Arsenic speciation: Sources of salinity and its impact on mobilization of arsenic and fluoride in groundwater of Rachna Doab

This work is submitted as a dissertation in partial fulfillment for the award of the degree of

Master of Philosophy

In

Environmental Sciences

By

Ambreen Parvaiz

Department of Environmental Sciences
Faculty of Biological Sciences
Quaid-i-Azam University
Islamabad, Pakistan,
2018

Certificate of Approval

It is to certify that the research work presented in this thesis, entitled "Arsenic Speciation: Sources of salinity and its impact on mobilization of arsenic and fluoride in groundwater of Rachna Doab" was conducted by Ms. Ambreen Parvaiz (02311613005) under the supervision of Dr. Abida Farooqi. No part of this thesis has been submitted else for any other degree. This thesis is submitted to the Department of Environmental Sciences, in the partial fulfillment of the requirements for the degree of **Master of philosophy** in the field of environmental science, Quaid-i-Azam University, Islamabad.

Ms. Ambreen Parvaiz (MPhil Scholar)

Supervisor:

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

abida

External Examiner:

Rohama Gill (Dr.)
Associate Professor/ Head of Department
Department of Environmental Sciences
Fatima Jinnah Women University

Rohama Gill

Incharge:

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

abida

Dated: 20-12-2018

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List of Abbreviations

As	Arsenic
F	Fluoride
EC	Electrical Conductivity
FAO	Food And Agriculture Organization
GAS	Groundwater Associated Salinity
IAS	Irrigation Associated Salinity
IGRAC	International Groundwater Resource Assessment Center
LBOD	Left Bank Outfall Drain
NAS	Non-groundwater Associated Salinity
PCRWR	Pakistan Center for Research on Water Resources
RBOD	Right Bank Outfall Drain
SCARP	Salinity Control and Reclamation Project
TDS	Total Dissolved Solids
UNICEF	United Nations International Children's Emergency Fund
WHO	World Health Organization

Abstract

The current research was based on studying the sources of groundwater salinity in Rachna Doab, Pakistan and its possible impact on the enrichment of arsenic and fluoride levels. For this purpose blanket sampling was conducted throughout Rachna Doab to test the occurrence of salinity, As and F^-. The groundwater was found to have varied TDS concentrations i.e., 233.6 to 4556.8mg/l. Based on the results of blanket sampling representative groundwater samples from all villages were selected. The samples were classified into three groups based on their TDS levels and analyzed for As, F^- and other physicochemical parameters. As and F^- concentrations in the study area ranged from below detection limits to 183.42µg/l and 3.9mg/l respectively with the prevalence of both arsenate and arsenite in the area.

Graphical biplots, stable isotopic analysis ($\delta\ ^{18}O$ and $\delta\ ^{2}H$ relative to VSMOW), Gibbs plot and hydrogeochemical modeling of the groundwater samples revealed mineral dissolution, ion exchange processes and partial input of evaporation towards groundwater salinity in the region. The results were in accordance with the conceptual model developed based on secondary data. Na^+ and Cl^- were the major cation and anion identified in the area with reference to elevated TDS levels.

Piper plot reflected NaCl as the dominant water type in moderately saline samples whereas $CaHCO_3$ mainly prevailed in non-saline water samples. The moderately saline samples were found to have high fluoride levels (greater than WHO level) with the exception of one sample suggesting a positive influence of groundwater salinization on groundwater F^- levels. Groundwater As levels showed an overall decreasing trend with increasing salinity identifying a negative effect of salinization on enrichment of arsenic in groundwater.

CHAPTER 1

INTRODUCTION

1. Introduction

Salinity in water is basically the amount of dissolved salt (often dominated by sodium chloride) content present in it (Podmore, 2009).Mainly the presence of dissolved K^+, Mg^{+2}, Na^+, Ca^{+2}, Cl^-, CO_3^{-2}, SO_4^{-2}, NO_3^-, and HCO_3^- in groundwater refers to its salinity (Rhoades, 1996). These salts are naturally found in sediments, soils and rocks. They make their way to the groundwater reservoirs by dissolving into the water that flows through the geologic material (Harter and Rollins, 2008). The phenomenon of salinization is of global concern to all. It is predicted that the changing climate is likely to increase the salinization with a rise in sea level impacting the coastal regions and increasing temperature that will enhance the evaporation rate and salinity (Shahid et al., 2013). Both excessive and inadequate use of water can result in surface and sub surface salinization. Groundwater salinity fluctuates with geography and depth of an area. However, the groundwaters of arid regions are found to be unvaryingly saline (Singh, 2005). Salinization of groundwater is a relatively grave issue in semi-arid and arid regions where it serves a major role in providing precious water resource and supports the ecosystem (Alaghmand et al., 2013)

