6
ARK-2	20–27	−7.46	−45.71	n.a	5.1
ARK-3	20–27	−7.23	−48.76	n.a	5.0
ARK-4	20–27	−7.70	−48.03	n.a	5.4
ARK-5	20–27	−7.82	−52.59	11.0	5.5
ARK-6	20–27	−7.87	−54.79	n.a	5.4
ARK-7	20–27	−7.22	−45.26	n.a	5.6
DN-1	20–27	−7.70	−47.90	n.a	n.a
DN-2	20–27	−7.88	−48.47	n.a	5.5
DN-3	20–27	−7.70	−47.09	12.5	5.0
DN-4	20–27	−7.90	−47.47	n.a	n.a
DN-5	20–27	−7.20	−46.00	9.40	5.4
DN-6	20–27	−8.13	−51.03	n.a	n.a
NK-1	20–27	−8.30	−49.91	n.a	5.8
NK-2	20–27	−8.30	−51.66	n.a	n.a
NK-3	20–27	−8.20	−50.59	n.a	5.8
NK-4	20–27	−8.20	−49.17	n.a	6.2
NK-5	20–27	−8.30	−55.03	n.a	n.a
NK-6	20–27	−8.37	−51.17	n.a	6.3
KA-1	20–27	−8.70	−53.86	n.a	5.6
KA-2	20–27	−7.50	−45.81	n.a	5.7
KA-3	20–27	−7.98	−48.06	8.1	5.6
BP-1	20–27	−8.37	−52.37	n.a	5.6
BP-2	20–27	−8.55	−54.13	n.a	5.3
BP-3	20–27	−7.91	−49.63	n.a	n.a
JK-1	20–27	−7.70	−48.14	15.0	3.7
JK-2	20–27	−7.80	−49.94	14.5	3.9
RPNA1	20–27	−8.28	−56.36	n.a	3.8
RPNA2	20–27	−7.30	−44.28	7.2	3.7

(continued)

Table 4.9 (continued)

Sample ID	Depth (m)	$\delta^{18}O^a$ (‰)	δD^a (‰)	$\delta^{15}N$ (‰)	$\delta^{34}S$ (‰)
CCO1	20–27	−9.60	−60.15	n.a	5.5
CCO2	20–27	−9.32	−58.05	n.a	5.6
ZAB-1	20–27	−7.30	−46.26	5.7	4.5
ZAB-2	20–27	−7.60	−46.56	5.0	4.3
ZAB-3	20–27	−7.00	−41.08	5.0	4.6
ZAB-4	20–27	−7.84	−48.75	5.0	4.4
ZAB-5	20–27	−7.03	−45.83	3.5	4.7
KLW25	40–80	−8.58	−56.29	n.a	5.3
ARK-1	40–80	−7.48	−48.06	n.a	4.4
ARK-8	40–80	−7.69	−46.18	n.a	5.4
WP-6	40–80	−8.15	−51.64	n.a	5.7
SKB-1	40–80	−8.39	−52.62	n.a	5.6
SKB-11	40–80	−8.79	−54.88	n.a	5.7
MM-10	40–80	−8.06	−49.81	n.a	5.7
KAD-3	40–80	−8.01	−50.59	n.a	5.6
KAD-4	40–80	−8.22	−52.67	n.a	5.6
KAD-5	40–80	−8.37	−53.09	n.a	5.5
KAD-9	40–80	−8.48	−53.75	n.a	5.6
KLW-29	40–80	−8.74	−57.26	n.a	n.a
CNG-3	40–80	−8.10	−50.69	n.a	n.a
SKB-7	40–80	−8.76	−57.08	n.a	5.7
WP-2	80–200	−8.17	−52.07	n.a	n.a
SKB25	80–200	−8.94	−58.90	n.a	5.6
MM-1	80–200	−7.94	−48.51	n.a	6.2
MM-13	80–200	−7.32	−45.22	n.a	5.6
KLW2	80–200	−8.28	−51.10	n.a	5.6
KLW-28	80–200	−8.25	−51.55	n.a	n.a
ARK-9	80–200	−7.67	−47.23	n.a	5.5
ARK-10	80–200	−8.15	−52.28	n.a	n.a

n.a represents not analyzed
bdl stands for below detection limit
Detection limits are the same as in Table 4.1
n.d stands for not detected. Detection limit for As^{III} is 5 ppb
[a]SMOW (Standard Mean Oceanic Water) is the standard used for determining δ^{18} O and δ^2 H in water

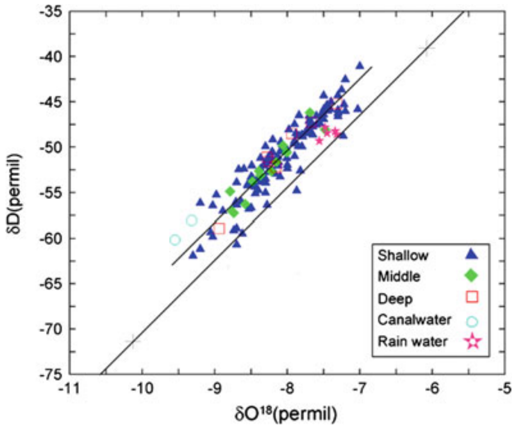


Fig. 4.9 Oxygen versus Hydrogen isotopes

Table 4.10 Isotopic data of rain

Sample ID	δ^{18}O	δD
Rain-1	−7.34	−48.23
Rain-2	−7.45	−48.45
Rain-3	−7.48	−47.80
Rain-4	−7.56	−49.30
Rain-5	−7.32	−48.60

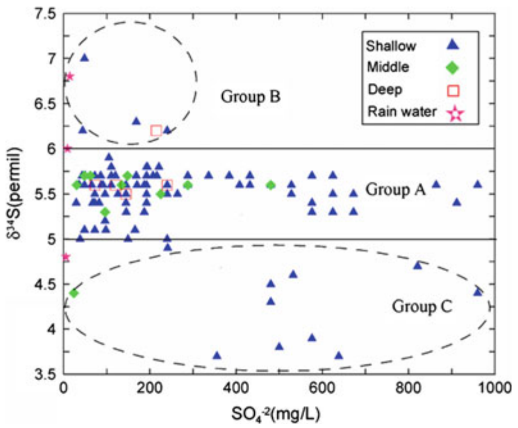


Fig. 4.10 The relationship between sulfur isotope values and sulfate concentrations

Table 4.11 The sulfur isotopic values of coals fertilizers and rainwater

Coal		Fertlizers		Rain	
Coal-1	10.0	DAP-1	5.9	Rain-1	6
Coal-2	7.8	DAP-2	5.8	Rain-2	5
Coal-3	3.5	DAP-3	6.0	Rain-3	7
Coal-4	4.5	DAP-4	3.4		
Coal-5	7.1	DAP-5	7.6		
Coal-6	3.6				
Coal-7	4.6				
Coal-8	8.9				

Table 4.12 Nitrogen isotope data

Sr No.	Sample ID	NO_3−N (mg/L)	δ^{15} N (‰, air)
1	MM-2	8.68	30.0
2	MM-3	7.42	14.0
3	MM-4	5.60	13.0
4	MM-5	46.00	25.0
5	MM-8	6.72	12.5
6	KLW-16	10.64	15.0
7	DN-3	18.90	12.5
8	DN-5	3.36	9.4
9	KA-3	11.48	8.1
10	ZAB-1	7.00	5.7
11	ZAB-2	7.56	5.0
12	ZAB-3	5.60	5.0
13	ZAB-4	14.00	5.0
14	ZAB-5	10.50	3.5
15	ARK-5	7.84	11.0
16	SKB-6	4.20	10.0
17	SKB-14	3.50	12.5
18	SKB-22	3.08	11.9
19	JK-1	10.50	15.0
20	JK-2	10.00	14.5
21	RPNA-2	10.00	7.2
22	Urea-1	na[a]	1.4
23	Urea-2	na	0.9
24	Urea-3	na	1.6

[a] *na* means not analyzed

4.2.3.3 Nitrogen Isotopes

The $\delta^{15}N_{NO3}$ isotopes were analyzed for 21 groundwaters to identify the sources of nitrogen contaminants. The $\delta^{15}N_{NO3}$ of groundwater and fertilizers is given in Table 4.12. Most of the groundwater samples give $\delta^{15}N_{NO3} > 5$ ‰, with the maximum value 30 ‰ and the mean 10 ‰.

The groundwaters from Zahir Abad (ZAB), the southwest village among the studied villages, showed the δ^{15}N within narrow range 3.5–5.7 ‰. The δ^{15}N of fertilizer samples (urea, n = 3) were also analyzed, and those values were <2 ‰, close to that of air. The range of the $\delta^{15}N$ of ZAB groundwaters is in concordant with that of soil organic nitrogen (e.g., Chapella 2001) and chemical fertilizers used in China but slightly larger than those used in this area.

4.3 Analytical Results of Soil Sampled in 2005

Soil and sediment samples were collected in April, 2005. Those can be categorized into three types (a) 42 surface soils (b) 41 taken from 30 cm depth at the same location where the surface soils were collected (c) Alluvial sediments including 3 sediments from the surface of alluvial plain of river bank, and 5 sets of sediments were also collected from outcrops up to 500 cm from the surface of alluvial plain.

4.3.1 Mineral Composition

The results of the chemical analyses of soil and surface sediments are summarized in Table 4.13 and those from outcrops are given in Table 4.14. No distinct difference of fraction distribution could be observed between surface and deep soil taken from 30 cm depth at the same location. All soils are silty and sandy with small amount of clay particles. The alluvial sediments contain >50 % fine sand fraction with fewer amounts of silt, and clay 1–5 %. Sediments taken from outcrops contain 7 to >80 % silt with an average value of 48 %. Results of XRD shows that the compositional minerals in the soil samples are abundant quartz, moderate muscovite, and minor clay minerals of chlorite or kaolinite were also detected (Fig. 4.11).

4.3.2 Relationship of Major Elements with As and F^-

The major chemical composition also shows almost the same pattern between surface and deep soil taken from 30 cm depth of the same location (Table 4.13).

Some physical and chemical properties of soils, such as chemical composition including aluminum, calcium, iron, pH, organic matter and clay content are the major parameters that impact the binding ability of As, and of F^- through adsorption, anion exchange, and precipitation (Fluhler et al. 1982; Murray 1984). Fluoride and As shows a slight positive correlation with clay fractions for surface and 30 cm deep soils (Figs. 4.10 and 4.12a, b) as well for outcrops 4.13. The positive correlation between F^- and content of clay particles shows that clay rich soils retain F^- better than sandy soils (Morshina and Fanaskova 1987) similarly the adsorption of As^{III} at low pH and desorption of As as As^{V} at higher pH by clay phases has been previously documented (Manning and Goldberg 1997).

Fluoride and As concentrations do not have any good correlation to major element concentration in most of the studied soils and sediments, except the sediments from outcrops in which, F^- show weakly positive correlation with Al_2O_3 ($r^2 = 0.28$), Fe_2O_3 ($r^2 = 0.40$), and significant with with those of MgO ($r^2 = 0.60$), CaO ($r^2 = 0.40$), and Na_2O ($r^2 = 0.43$) as shown in Fig. 4.14a–f. The positive correlation of F^- with Ca^{2+} and Mg^{2+} suggests that those ions are retained in the soil, as usually observed in those from the agricultural lands (Fluhler et al. 1982).

The relationships among concentrations of F^-, As and P_2O_5 of surface and 30 cm deep soils, and alluvial sediments are given in Figs. 5.2 and 5.3. Five end members could be identified from these Figures; soil almost free from F^- (<0.1 mg/kg) ca. 7.0 mg/kg As and 1–2 g/kg of P_2O_5 (Point A), enormously high F^- (ca. 16 mg/kg) and As (35 mg/kg) and low P_2O_5 approximately 2.4 g/kg (point B), moderate F^- (2 mg/kg), high As (10 mg/kg) and high P_2O_5 11.5 g/kg (Point C), high F^- (5.2 mg/kg), low As (7 mg/kg) and high P_2O_5 6.5 g/kg (Point D), and high As (19 mg/kg), low F^- (0.1 mg/kg) and low P_2O_5 1.8 g/kg (Point E).

End member A contains the least F^-, As and P_2O_5, implying the background soil in this area.

Table 4.13 Major chemistry, particle size and F and As concentrations of soil samples taken from Punjab, Pakistan

Sample ID	Depth (cm)	Particle size distribution in %			pH	As (mg/kg)	F (mg/kg)	SiO_2 (%)	TiO_2 (%)	AL_2O_3 (%)	Fe_2O_3 (%)	MnO (%)	MgO (%)	CaO (%)	Na_2O (%)	K_2O (%)	P_2O_5 (%)	LOI (%)
		Clay	Silt	Sand														
KLW-2B	0	7.1	70.0	22.8	8.1	10	0.4	66.7	0.73	13.1	5.26	0.09	2.15	2.39	1.44	2.78	0.23	5.7
KLW-2A	30	16.3	68.6	15.1	7.9	10	0.6	68.2	0.73	13.1	4.30	0.08	2.12	2.42	1.53	2.66	0.21	5.1
KLW-3B	0	17.6	68.5	13.9	7.6	10	0.7	66.3	0.74	12.9	5.11	0.09	2.23	4.55	1.54	2.59	0.20	4.2
KLW-3A	30	18.5	68.6	12.8	8.5	8	1.4	68.6	0.74	13.1	5.03	0.09	2.18	2.79	1.58	2.76	0.20	3.4
KLW-4B	0	19.2	70.7	10.1	7.8	12	0.3	68.9	0.69	11.9	4.23	0.08	1.92	3.09	1.59	2.49	0.21	5.1
KLW-4A	30	17.8	68.6	13.7	8.2	10	1.5	68.2	0.76	13.2	4.80	0.09	2.09	2.15	1.61	2.73	0.18	4.7
KLW-5B	0	21.1	68.7	10.3	8.2	13	1.0	70.1	0.85	12.1	5.18	0.10	2.58	2.50	1.65	3.36	0.25	1.2
KLW-5A	30	19.5	65.3	15.2	8.2	11	1.2	70.4	0.78	12.6	5.10	0.09	2.29	2.37	1.53	2.94	0.19	2.3
KLW-6B	0	19.4	69.4	11.1	8.7	15	1.4	74.5	0.45	10.4	3.08	0.06	1.28	2.69	1.76	2.46	0.12	3.2
KLW-6A	30	21.4	66.4	12.1	8.7	12	2.1	72.5	0.45	12.4	3.18	0.06	1.18	2.56	1.84	2.46	0.12	3.2
KLW-7B	0	18.1	71.9	10.0	8.9	13	2.1	64.7	0.73	14.4	5.47	0.09	2.37	2.00	1.42	3.03	0.31	5.6
KLW-7A	30	18.8	70.0	11.2	9.1	12	2.5	68.6	0.74	13.9	5.23	0.09	2.32	2.19	1.57	2.89	0.35	2.8
KLW-8B	0	17.7	70.1	12.2	8.2	14	0.9	72.2	0.76	12.2	4.27	0.09	2.23	2.06	1.57	2.95	0.22	2.1
KLW-8A	30	19.1	66.7	14.2	8.8	10	2.1	66.3	0.77	14.0	5.55	0.10	2.18	1.52	1.53	2.82	1.14	4.6
KLW-9B	0	15.5	66.4	18.1	8.8	15	1.9	66.4	0.72	13.0	5.09	0.09	2.38	3.38	1.92	2.65	0.22	4.7
KLW-9A	30	16.7	65.5	17.7	8.8	10	2.0	67.3	0.73	13.7	5.29	0.09	2.22	2.69	1.52	2.87	0.18	3.5
KLW-10B	0	17.4	72.4	10.1	9.4	10	1.4	64.2	0.71	13.0	5.14	0.10	2.42	7.38	1.60	2.68	0.17	3.1
KLW-10A	30	13.6	68.1	18.3	8.2	8	3.2	62.6	0.68	11.9	4.60	0.08	2.17	7.64	1.52	2.38	0.50	6.4
KLW-11B	0	16.8	65.1	18.0	8.8	12	1.7	68.7	0.72	12.6	4.72	0.09	2.10	3.28	1.46	2.59	0.21	4.4
KLW-11A	30	18.9	67.4	13.7	9.0	9	2.5	66.2	0.72	12.3	5.08	0.09	2.12	3.46	1.52	2.69	0.17	5.7
WP-1B	0	19.0	71.0	10.0	8.7	12	1.9	61.2	0.61	13.3	5.24	0.07	3.89	6.06	3.52	2.80	0.13	3.3
WP-1A	30	18.0	68.4	13.6	8.7	10	2.5	66.4	0.74	14.4	5.64	0.10	2.38	2.76	1.44	3.00	0.15	2.8
WP-2B	0	14.2	70.2	15.6	8.2	12	1.2	64.4	0.71	15.7	6.06	0.09	2.62	2.84	1.65	3.96	0.16	2.3
WP-2A	30	18.3	67.7	14.1	8.3	11	1.4	67.8	0.72	12.2	4.51	0.08	2.14	3.68	1.61	2.49	0.26	5.1
WP-3B	0	12.1	69.2	18.7	7.6	19	0.1	70.3	0.74	12.1	5.10	0.08	2.35	2.27	1.61	2.92	0.18	2.7

(continued)

Table 4.13 (continued)

Sample ID	Depth (cm)	Particle size distribution in %			pH	As (mg/kg)	F (mg/kg)	SiO_2 (%)	TiO_2 (%)	AL_2O_3 (%)	Fe_2O_3 (%)	MnO (%)	MgO (%)	CaO (%)	Na_2O (%)	K_2O (%)	P_2O_5 (%)	LOI (%)
		Clay	Silt	Sand														
WP-3A	30	15.1	70.9	14.0	7.7	17	0.2	68.1	0.73	13.3	5.10	0.08	2.27	2.58	1.51	2.78	0.17	3.9
WP-4B	0	16.6	65.1	18.2	8.3	10	0.6	71.3	0.73	12.5	4.59	0.08	1.97	1.86	1.54	2.58	0.19	2.9
WP-4A	30	16.4	66.1	17.4	8.3	7	0.6	70.3	0.71	12.6	4.69	0.09	2.04	2.40	1.48	2.58	0.19	3.4
WP-5B	0	15.4	71.9	12.7	8.6	9	1.1	71.8	0.75	13.5	1.88	0.09	2.16	2.80	1.59	2.76	0.23	3.1
WP-5A	30	16.4	71.5	12.1	8.8	9	1.9	65.6	0.74	13.5	5.39	0.10	2.25	4.12	1.43	2.67	0.16	4.3
WP-6B	0	15.1	73.3	11.6	8.3	10	0.9	66.2	0.73	14.1	5.28	0.09	2.35	2.33	1.50	2.91	0.19	4.7
WP-6A	30	15.2	69.0	15.8	8.3	9	1.3	69.6	0.74	13.8	5.09	0.09	2.14	1.61	1.58	2.87	0.18	2.8
WP-7B	0	16.9	69.6	13.6	8.0	8	0.7	71.5	0.72	12.5	4.55	0.07	1.95	2.00	1.53	2.57	0.17	2.5
WP-7A	30	16.9	69.6	13.6	8.2	8	1.2	68.2	0.78	12.2	5.40	0.09	2.33	3.73	1.47	2.82	0.18	3.4
WP-8B	0	15.9	65.8	18.2	8.1	7	0.8	68.6	0.69	11.9	4.27	0.08	2.16	3.73	1.65	2.56	0.26	4.2
WP-8A	30	16.3	63.8	20.2	8.2	6	1.1	70.6	0.69	12.9	3.27	0.08	1.25	4.56	1.65	2.56	0.26	2.3
WP-9B	0	11.1	63.9	24.8	8.0	8	0.4	64.8	0.72	13.8	5.50	0.09	2.51	3.48	1.35	2.87	0.16	4.8
WP-9A	30	8.3	59.2	32.1	8.1	7	0.9	79.2	0.96	7.6	2.90	0.06	0.95	1.58	1.33	1.36	0.17	4.3
WP-10B	0	12.2	65.7	19.6	7.9	16	0.4	69.5	0.73	13.5	5.03	0.09	2.12	1.90	1.53	2.82	0.19	3.2
WP-10A	30	11.3	63.3	21.3	8.0	14	0.5	69.5	0.73	13.5	5.03	0.09	2.12	1.90	1.53	2.82	0.19	3.2
WP-11B	0	13.4	64.3	17.3	8.2	8	0.8	69.5	0.73	13.5	5.03	0.09	2.12	1.90	1.53	2.82	0.19	3.2
WP-11A	30	16.8	66.3	18.6	8.2	7	1.0	62.7	0.72	15.7	4.20	0.09	2.27	4.05	1.47	3.62	0.26	5.0
WP-12B	0	18.6	69.4	12.1	8.1	10	0.7	68.2	0.74	13.3	5.08	0.09	2.05	1.50	1.43	2.74	0.18	4.9
WP-12A	30	17.6	68.3	14.1	8.2	9	1.0	68.2	0.74	13.3	5.08	0.09	2.05	1.50	1.43	2.74	0.18	4.9
MM-1B	0	17.0	71.3	11.7	9.4	15	0.6	73.1	0.64	10.9	4.15	0.07	1.63	1.81	1.43	2.53	0.26	3.5
MM-1A	30	16.2	65.6	18.2	8.0	7	5.2	63.7	0.72	12.7	5.20	0.09	2.27	5.05	1.47	2.62	0.65	5.9
MM-2B	0	21.6	65.1	13.4	8.2	8	0.5	66.7	0.72	13.7	5.42	0.10	2.28	1.93	1.41	2.94	0.23	4.2
MM-2A	30	17.7	70.2	12.1	8.3	10	0.7	67.4	0.72	12.4	4.32	0.10	2.68	2.04	1.41	2.62	0.23	4.4
MM-3B	0	18.2	67.2	14.3	8.3	11	0.6	70.0	0.72	13.3	5.10	0.09	2.22	3.00	1.46	2.82	0.25	1.3