Generally, there are two major types of salinity. For instance the natural occurrence of salts in water and soil (tidal swamps and salt marshes) is known as primary salinity whereas the contribution of human activity (urbanization, intensive irrigation practices and excessive use of fertilizers) towards the salinity in the environment is referred to as secondary salinity (Podmore, 2009; Rao, 2008). However diverse processes are responsible for triggering the groundwater salinity in inland and coastal areas.

Primary indicators of salinity may include electrical conductivity (EC) and total dissolved solids (TDS) (Singh, 2005). The ability of water to pass electrical flow (Electrical conductivity) is directly related to the concentration of ions in the water. Whereas, TDS is referred to as the total amount of dissolved inorganic salts (mainly sodium, magnesium, calcium, potassium, chlorides, sulphates and bicarbonates) and organic matter present in water (Fawell et al., 2003).Salts that dissolve in water basically contribute to the basis of conductivity in water by producing anions and cations. Since dissolved ions increase salinity as well as conductivity, the two measures are related.

The problem of groundwater and soil salinity evolved in Indus Basin after the development of canal irrigation system in 1859. Moreover, As contamination in the groundwater has found to be a growing concern in Pakistan since the first incident in Kalanlanwala happened in year 2000. Similarly, increased fluoride pollution has also been known to occur in groundwater of various regions of Pakistan.

The dissolution of salts to water imparts a change in its pH (redox conditions); however, the direction of change depends on the type of salt added. Chemically if a salt of a strong base and weak acid (Na_3PO_4) is dissolved in water the solution acquires a basic character and vice versa. Nevertheless, the addition of a neutral salt (salt with a strong acid and strong base or weak acid and weak base) has negligible or no effect on the pH of water. Therefore, salinity and pH play a significant role in characterizing the chemistry of water. As the major mechanism of arsenic release is based on redox conditions whereas elevated fluoride levels are found to be mostly associated with higher Na^+ levels hence salinity may affect their enrichment in water.

1.1. Overview of Global Occurrence of Groundwater Salinization

Groundwater is one main source of drinking water mainly for the people living in the dry regions of the world. The continuous increase in the world population is leading towards an expanding demand for water. Over extraction of water to meet the demands cause various serious water crises in terms of its quality as well as quantity. According to an estimate 884 million people in the world do not have access to clean drinking water. Increasing groundwater salinity is informed to be one of the many reasons of this crisis (Vineis et al., 2011). Groundwater salinization is one of the significant types of aquifer degradation from both practical and hypothetical aspect (Greene et al., 2016). More than hundred countries in the world including India, China and US are affected by aquifer and land salinization (Shahid, 2013). International Groundwater Resource Assessment Center (IGRAC) has developed an inventory (global scale) along with a map on an overview of the global occurrence of saline groundwater based on yet available data including scientific reports, flood and storm recurrence data and geological, hydro-geological, scientific reports, flood and storm recurrence data and geological, hydro-geological, geographical, soil, elevation and land use maps. In line with this inventory 16% of the total area of Earth i.e., 24 million km^2 has occurrence of saline groundwater. The contribution of various factors towards groundwater salinity identified on global scale is shown in Figure 1.1 (Van Weert and Van Der Gun, 2012).Various processes are identified to be responsible for aquifer salinization in inland and coastal regions.

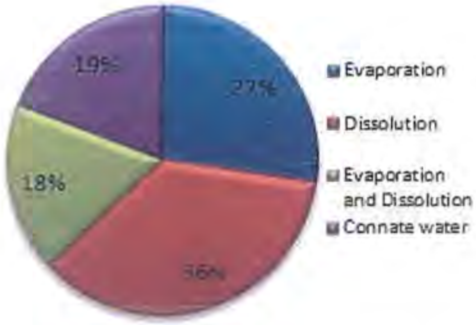


Figure 1.1: Contributions of different factors towards groundwater salinity - on global scale