(continued)

Table 4.13 (continued)

Sample ID	Depth (cm)	Particle size distribution in %			pH	As (mg/kg)	F (mg/kg)	SiO_2 (%)	TiO_2 (%)	AL_2O_3 (%)	Fe_2O_3 (%)	MnO (%)	MgO (%)	CaO (%)	Na_2O (%)	K_2O (%)	P_2O_5 (%)	LOI (%)
		Clay	Silt	Sand														
MM-3A	30	17.4	68.6	14.3	8.2	10	1.2	68.4	0.82	12.3	4.10	0.09	2.32	3.00	1.66	2.92	0.25	4.2
MM-4B	0	18.5	67.3	14.2	8.1	10	0.6	64.3	0.67	14.3	4.87	0.09	2.12	4.36	1.36	2.57	0.20	5.1
MM-4A	30	17.6	66.2	16.2	8.2	9	1.2	66.4	0.67	12.3	5.37	0.09	2.02	4.16	1.34	2.37	0.20	4.9
MM-5B	0	16.3	66.3	17.4	8.1	10	0.5	66.6	0.71	12.6	4.75	0.08	2.12	4.31	1.50	2.60	0.20	4.8
MM-5A	30	16.3	65.0	18.7	8.1	9	0.5	66.1	0.75	13.2	5.32	0.09	2.21	4.01	1.44	2.67	0.20	4.6
MM-9B	0	13.7	71.8	14.5	8.0	7	0.2	67.6	0.73	12.6	4.74	0.08	2.12	4.12	1.45	2.56	0.10	4.2
MM-9A	30	14.4	69.8	16.5	8.0	6	0.3	68.4	0.73	14.0	5.22	0.08	2.33	2.28	1.46	2.88	0.21	3.2
MM-10B	0	18.5	67.5	14.0	8.1	10	0.7	64.0	0.76	13.2	5.89	0.09	2.15	4.61	1.37	2.56	0.21	5.7
MM-10A	30	16.1	67.0	16.9	8.2	12	1.1	67.6	0.73	12.6	4.74	0.08	2.12	4.12	1.45	2.56	0.20	4.2
MM-11B	0	17.3	62.9	13.8	9.3	10	4.3	69.1	0.72	13.3	4.94	0.09	2.11	2.01	1.64	2.74	0.6	3.8
MM-11A	30	18.0	61.3	14.9	9.3	11	4.8	66.5	0.71	14.1	5.16	0.08	2.27	1.92	1.50	2.96	0.58	4.8
MM-12B	0	18.1	67.3	14.6	8.2	9	0.8	72.6	0.67	13.2	3.46	0.07	2.53	1.68	1.26	1.77	0.13	3.3
MM-12A	30	13.0	71.7	15.3	8.2	9	1.0	75.6	0.67	10.2	3.96	0.07	1.53	1.98	1.36	1.97	0.13	3.1
MM-13B	0	17.8	63.9	18.3	8.2	8	0.4	67.8	0.73	12.9	5.16	0.10	2.17	3.08	1.47	2.64	0.22	3.9
MM-13A	30	17.4	63.9	18.6	8.2	9	0.8	74.0	0.94	8.5	3.33	0.11	1.12	3.69	1.53	1.71	0.25	5.3
MM-14B	0	14.7	63.7	21.6	8.4	8	1.6	65.6	0.81	13.6	6.29	0.09	1.99	3.30	1.38	2.50	0.22	4.4
MM-14A	30	17.7	64.7	17.6	8.4	7	1.7	65.6	0.81	13.6	6.28	0.09	1.98	3.28	1.38	2.50	0.22	4.2
RWR-1B	0	14.0	66.1	19.9	8.2	7	0.3	66.5	0.69	11.9	4.86	0.08	2.07	4.64	1.43	2.55	0.29	5.9
RWR-1A	30	18.1	67.4	14.5	8.2	7	0.5	64.9	0.65	13.1	4.90	0.08	2.63	4.30	1.68	2.90	0.15	4.7
RWR-2B	0	16.9	70.2	12.9	8.2	10	0.3	66.5	0.76	15.0	5.72	0.09	2.48	2.12	1.38	3.10	0.20	3.4
RWR-2A	30	16.0	67.1	16.9	8.2	13	0.5	69.1	0.72	12.7	4.72	0.09	2.17	2.98	1.56	2.82	0.26	3.3
RWR-3B	0	23.2	67.6	9.2	8.3	11	0.5	64.1	0.75	14.9	6.25	0.11	2.71	1.93	1.19	3.30	0.27	4.6
RWR-3A	30	16.4	67.0	16.7	8.3	10	0.5	69.2	0.74	13.9	5.40	0.10	2.24	2.03	1.46	2.93	0.23	2.1

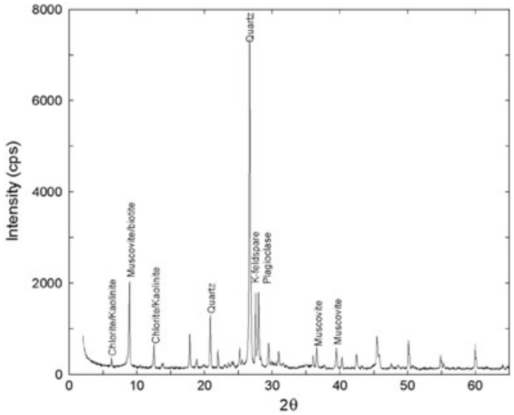
(continued)

Table 4.13 (continued)

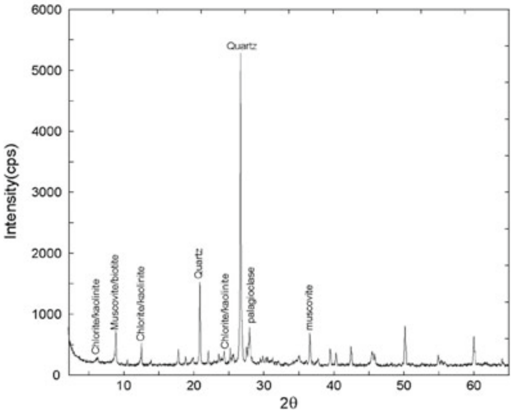
Sample ID	Depth (cm)	Particle size distribution in %			pH	As (mg/kg)	F (mg/kg)	SiO_2 (%)	TiO_2 (%)	AL_2O_3 (%)	Fe_2O_3 (%)	MnO (%)	MgO (%)	CaO (%)	Na_2O (%)	K_2O (%)	P_2O_5 (%)	LOI (%)
		Clay	Silt	Sand														
RWR-4B	0	18.7	65.7	15.7	8.3	7	0.6	66.8	0.74	14.2	5.64	0.10	2.40	1.30	1.42	3.06	0.21	4.7
RWR-4A	30	23.4	70.5	6.2	8.3	9	0.6	68.6	0.77	14.0	5.41	0.09	2.22	1.48	1.54	2.86	0.18	3.2
RWR-6B	0	15.2	73.4	11.4	8.3	6	0.8	63.2	0.62	11.7	4.85	0.07	2.44	6.72	1.58	2.32	0.18	4.6
RWR-6A	30	14.8	76.7	8.5	8.3	10	0.9	61.2	0.62	12.7	4.85	0.07	3.44	8.00	1.48	2.72	0.18	4.8
RWR-7B	0	24.0	75.1	0.8	10.0	35	16	67.4	0.71	13.2	4.67	0.08	2.31	2.32	1.54	2.57	0.24	4.8
RWR-8B	0	14.7	63.0	22.2	8.3	10	0.5	68.4	0.71	12.2	4.60	0.08	1.95	3.00	1.54	2.57	0.24	4.5
RWR-8A	30	15.4	64.9	19.7	8.4	7	1.5	71.5	0.75	11.9	4.18	0.08	2.24	3.11	1.58	2.88	0.23	2.1
RWR-9B	0	22.0	68.8	9.1	9.2	12	2.3	63.8	0.65	12.7	4.83	0.07	2.78	5.32	1.46	2.84	0.33	5.9
RWR-9A	30	22.3	70.1	7.6	9.2	9	3.5	65.6	0.71	13.1	5.06	0.09	2.26	4.44	1.45	2.73	0.34	4.3
RWR-10B	0	18.6	67.6	14.8	8.4	12	1.0	70.3	0.75	11.7	5.31	0.09	2.44	2.82	1.52	2.96	0.25	2.3
RWR-10A	30	16.6	69.6	13.8	8.3	16	0.6	66.5	0.67	11.3	3.87	0.07	2.31	6.26	2.45	2.35	0.19	3.9
MM-8B	Alluvial-0	5.0	36.2	50.7	7.7	10	0.2	69.3	0.60	11.2	3.32	0.06	2.135	4.56	1.68	2.31	0.10	4.5
MM-8A	Alluvial 30	5.2	36.7	51.2	7.5	9	bdl	69.2	0.62	10.3	3.45	0.05	2.21	3.67	1.54	2.14	0.10	6.4
BRB-1B	Alluvial-0	4.9	45.2	55.4	7.8	10	0.2	68.1	0.77	13.8	5.21	0.09	2.20	3.60	1.49	2.76	0.18	2.3
BRB-1A	Alluvial 30	4.1	47.3	53.2	7.8	9	bdl	60.8	0.62	13.0	4.83	0.08	2.99	4.19	4.38	2.75	0.17	6.5
BRB-2B	Alluvial-0	2.0	37.6	54.1	7.6	10	0.2	69.1	0.61	11.3	3.24	0.06	2.01	3.67	1.73	2.65	0.11	5.2
BRB-2A	Alluvial 30	2.4	38.0	52.9	7.6	9	bdl	70.1	0.53	10.7	3.56	0.06	1.79	3.68	1.78	2.42	0.13	5.6

Table 4.14 Major chemistry, particle size and F and As concentrations of outcrops taken from Punjab, Pakistan

Outcrops	Sample	Depth particle size distribution in %				pH	As (mg/kg)	F^- (mg/kg)	SiO_2 (%)	TiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	MnO (%)	MgO (%)	CaO (%)	Na_2O (%)	K_2O (%)	P_2O_5 (%)	LOI (%)
		cm	Clay	Silt	Fine sand														
Outcrop-1	KLW-1A	0	13.2	67.7	19.1	8.2	16.0	1.10	65.0	0.73	13.0	4.88	0.09	2.28	3.15	1.52	2.82	2.630	4.2
	KLW-1B	50	15.1	69.4	15.6	8.1	17.0	0.35	77.6	0.62	9.1	3.20	0.06	1.27	1.80	1.41	1.79	0.108	3.7
	KLW-1C	100	18.3	61.6	20.0	8.3	6.0	1.00	65.2	0.76	13.2	5.40	0.09	2.66	3.98	1.58	2.89	0.217	4.2
	KLW-1D	150	20.4	70.7	8.9	8.2	14.0	0.48	70.1	0.63	10.7	3.34	0.06	1.69	4.31	1.90	2.21	0.163	5.1
	KLW-1E	200	22.3	66.8	10.9	8.3	8.0	1.03	71.7	0.47	10.2	3.67	0.06	1.55	3.16	1.72	2.45	0.100	5.2
	KLW-1F	250	1.0	21.9	70.6	8.1	4.0	0.26	68.3	0.71	12.2	4.44	0.08	2.07	3.55	1.56	2.49	0.172	4.8
	KLW-1G	300	0.0	7.1	87.4	8.1	8.0	0.28	80.7	0.81	8.2	2.87	0.06	1.14	1.64	1.34	1.52	0.124	2.1
	KLW-1H	350	0.2	31.5	62.0	8.1	4.0	0.17	68.0	0.63	12.2	4.49	0.07	2.13	4.17	1.73	2.65	0.142	3.4
	KLW-1I	400	0.4	33.2	61.4	8.1	4.0	0.33	71.2	0.75	13.1	3.67	0.09	2.36	2.41	1.61	2.93	0.131	2.3
Outcrop-2	MM-6A	0	17.9	68.1	14.0	8.1	5.0	0.34	64.2	0.72	12.6	4.85	0.09	2.15	5.88	1.68	2.63	0.174	5.6
	MM-6B	100	17.5	68.5	14.1	8.3	6.0	2.55	62.7	0.68	12.4	4.70	0.08	2.80	7.01	2.85	2.44	0.148	4.3
	MM-6C	200	12.5	80.6	6.8	8.6	19.0	4.17	56.8	0.61	13.3	5.24	0.07	3.89	6.06	3.53	2.81	0.133	7.8
	MM-6D	300	10.0	76.1	13.9	8.5	19.0	2.88	66.1	0.67	12.9	5.34	0.08	3.07	3.41	1.81	2.67	0.156	4.1
	MM-6E	400	3.7	69.0	27.2	8.2	5.0	0.62	64.5	0.59	11.2	3.89	0.06	2.03	6.34	3.06	2.27	0.149	5.8
	MM-6F	500	0.5	18.1	76.0	8.3	9.0	0.74	76.1	0.64	9.9	3.30	0.06	1.50	1.80	1.81	2.06	0.111	3.2
Outcrop-3	MM-7A	0	6.9	64.1	28.6	8.3	9.0	1.53	68.6	0.72	11.7	5.25	0.09	2.52	3.52	1.59	2.82	0.263	3.2
	MM-7B	50	7.5	81.6	10.8	8.2	8.0	0.55	80.5	1.34	7.7	3.43	0.09	1.00	1.30	1.18	1.41	0.176	2.4
	MM-7C	100	1.2	41.0	57.3	8.2	8.0	0.35	63.9	0.72	13.5	5.35	0.09	2.71	3.94	1.64	2.84	0.160	5.7
	MM-7D	150	3.6	58.2	37.3	8.1	6.0	0.30	79.8	0.51	9.2	2.96	0.05	1.16	1.26	1.45	1.99	0.080	2.1
	MM-7E	200	5.5	81.6	12.8	8.1	7.0	0.27	75.3	0.67	10.2	3.96	0.07	1.52	1.98	1.36	1.97	0.129	3.2
Outcrop-4	BRB-3A	100	1.1	30.3	68.0	8.2	6.0	0.54	72.8	0.81	9.1	3.16	0.08	1.31	3.83	1.70	1.88	0.216	5.4
	BRB-3B	110	5.5	72.5	22.1	8.2	7.0	1.30	66.2	0.68	12.4	4.54	0.07	2.25	4.57	1.86	2.69	0.141	4.7
	BRB-3C	120	0.9	18.8	81.0	8.1	4.0	0.39	65.7	0.72	13.6	5.24	0.09	2.37	3.33	1.39	2.92	0.222	4.6
	BRB-3D	130	0.9	54.6	44.3	8.3	10.0	1.07	73.8	0.81	8.1	3.16	0.08	1.31	1.87	1.40	1.86	0.119	3.9
	BRB-3E	140	0.0	18.0	81.2	8.1	4.0	0.62	76.4	0.70	9.2	3.47	0.06	1.35	6.76	4.59	3.54	0.180	5.7
	BRB-3F	200	1.1	42.7	52.3	8.0	1.0	0.63	56.4	0.66	15.4	6.14	0.09	3.86	6.06	3.53	2.81	0.133	5.4



From surface KLW-2b



From 30 cm depth Wp-4a

Fig. 4.11 Selected XRD plots from the study area showing the principal minerals in soil samples

While, most of the studied soils and sediments are contaminated by some anthropogenic sources, which corresponds to other four end members. This will be discussed in detail later.

The soluble F^- shows good positive correlation with pH for surface and 30 cm deep soils (r^2 = 0.88, Fig. 4.16a). The similar correlation can be observed from most of the sediments taken from outcrops (r^2 = 0.66, Fig. 4.16b). Figure 4.16c shows the good relationship of As with pH of the samples from outcrops ($r^2 = 0.63$). Alkaline pH is favorable for F^- dissolution into the solution, because F^- ions are adsorbed by clay particles in acidic solution; however, they are desorbed in alkaline solution (Sexena 2003). Similarly As^V is most effectively adsorbed on the Fe-oxyhydroxide/oxide at weakly acid to neutral pH conditions, and it releases into the solution with increasing pH at alkaline condition (Anderson et al. 1976; Pierce and Moore 1982; Dzombak and Morel 1990; Gustafsson and Jacks 1995; Lindberg et al. 1997). Thus, alkaline soils from temperate arid and semi-arid areas leach relatively large amounts of F^- (Wang et al. 2002). Our obtained results also explain that if water infiltrates into the soils and F^- and As are released into the groundwater through leaching and desorption of As in association with increasing pH.

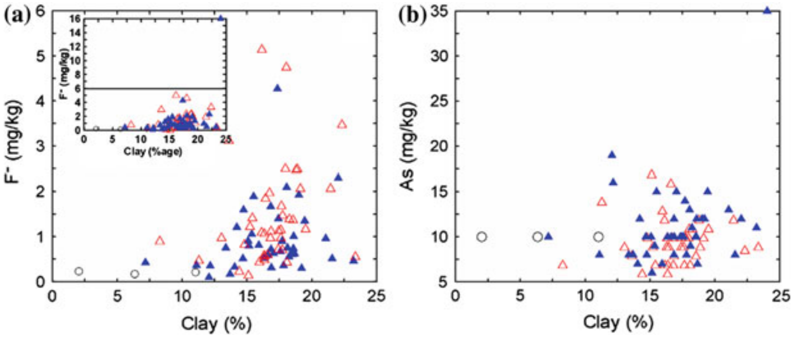


Fig. 4.12 Relationship of F^- with clay (**a**) and As with clay (**b**). *Soil triangles* are symbol for surface samples, *open triangles* for 30 cm depth and circle for alluvial samples

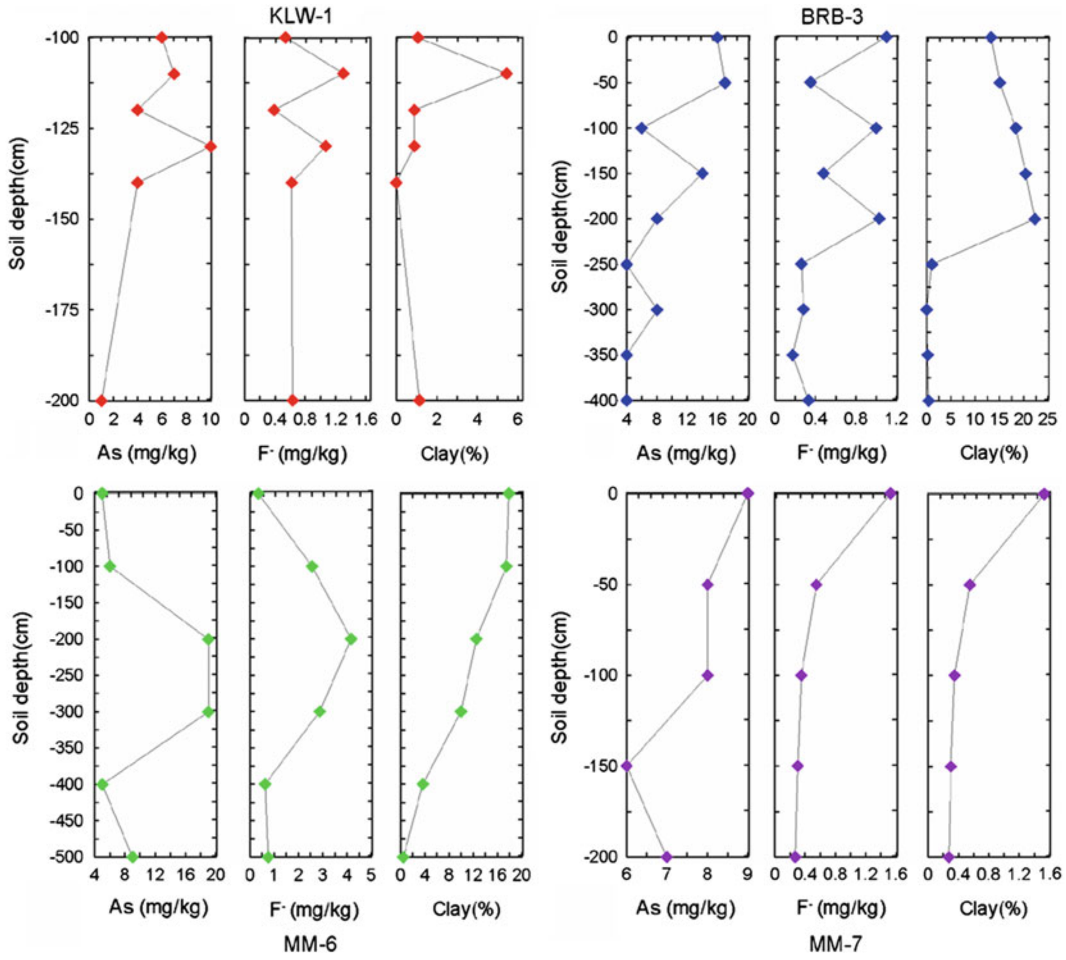


Fig. 4.13 Relationship of As, F^- and clay fraction with depth for outcrops

4.3.3 Geographic Distribution of As and F^-

Geographic distribution of As and F^- is given in Fig. 4.17. As concentration is comparatively higher in the surface samples than the deep samples; the surface soils contain As ranging 6–35 mg/kg with an average value of 10.2 mg/kg, while, deep soils contain As in the range of 1.0–17.0 mg/kg with mean value of 9.0 mg/kg. The higher concentrations of total As of the surface soil than 30 cm deep soils and alluvial sediments could be explained by the accumulation of this element derived from anthropogenic activities on the surface soils; as soils highly polluted by the industrial emission or other anthropogenic activities tend to have their highest concentrations at the surface of the profile (Robinson and Edgingion 1946).

Arsenic concentration of the soils is unevenly distributed in the area, and highly As containing soils are concentrated in two areas, 1 and 2, enclosed with dashed lines in Fig. 4.17; The area 1 include southern part of the Manga Mandi and Kalalanwala, where the high As >15 mg/kg is included in the soil. The other is area 2 including Waran Piran Wala (WP-3, 10, and 13) and Raiwind road, where the maximum concentration 35 mg/kg was detected in a soil (RWR-7B) from east of the study area. One sample MM-1, which

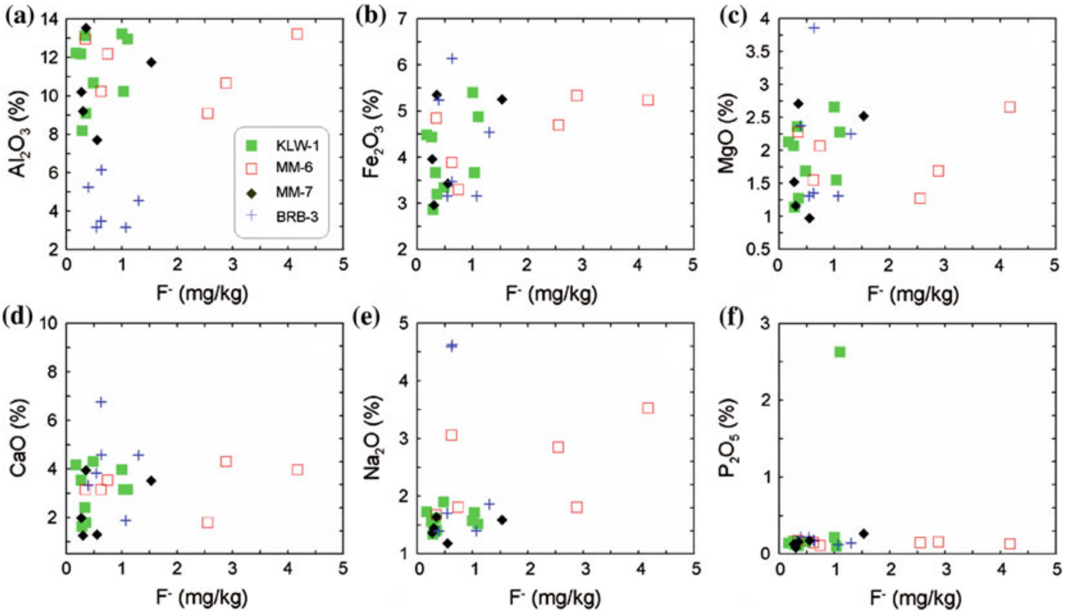


Fig. 4.14 Relationship of F$^-$ with Al$_2$O$_3$ (**a**) Fe$_2$O$_3$ (**b**), MgO (**c**), CaO (**d**), Na$_2$O (**e**) and P$_2$O$_5$ (**f**) for outcrops

was collected very near to the brick kilns contain high amount of As (15.0 mg/kg). Coals including 4–12 mg/kg As are used by brick factories in the area, thus dry deposition via coal would be a source of As in the studied soils and sediments.

Soluble F$^-$ is comparatively higher in the deep soils taken from 30 cm depth than in the surface soils taken from the same localities; concentrations ranging 0.1–5.2 mg/kg with mean value of 1.9 mg/kg were obtained for the former samples, while those ranged from 0.1 to 2.1 mg/kg with the mean value of 0.8 mg/kg for the latter ones. The higher F$^-$ concentration in the deep soils than in the surface soils suggests the migration of these elements from the surface into deeper layer due to the infiltration of surface water (Fluhler et al. 1982).

The distribution of high F$^-$ is similar to that of As, however, the highly F$^-$ contaminated areas seems to be narrower than that of As (Zones 1/ and 2/). Such a coincidental distribution pattern implies that those two elements have the same sources and polluting paths.

4.4 Underground Profiles by Drilling March 2006

Drilling was done at 6 sites from the study area in March-2006. At only one site KL-ES the undisturbed sediment cores were obtained, while at other five locations the drilling was done by conventional method to observe lithology in relation to aquifer structure. As a result, at least three aquifers were identified in the study area; unconfined aquifer shallower than ca 10 m in the aeolian sediments, shallower confined aquifer at the depth of 20–30 m depth, and the deeper confined aquifer at 55–60 m depth in mostly fine to medium sand formations. The shallower confined aquifer is mainly used for obtaining water of daily purpose, and heavily polluted by As, F$^-$ and other anthropogenic pollutants. Impermeable layer between two confined acquirers is not well developed, and mostly observed as the layer including a few to tens cm thick silt to clay lenses. The lithology and the aquifer structure is given in Fig. 4.18a–c.

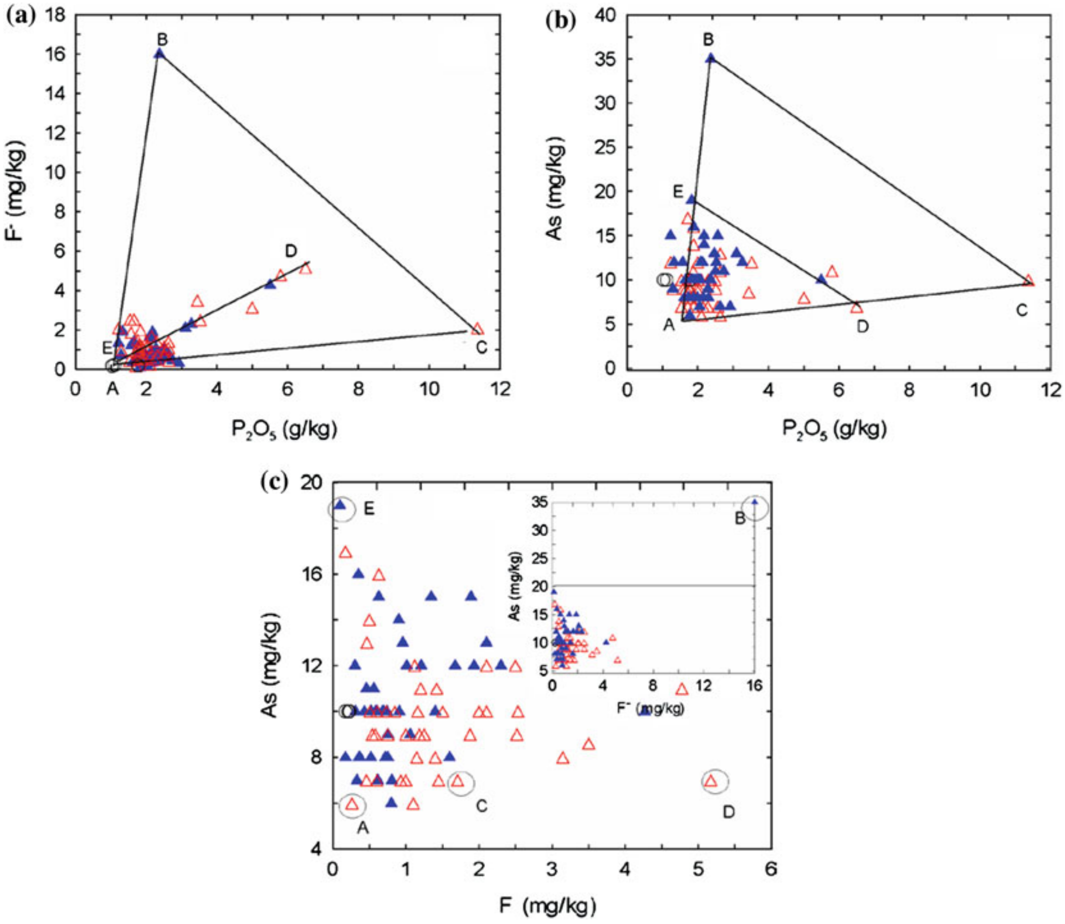


Fig. 4.15 Relationship of F^- with P_2O_5 (**a**) As with P_2O_5 (**b**), and F^- with As (**c**)

4.5 Mineral Saturation

Saturation index (SI) indicates the state of saturation of groundwater for a certain mineral. SI is defined to be equal to log (*IAP/K*). Where *IAP* is the ionic activity product and *K* is the solubility product constant. For example, as mineral gypsum, the precipitation dissolution can be expressed by the equation;

$$CaSO_4 \cdot 2H_2O \leftrightarrow Ca^{2+} + {SO_4}^{2-} + 2H_2O \tag{4.1}$$

The SI is expressed as:

$$SI(gyp) = \frac{IAP_{gyp}}{K_{gyp}} \tag{4.2}$$

K_{gypsum} = $[Ca^{2+}]$ $[{SO_4}^{2-}]$ (Solubility product)

IAP_{gypsum} = $[Ca^{2+}]$ $[{SO_4}^{2-}]$ (Solubility product)

Thus, from the value of SI, three cases can be examined:

If $SI > 0$ over-saturated by certain mineral, which can be stably present in solution.

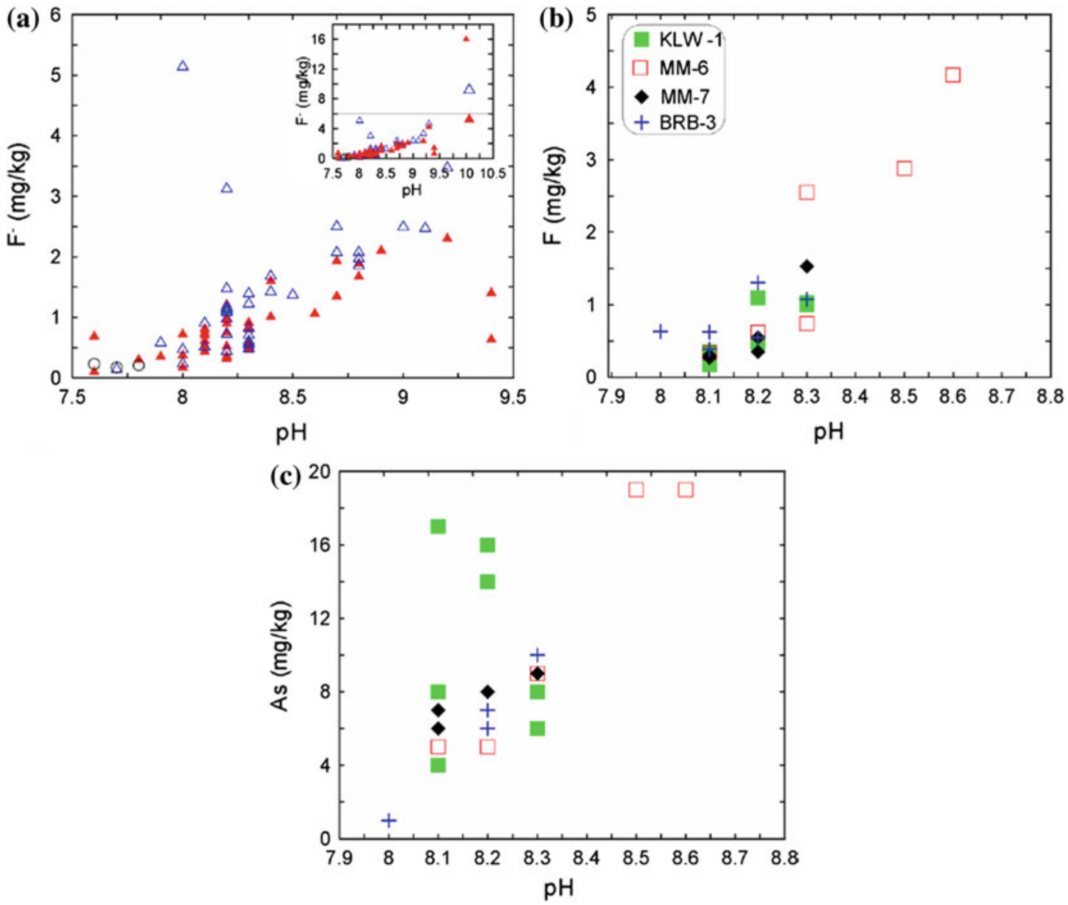


Fig. 4.16 Relationship of F^- with pH for surface and 30 cm samples (**a**) F^- with pH for outcrops (**b**), As with pH for outcrops (**c**)

SI = 0 equilibrium condition between the mineral and aqueous solution.

SI < 0 under-saturation of the mineral which will not be present in the aqueous solution.

A computer programme PHREEQC developed by USGS (version 2.11, http://wwwbrr.cr.usgs.gov/projects/GWC_coupled/phreeqc/) was used to calculate the SI of the minerals fluorite, calcite, dolomite and gypsum for groundwaters. The results of calculation would be useful to discuss the water rock interaction of the four minerals.

The saturation indices (SI) of the minerals are expressed as follows except gypsum. For fluorite (Eq. 4.3), calcite (Eq. 4.4), and dolomite (Eq. 4.5):

$$\mathrm{SI(Fluorite)} = \frac{\mathrm{IAP_{fluorite}}}{\mathrm{K_{fluorite}}} \qquad (4.3)$$

$$\mathrm{SI(calcite)} = \frac{\mathrm{IAP_{calcite}}}{\mathrm{K_{calcite}}} \qquad (4.4)$$

$$\mathrm{SI(dolomite)} = \frac{\mathrm{IAP_{dolomite}}}{\mathrm{K_{dolomite}}} \qquad (4.5)$$

The solubility product constants (Ksp) used for the calculation at 25 °C are as follows: 3.45×10^{-11} for CaF_2 (fluorite), 3.36×10^{-9} for $CaCO_3$ (calcite); 6.82×10^{-6} for dolomite ($MgCO_3$); and, 3.14×10^{-5} for gypsum ($CaSO_4 \cdot 2H_2O$).

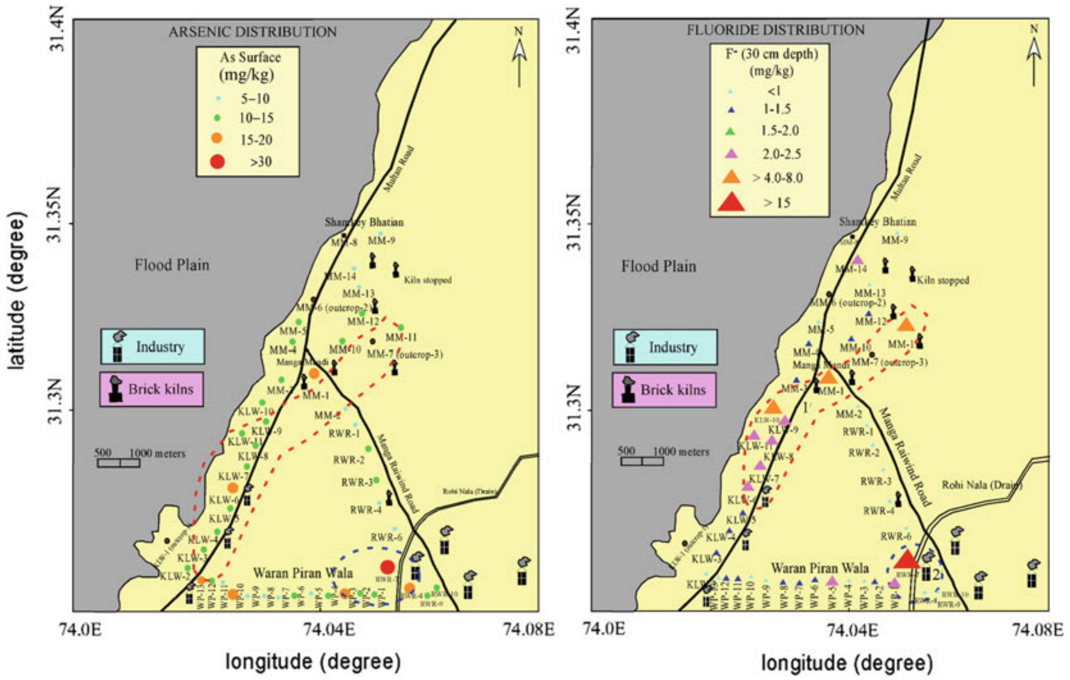


Fig. 4.17 Geographic distribution of As and F⁻ in soil samples

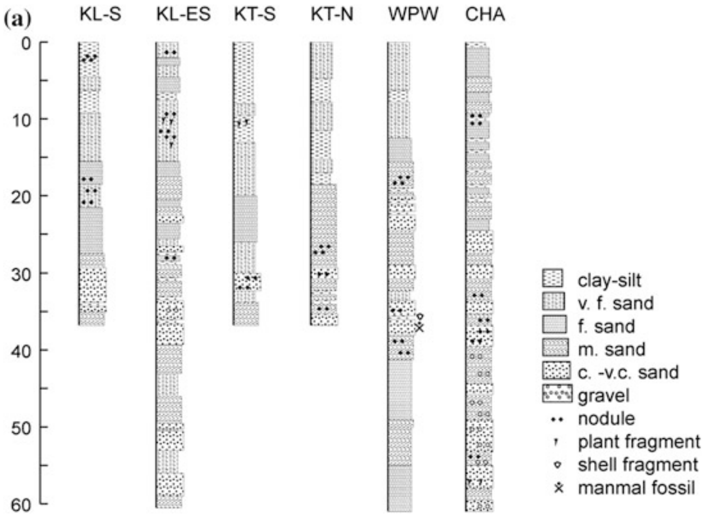


Fig. 4.18 **a** Underground geological profiles from the study area collected in March 2006. **b** Underground geological profiles from west to east and the aquifer structure. **c** Underground geological profiles from south to north and the aquifer structure

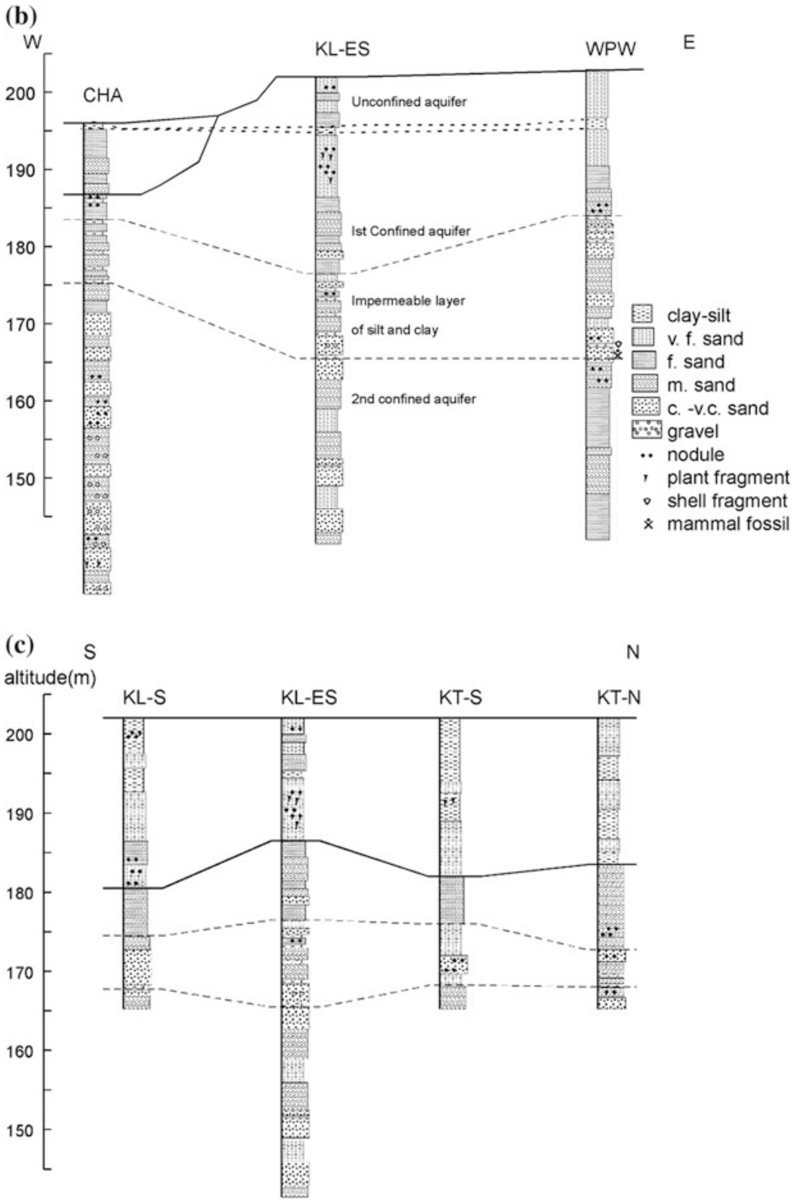


Fig. 4.18 (continued)

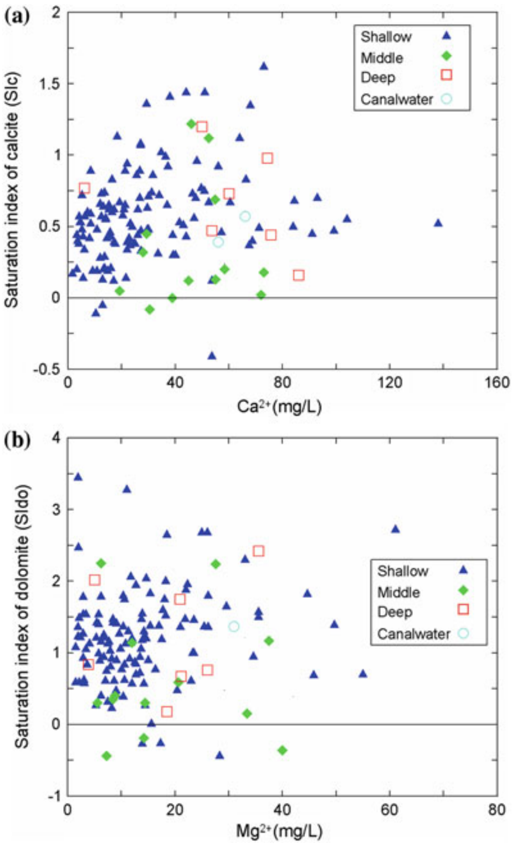


Fig. 4.19 The Ca^{2+} and Mg^{2+} concentrations versus saturation index (SI) of calcite (**a**) and dolomite (**b**)

4.5.1 Minerals Calcite and Dolomite

The Ca^{2+} and Mg^{2+} concentrations versus saturation index (SI) of calcite and dolomite from the extended study area are shown in Fig. 4.19a, b, the groundwater samples from single village Kalalanwala also show the similar behavior. Almost all the groundwaters lie above SI = 0 indicating the saturation or the precipitation of Ca^{2+} and Mg^{2+} in the studied groundwaters. As discussed before in Sect. 4.2.1, the major chemical composition of the studied groundwater is characterized by high concentrations of HCO_3^-, Na^+ and SO_4^{2-}, with depletion of Ca^{2+} and Mg^{2+}. The depletion of Ca^{2+} and Mg^{2+} must be caused by precipitation of calcite and dolomite due to enrichment of carbonate ions and increasing pH.