1.1.1. Processes leading to Groundwater Salinity in Inland areas

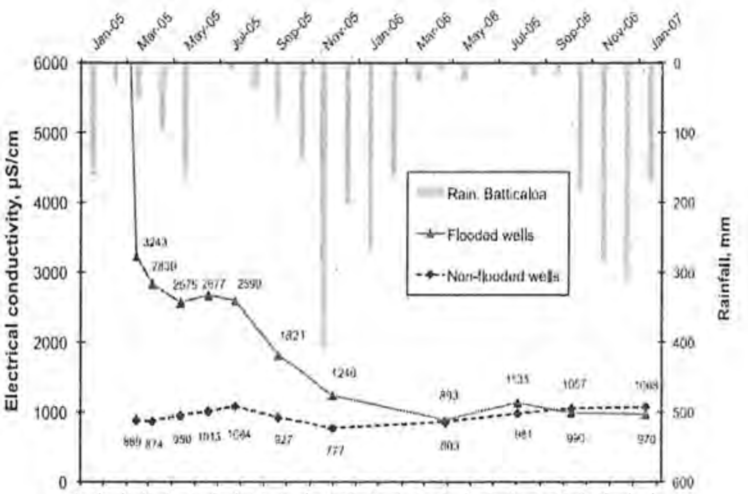
The term Inland areas encompass regions lying in the middle of a country away from the sea resource. Foster and Chilton (2003) summarized the possible processes responsible for the salinization of aquifers in the inland regions. These processes include the rise in groundwater level due to excessive irrigation and poor drainage, mobilization of naturally present salts because of land clearing and construction of wells along with over extraction leading to the disturbance of naturally existing salts in the stratigraphy (upconing of brines). Moreover, other causes of groundwater salinity are the application of excessive fertilizers and use of irrigation return flow (Rao, 2008).

Many parts of India particularly semi-arid regions of Punjab are suffering from severe inland groundwater salinity problems due to reasons such as increased evapotranspiration, development of canal network system and poor drainage. High levels of salinity have been reported in ground waters of Bathinda District, Ganga Plain, Delhi – Haryana State and Andra Pradesh India (Krishan et al., 2017; Lorenzen et al., 2012;

Misra and Mishra, 2007; Rao, 2008; Rao et al., 2017). Similarly in China, the groundwater of Yuncheng Basin is highly saline due to salt lake water intrusion whereas the groundwater of inland Dunhuang Basin shows TDS ranging between 400 to 41000 mg/l (Gao et al., 2007; 2013; Sun et al., 2016).

1.1.2. Processes leading to Groundwater Salinity in Coastal areas

Coastal plains are found to serve as the main agricultural areas globally, utilizing water from both surface and groundwater resources. In times of low-flow the groundwater plays a major role in improving the surface supplies (Greene et al., 2016). Almost 50% of the world's total population dwells in coastal regions (Post, 2005). Excessive pumping of groundwater at rates greater than the upstream fresh water recharge results in the reduction of hydraulic head in inland regions permitting the intrusion of sea water inland thus, salinizing the resource. Werner et al. (2013) has reported the rise in sea level as another reason contributing to the exacerbation of the issue of groundwater salinization in coastal aquifers. The main factors responsible for salinity buildup in groundwater of coastal areas include sea water intrusion into the aquifers, excessive pumping of groundwater, relatively less recharge, tidal water intrusion and poor land and water administration (Arora et al., 2017). Khan et al.(2011) and Vineis et al.(2011) reported in their studies that the drinking water sources of coastal Bangladesh are contaminated by saline water intrusion from the Bay of Bengal as a result of rising sea level due to changing climate. Khan et al. (2006) has also studied the potential for the disappearance of interface between fresh and saline waters in the coastal areas of Bangladesh due to the expected rise in sea level caused by the increasing trend of global warming. Storms and floods acts as drivers of sea water intrusion in coastal regions by land surface inundations particularly in low lying floodplains (Ketabchi et al., 2016; Wong et al., 2015). For instance the unconfined aquifers along the bank of eastern Srilanka were salinized as a result of December 2004 Tsunami in Indian Ocean. Condition of salinity in aquifers before and after flooding can be seen in figure 1.2 (Villholth et al., 2010). Furthermore, the natural balance of groundwater is also vulnerable to the fluctuations in discharge and recharge caused by the changing climate.



Source: Villholth et al. 2011

***Figure 1.2: Salinity of aquifers before and after flooding in Eastern Srilanka, taken from** (Villholth et al., 2010)*

The aquifers in the major coastal irrigation areas in the world such as Queensland in Australia (Narayan et al., 2007), Florida, California and New Jersey in United States, Cyprus, Israel, Egypt, Atlantic Coastline of Lebanon and Spain have found to be affected by sea water intrusion (Barlow and Reichard, 2010). The groundwater in coastal aquifer of Jeju Island in Korea has found to have 67% mixing of sea water with TDS ranging from 77 to 21,782 mg/l. Seawater has intruded 2.5 km inland in the region (Kim et al., 2003). Likewise, in Mexico the Western State of Sonora has suffered seawater intrusion of 20-25 km inland from the coastline (Jakeman et al., 2016).

Groundwater salinity in different regions of the World along with its type and causative processes are presented in table 1.1.

Table 1.1: Groundwater salinity in different regions of the World along with its type and causative processes

Location	Type of salinity	TDS mg/l	Processes leading to salinity	References
Western Delhi, Haryana State, India	Inland	350- 23,000	Surface and groundwater influx, Limited flushing of solutes, Traditional canal system, evapotranspiration	(Lorenzen et al., 2012)
Bathinda District, India	Inland	300.8 – 1932.8	High Evaporation	(Krishan et al., 2017)
Ganga Plain, India	Inland	725- 2200	Canal network, evapotranspiration	(Misra and Mishra, 2007)
Guntur District, Andra Pradesh India	Inland	1260 - 3360	Evapotranspiration, intensive and long-term irrigation, irrigation-return-flow, application of unlimited agricultural fertilizers and recycling of saline groundwater	(Rao, 2008)
Southern India	Inland	499-39100	Water rock interaction, saline water mixing and anthropogenic pollution (untreated tannery effluent)	(Mondal and Singh, 2011)
Southeastern India	Coastal	Upto 8320	tsunami	(Violette et al., 2009)
Meghna Basin, Bangladesh	Coastal	93.44 – 3193.6	Mixing of Sea water with fresh water, Silicate weathering	(Hasan et al., 2009)
South West Bangladesh	Coastal	615.7 – 5996.8	Hydro geochemical processes and sea water influence	(Bahar and Reza, 2010)
Yuncheng Basin, China	Inland	9020 – 268100	Salt Lake water intrusion	(Gao et al., 2007)
Dunhuang Basin, China	Inland	400 – 41000	Evaporation, transpiration, water-rock interaction (Mineral dissolution)	(Sun et al., 2016)

Pearl River Delta, China	Coastal	1000 – 26800	Sea water intrusion	(Wang and Jiao, 2012)
Jeju volcanic Island, Korea	Coastal	77 – 21,782	Sea Water Intrusion	(Kim et al., 2003)
Rhône delta, Southern France	Coastal	2560 – 37120	Mixing between fresh water and Mediterranean sea water	(De Montety et al., 2008)

1.2. Overview of Global Occurrence of Soil Salinization

The phenomenon of soil and groundwater salinization is interrelated. Contribution of salts from aeolian dust, physical and chemical weathering of rocks, evapotranspiration, drought, lack of precipitation and human activities such as salt-rich irrigation, inefficient water use, poor drainage and construction of dams result in salinization of soils in an area (Taghadosi and Hasanlou, 2017). According to a report by Food and Agriculture Organization (FAO) in 2000, an estimated area of soils affected by salts globally is 831 million ha with 38% saline and 62% sodic soils. Szabolcs 1989 defined the continent wise distribution of saline soils globally shown in figure 1.3.According to which Asia is the continent with highest occurrence of saline soils (Rengasamy, 2006). Current worldwide estimates however, show that more than 1 billion ha are influenced by different degrees of soil salinization (Jakeman et al., 2016). Pakistan, United States, India, China, Argentina, Sudan, various countries in Western and Central Asia and Mediterranean Coastline are the worldwide hotspots of soil salinization (Daliakopoulos et al., 2016). These salts accumulated on the surface can raise groundwater salinity whenever mobilized through irrigation or drainage.

Globally, three main types of salinity have been identified based on the different groundwater and soil interactions.

- Groundwater associated salinity
- Non-groundwater associated salinity
- Irrigation associated salinity

1.2.1. Groundwater Associated Salinity (GAS)

Groundwater associated salinity (seepage salinity) is usually observed at the discharge zones, valley floors and foot slants as they possess shallow water tables. It is associated with areas having water tables very close to the soil surface. The clearance of perennial vegetation and its replacement by agricultural crops disturb the equilibrium of water table. Elevated recharge and movement of salts from the regolith increases the salinity. Furthermore, the salts reach the surface via capillary rise. Shallow water tables lead to salt accumulation in soils particularly in areas where water table is <4m from the surface.