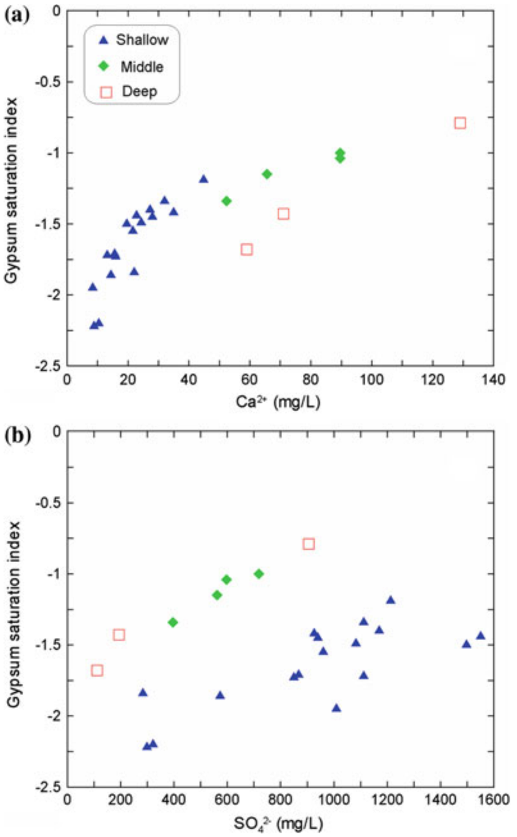


Fig. 4.20 **a**, **b** The Ca^{2+} and SO_4^{2-} concentrations versus saturation index (SI) of gypsum from Kalalanwala area

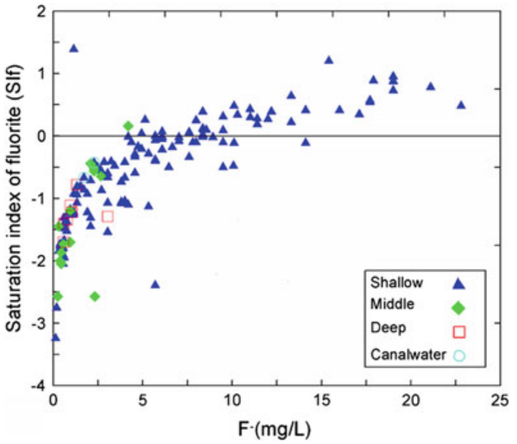


Fig. 4.21 The F^- concentrations versus saturation index (SI) of fluorite

4.5.2 Mineral Gypsum Saturations

The saturation index of gypsum (SI_g) shows a good correlation with Ca^{2+} and SO_4^{2-} (Fig. 4.20a, b) from Kalalanwala, (samples from extended study area also shows the similar pattern), although all of the groundwater is under saturated with respect to this mineral. Instead of higher concentration of SO_4^{2-} in the shallow groundwater than in the middle and deep groundwater, SI_g is much lower in the former groundwaters than in the latter ones, because Ca^{2+} depletion from the groundwater is more intense in the shallow groundwater.

4.5.3 Mineral Fluorite Saturations

The saturation index of fluorite (SI_f) increases with increasing F^- concentration, and reaches the saturation state when the F^- concentration is >8 ppm (Fig. 4.21). As described before, F^- concentration increased with decreasing Ca^{2+} and Mg^{2+} and increasing Na^+ concentrations under alkaline condition. Calcium and Mg^{2+} concentrations were low and controlled mainly by the solubilities of calcite and dolomite due to high HCO_3^- concentrations.

Appendix

Table A.1 Cations, anions and arsenic results from the study area

Sample ID	Depth (m)	F^-		Cl^-		Br^-		NO_3–N		PO_4^{3-}		SO_4^{2-}	
		Mar-04	Sep-04	Mar-04	Sep-04	Mar-04	Sep-04	Mar-04	Sep-04	Mar-04	Sep-04	Mar-04	Sep-04 mg/L
CNG-1	20-27	4.94	4.95	131	130	0.33	0.31	7.00	6.00	bdl	bdl	192	200
CNG-2	20-27	2.67	2.52	78	73	0.23	0.20	bdl	bdl	bdl	bdl	120	125
CNG-4	20-27	8.36	8.14	96	90	0.30	0.30	bdl	bdl	bdl	bdl	165	170
CNG-5	20-27	6.08	6.00	51	50	0.14	0.14	bdl	bdl	bdl	bdl	116	116
SUN1	20-27	10.1	9.70	21	20	bdl	bdl	bdl	bdl	0.4	0.4	120	120
SUN2	20-27	8.36	8.22	60	57	0.16	0.16	0.98	0.90	bdl	bdl	192	195
SUN3	20-27	4.75	4.70	178	176	0.36	0.36	4.20	4.00	bdl	bdl	432	442
SUN4	20-27	4.18	4.15	142	140	0.34	0.34	1.68	1.60	0.7	0.7	336	340
SUN5	20-27	1.52	1.50	177	173	0.45	0.44	4.48	4.49	bdl	bdl	432	435
SKB-2	20-27	3.80	3.76	28	29	bdl	bdl	bdl	bdl	bdl	bdl	106	110
SKB-3	20-27	1.14	1.10	41	40	0.16	0.15	bdl	bdl	bdl	bdl	105	110
SKB-4	20-27	5.70	5.50	19	19	bdl	bdl	bdl	bdl	bdl	bdl	96	100
SKB-5	20-27	10.07	10.00	10	10	0.04	0.04	0.42	0.4	0.6	0.3	50	55
SKB-6	20-27	3.04	3.00	10	10	bdl	bdl	4.20	4.20	2.9	2.3	38	40
SKB-8	20-27	5.70	5.20	9	8	bdl	bdl	2.24	2.20	0.8	0.6	35	38
SKB-9	20-27	5.32	5.25	11	11	bdl	bdl	0.70	0.50	1.4	1.2	48	50
SKB-10	20-27	4.56	4.50	6	6	bdl	bdl	bdl	bdl	bdl	bdl	43	45
SKB-12	20-27	0.95	0.90	13	12	bdl	bdl	2.38	2.30	bdl	bdl	44	47
SKB-13	20-27	3.42	3.34	21	20	0.06	0.06	0.84	0.74	bdl	bdl	58	60
SKB-14	20-27	3.04	3.00	50	48	0.15	0.15	3.50	3.50	bdl	bdl	110	112
SKB-15	20-27	4.56	3.50	14	13	0.06	0.05	0.56	0.55	bdl	bdl	91	95
SKB-16	20-27	1.90	1.87	7	7	bdl	bdl	1.54	1.50	bdl	bdl	48	50

(continued)

Table A.1 (continued)

Sample ID	Depth (m)	F^-		Cl^-		Br^-		NO_3−N		PO_4^{3-}		SO_4^{2-}	
		Mar-04	Sep-04	Mar-04	Sep-04	Mar-04	Sep-04	Mar-04	Sep-04	Mar-04	Sep-04	Mar-04	Sep-04 mg/L
SKB-17	20-27	5.32	5.30	8	8	bdl	bdl	0.14	0.10	bdl	bdl	44	46
SKB-18	20-27	17.1	17.00	49	45	0.16	0.15	0.84	0.80	bdl	bdl	110	110
SKB-19	20-27	8.55	8.51	29	26	0.13	0.13	bdl	bdl	bdl	bdl	86	88
SKB-20	20-27	5.70	5.60	13	13	0.05	0.05	bdl	bdl	bdl	bdl	72	75
SKB-21	20-27	7.03	7.00	24	24	0.09	0.09	bdl	bdl	bdl	bdl	87	90
SKB-22	20-27	2.09	2.00	14	14	0.06	0.06	3.08	3.00	bdl	bdl	88	90
SKB-23	20-27	4.94	4.90	5	5	bdl	bdl	1.12	1.00	bdl	bdl	43	45
SKB24	20-27	3.04	3.00	5	5	bdl	bdl	4.20	4.20	0.2	0.2	48	50
MM-2	20-27	1.14	1.10	106	103	0.30	0.27	8.68	8.61	bdl	bdl	217	225
MM-3	20-27	1.33	1.26	80	78	0.21	0.22	7.42	7.40	bdl	bdl	165	170
MM-4	20-27	0.86	0.80	68	67	0.20	0.20	5.60	5.20	bdl	bdl	149	150
MM-5	20-27	2.28	2.23	262	262	0.76	0.72	46.00	48.00	bdl	bdl	499	505
MM-6	20-27	3.04	3.00	124	125	0.40	0.40	bdl	bdl	2.0	2.0	480	485
MM-7	20-27	1.33	1.31	50	51	0.20	0.20	0.84	0.80	bdl	bdl	259	260
MM-8	20-27	1.14	1.10	67	65	0.23	0.21	6.72	6.67	bdl	bdl	113	120
MM-9	20-27	1.90	1.87	110	106	0.30	0.27	7.56	7.50	bdl	bdl	207	210
MM-11	20-27	0.76	0.65	62	60	0.23	0.21	bdl	bdl	bdl	bdl	187	190
MM-12	20-27	0.46	0.40	28	25	0.10	0.10	1.26	1.20	bdl	bdl	82	87
MM-14	20-27	0.57	0.50	23	22	0.06	0.06	bdl	bdl	bdl	bdl	75	80
MM-15	20-27	0.57	0.50	99	98	0.63	0.61	bdl	bdl	bdl	bdl	336	340
MM-16	20-27	0.60	0.60	117	113	0.37	0.34	bdl	bdl	bdl	bdl	355	368
MM-17	20-27	4.18	4.14	11	10	bdl	bdl	0.84	0.84	0.6	0.5	65	70

(continued)

Table A.1 (continued)

Sample ID	Depth (m)	HCO_3^-		Na^+		K^+		Ca^{2+}		Mg^{2+}		As(V)	
		Mar-04	Sep-04	Mar-04	Sep-04	Mar-04	Sep-04	Mar-04	Sep-04	Mar-04	Sep-04	Mar-04	Sep-04 μg/L
CNG-1	20-27	976	976	460	455	8.97	8.00	48	45	13	11	6	5
CNG-2	20-27	549	549	230	231	4.76	4.00	39	32	18	15	71	65
CNG-4	20-27	671	671	322	320	5.07	5.00	34	31	15	15	23	21
CNG-5	20-27	610	610	299	300	3.90	4.00	42	40	14	12	14	16
SUN1	20-27	884	884	380	382	4.68	4.23	8	7	4	4	92	93
SUN2	20-27	732	732	368	367	3.12	3.02	20	22	8	7	57	55
SUN3	20-27	854	854	575	570	7.80	7.50	31	30	18	16	85	86
SUN4	20-27	915	915	483	480	8.58	8.53	51	52	24	21	19	20
SUN5	20-27	1037	1037	575	573	11.7	11.00	37	35	35	32	1	1
SKB-2	20-27	671	671	299	300	3.90	4.00	6	5	3	3	91	90
SKB-3	20-27	610	610	207	205	5.46	5.34	40	41	23	21	70	72
SKB-4	20-27	854	854	345	341	5.07	5.00	12	10	7	6	92	90
SKB-5	20-27	732	732	276	273	3.90	3.70	3	3	13	12	443	445
SKB-6	20-27	732	732	288	285	1.95	2.00	3	3	6	6	283	285
SKB-8	20-27	636	636	276	270	3.90	4.00	2	2	3	3	195	200
SKB-9	20-27	549	549	230	230	3.90	4.00	4	4	2	2	231	232
SKB-10	20-27	366	366	115	112	4.29	4.19	16	15	13	11	223	225
SKB-12	20-27	549	549	69	65	9.75	9.78	71	70	46	44	3	3
SKB-13	20-27	488	488	184	180	6.24	6.22	23	21	12	12	56	60
SKB-14	20-27	732	732	322	320	6.78	6.76	25	23	11	11	15	16
SKB-15	20-27	732	732	299	295	4.68	4.62	11	10	4	4	43	45
SKB-16	20-27	427	427	138	136	6.24	6.20	27	25	14	14	12	12

(continued)

Table A.1 (continued)

Sample ID	Depth (m)	HCO_3^-		Na^+		K^+		Ca^{2+}		Mg^{2+}		As(V)	
		Mar-04	Sep-04	Mar-04	Sep-04	Mar-04	Sep-04	Mar-04	Sep-04	Mar-04	Sep-04	Mar-04	Sep-04 µg/L
SKB-17	20-27	457	457	161	160	3.90	3.75	15	15	10	10	41	40
SKB-18	20-27	854	854	368	365	7.80	7.72	8	8	3	4	63	65
SKB-19	20-27	427	427	207	205	4.68	4.65	14	15	6	5	79	80
SKB-20	20-27	549	549	207	206	5.85	5.82	22	20	11	10	30	32
SKB-21	20-27	702	702	276	274	7.80	7.73	18	16	13	11	155	156
SKB-22	20-27	671	671	207	205	8.19	8.11	42	40	24	22	27	28
SKB-23	20-27	488	488	161	159	5.07	5.00	22	20	14	12	33	40
SKB24	20-27	549	549	230	232	3.90	4.00	9	9	5	5	38	39
MM-2	20-27	445	445	170	172	11.70	11.63	93	91	50	46	36	38
MM-3	20-27	457	457	161	160	15.60	15.56	84	80	36	32	10	12
MM-4	20-27	323	323	124	120	8.97	8.87	68	65	26	25	4	5
MM-5	20-27	549	549	460	464	39.00	40.00	84	80	55	51	8	9
MM-6	20-27	427	427	414	415	12.87	12.46	27	25	15	13	46	48
MM-7	20-27	610	610	253	250	19.50	19.30	73	70	33	30	23	25
MM-8	20-27	488	488	230	232	8.19	8.07	44	40	11	11	4	4
MM-9	20-27	458	458	253	250	9.36	9.31	51	50	26	22	5	5
MM-11	20-27	366	366	138	135	9.36	9.32	68	65	25	24	68	70
MM-12	20-27	213	213	46	48	5.85	5.80	56	53	19	15	42	45
MM-14	20-27	201	201	46	43	5.46	5.42	36	32	18	16	134	135
MM-15	20-27	549	549	368	365	8.97	8.92	29	28	12	10	70	71
MM-16	20-27	506	506	299	296	7.80	7.74	38	35	61	58	75	74
MM-17	20-27	610	610	276	274	2.73	2.70	5	5	2	2	424	420

(continued)

Table A.1 (continued)

Sample ID	Depth (m)	F^-		Cl^-		Br^-		$NO_3{-}N$		PO_4^{3-}		SO_4^{2-}	
		Dry	October	April	October	April	October	April	October	April	October	April	October mg/L
WP-1	20-27	6.08	6.00	13	12	bdl	bdl	bdl	bdl	bdl	bdl	72	72
WP-3	20-27	5.70	5.50	113	100	0.22	0.2	5.88	6.00	bdl	bdl	241	241
WP-4	20-27	3.80	3.76	42	40	bdl	bdl	2.52	2.50	bdl	bdl	98	100
WP-5	20-27	6.65	6.60	129	126	0.66	0.56	2.38	2.38	bdl	bdl	240	245
WP-7	20-27	7.03	7.00	96	94	0.26	0.24	bdl	bdl	bdl	bdl	288	290
WP-8	20-27	7.98	7.90	103	100	0.24	0.24	bdl	bdl	bdl	bdl	254	260
WP-9	20-27	8.36	8.32	66	60	0.17	0.17	bdl	bdl	0.5	0.5	221	225
WP-10	20-27	11.02	11.00	71	70	0.18	0.18	bdl	bdl	bdl	bdl	206	210
WP-11	20-27	2.09	2.00	16	16	bdl	bdl	bdl	bdl	2.0	2.0	72	75
KAD-1	20-27	7.60	7.50	241	240	0.60	0.60	bdl	bdl	bdl	bdl	624	630
KAD-2	20-27	7.80	7.60	216	213	0.55	0.51	1.96	1.87	bdl	bdl	624	628
KAD-6	20-27	11.0	11.00	250	250	0.57	0.52	bdl	bdl	bdl	bdl	576	580
KAD-7	20-27	12.2	12.00	214	207	0.50	0.46	bdl	bdl	bdl	bdl	672	680
KAD-8	20-27	9.50	9.30	213	210	0.53	0.53	bdl	bdl	bdl	bdl	528	532
KAD-10	20-27	19.0	19.00	184	180	0.50	0.50	bdl	bdl	bdl	bdl	528	530
KAD-11	20-27	13.3	13.00	238	235	bdl	bdl	bdl	bdl	bdl	bdl	624	628
KAD-12	20-27	9.50	9.30	177	176	0.50	0.47	bdl	bdl	bdl	bdl	480	492
KLW1	20-27	3.23	3.20	43	42	0.17	0.14	bdl	bdl	bdl	bdl	192	200
KLW3	20-27	9.50	9.20	32	32	bdl	bdl	bdl	bdl	0.5	0.3	178	180
KLW4	20-27	2.70	2.50	42	42	bdl	bdl	bdl	bdl	bdl	bdl	192	200
KLW5	20-27	7.60	7.50	36	35	bdl	bdl	0.84	0.80	bdl	bdl	144	145
KLW6	20-27	19.0	19.00	50	51	0.15	0.13	bdl	bdl	bdl	bdl	264	270
KLW7	20-27	11.4	11.00	34	32	bdl	bdl	0.7	0.70	bdl	bdl	168	170

(continued)

Table A.1 (continued)

Sample ID	Depth (m)	F^-		Cl^-		Br^-		$NO_3{-}N$		PO_4^{3-}		SO_4^{2-}	
		Dry	October	April	October	April	October	April	October	April	October	April	October mg/L
KLW8	20-27	17.9	17.00	200	201	0.50	0.46	2.52	2.50	bdl	bdl	576	580
KLW9	20-27	19.0	18.70	163	164	0.35	0.35	bdl	bdl	bdl	bdl	432	442
KLW10	20-27	17.7	17.40	62	60	bdl	bdl	bdl	bdl	bdl	bdl	192	198
KLW11	20-27	19.0	19.00	167	162	0.40	0.40	0.14	0.10	bdl	bdl	408	410
KLW12	20-27	17.7	17.80	217	215	0.45	0.42	bdl	bdl	1.2	1.0	576	580
KLW13	20-27	16.0	16.10	344	341	0.83	0.8	1.12	1.10	bdl	bdl	912	920
KLW14	20-27	14.1	14.00	220	220	0.45	0.41	bdl	bdl	bdl	bdl	624	630
KLW15	20-27	10.1	10.00	328	322	0.71	0.71	3.92	3.90	bdl	bdl	864	870
KLW16	20-27	3.99	4.00	160	158	0.43	0.43	10.64	10.00	bdl	bdl	384	385
KLW17	20-27	7.98	8.00	249	246	0.53	0.53	2.38	2.38	bdl	bdl	672	680
KLW18	20-27	3.99	4.00	18	18	bdl	bdl	bdl	bdl	1.2	1.0	48	50
KLW19	20-27	8.93	9.00	107	103	0.27	0.27	2.24	2.20	0.8	0.6	336	340
KLW20	20-27	14.1	14.00	51	50	bdl	bdl	2.8	2.80	bdl	bdl	192	190
KLW21	20-27	6.46	6.40	34	32	bdl	bdl	bdl	bdl	bdl	bdl	96	96
KLW22	20-27	21.1	21.00	17	16	bdl	bdl	0.42	0.42	bdl	bdl	96	101
KLW23	20-27	10.3	10.00	39	37	0.12	0.12	bdl	bdl	bdl	bdl	187	190
KLW24	20-27	6.08	6.00	21	20	0.07	0.07	bdl	bdl	bdl	bdl	96	100
KLW26	20-27	8.36	8.30	16	15	bdl	bdl	bdl	bdl	bdl	bdl	82	85
KLW27	20-27	22.8	23.00	18	16	bdl	bdl	bdl	bdl	0.5	0.3	126	128
MPU-1	20-27	0.12	0.10	213	214	0.63	0.63	bdl	bdl	bdl	bdl	605	610
MPU-2	20-27	0.57	0.55	62	62	0.20	0.20	bdl	bdl	bdl	bdl	211	218
MPU-3	20-27	0.19	0.15	200	200	0.70	0.70	bdl	bdl	bdl	bdl	960	976

(continued)

Table A.1 (continued)