However, higher salinity levels are found to occur in soils with water table <1.5m from surface.

Evapotranspiration is the major cause concentrating salts in shallow soil layers. Western Australia is facing severe ground water associated salinity issues. According to the National Land and Water Resource Audit, around 570000 km^{2}of Australian agricultural land possess the ability to develop groundwater associated salinity (Rengasamy, 2006). Similarly NorthWest India and Xinjiang Province of China have also been reported to suffer from GAS due to rise in water table, water logging and intense evapotranspiration leading to soil salinization (Datta and De Jong, 2002; Wang et al., 2008).

1.2.2. Non-groundwater Associated Salinity (NAS)

Non-groundwater associated salinity occurs in areas with deep groundwater tables. Salinity levels however do vary with seasonal variability. The salts introduced by precipitation, weathering or through wind, accumulate in the soil layers due to poor drainage and evapotranspiration. This type of salinity is commonly found in regions with sodic soils as sodic soils have poor hydraulic conductivity thereby leading to reduced leaching and accumulation of salts in top and sub soil layers (Greene et al., 2016).

1.2.3. Irrigation Associated Salinity (IAS)

Salinity induced basically due to application of saline, effluent or poor quality water for irrigation is called irrigation associated salinity. Increased evaporative conditions, improper drainage and poor soil management further aggravate the problem. Moreover, insufficient leaching due to low hydraulic conductivity of soils determines the time taken to salinize a particular area. The Murray Darling Basin of Australia is known to be affected by irrigation induced salinity as the river water used for irrigation has increased salinity due to drainage and effluent discharge into it. The flat lands in some irrigated areas lead to the rise in water table. The pumping of saline water and its reuse for irrigation to decrease the water table has ended up in salinizing the soil layers. Mostly the soils are sodic, however the soils with good hydraulic conductivity are becoming sodic due to sufficient leaching (Rengasamy, 2006).

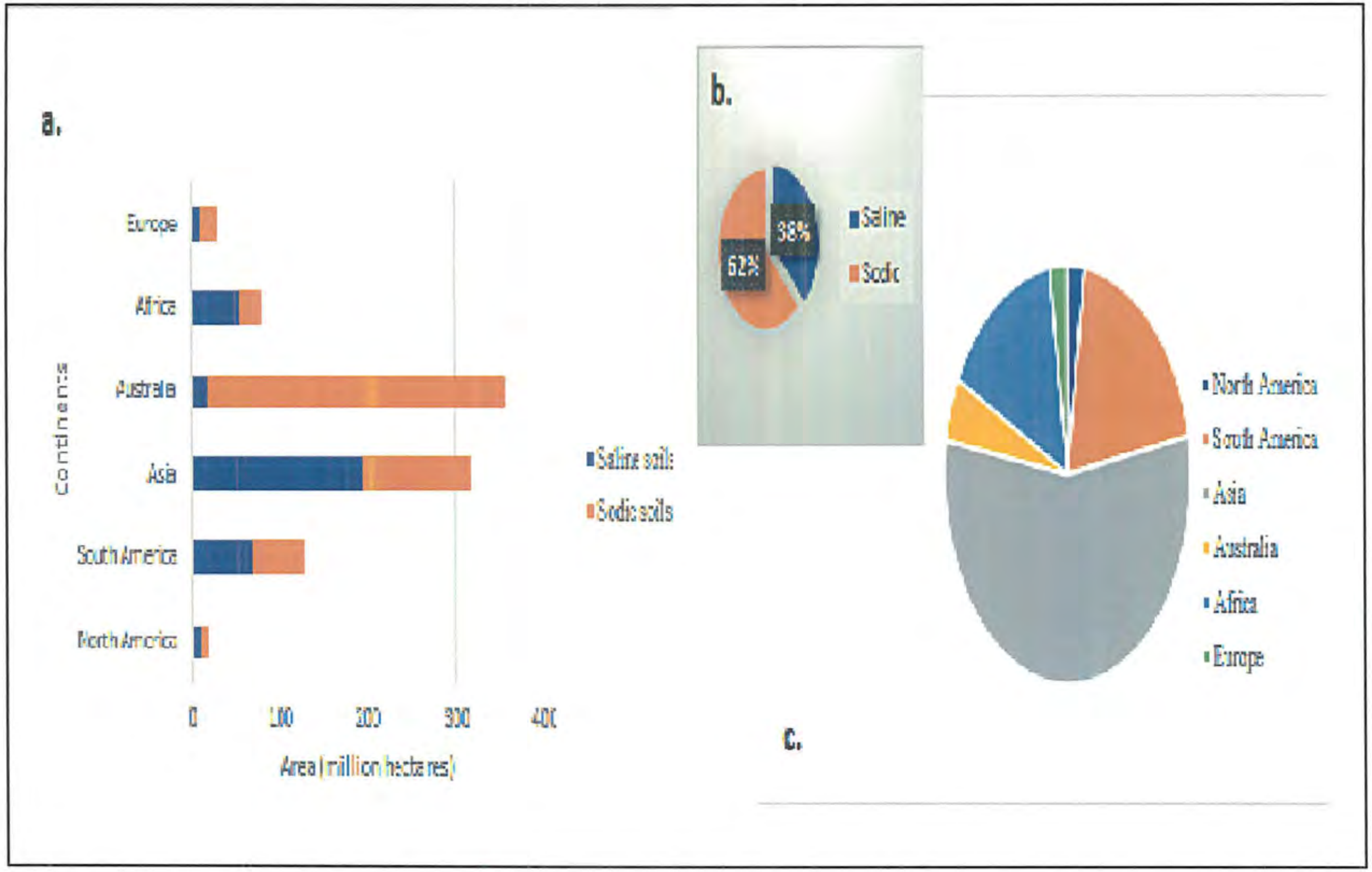


Figure 1.3: (a) Continent wise distribution of saline and sodic soils, (b)Percentage of global occurrence of saline and sodic soils, (c) Continent wise distribution of saline soils showing highest soil salinization in Asia *(Rengasamy, 2006)*

1.3. Effects of salinization

Water with increased TDS level affects the human health if consumed for a long period of time. As TDS is a mere count of the number of different ions dissolved in water therefore the type of health effect would depend on the fact that excess of which ion is responsible for the elevated TDS levels in water (for instance excess Ca can result in kidney stones).

Increased salinization becomes a threat to the ecosystem. It affects the plant growth and reduces crop yield by accumulation in the root zone (Kobryn et al., 2015). Drinking water with increased salinity causes high bloodpressure incidences in the young adults leading to cardiovascular problems (Talukder et al., 2016). The populations living in the coastal areas of Bangladesh are reported to suffer from a range of health issues such as hypertension (Khan et al., 2011), skin diseases, respiratory infections, diarrheal diseases and miscarriages associated with enhanced exposure to salts (Vineis et al., 2011).Groundwater with TDS >1000mg/l is not considered safe for human (WHO, 2011) whereas TDS> 2000mg/l is harmful for many plant species (Jia et al., 2017).

1.4. Groundwater Salinity in Indus Basin Pakistan

Groundwater has turned out to be a resource of strategic significance due to its elevated demand in domestic and agricultural uses. Good quality assurance of groundwater is a key issue as 90% of the inhabitants of the most populated province i.e., Punjab relies on groundwater for their everyday domestic needs (Qureshi et al., 2010). Investigations of groundwater quality of Pakistan through British Geological Survey have identified increased salinization of groundwater as a major concern prompting towards the confinement in the availability of precious resource (Smedley, 2001). Moreover, events of excessive arsenic and fluoride contamination in some ground water sources within Indus Plain are reported to be additional water quality concerns faced by Pakistan.

Pakistan possesses a blend of climatic zonation from humid to arid conditions as shown in figure 1.4. However, the climate is mainly classified as arid to semi-arid (Chaudhry and Rasul, 2004). Irrigation developments in such regions often result in problems of salinity. The balance between the accessible water and population already makes Pakistan a water stressed country. This status is soon expected to be water scarce with the continuous rising population. Indus River which has suffered a huge human foot print is the major river holding the dependence of the agrarian economy and population of the country (Briscoe et al., 2006). The incidence of most of the groundwater and soil salinization in the Indus Basin is a legacy of the development of the canal irrigation system in 1859. Waterlogging, high evaporation due to climatic conditions, industrial pollution and sea water intrusion in coastal areas are the reasons accounted responsible for salinity. The issue influences groundwater in considerable parts of Sindh, Punjab, Balouchistan and Khyber Pakhtunkhwa. Sodium and Chloride are found to be the dominant ions in the groundwaters with elevated TDS (Smedley, 2001).