Sample ID	Depth (m)	F^-		Cl^-		Br^-		NO_3−N		PO_4^{3-}		SO_4^{2-}	
		Dry	October	April	October	April	October	April	October	April	October	April	October mg/L
ARK-2	20-27	0.38	0.30	4	4	bdl	bdl	bdl	bdl	bdl	bdl	48	50
ARK-3	20-27	0.65	0.62	5	5	0.04	0.04	0.42	0.40	bdl	bdl	38	42
ARK-4	20-27	0.61	0.58	6	6	0.04	0.04	0.42	0.38	bdl	bdl	72	76
ARK-5	20-27	0.31	0.30	61	60	0.09	0.09	7.84	8.00	bdl	bdl	144	145
ARK-6	20-27	0.38	0.30	25	23	0.05	0.05	0.42	0.40	bdl	bdl	67	68
ARK-7	20-27	0.59	0.55	39	35	0.09	0.09	bdl	bdl	bdl	bdl	110	115
DN-1	20-27	0.76	0.70	122	120	0.33	0.33	2.52	2.52	bdl	bdl	192	196
DN-2	20-27	2.85	2.80	81	78	1.80	1.80	1.26	1.20	bdl	bdl	240	245
DN-3	20-27	6.08	6.00	136	135	0.30	0.30	18.9	20.00	bdl	bdl	240	242
DN-4	20-27	2.47	2.42	36	32	bdl	bdl	1.4	1.40	bdl	bdl	144	148
DN-5	20-27	5.13	5.00	110	113	0.33	0.31	3.36	3.30	bdl	bdl	144	143
DN-6	20-27	15.4	15.00	12	10	bdl	bdl	bdl	bdl	bdl	bdl	96	98
NK-1	20-27	1.71	1.70	56	52	0.15	0.11	0.7	0.70	bdl	bdl	192	198
NK-2	20-27	0.61	0.60	14	13	bdl	bdl	0.42	0.40	bdl	bdl	96	100
NK-3	20-27	0.57	0.55	64	61	0.16	0.16	0.42	0.40	bdl	bdl	194	200
NK-4	20-27	1.33	1.30	70	67	0.18	0.18	bdl	bdl	bdl	bdl	240	242
NK-5	20-27	11.4	11.00	20	18	bdl	bdl	bdl	bdl	bdl	bdl	96	98
NK-6	20-27	8.40	8.00	57	52	0.14	0.14	0.70	0.65	bdl	bdl	168	170
KA-1	20-27	1.14	1.10	75	73	0.20	0.20	0.14	0.10	bdl	bdl	192	199
KA-2	20-27	2.09	2.00	54	52	0.17	0.17	1.54	1.51	0.7	0.6	216	219
KA-3	20-27	4.37	4.32	121	120	0.30	0.26	11.48	12.00	bdl	bdl	288	294
BP-1	20-27	3.99	4.00	52	50	0.14	0.14	1.96	2.00	bdl	bdl	170	174

(continued)

Table A.1 (continued)

Sample ID	Depth (m)	F^-		Cl^-		Br^-		$NO_3{-}N$		PO_4^{3-}		SO_4^{2-}	
		Dry	October	April	October	April	October	April	October	April	October	April	October mg/L
BP-2	20-27	12.0	12.00	41	38	0.11	0.11	2.52	3.00	bdl	bdl	145	148
BP-3	20-27	1.01	1.00	43	41	0.12	0.12	0.42	0.40	bdl	bdl	67	70
JK-1	20-27	13.3	13.00	224	221	bdl	bdl	10.5	10.00	bdl	bdl	638	642
JK-2	20-27	9.50	9.30	390	387	1.02	1.00	10.0	10.00	bdl	bdl	576	576
RPNA1	20-27	4.56	4.45	107	104	0.25	0.25	2.59	2.52	bdl	bdl	500	507
RPNA2	20-27	1.71	1.65	144	140	0.27	0.27	10	10.00	bdl	bdl	355	359
CCO1	20-27	2.28	2.23	15	14	bdl	bdl	bdl	bdl	bdl	bdl	72	75
CCO2	20-27	1.71	1.7	10	9	bdl	bdl	bdl	bdl	bdl	bdl	36	38
ZAB-1	20-27	3.80	3.6	213	205	bdl	bdl	7.00	7.00	bdl	bdl	480	487
ZAB-2	20-27	8.36	8.35	252	252	bdl	bdl	7.56	7.00	bdl	bdl	480	486
ZAB-3	20-27	7.60	7.6	295	290	bdl	bdl	5.60	5.60	bdl	bdl	532	538
ZAB-4	20-27	3.80	3.7	415	409	0.64	0.61	14.00	14.00	bdl	bdl	960	968
ZAB-5	20-27	5.70	5.5	355	351	bdl	bdl	10.50	10.00	bdl	bdl	821	828
KLW25	40-80	2.28	2.25	7	6	bdl	bdl	bdl	bdl	bdl	bdl	96	100
ARK-1	40-80	0.30	0.3	4	4	bdl	bdl	bdl	bdl	bdl	bdl	24	28
ARK-8	40-80	0.38	0.35	4	4	bdl	bdl	bdl	bdl	bdl	bdl	29	32
WP-6	40-80	0.95	0.9	67	62	0.14	0.14	bdl	bdl	bdl	bdl	148	151
SKB-1	40-80	2.28	2.23	96	95	0.30	0.30	bdl	bdl	bdl	bdl	288	293
SKB-11	40-80	2.66	2.62	9	9	0.04	0.04	0.70	0.70	bdl	bdl	62	65
MM-10	40-80	0.57	0.5	14	13	0.06	0.06	0.28	0.24	bdl	bdl	48	50
KAD-3	40-80	0.44	0.4	57	54	0.15	0.11	0.28	0.20	bdl	bdl	134	137
KAD-4	40-80	0.44	0.4	5	5	bdl	bdl	0.28	0.25	bdl	bdl	30	34
KAD-5	40-80	4.20	4	117	115	0.28	0.24	0.56	0.53	bdl	bdl	225	228

(continued)

Table A.1 (continued)

Sample ID	Depth (m)	F^-		Cl^-		Br^-		NO_3-N		PO_4^{3-}		SO_4^{2-}	
		Dry	October	April	October	April	October	April	October	April	October	April	October mg/L
KAD-9	40-80	2.09	2.00	249	246	0.54	0.50	bdl	bdl	bdl	bdl	480	485
KLW-29	40-80	2.32	2.30	36	34	bdl	bdl	bdl	bdl	bdl	bdl	96	98
CNG-3	40-80	0.25	0.20	12	12	0.04	0.04	bdl	bdl	bdl	bdl	29	32
SKB-7	40-80	0.95	0.90	134	131	bdl	bdl	bdl	bdl	bdl	bdl	62	65
WP-2	80-200	1.03	1.00	100	97	0.25	0.25	0.70	0.64	bdl	bdl	341	345
SKB25	80-200	3.10	3.00	10	10	bdl	bdl	0.84	0.80	3.3	3.0	73	75
MM-1	80-200	1.33	1.25	78	75	0.30	0.30	0.70	0.62	bdl	bdl	215	218
MM-13	80-200	0.57	0.55	45	43	0.14	0.14	0.14	0.10	bdl	bdl	120	122
KLW2	80-200	0.78	0.72	159	155	0.40	0.36	bdl	bdl	bdl	bdl	240	245
KLW-28	80-200	0.95	0.93	25	23	bdl	bdl	bdl	bdl	bdl	bdl	77	80
ARK-9	80-200	0.59	0.53	71	70	0.18	0.15	bdl	bdl	bdl	bdl	144	148
ARK-10	80-200	0.50	0.50	19	16	bdl	bdl	bdl	bdl	bdl	bdl	32	38

Sample ID	Depth (m)	HCO_3^-		Na^+		K^+		Ca^{2+}		Mg^{2+}		As(V)	
		April	October	April	October	April	October	April	October	April	October	April	October µg/L
WP-1	20-27	518	518	219	215	3.90	3.87	13	11	7	7	33	30
WP-3	20-27	610	610	391	387	7.80	7.72	30	28	16	13	166	170
WP-4	20-27	519	519	276	272	3.90	3.86	5	5	2	2	242	245
WP-5	20-27	616	616	437	435	5.07	5.00	15	16	7	7	153	156
WP-7	20-27	550	550	391	386	5.46	5.34	16	18	10	10	69	70
WP-8	20-27	518	518	368	365	5.46	5.41	26	24	10	10	86	90
WP-9	20-27	610	610	368	362	4.68	4.65	14	13	7	7	46	50
WP-10	20-27	610	610	363	360	5.07	5.00	19	16	12	10	70	72
WP-11	20-27	488	488	230	232	2.73	2.69	4	4	2	2	677	675
KAD-1	20-27	549	549	621	620	7.80	7.60	17	16	9	6	42	40
KAD-2	20-27	549	549	621	621	7.80	7.65	13	12	8	7	142	145

(continued)

Table A.1 (continued)

Sample ID	Depth (m)	HCO_3^-		Na^+		K^+		Ca^{2+}		Mg^{2+}		As(V)	
		April	October	April	October	April	October	April	October	April	October	April	October µg/L
KAD-6	20-27	549	549	598	595	6.63	6.60	22	20	12	10	42	45
KAD-7	20-27	537	537	621	622	7.80	7.74	17	15	10	10	158	160
KAD-8	20-27	671	671	621	625	7.80	7.83	14	10	9	9	10	10
KAD-10	20-27	793	793	621	618	6.24	6.21	26	23	9	9	62	65
KAD-11	20-27	1037	1037	782	778	8.97	8.78	30	27	16	13	34	35
KAD-12	20-27	915	915	621	623	7.80	7.72	25	23	14	12	171	172
KLW1	20-27	805	805	345	342	7.80	7.81	35	32	13	11	38	40
KLW3	20-27	854	854	414	410	4.29	4.22	8	8	3	3	615	618
KLW4	20-27	793	793	345	342	4.68	4.65	22	20	15	12	90	92
KLW5	20-27	793	793	345	344	7.80	7.82	16	15	6	6	82	80
KLW6	20-27	854	854	460	462	5.85	5.80	21	20	2	2	131	135
KLW7	20-27	671	671	334	331	5.85	5.81	16	15	6	6	159	162
KLW8	20-27	915	915	713	710	7.80	7.75	26	23	11	9	217	215
KLW9	20-27	701	701	552	550	11.70	11.56	19	18	2	2	213	211
KLW10	20-27	976	976	460	455	3.90	3.82	12	10	16	15	234	234
KLW11	20-27	841	841	575	573	5.85	5.80	21	23	14	13	157	152
KLW12	20-27	915	915	736	731	5.85	5.82	23	20	12	10	103	101
KLW13	20-27	1281	1281	1058	1045	12.09	12.00	27	25	30	27	111	108
KLW14	20-27	945	945	736	732	7.80	7.74	30	32	17	15	79	79
KLW15	20-27	1281	1281	1012	1008	11.70	11.62	32	30	22	20	185	186
KLW16	20-27	549	549	483	481	5.46	5.42	13	11	9	9	250	252
KLW17	20-27	1098	1098	805	801	8.58	8.55	27	25	22	20	137	135
KLW18	20-27	732	732	299	300	3.90	3.86	5	5	3	3	2400	2409
KLW19	20-27	1037	1037	575	571	6.63	6.61	14	16	10	12	460	462
KLW20	20-27	915	915	460	462	4.68	4.62	5	5	3	3	634	638
KLW21	20-27	702	702	311	308	3.90	3.87	7	7	6	6	23	25
KLW22	20-27	671	671	288	285	4.68	4.62	12	10	9	9	120	122

(continued)

Table A.1 (continued)

Sample ID	Depth (m)	HCO_3^-		Na^+		K^+		Ca^{2+}		Mg^{2+}		As(V)	
		April	October	April	October	April	October	April	October	April	October	April	October µg/L
KLW23	20-27	793	793	391	389	5.07	5.00	16	16	7	7	30	32
KLW24	20-27	671	671	276	273	5.46	5.41	24	23	8	7	639	635
KLW26	20-27	610	610	253	250	3.90	3.88	13	11	5	5	52	50
KLW27	20-27	793	793	368	365	3.90	3.82	6	6	2	2	124	125
MPU-1	20-27	915	915	667	663	7.80	7.76	50	52	11	10	64	62
MPU-2	20-27	610	610	299	287	6.24	6.22	34	31	14	12	59	55
MPU-3	20-27	1159	1159	805	801	11.70	11.72	57	53	23	21	52	50
ARK-2	20-27	335	335	23	21	7.80	7.78	99	92	10	9	8	8
ARK-3	20-27	195	195	23	20	4.68	4.62	54	51	7	7	56	55
ARK-4	20-27	244	244	30	27	4.68	4.61	69	65	14	12	2	2
ARK-5	20-27	366	366	51	48	23.4	23.1	138	135	20	18	1	1
ARK-6	20-27	274	274	23	20	5.85	5.82	91	86	14	16	40	42
ARK-7	20-27	305	305	46	43	27.30	27.24	104	101	9	8	73	70
DN-1	20-27	610	610	299	289	7.80	7.76	52	50	28	25	8	8
DN-2	20-27	640	640	345	343	7.80	7.72	46	42	22	20	31	30
DN-3	20-27	915	915	506	500	11.70	11.65	27	26	18	15	8	8
DN-4	20-27	671	671	299	292	7.80	7.78	27	24	18	15	33	30
DN-5	20-27	610	610	276	273	11.70	11.62	48	46	2	2	37	35
DN-6	20-27	732	732	276	272	7.80	7.74	64	61	8	8	38	35
NK-1	20-27	610	610	276	270	7.80	7.75	43	41	15	13	61	60
NK-2	20-27	793	793	230	228	15.60	15.52	66	62	35	32	39	35
NK-3	20-27	671	671	253	250	11.70	11.65	60	63	26	24	65	62
NK-4	20-27	488	488	253	251	11.70	11.62	44	42	25	23	41	40
NK-5	20-27	915	915	368	365	15.60	15.52	11	10	6	6	46	42
NK-6	20-27	854	854	391	387	11.70	11.63	17	15	8	8	94	96
KA-1	20-27	610	610	253	251	8.97	8.92	47	45	28	25	177	175

(continued)

Table A.1 (continued)

Sample ID	Depth (m)	HCO_3^-		Na^+		K^+		Ca^{2+}		Mg^{2+}		As(V)	
		April	October	April	October	April	October	April	October	April	October	April	October µg/L
KA-2	20-27	671	671	368	365	3.90	4.00	6	6	3	3	621	623
KA-3	20-27	610	610	368	366	11.70	11.68	37	36	21	20	392	390
BP-1	20-27	549	549	299	300	5.07	5.00	21	20	6	5	109	106
BP-2	20-27	494	494	276	271	4.29	4.25	10	8	4	4	40	42
BP-3	20-27	213	213	69	65	4.68	4.62	39	35	17	16	54	52
JK-1	20-27	1019	1019	851	845	12.87	12.8	12	10	11	10	103	100
JK-2	20-27	976	976	874	872	46.80	46.78	54	52	45	43	6	6
RPNA1	20-27	494	494	445	442	11.7	11.62	23	21	14	12	23	20
RPNA2	20-27	495	495	239	235	23.4	23.24	4	4	5	5	70	65
CCO1	20-27	427	427	19	17	19.5	20.00	66	60	47	46	1	1
CCO2	20-27	366	366	12	10	27.3	27.34	60	62	31	30	1	1
ZAB-1	20-27	671	671	598	595	9.75	9.70	6	6	2	2	56	53
ZAB-2	20-27	590	590	575	570	15.60	15.62	14	15	8	7	27	25
ZAB-3	20-27	488	488	598	594	9.75	9.70	8	8	7	6	32	30
ZAB-4	20-27	518	518	874	870	19.50	1.46	14	16	12	10	22	20
ZAB-5	20-27	793	793	897	893	15.60	15.52	15	13	13	12	14	12
KLW25	40-80	732	732	207	204	7.80	7.75	53	50	21	20	80	78
ARK-1	40-80	153	153	16	15	3.90	3.93	39	35	6	6	53	50
ARK-8	40-80	183	183	16	15	3.90	3.91	45	42	7	7	881	878
WP-6	40-80	244	244	115	113	5.85	5.80	55	52	14	12	68	65
SKB-1	40-80	732	732	322	320	8.58	8.55	58	55	37	35	91	90
SKB-11	40-80	610	610	184	181	7.80	7.87	29	25	21	20	34	32
MM-10	40-80	366	366	92	90	3.90	3.85	46	44	12	10	52	50
KAD-3	40-80	213	213	69	65	5.85	5.80	55	53	28	25	24	20
KAD-4	40-80	165	165	28	25	3.12	3.08	30	34	8	8	25	22
KAD-5	40-80	213	213	115	113	7.80	7.78	72	73	40	43	22	20

(continued)

Table A.1 (continued)

Sample ID	Depth (m)	HCO_3^-		Na^+		K^+		Ca^{2+}		Mg^{2+}		As(V)	
		April	October	April	October	April	October	April	October	April	October	April	October µg/L
KAD-9	40-80	244	244	322	320	6.63	6.61	73	72	33	30	64	62
KLW-29	40-80	549	549	276	272	3.90	3.87	28	25	9	9	672	670
CNG-3	40-80	183	183	46	43	1.95	1.90	28	26	6	6	45	44
SKB-7	40-80	610	610	299	295	4.68	4.62	19	15	14	12	61	60
WP-2	80-200	439	439	306	303	6.24	6.20	54	52	18	16	60	58
SKB25	80-200	671	671	276	274	4.00	3.98	6	7	4	4	242	240
MM-1	80-200	262	262	124	121	8.58	8.55	76	72	21	20	80	82
MM-13	80-200	263	263	92	90	4.68	4.62	50	45	21	20	611	610
KLW2	80-200	610	610	283	280	7.80	7.82	75	72	36	32	38	35
KLW-28	80-200	244	244	62	60	4.00	4.03	60	56	5	5	43	40
ARK-9	80-200	146	146	23	20	7.80	7.86	86	82	26	22	50	52
ARK-10	80-200	244	244	92	90	6.63	6.60	19	16	19	18	8	8

Note Abbreviations for villages are the same as in those Table 2.1
n.a represents not analyzed
bdl stands for below detection limit
detection limits are the same as in Table 4.1
n.d stands for not detected. Detection limit for As^{III} is 5ppb

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Sources of Pollution, Discussion: Case Study

5

5.1 Probable Anthropogenic Sources of Pollutants

Although As and F^{-} polluted groundwaters are well known to occur naturally in many parts of the world, the present study shows the significant contribution of anthropogenic sources for these elements in association with SO_4^{2-} and NO_3 in the studied groundwaters. In present study area the average concentration of soil As is 10 mg/kg which is comparably higher than the soils unaffected by human activities (Wauchope 1983; Shacklette and Boerngen 1984).

The anthropogenic sources of As and F^{-} has been well described in Chap. 1; among these anthropogenic sources phosphate fertilizers, coal combustion and the industrial waste seems to increase the As, F^{-} and SO_4^{2-} concentrations, while the animal, human and household waste increase the concentrations of SO_4^{2-} and $NO_{3,}$ significantly to the soils and ultimately into the groundwaters.

5.1.1 Contribution of Coal Combustion

Burning mineralized coal is known to emit toxic elements such as As and F^{-} (Robert et al. 2002). In the southwest Guizhou Province, 3,000 people have been affected by As and F^{-} pollution due to domestic combustion of coal, which contains highly concentrated As (Ding et al. 2001). People are ingesting those elements directly from the air inside local residences, and indirectly from the contaminated groundwater (Zheng et al. 1996).

The presence of high concentrations of As near the brick kilns (Fig. 5.1) suggests the contribution of As and F^{-} due to combusted coal in the study area. The As and F^{-} contamination process of those elements in our studied area seems to be analogous to the case in China. Coal samples contained total F^{-} ranging 5.12–20.1 mg/kg with an average value of 10.2 mg/kg, while, samples contain As ranging from 4 to 12 mg/kg with an average value of 8 mg/kg. In the study area, coal is combusted in the open air, thus the direct effects from the air on the people are not as serious as in the case in China. However, the semiarid climate can promote intense soil pollution due to the condensation of those elements, causing more serious groundwater contamination.

Atmospheric precipitation, surface water, and aquifer materials are potential sources of As in ground water. Precipitation in unpolluted areas generally contains much less than 1 µg/L dissolved As (Andreae 1980). Substantially greater concentrations have been found in precipitation affected by anthropogenic sources. For instance, As concentrations averaging 17 µg/L (Crecelius 1975) were found in rain and snow collected downwind from a smelter (now dismantled) in

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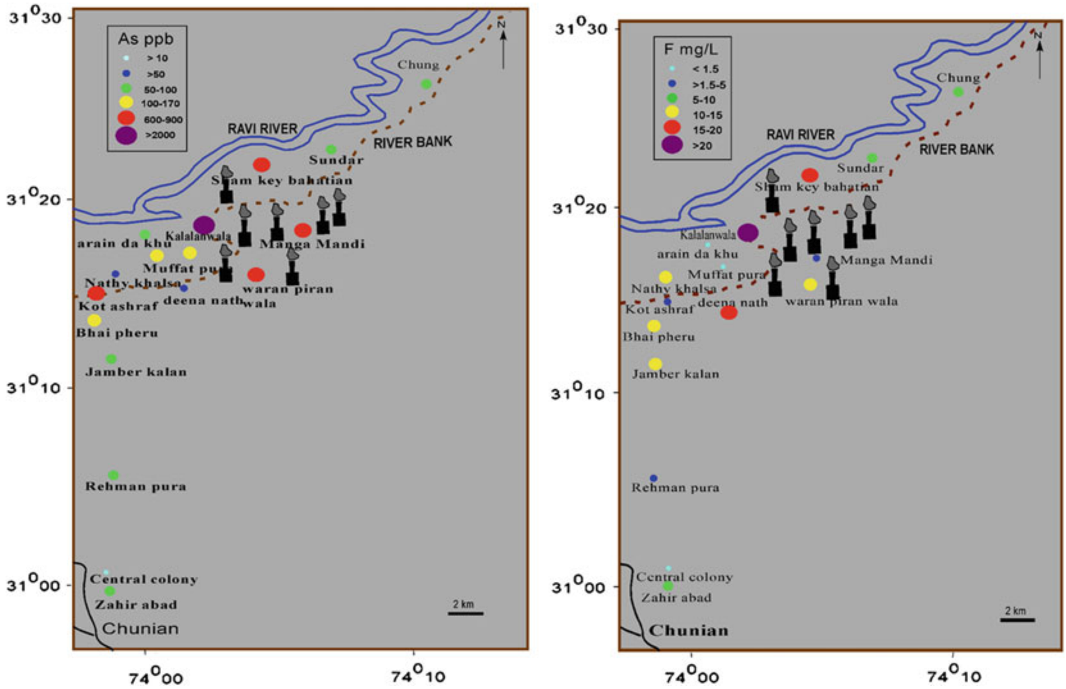


Fig. 5.1 Topographic distribution of As and F^{-} in the groundwater of Kalalanwala and its surrounding villages

Tacoma, Washington. In the present study area the SO_2 concentrations in the ambient air was 133–212 µg/m^3/h in Lahore (Punjab EPD 1998–99). High concentration of As (<10–90 µg/L), with SO_4^{2-} (5–14 mg/L) in the local rainwater has been reported. Although the concentration of SO_2 in ambient air is lower than the WHO standard for SO_2 in air, i.e. 350 µg/m^3/h, the presences of As in the air and rainwater support that those elements in the studied groundwater are partly derived via ambient air.

5.1.2 Contribution of Phosphate Fertilizers

Based on the preliminary results of Kalalanwala groundwater analysis and the detection of As and F^{-} in rainwater, it was hypothesized that As and F^{-} are in part contributed by the coal combusted by brick factories in the area. However, the topographic distribution of As and F^{-} in the groundwater from the extended study shows the presence of two or more anthropogenic sources for As and F^{-}, since highly concentrated groundwaters observed in four villages (KLW, SKB, WP and MM) are not always corresponding to the F^{-} concentrated waters found in KLW, SKB and WP. Especially, the low F^{-} concentrations of groundwater from MM imply the presence of another big source than the coal combusted in the brick kilns in and around MM (Fig. 5.1). Fluoride can be released in the environment from phosphate fertilizers, which include fluorine as an impurity (Pickering 1985; Skjelkvale 1994), from 1.3 to 3.0 %. Soil fluorine concentration continues to increase in cultivated soils receiving regular applications of phosphate fertilizer causing a future risk to groundwater quality. Pakistan is an agricultural country and its economy mostly depends on the agriculture. The annual consumption of fertilizers in 1999 was 2,824 thousands metric tonnes with 129 kg/ha cropland in Pakistan and mostly in Punjab (http://earthtrends.wri.org).

The locally consumed fertilizers contained soluble F^- ranging from 60 to 255 mg/kg with an average value of 175 mg/kg, while, water soluble As in fertilizers (DAP) is estimated to be 5–10 mg/kg with an average value of 7.4 mg/kg. The topographic distribution of As and F^- and the presence of very high concentrations of soluble F^- in fertilizers suggests that phosphate fertilizers are among the significant anthropogenic sources of F^- in the area, while, As in fertilizers would be the minor pollutant source of surface soil and underlying groundwater associating with cultivation in the study area.

Application of phosphate fertilizers changes the aquifer condition to release As into the ground water. Laboratory studies suggest that As was released into the coexisting water from the soils contaminated with lead arsenate when phosphate was applied. Application of phosphate onto uncontaminated soil also may increase arsenic concentrations in ground water due to releasing adsorbed As (Woolson et al. 1971; Davenport and Peryea 1991). Thus, the As could be released into the studied groundwater associating with the excessive application of phosphate fertilizers if this element was derived from the different source materials.

5.1.3 Contaminated Soils—The Evidence of Anthropogenic Sources

As noted that five end members can be presumed to explain the sources of high As, and F^- of the studied soils (points A, B, C, D and E in Figs. 5.2 and 5.3). Point A is for the background soil, which

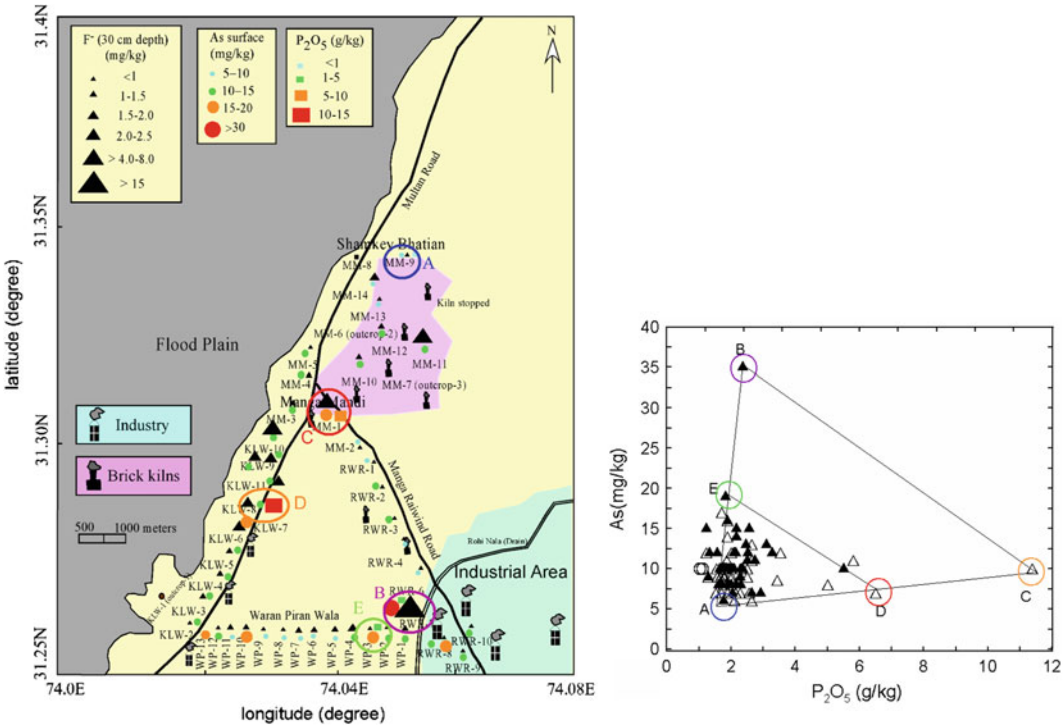


Fig. 5.2 End members identified in the study area based on the As distribution and in relation to As and P_2O_5

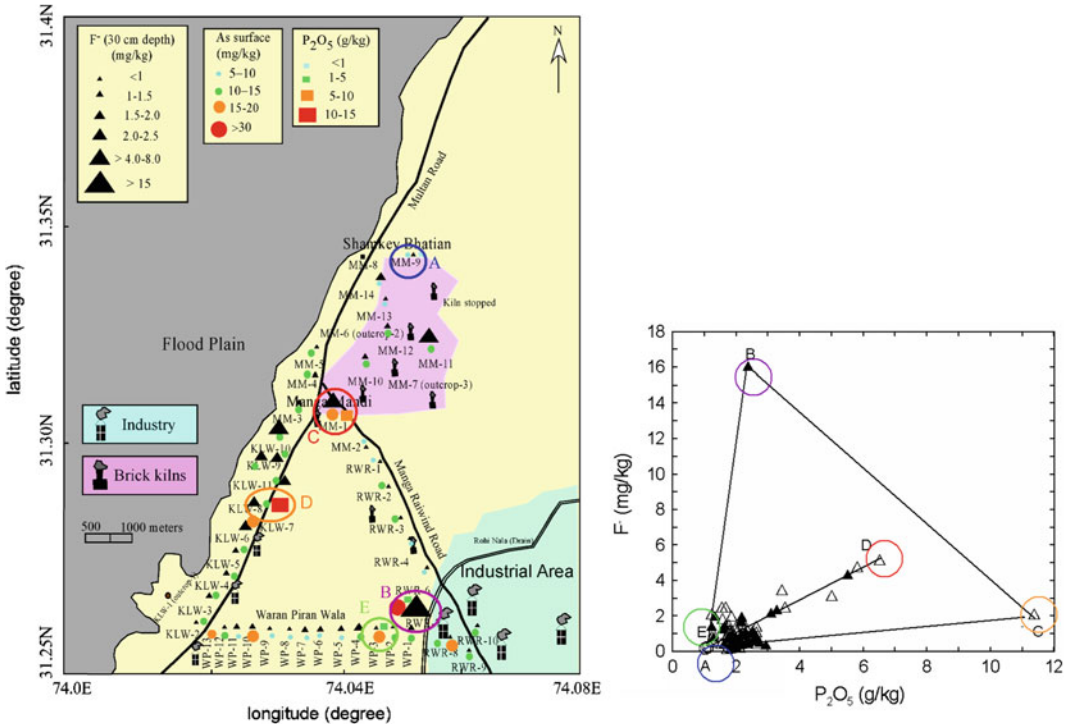


Fig. 5.3 End members identified in the study area based on the F^{-} distribution and in relation to F^{-} and P_2O_5

is almost free of contamination, free from F^{-} (<0.1 mg/kg), As 5 mg/kg and 1–2 g/kg of P_2O_5. End member B highly contains both As (35 mg/kg) and F^{-} (16 mg/kg), and P_2O_5 (2.1 g/kg). The end member B (RWR-7B) is a surface samples collected near the industrial zone which is located at the eastern part along Manga Mandi Raiwind road. This area is a famous industrial zone for fertilizer and other chemicals. Those factories do not have any waste treatment plants, and, the waste material is directly dumped outside or drained out. Thus, enormously high concentrations of As and F^{-} of this end member (B) would be the result of industrial activities.

End member C (KLW-8A) was a soil taken from 30 cm depth from the surface. This soil contain high P_2O_5 (11.4 g/kg), moderate F^{-} (2.1 mg/kg) and As (10 mg/kg). This end member must represent contribution of phosphate fertilizers consumed in the area, since the locally consumed fertilizers contained 55–265 mg/kg of F^{-} and As 5–10 mg/kg with an average value of 7.4 mg/kg. Phosphate fertilizers were introduced in Pakistan in 1959/60. Fertilizer consumption has increased threefold during the past 30 years; it reached one million nutrient tonnes in 1980/81, two million tonnes in 1992/93 and three million tonnes in 2002/03. It is projected that over the next 10 years fertilizer nutrient consumption will grow at the rate of 2–3 % per annum. Punjab has the largest agricultural area and therefore consumes the greatest share of fertilizers (FAO 1996).

End member D contains P_2O_5 concentration of 6.50 g/kg, high F^{-} 5.2 and As 7.0 mg/kg. This end member D is not derived from only one source(s), rather this end member represents the mixed anthropogenic sources e.g. fertilizers, waste material of industries and coal combusted in the study area. The F^{-} with increasing P_2O_5 concentration is possible due to the fertilizers used in the study area and the contribution of F^- by coal combustion (coals contain F^- 5.12–20.1 mg/kg with an average value of 10 mg/kg and As 4–12 mg/kg with average value of 8 mg/kg; while As is contributed mostly by the coal combusted in the study area.

The end member E that contains high As 19 mg/kg, low F^- (<0.1 mg/kg) and low P_2O_5 (1.8 g/kg) must represent contribution of air born As by brick factories or industries via dry deposition in the area. Arsenic in the ambient air in the Lahore district is 230–2,230 ng/m^3 (JICA and Pakistan EPA 2000), which is much higher than those reported in the other areas in the world; e.g. 91–512 ng/m^3 in Calcutta, India (Chakraborti et al. 1992), 25 ng/m^3 in Wuhan City, China (Waldman et al. 1991), and 1.2–44 ng/m^3 in Los Angles, USA (Rabano et al. 1989).

From these results it is concluded that fertilizers (DAP) consumed in the study area would be the most important as an anthropogenic source of F^-, while the presence of As in rainwater coal samples 4–12 mg/kg with average value of 8 mg/kg (though not so high) shows the contribution of combusted coal; and air born As, moreover, the high concentrations of As and F^- are also contributed by the presence of industries (Phosphate fertilizer and chemical industries) and the waste disposal by the factories in the surroundings of the study area.

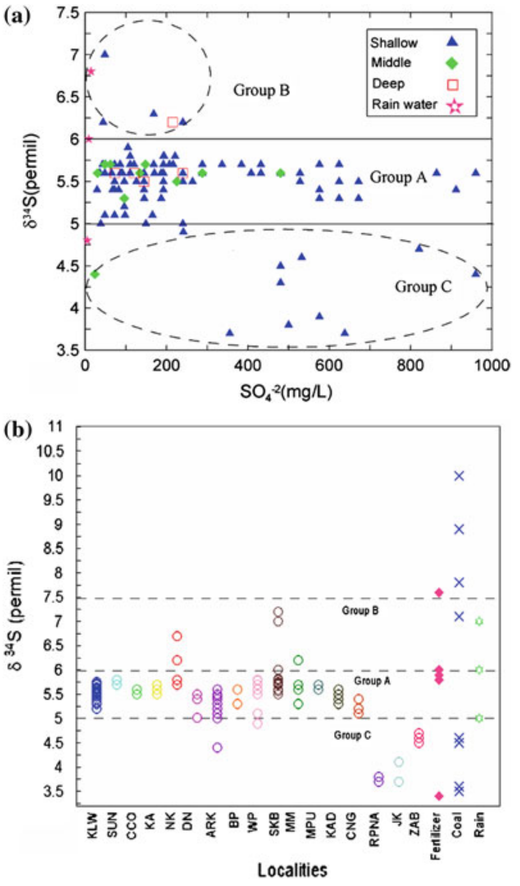


Fig. 5.4 **a**, **b** The relationship between sulfur isotope values and sulfate concentrations (**a**), and the sulfur isotope ratios of groundwater samples corresponding to the sampling villages, coal, fertilizers and rainwater samples (**b**)

5.1.4 Sulfate and Sources of Sulfur in Rainwater and Groundwater

Sulfur isotopic composition is an efficient tool for tracing and identifying the SO_4^{2-} pollutant sources. Anthropogenic sulfates mainly derived from fertilizers (DAP) and detergents are the major pollutant sources of the studied groundwaters. SO_x produced by fossil fuel combustion, is another source of anthropogenic sulfur in the study area. The oxidized sulfur compounds, originated from the combustion of coal occur in variety of solid, liquid and gaseous phases in the atmosphere. Such pollutants finally deposit upon the soil surface via either dry or wet fall out processes.

The δ^{34}S values of the studied groundwaters range from +3.7 to +7.0 ‰ with average value of 6.2 ‰. As shown before three groups were identified from the data (Fig. 5.4a); groundwaters having constant δ^{34}S values (5.5–5.7 ‰) irrespective to the SO_4^{2-} concentration (A), those with high δ^{34}S values (6.3–7.0 ‰) and low SO_4^{2-} (B), those with low δ^{34}S values (3.7–4.8 ‰) and high SO_4^{2-} (C).

The $\delta^{34}S$ values of rainwater (n = 3) is 5.0–7.0 ‰. The $\delta^{34}S$ values of coal collected from the study area (n = 8) range within 3.5–10 ‰ with an average value of 6.2 ‰, close to the average value of $\delta^{34}S$ of Chinese coal +6.9 ‰ (Ohizumi et al. 1997). Large amount of agricultural fertilizer have been added to the soils of the study area over past 20 years (FAO 2004). The currently applied superphosphate fertilizers include SO_4^{2-} as impurities giving the $\delta^{34}S$ values (DAP, n = 5) within 3.4–7.6 ‰ with the mean value of 5.7 ‰. The $\delta^{34}S$ values of fertilizers from China mostly superphosphate ranged from −5.6 to +8.9 ‰ (Li et al. 2006), while in England the $\delta^{34}S$ of fertilizers (superphosphate) was between +5.4 and +8.5 (Moncaster et al. 2000).

In group A, all samples had $\delta^{34}S$ values around 5.5–5.7 ‰ with widely varying SO_4^{2-} concentrations. One of the SO_4^{2-} sources must be the atmospheric pollution, since rainwater and coal samples also showed average $\delta^{34}S$ value around 6.0 ‰ and SO_4^{2-} concentration in the rain was 14 mg/L. The range is also concordant with the average $\delta^{34}S$ value of the fertilizers. Combining with the fact that considerable evaporation-condensation does not occur after the recharge, high SO_4^{2-} concentration in the groundwaters of this group must be caused by the fertilizers distributed in the study area, although the recharging water was already contaminated by air born sulfur.

The group B is characterized by the $\delta^{34}S$ values >6 ‰ with low SO_4^{2-} concentrations <250 mg/L. The maximum δ^{34} S value is 7.0 ‰, which is close to that of household detergents (+8.5 to +13.6 ‰; Laura et al. 2004; +15.2 to 17.2 ‰; Li et al. 2006).

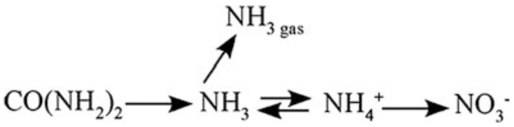
The group C groundwaters had low $\delta^{34}S$ and high SO_4^{2-} concentrations. All waters of this group were obtained from the villages RPNA, JK and ZAB, located at southwest of the study area in Fig. 5.7b, away from the brick kiln area. The effect of atmospheric pollution and fertilizers would be smaller in this area among the studied area (Fig. 5.4b). The sulfur source can not be well specified, since the $\delta^{34}S$ are overlapping between fertilizers and air pollutants. However, the SO_4^{2-} in the groundwaters of the study area appears generally to have originated from fertilizers, air pollutants and household waste water including detergent used in the area.

5.1.5 Nitrogen and Sources of Nitrogen

In 20 % of the studied groundwaters NO_3^-–N concentrations exceeded 10 mg/L, the WHO standard. The high NO_3^- containing groundwaters were found from the shallow tube wells installed inside the house yards, where the house owners raise live stocks. Also there is no sewer system in the local residences and the pit latrines directly connect with the unconfined groundwater aquifer. Thus, the major sources of this component should be the animal and human waste distributed in the study area.

The δ^{15} N_{NO3} isotopes were analyzed for 21 groundwaters to identify the sources of nitrogen contaminants. Most of the groundwater samples give δ^{15} N_{NO3} >5 ‰, with the maximum value 30 ‰ and the mean one 10 ‰ (Table 4.12).

The rise in NO_3^--N concentrations of groundwaters (5–30 ‰) is probably due to nitrogen from animal excrement. Nitrogen in excretory waste mainly appears as urea, which is hydrolyzed to NH_3 and converted to NH_4^+ and finally NO_3^- as follows:



$$CO(NH_2)_2 \longrightarrow \overset{\nearrow NH_{3\,gas}}{NH_3} \rightleftarrows NH_4^+ \longrightarrow NO_3^-$$

The hydrolysis of urea is associated with a rise in pH, promoting the formation of NH_3 which is easily lost by volatilization into the atmosphere. Volatilization and denitrification by microbial activities cause the N isotope fractionation to enrich in ^{15}N in soil, although those two processes can not increase δ^{15} N > 10 ‰ (Gormly and Spalding 1979). The kinetic fractionation accompanying the above hydrolysis and volatilization and the equilibrium fractionation between NH_3 and NH_4^+ result in the formation of NH_3 which is depleted in ^{15}N, while the reaming NH_4^+ is strongly enriched in ^{15}N. Most of this NH_4^+ is subsequently converted into ^{15}N-enriched NO_3^-.

The δ^{15} N_{NO3} of the groundwater samples are in the same range of those of animal waste as reported from literatures; e.g., the NO_3 originating from animal excrement displays δ^{15} N_{NO3} values typically in the range within +10 to 20 ‰ (Heaton 1986; Widory et al. 2005), and +8 to 25 ‰ (Fogg et al. 1998), implying that δ^{15} N_{NO3} in the study area is contributed by the animal and human waste.

The groundwaters from Zahir Abad (ZAB), the southwest village among the studied villages, showed the δ^{15} N within narrow range from 3.5 to 5.7 ‰. The δ^{15} N of fertilizer samples (urea, n = 3) were also analyzed, and those values were <2 ‰, close to that of air. The range of the $\delta^{15}N$ of ZAB groundwaters is in concordant with that of soil organic nitrogen (e.g., Chapella 2001) and chemical fertilizers used in China (Li et al. 2006) but slightly larger than those used in this area. Since the concentration of NO_3^--N is not very low in those waters among the analyzed ones, the soil organic nitrogen would not be the only source for this component. Denitrification of urea in the fertilizers would promote to enrich in ^{15}N in those waters.

5.2 Redox Reactions and Stability of Inorganic As

Arsenic is a unique element among the heavy metalloids and oxyanions-forming elements (e.g. As, Se, Sb, Mo, V, Cr, U, Re) in its sensitivity to mobilization at the pH values typically found in groundwaters (pH 6.5–8.5) and under both oxidizing and reducing conditions. Relative to other oxyanions forming elements, As is the most problematic in the environment because of its high mobility over a wide range of redox conditions. Arsenic can occur in environment in several oxidation states (−3, 0, +3 and +5) but in natural waters is mostly found as inorganic form as oxyanions of trivalent arsenite As^{III} or pentavalent arsenate As^{IV}.

Redox potential (Eh) and pH are the most important factors controlling As speciation (Smedley et al. 2002). Under oxidizing conditions $H_2AsO_4^-$ is dominant at low pH (less than about pH 6.9), whilst, at higher pH $HAsO_4^{2-}$ becomes dominant (Fig. 5.5), $H_3AsO_4^0$ and AsO_4^{3-} may be present in extremely acidic and alkaline conditions respectively.

In the present study the speciation analysis of the studied groundwaters shows that most of the As is present in the form of As^v. As shown in Fig. 5.5, the plot of Eh and pH of the studied groundwaters are mostly in the field of $HAsO_4^{2-}$. Thus, the As^v is thermodynamically stable phase in the studied groundwaters.