Furthermore, much of the soil salts in Indus are of inherited origin brought in by the Indus River and its tributaries during soil formation. A portion of fossil salts also occupies the deeper strata of Indus deposited during course of its formation exploited while pumping through deep tube wells. Qureshi et al. (2008) has studied the distribution of Groundwater quality in Indus Basin demonstrated in figure 1.5.

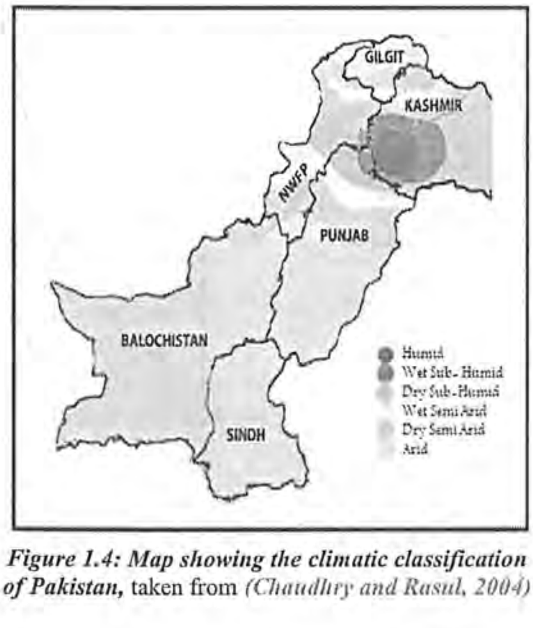


Figure 1.4: Map showing the climatic classification of Pakistan, taken from *(Chaudhry and Rasul, 2004)*

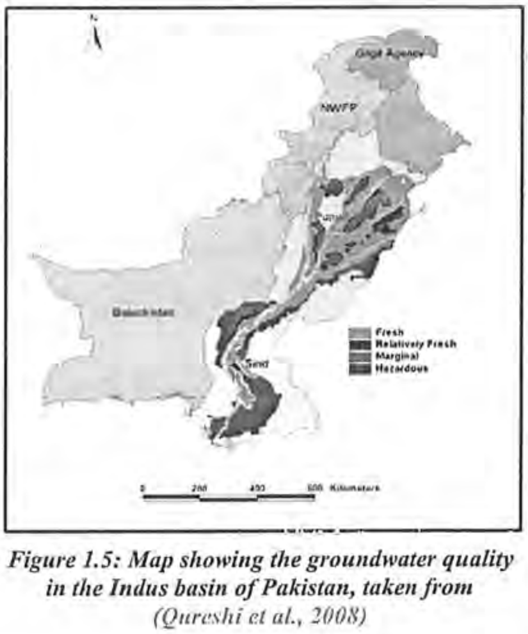


Figure 1.5: Map showing the groundwater quality in the Indus basin of Pakistan, taken from *(Qureshi et al., 2008)*

1.4.1. Development of Indus Basin Irrigation System- Rise of Water tables

The Indus Basin Irrigation System was developed with three basic concepts of avoiding famine, to prevent crop damage and for the effective provision of water to as large an area possible. Before development of canal system, the water table was 20 to 30 m below the soil surface therefore the need for a proper drainage system was not anticipated at that time. However soon after the introduction of the huge canal network the ground water table rose to 1.5m of the soil surface as shown in figure 1.6 resulting in the problems of water logging and salinization in the area. The hydrological balance of the Indus Basin was severely disturbed. Furthermore, the excessive use of groundwater for irrigation also contributed to the secondary salinity in the basin. As a result approximately 4.5 million ha of the area was gradually subjected to this menace (Qureshi et al., 2008).