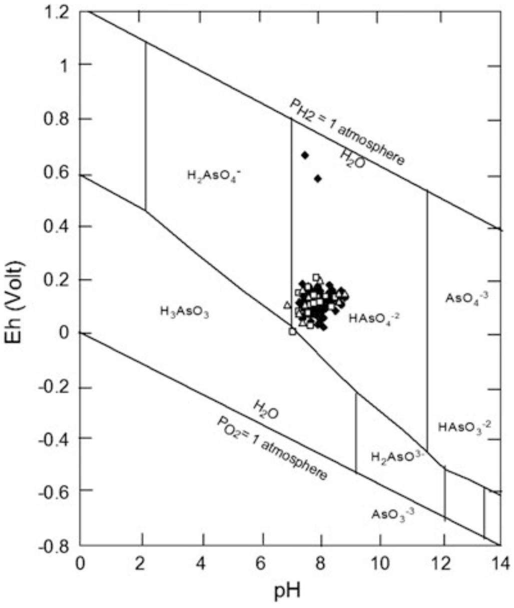


Fig. 5.5 Eh-pH diagram for aqueous As species for the studied groundwaters. The dominant species is $HAsO_4^{2-}$

5.3 Role of Major Chemistry and Geochemical Factors Controlling As Mobilization

There appear to be two key factors involved in the formation of high As groundwaters on a regional scale where natural pollutants are accounted beside the anthropogenic activities increasing the concentration of pollutants: firstly, there must be some form of geochemical trigger which releases As from the aquifer solid phase into the groundwater. Secondly, the released As must remain in the groundwater and not be flushed away. There are a number of possible geochemical triggers. In mining ad mineralized area, oxidation of sulfide ores would be triggered by influxes of O_2 or other oxidizing agents. However, in most As affected aquifers, the most important trigger appears to be the desorption/dissolution of As from oxide minerals, particularly Fe oxides. This process is controlled by number of factors pH, Eh and associated water quality parameters of the aquifer.

5.3.1 Desorption at High pH Under Oxidizing Conditions

High concentrations of As were found in groundwaters from shallow depths of 20–27 m. The highly contaminated waters are characterized by high EC values >2 mS/cm. The groundwater chemistry of the studied area shows that the pH is predominantly alkaline 65 % samples show pH > 8.0. In general high pH of the groundwaters is caused by the weathering reactions (Silicate hydrolysis) (Robertson 1989).

Naturally As contaminated groundwater is caused by mainly two different ways; oxidation of arsenic-bearing sulfide minerals (Schreiber et al. 2000) and desorption from and/or following reduction of FeOOH adsorbing As (Matisoff et al. 1982; Robertson 1989; Nimick 1998; Nickson et al. 2005; McArthur et al. 2001) in response to increase of pH of groundwater. Based on the laboratory experiments of As adsorption on the metal oxides, such as Fe, Mn and Al oxyhydroxide/oxides (Anderson et al. 1976; Pierce and Moore 1982; Dzombak and Morel 1990; Gustafsson and Jacks 1995; Lindberg et al. 1997) and clay fractions (Jacobs et al. 1970), As^V is most effectively adsorbed on the Fe-oxyhydroxide/oxide at weakly acid to neutral pH conditions, and it releases into the solution with increasing pH at alkaline condition.

As noted in this study, the As concentration increases with increasing pH in groundwaters (Fig. 5.6) as well as in soils discussed before. The increase of pH is due to the uptake of protons by mineral weathering and ion exchange reactions. The pH increase is commonly associated with the development of salinity and the salinisation of soils (Smedley et al. 2002). The Eh values (218–715 mV) suggests oxidizing conditions of the aquifers, under such oxidizing conditions As is commonly present in the form of As^V. In this study the speciation analysis shows that 97 % samples are in the form of As^V, while only 3 % samples from ARK the only village that is located in the flood plain is dominated by As^{III}.

Concentration of Fe was low in the studied groundwaters in concordance with the highly positive Eh, indicating the oxidizing condition to

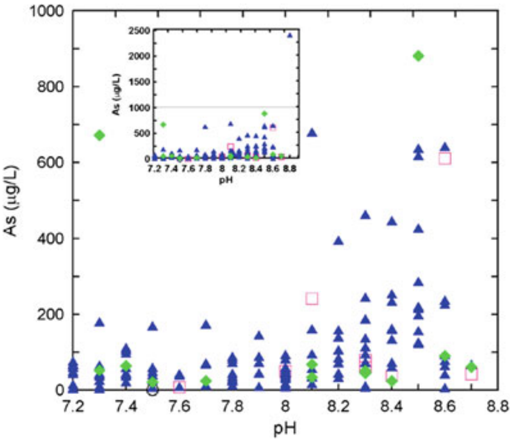


Fig. 5.6 Relationship between As and pH. *Solid triangles* are symbols for shallow, *diamond* for middle, *square* for deep groundwaters and *circles* for canal water

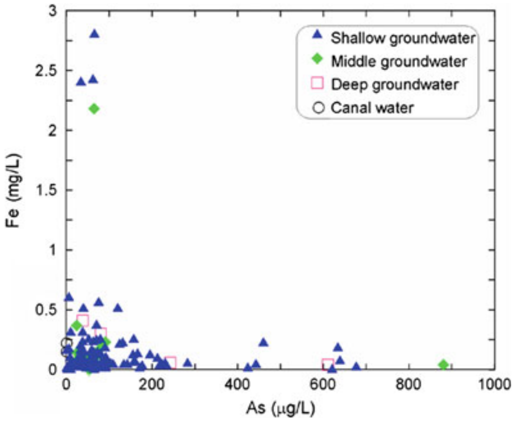


Fig. 5.7 Relationship between As and Fe

prohibit high Fe dissolution. Most of the studied groundwater showed the Fe concentrations below the detection limit, 0.01 mg/L. Figure 5.7 shows that As and Fe have a negative correlation, and the groundwater containing <0.2 mg/L Fe, contains >400 μg/L As. Thus, FeOOH, if it controls the As concentration in the studied groundwater, would fix the As to prohibit the dissolution of this element into the groundwater. Arsenate is desorbed from Fe oxides at alkaline pH (Dzombak and Morel 1990). Many researchers have pointed out that desorption of As from mineral oxides is responsible for the highly As containing groundwater in Quaternary sedimentary aquifers, e.g., As release into the groundwater can occur without apparent reduction in the arid basins of Argentina (Smedley et al. 2002).

So in this study we can say that the alkaline nature promotes the dissolution/desorption of As from mineral oxides into the studied groundwaters, or whichever the As is derived from the anthropogenic or natural sources the alkaline environment of the groundwaters is promoting the release of this As into the groundwaters.

5.3.2 Arsenic and Intense Evaporation

Evaporation concentration can increase As concentrations. This process is particularly important in closed hydrologic basins in the semiarid regions where evaporation rates exceed precipitation. For example, in the Carson Desert and southern San Joaquin Valley, western USA, evaporation appears to be a contributing factor producing high arsenic concentrations (Fujii and Swain 1995). However, this mechanism could not explain the case of this studied area, since the As concentrations did not have the linear relationship with Cl^- (Fig. 4.7) which is the most conservative component in the hydrosphere. The study area is semiarid region and the Fig. 4.9, plots of δD and $\delta^{18}O$ were parallel to the global meteoric water line (GMWL, Fig. 4.9), explaining that the studied waters were not largely affected by the evaporation and condensation. Thus, these results show that in the study area the high concentrations of As are not as a result of evaporation condensation.

5.4 Role of Major Chemistry and Geochemical Factors Controlling F^- Mobilization

The release of F^- into the groundwater depends on such factors such as temperature, pH, presence or absence of complexing or precipitating ions and colloids, solubility of fluorine-bearing minerals, anion exchange capacity of aquifer materials (OH^- for F^-), the size and type of geological formations traversed by water, and the amount of time that water is in contact with a particular formation.

In the studied area, the sources of As and F^- were not only the factor, but also the major chemistry of the groundwater, which controls the dissolution rates of those contaminants must play an important role on the formation and extension of contaminated groundwater.

5.4.1 Alkaline pH and Desorption of F^-

In this study high concentrations of F^- were found in groundwaters from shallow depths of 20–27 m. As noted above the highly contaminated waters are characterized by high EC values >2 mS/cm. The groundwater chemistry of the studied area shows that the pH is predominantly alkaline; 65 % samples give pH > 8.0. As noted in results, the studied soils were also alkaline with pH > 8.0. The F^- concentrations increase with the increase of pH in soil samples (Fig. 4.16a, b) although this behavior is not so consistent in groundwaters (Fig. 5.8f).

General trend of increasing F^- concentration in soils with increasing pH (Fig. 4.16a, b) is in good agreement with observations in soils from UK by Larsen and Widdowson (1971) and soils from Pennsylvania, USA by Gilpin and Johnson (1980). Fluoride ion is readily bound to the soil surfaces at neutral pH and is adsorbed by clays in acidic solution; however, they are desorbed in alkaline solution (Sexena 2002). In the study F^- is easily released from the alkaline soil when groundwater infiltrates. Thus, the alkaline environment of the soil must be one of the major factors of highly F^- contaminated groundwater.

5.4.2 Evaporation Transpiration and Release of F^-

Fluoride concentration in groundwater in arid and semiarid regions is promoted by evaporation and evapotranspiration (Jacks et al. 2005). This mechanism could not explain the case of our studied area, since the F^- concentrations did not have the linear relationship with Cl^- (Fig. 4.7e), which is the most conservative component in the hydrosphere. Also, as shown in Fig. 4.9, plots of δD and $\delta^{18}O$ were parallel to the global meteoric water line (GMWL, Fig. 4.9), explaining that the studied waters were not affected by the evaporation and condensation. Thus, the high concentrations of Cl^-, F^- and also SO_4^{2-} would be explained by one or more sources distributed on

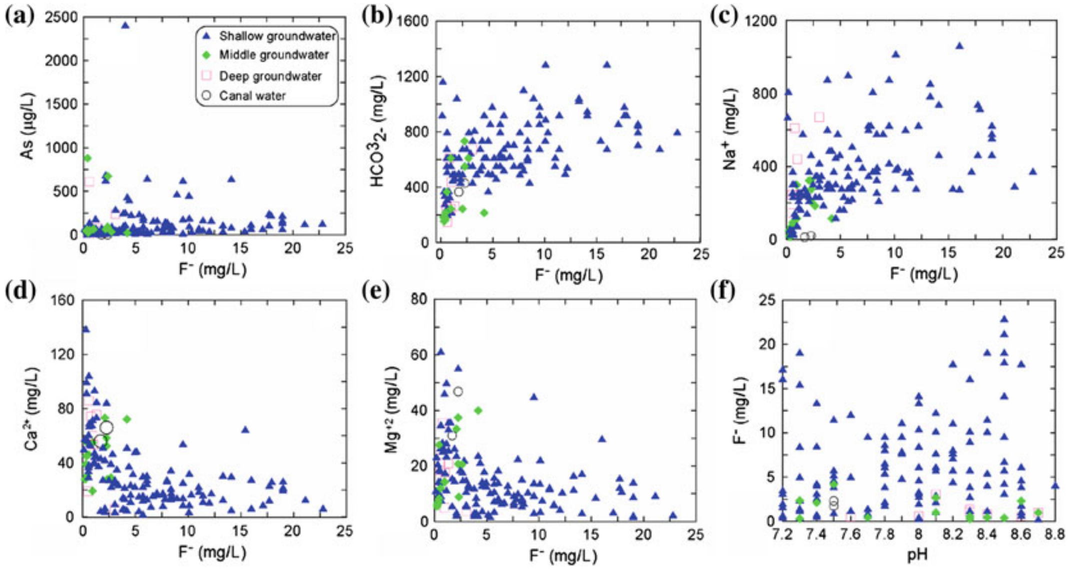


Fig. 5.8 Relationship of F^- with As (**a**), HCO_3^-(**b**), Na^+ (**c**), Ca^{2+} (**d**), Mg^{2+} (**e**), and pH (**f**)

the land surface or intruded directly into the aquifer. Directly supplied pollutants and wet and dry deposition must be condensed on the land surface.

5.4.3 Mineral Solubility

As mentioned above that the groundwater is dominated by Na-HCO$_3$-SO$_4$ type, with very low Ca^{2+} and Mg^{2+} concentrations. Fluoride concentrations increase with decreasing Ca^{2+} (Fig. 5.8d) and Mg^{2+} (Fig. 5.8e) and increases with increasing Na$^+$ (Fig. 5.8c) and HCO$_3$$^-$ (Fig. 5.8d). High F$^-$ concentrations were found in alkaline water, although the F$^-$ and pH did not have clear correlation (Fig. 5.8f). As described above, F$^-$ concentration increased with decreasing Ca^{2+} and Mg^{2+} and increasing Na$^+$ concentrations under alkaline condition. Calcium and Mg^{2+} concentrations were low and controlled mainly by the solubilites of calcite and dolomite due to high HCO$_3$$^-$ concentrations. Saturation indices (SI) calculated by the hydrogeochemical code PHREEQE using the groundwater chemical data from selected areas of the study shows that the groundwaters are saturated with respect to calcite and dolomite as shown in Fig. 5.9a, b. The saturation index of fluorite (SI$_f$) increased with increasing F$^-$ concentration (Fig. 5.9c), while, Ca^{2+} did not show a clear relationship with SI$_f$ (Fig. 5.9e).

The following equations explain the saturation of groundwater with respect to calcite and fluorite (Handa 1975).

$$CaCO_3 + H^+ \rightarrow Ca^{2+} + HCO_{3^-} \tag{5.1}$$

$$Ksp_1 = \frac{\left[Ca^{2+}\right]\left[HCO_3^{2-}\right]}{H^+} \tag{5.2}$$

Similarly for the dissociation reactions of (CaF$_2$) dissolved in water

$$CaF_2 \rightarrow Ca^{2+} + 2F^- \tag{5.3}$$

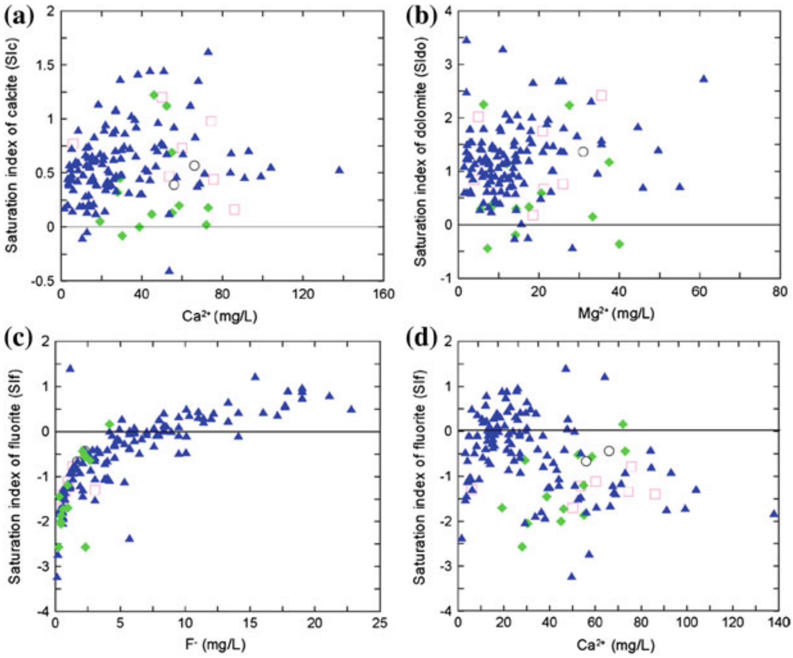
the equilibrium constant K$_2$ is described as

$$Ksp_2 = \left[Ca^{2+}\right][F^-]^2 \tag{5.4}$$

From Eqs. 5.2 and 5.4, the following relation is written

$$\frac{[HCO_3{}^-]}{[H^+][F^-]^2} = \frac{Ksp_1}{Ksp_2} \tag{5.5}$$

Fig. 5.9 Relationships between calcite saturation index (SI$_c$) and Ca^{2+} (**a**), dolomite saturation index and Mg^{2+} (**b**), fluorite saturation index (SI$_f$) and F$^-$ (**c**), fluorite saturation index (SI$_f$) and Ca^{2+} (**d**)



Equation 5.4 demonstrates that decrease in calcium would be followed by increase in fluoride ions. However, if pH is constant, enrichment in bicarbonate ions is usually accompanied by enrichment in fluoride ions (Eq. 5.5), as also reported by Kakar et al. (1988).

Fluoride content showed a positive correlation with bicarbonate and sodium concentrations and a negative correlation with calcium concentrations.

The following reaction takes place during the water mineral (fluorite) interaction (Sexena and Ahmed 2003).

$$\mathrm{CaF_2 + Na_2CO_3 \leftrightarrow CaCO_3 + 2F^- + 2Na^+} \quad (5.6)$$

$$\begin{aligned}\mathrm{CaF_2 + 2NaHCO_3(aq)} &\leftrightarrow \mathrm{CaCO_3 + 2Na^+} \\ &\quad \mathrm{+ 2F^- + H_2O + CO_2(aq)}\end{aligned} \quad (5.7)$$

In the above reactions, the $NaHCO_3$ rich water in a weathered rock formation accelerates the dissolution of CaF_2 and thereby releases F^- into groundwater and allows calcite precipitation from Ca^{2+} and CO_3^{2-} ions is the same way the concentration of dissolved ionic species and the pH of water play an important role in the study area, thereby enhancing F^- concentrations. Therefore, the low concentrations of Ca^{2+} (and probably Mg^+) must promote high concentrations of F^- in the studied groundwater, and that the upper limit of F^- concentrations is controlled by fluorite solubility as seen in Fig. 5.9c. Moreover, shells of $CaCO_3$ were observed in the aeolian and drilled sediments that also confirms the $CaCO_3$ precipitation. The presence of high concentrations of Na^+ and low Ca^{2+} concentrations in the study area would also be a result from the intense cation exchange reaction between Ca^{2+} and Na^+ (Sarma and Rao 1997).

5.5 Topographic Constrains

Since the topography would reflect the groundwater aquifer structure, and would affect to concentrate the pollutants into the local groundwaters and soils. Highly As and F^- polluted groundwaters were concentrated in eastern and western part of the study area (Fig. 5.1); e.g. KLW, KAD, SKB, and MM. Altitude of these villages are slightly lower (200–205 m) among the other villages in the study area (Fig. 5.10). Villages, where the groundwater contains less amounts of As, are located in the surrounded area of the above villages; CNG and SUN at northeast, BP at south and JK, ZAB, and RPNA at southwest. These villages are located at slightly higher altitude 210 m or >210 m (Fig. 5.10). If the surface topography was concordant with the structure of the aquifer, the groundwater would flow parallel to the altitude toward topographic low. The groundwater flow system including flowing rate and direction would deeply affect the groundwater chemistry and formation of the studied highly polluted groundwater.

The distribution pattern of As and F^- in the soils also shows the similar behavior. As noted before, highly contaminated areas are found in two distinct zones, (Fig. 4.17, zones 1 and 2 $1'$ and $2'$). One of the zones (encircled by dotted lines) is extended along the edge of terrace bordered by the flood plain of Ravi River from the southern part of Manga Mandi. Another one is in the southwestern part of the studied area. Topographically these areas are located slightly lower than the surroundings. The north eastern and eastern parts where less contaminated soils were distributed, are located at slightly higher altitude >200 m than the above mentioned higher polluted villages located at about 195 m altitude (Fig. 5.11).

5.6 Aquifer Structure and Mechanism of Pollutant Migration

The highest concentrations of As and F^- in the study area are detected from the shallowest aquifer at the depth of 20–27 m, although the deeper aquifers are also not completely free of As and F^-. This presence of As and F^- at deeper depths suggests that the shallow and deeper aquifers are

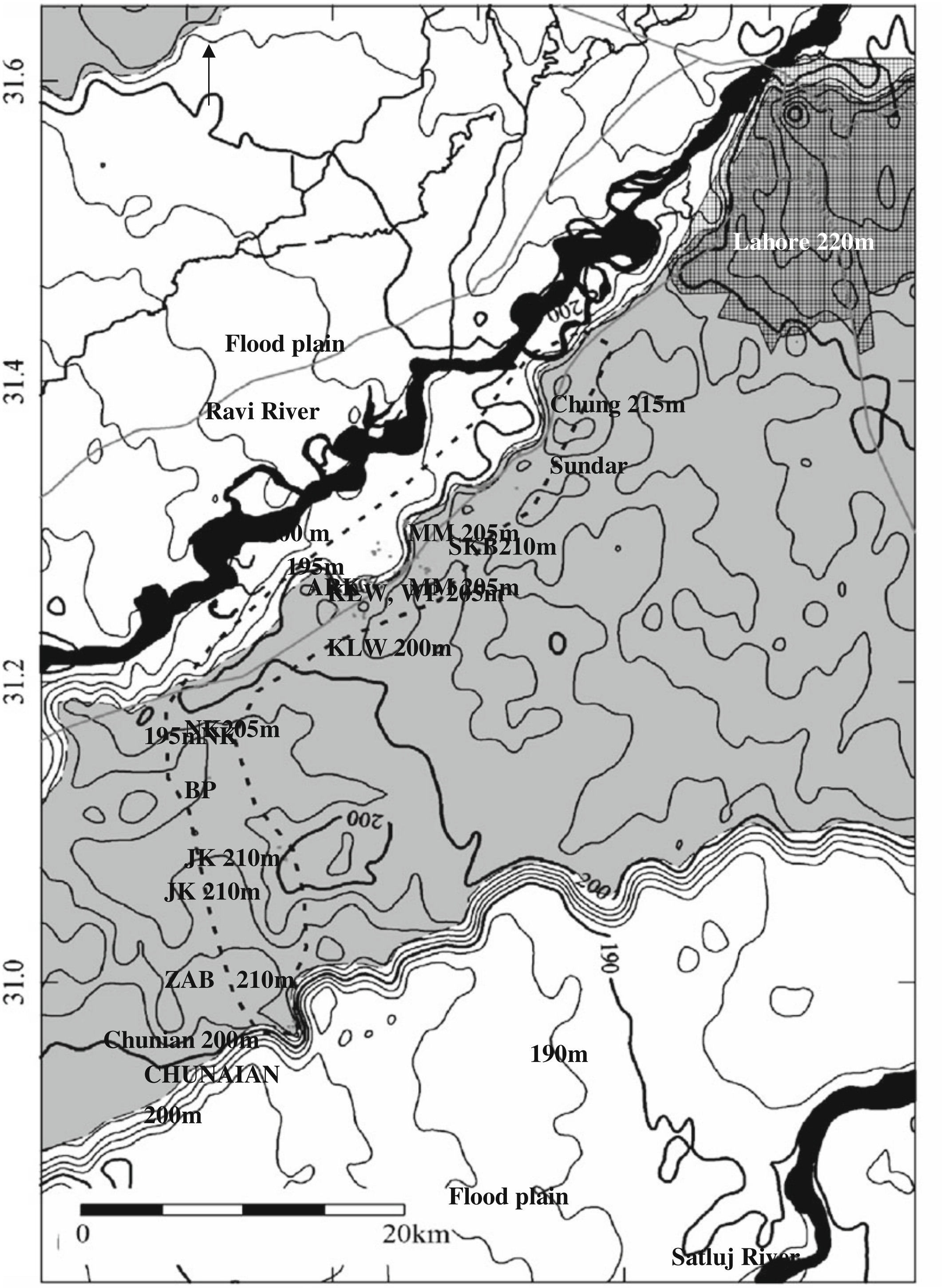


Fig. 5.10 General topography of the studied area with groundwater sampling locations

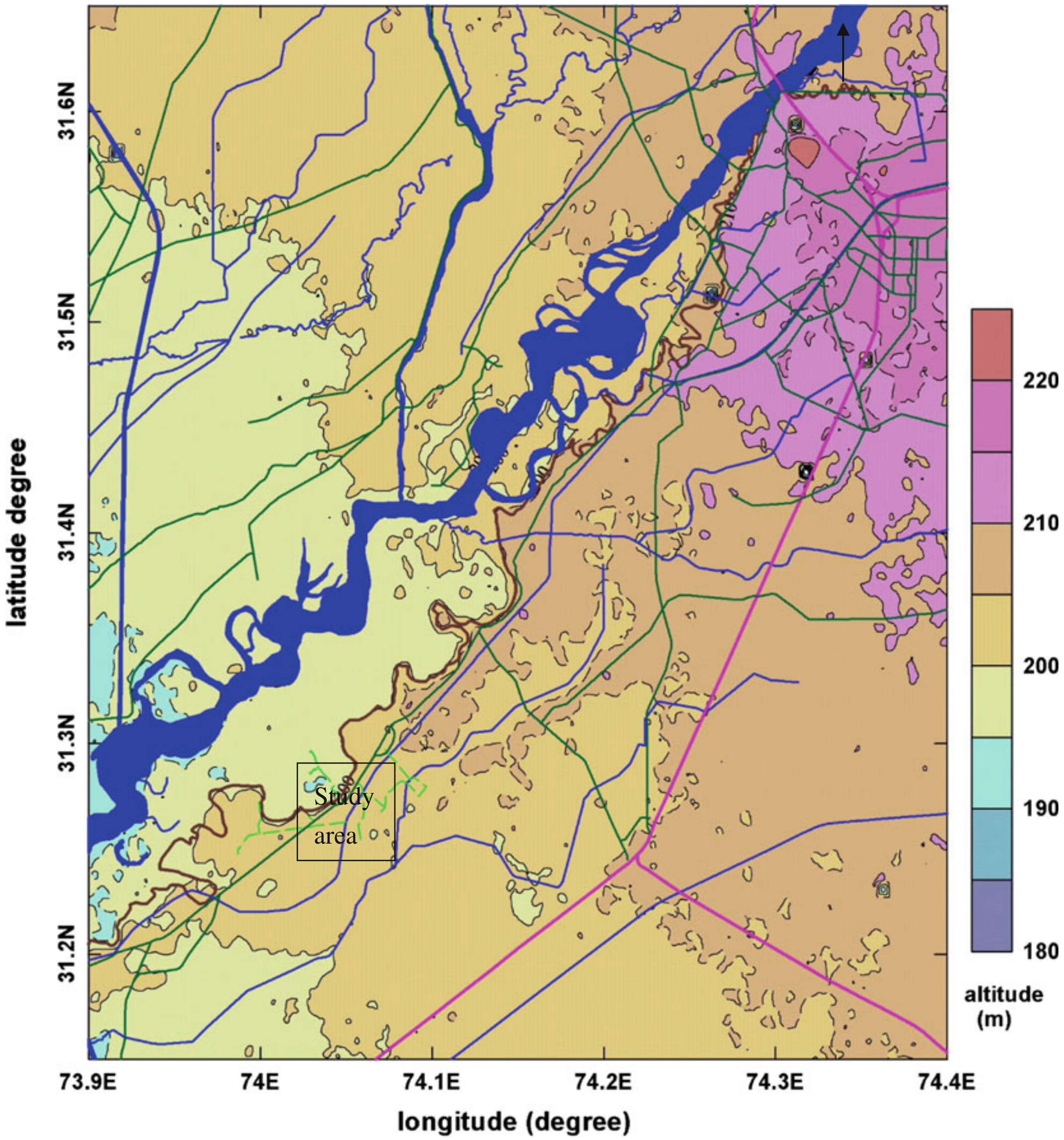


Fig. 5.11 General topography of the studied area with soil sampling location

in hydraulic connectivity with each other. The evaluation of the relationship between aquifer structure and polluted groundwater formation could be explained by the study of underground geological profiles obtained in March 2006.

The underground geological profiles of the highly polluted waters are given in Fig. 4.18a–c. This shows that the shallowest aquifer at the depth of 20–27 m developed in freshwater formation comprising fine to medium sand and this aquifer is not completely impermeable rather it is slightly permeable. The second deeper aquifer was at the depth of 60–90 m and it is silty and sandy in nature. In-between these two aquifers there are impermeable layers that are not well developed, and mostly observed as the layer

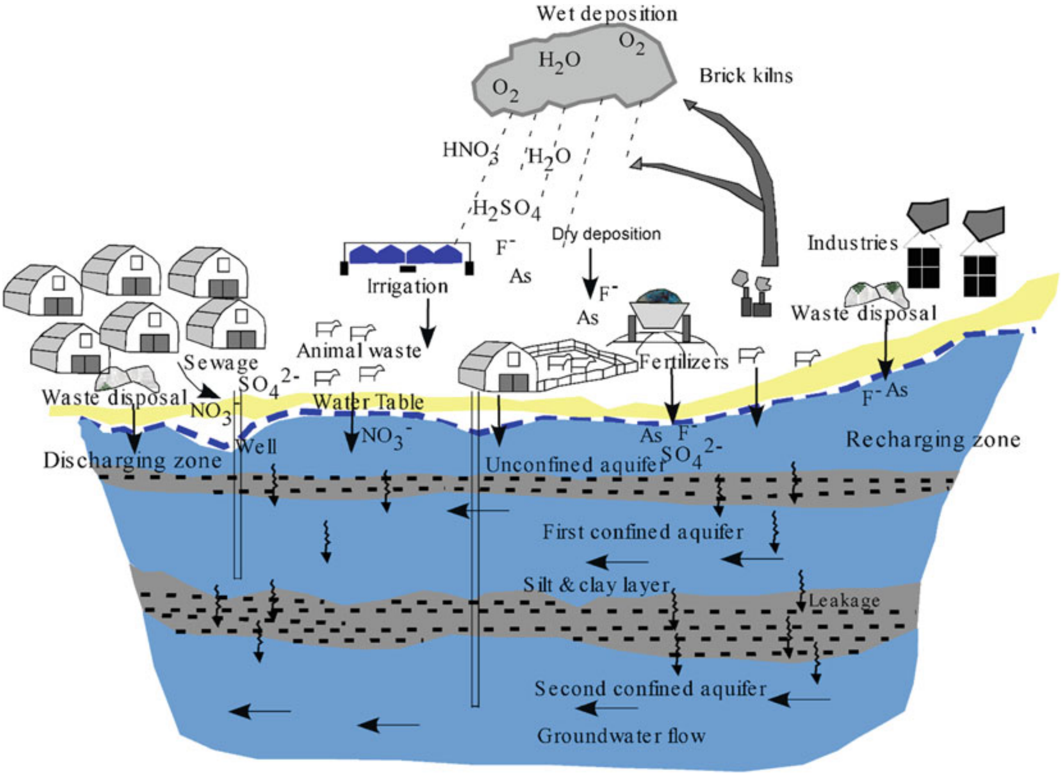


Fig. 5.12 Possible pollutant sources and pollutant migration into groundwater

including a few to tens cm thick silt to clay lenses. It is proposed that the pollutants distributed on and in the surface sediment by the man made pollution could directly penetrate into deeper aquifer. Also, the highly polluted area was located along the buried river channels, implying that the vertical migration of pollutants was promoted in association with increasing uptake of groundwater and accumulation of pollutants in the depression of the aquifer.

The groundwater flow system including flowing rate and direction would deeply affect the groundwater chemistry and formation of the studied highly polluted groundwater. The major chemistry of highly As and F^- polluted groundwaters are highly alkaline and Na-HCO_3^- dominant type, indicating typical characteristics of the groundwater chemistry formed in stagnant aquifer (e.g., Hinkle 1997). Thus, it is probable that the As and F^- are coincidently dissolved into the stagnant groundwater (Fig. 5.12).

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6 Arsenic Health Risk Assessment

6.1 Health Risk Assessment Model

A health risk assessment model derived from the USEPA (Integrated Risk Information System (IRIS): arsenic CASRN 7440-38-2, 1998) was applied to compute the non-carcinogenic and carcinogenic effects to individuals who consume groundwater as their drinking water source.

$$ADD = \frac{C \times IR \times EF \times ED}{AT \times BW} \tag{6.1}$$

where ADD: Average daily dose from ingestion (mg kg^{-1} day^{-1}); C: Arsenic concentration in ground water (mg L^{-1}); IR: Water ingestion rate (L day^{-1}); EF: Exposure frequency (day year^{-1}); ED: Exposure duration (year); AT: Average time/life expectancy (day); BW: Body weight (kg)

$$HQ = \frac{ADD}{RFD} \tag{6.2}$$

where HQ: Hazard Quotient (Toxic risk is considered occurring if HQ > 1.00); RfD: Oral reference dose (RfD = 3×10^{-4} mg kg^{-1} day^{-1});

$$CR = 1 - \exp(-SF * ADD) \tag{6.3}$$

where SF is the slope factor, equal to 1.5 mg kg^{-1} day^{-1}.

If

HQ > 1 Adverse non-carcinogenic effects of concern

HQ < 1 Acceptable level (no concern)

For the carcinogenic effect, calculated Cancer Risk used the following Eq. (6.4).

$$Risk = CDI \times SF \tag{6.4}$$

If acceptable level is 10^{-6}, means the probable possibility that about 1 cancer patients among 1,000,000 people happen.

Cancer Risk > 10^{-6} Carcinogenic effects

Cancer Risk < 10^{-6} acceptable level (no concern)

6.2 Exposure Assessment

Exposure assessment was done for the present study (Table 6.1). Toxic and cancer risk indices were calculated by expressions (6.2) and (6.3), respectively. Computational results showed that the residents in the Lahore and Kasur districts study areas had toxic risk indices (HQ) ranging from 1.11 to 7.407 (n = 64) 2.6×10^{-2} to 2.08×10^{-4}. In some study areas from district Lahore and Kasur residents exceed the toxic risk index 1.00.

Table 6.1 summarizes as concentrations, HQ and cancer risk in ground water samples from

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Table 6.1 Arsenic concentrations in drinking water samples along with HQ and CR values

Sample ID	N		As (μ/L)	HQ	CR
CNG	5	Mean	32	3	1.33E−03
		SD	26	2	1.10E−03
		Range	6.1–71	0.56−6.57	2.50E−04–2.96E−03
SUN	5	Mean	51	5	2.12E−03
		SD	40	4	1.67E−03
		Range	1.1–92	0.093–8.519	4.17E−05–3.83E−03
SKB	25	Mean	106	10	4.42E−03
		SD	107	10	4.46E−03
		Range	3.00–443.0	0.278–41.019	1.25E−04–1.85E−02
MM	17	Mean	100	9	4.15E−03
		SD	164	15	6.85E−03
		Range	4.00–611	0.37–56.57	1.67E−04–2.55E−02
WP	11	Mean	152	14	6.33E−03
		SD	185	17	7.71E−03
		Range	33.0–677	3.056–62.685	1.38E−03–2.82E−02
KAD	12	Mean	81	7	3.36E−03
		SD	60	6	2.50E−03
		Range	10.00–171	0.926–15.83	4.17E−04–7.13E−03
KLW	29	Mean	106	13	1.21E−02
		SD	454	42	1.89E−02
		Range	23–2400	2.13–222	9.58E−04–1.00E−01
MPU	3	Mean	58	5	2.43E−03
		SD	6	1	2.51E−04
		Range	52–64	4.81–5.93	2.17E−03–2.67E−03
ARK	10	Mean	117	11	4.88E−03
		SD	270	25	1.12E−02
		Range	1.00–881	0.93–81.57	4.17E−05–3.67E−02
DN	6	Mean	26	2	1.08E−03
		SD	14	1	5.85E−04
		Range	8.00–38.00	0.741–3.52	3.33E−04–1.58E−03
NK	6	Mean	58	5	2.40E−03
		SD	21	2	8.63E−04
		Range	39–94	3.61–8.7	1.63E−03–3.92E−03
KA	3	Mean	397	37	1.65E−02
		SD	222	21	9.25E−03
		Range	177–621	16.4–57.5	7.38E−03–2.59E−02

(continued)

Table 6.1 (continued)

Sample ID	N		As (μ/L)	HQ	CR
BP	3	Mean	68	6	2.82E−03
		SD	36	3	1.52E−03
		Range	40–109	3.7–10.1	1.67E−03–4.54E−03
JK	2	Mean	55	5	2.27E−03
		SD	69	6	2.86E−03
		Range	6–103	0.56–9.54	2.50E−04–4.29E−03
RPNA	2	Mean	47	4	1.94E−03
		SD	33	3	1.38E−03
		Range	23–70	2.13–6.5	9.58E−04–2.92E−03
CCO	2	Mean	1	0	4.08E−05
		SD	0	0	1.17E−06
		Range	1.00–1.5	0.093–0.097	4.00E−05–4.17E−05
ZAB	5	Mean	30	3	1.26E−03
		SD	16	1	6.62E−04
		Range	14.00–56.00	1.296–5.19	5.83E−04–2.33E−03

study area. Study areas had toxic risk indices (HQ) ranging from 0.093–222 (n = 143) to CR 1.0×10^{-1} to 4.17×10^{-5}. The upper end of the ranges for study area residents exceeds the typical toxic risk index 1.00, confronting significant adverse toxic health impacts. Toxic risk indices (HQ) found in the CNG ranging 0.55–6.6 and Cancer risk indices found between 9.58×10^{-4} and 1.88×10^{-3}. In SUN HQ were between 0.093 and 8.51 while CR were ranged between 4.17×10^{-5} and 3.83×10^{-3}. SKB HQ values were 0.278–41.01, CR values were 1.25×10^{-4} to 1.85×10^{-2}. In MM HQ were calculated between 0.37 and 56.5 and CR ranged between 1.67×10^{-4} and 2.55×10^{-2}. WP HQ was between 3.05 and 62.68 and CR was between 1.38×10^{-3} and 2.8×10^{-2}. KAD HQ ranged between 0.925 and 15.8 and CR ranged between 4.17×10^{-4} and 712×10^{-3}. KLW HQ was between 2.13 and 59.17 and CR was calculated 1.25×10^{-3} and 2.66×10^{-2}. In MPU study areas HQ ranged 4.81–5.92 and CR ranged between 2.17×10^{-3} and 2.63×10^{-3}. ARK HQ ranged between 0.0926 and 81.57 and CR ranged 4.2×10^{-5} to 1.67×10^{-3}. In DN HQ range was found between 3.5185 and 0.7407 and CR was between 1.29×10^{-3} and 3.33×10^{-4}. In NK HQ were calculated between 8.7037 and 3.6111 and CR was found 3.92×10^{-3} to 1.63×10^{-3}. At KA HQ was found 57.50–16.4 and CR was calculated 1.63×10^{-2} to 7.4×10^{-3}. In BK, HQ was found between 10.1 and 3.70 and CR was 1.67×10^{-3} to 4.54×10^{-3}. JK HQ ranged between 9.54 and 0.56 and CR was 4.29×10^{-3} to 2.50×10^{-4}. RPNA HQ was calculated between 6.5 and 2.123 and CR was found 2.92×10^{-3} to 9.58×10^{-4}. CCO HQ ranged between 0.0940 and 0.093 and CR was 4.18×10^{-5} to 4.17×10^{-5} ZAB HQ was calculated 5.18–1.3 and CR was 9.17×10^{-4} to 1.13×10^{-3}. The CR value greater than one in a million (10^{-6}) was generally considered significant by US EPA.

In some areas in previous study like Bhai Kot in district Lahore and Central Colony in district Kasur HQ value was less than 1.00.

7

Remedies of Arsenic Problem and Environmental Legislation in Pakistan Regarding Arsenic

7.1 Remedies of Arsenic Problem

Worldwide huge number of technologies are available for arsenic removal from arsenic-contaminated water. Some of these technologies include pre-oxidation of arsenic(III) to arsenic(V) by the use of different oxidants, as As(V) has high adsorbance capacity and reacts more strongly than As(III) (Ahmed et al. 2001). Some developed countries like Germany has developed Granular Ferric Hydroxide (GFH) that removes arsenic by adsorption with ability to remove both arsenite and arsenate, without oxidation. But besides other limitations, it is costly and more applicable to small systems. Other techniques include ion exchange, reverse osmosis, conventional method of coagulation/filtration, use of activated aluminas doped with iron (Rubel 2003), use of low-cost adsorbents like rice husk (Amin et al. 2006), use of industrial wastes like lignite, peat chars, (Mohan et al. 2006) bonechar, (Sneddon et al. 2005) red mud (generated during Bayer process), (Altundogan et al. 2002), fly ash (generated by coal power stations) for As(V) removal from water that restricts As(V) movements in the solid wastes or the soil (Diamadopoulos et al. 1993).

However, achieving low standards will put increased economic pressure on rural communities having high levels of arsenic in drinking water (Frey et al. 1998) and some of the technologies mentioned above cannot be practically applicable because of the desired objectives and feasibility. Experience with point-of-use methods in Pakistan, India and elsewhere have indicated their success in small communities, individual households seeking arsenic removal from their drinking water. Point-of-use methods are: Coagulation, precipitation, adsorption, filtration or the combination of these different techniques. The application of the method may vary from point to point depending on economic cost and thickness of contaminated water source. Considering the socio-economic background of rural and urban population of different areas in Pakistan, PCRWR has conducted different research studies on the development of low cost arsenic removal technologies i.e. clay pitcher, gravity flow and ceramic cartridge arsenic removal filters. PCRWR in collaboration with UNICEF has developed a low cost technology for the removal of arsenic from drinking water and the cost of the filter is in the range of Rs. 600–1,000 with useful life of 6 months. However, the implementation and efficiency of this project should be monitored for achieving the real targets (http://www.pcrwr.gov.pk/islamabadregional.aspx).

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7.2 Environmental Legislation in Pakistan Regarding Arsenic

Due to As toxicity and harmful effects, it is considered in National Environmental Quality Standards (NEQS) and set its permissible limit. Pakistan Environmental Protection Ordinance (PEPO 1983) provides the basis for future legislation and guidelines regarding monitoring of toxic and essential pollutants in the water (Government of Pakistan 1983). As per PEPO (1983), Pakistan Environmental Protection Council (PEPC) and Pakistan Environmental Protection Agency (Pak-EPA) was formed. The first meeting of PEPC was held in 1993, after 10 years of huge gap after the approval of PEPO. In this meeting, Pak-EPA with the prior approval of PEPC established the NEQS in pursuance of the powers conferred by clause (d) of Sect. 6 of PEPO (1983). The maximum allowable limit, set by Pak-EPA for arsenic was 1 mg/L (1,000 µg/L) (NEQS 1993) which were very high as compared to WHO limits. In 1997, Pakistan Environmental Protection Act (PEPA 1997), a regulatory framework, was approved (Government of Pakistan 1997). In 2000, NEQS were revised in pursuance of the powers conferred by PEPA (1997) but maximum allowable limit for As were remain as such and did not change according to the situation. In this situation PCRWR conducted a detailed study in order to evaluate water quality of Pakistan (PCRWR 2004). Their reports showed alarming situation regarding As in the country, especially in South Punjab and some parts of Sindh province. NEQS were again then revised in 2010, considered As as essential inorganic chemical whose limit should be ≤0.05 mg/L (≤50 µg/L) in drinking water (NEQS 2010). Although this limit is still high as compared to WHO guidelines (0.01 mg/L) but this is strongly attributed to poor infrastructure, costly instrumentation and lack of precision in results (Farooqi et al. 2007). It is reported by Azizullah et al. (2011) that industries in Pakistan still do not follow the criteria of national standards in their waste effluents. Different programs have introduced by Government owing to control the pollution but due to weak law enforcement not any industry is willing to follow these standards.

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