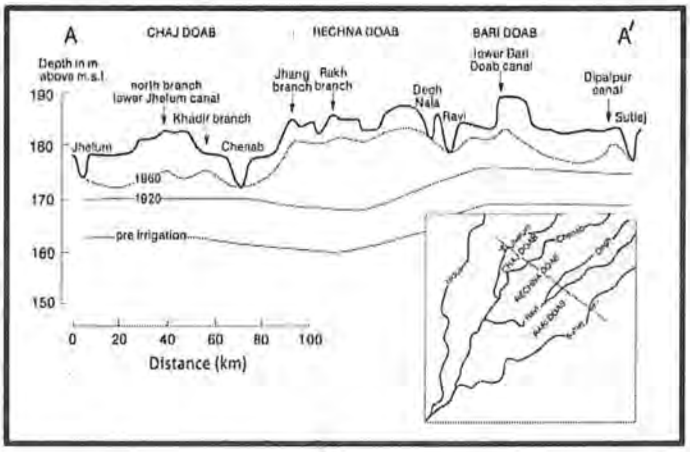


***Figure 1.6: Groundwater profiles for the pre-irrigation period, years 1920 and 1960 are shown highlighting the rise in groundwater level after the development of canal irrigation system, taken from** (Qureshi et al., 2008)*

1.4.2. Land Reclamation initiatives

To study the effect of irrigation on the depth of groundwater table, monitoring wells were installed in 1870. Based on the findings of these studies several efforts including lowering the full supply levels of canals, lining of the canals, surface drains development and shifting of irrigation from perennial to non-perennial was carried out (Rehman et al., 1997a). All of these measures turned out to be nothing more than a temporary relief. Later on, based on the results of US Geological Survey various measures to alleviate the problem such as SCARP tube well programs, Left Bank outfall Drain (LBOD) and Right

Bank outfall Drain (RBOD) were initiated. However, the efforts proved out to be successful initially but ultimately resulted to be a burden due to lack of proper maintenance, operation and disposal facilities (Qureshi et al., 2008).

1.5 Distribution of Arsenic and Fluoride in Indus Basin Pakistan

Arsenic and fluoride are currently perceived as the most severe inorganic contaminants found in drinking water (Smedley and Kinniburgh, 2002) and unfortunately ground waters in some areas of Pakistan are known to be a victim of these contaminants.

1.5.1. Arsenic

Arsenic occurs in environment in both organic and inorganic forms. However, inorganic form has greater abundance i.e., 90% all over the world relative to the organic forms. It primarily occurs in groundwater as oxyanion in two oxidation states i.e., arsenite (As^{+3}) and arsenate (As^{+5}) within the pH range of 6 to 9 (Shankar and Shanker, 2014). The speciation of arsenic is governed by two major factors, redox conditions and pH. Albeit Oxic conditions of groundwater support the presence of arsenate (As^{+5}) whereas arsenite (As^{+3}) is dominant in anoxic environments (Jiang et al., 2012). The reducing form of arsenic (As^{+3}) is more toxic and mobile. Groundwater arsenic contamination is a worldwide concern with 150 million people affected globally (Ravenscroft et al., 2009). Bangladesh has suffered 'The largest poisoning of a population in history' through elevated arsenic groundwater levels (Smith et al., 2000). Arsenic was declared a major public health concern by World Health Organization in 1999 to be dealt with on an emergency basis (WHO, 1999). The permissible limit of arsenic given by WHO is 10µg/l. The contamination of this known carcinogen in the ground waters of Pakistan is an important issue which was first officially recognized in year 2000. Many research studies have then been conducted as mentioned in table 1.2 by various authors with reference to arsenic in ground waters of different areas of Pakistan followed by the joint screening and detailed survey carried out by PCRWR and UNICCEF (Baig et al., 2009; Baig et al., 2010; Brahman et al., 2013; Farooqi et al., 2007a; Farooqi et al., 2007b; Gilani et al., 2013; Haque et al., 2008; Jabeen et al., 2014; Malana and Khosa, 2011; Muhammad et al., 2010; Mushtaq et al., 2018; Nickson et al., 2005; Rasool et al., 2016).

In the light of this survey the levels of As contamination in ground waters of Sindh and Punjab were found to be 10 – 50µg/l and 10 – 200µg/l respectively

.

Table 1.2: Distribution of Arsenic in ground waters of different regions of Pakistan along with their respective water types and salinity levels

Location	**Climate**	**Dominant Water type**	**As (µg/l)**	**TDS (mg/l)**	**Environmental Factors**	**References**
DG Khan	Arid	$CaSO_4$, $MgSO_4$	1 - 29	1484 - 8401	Metal leaching, Microbial contamination, Reduction of HFO, evaporative concentration	(Malana and Khosa, 2011)
Rahim yar Khan	———	———	150 - 400	———	Reductive dissolution of FeOOH, Enhanced application of phosphatic fertilizers	(Haque et al., 2008)
Jamshoro	Sub-arid, tropical, Continental	———	13 - 106	188 - 2214	Water logging, Reduction of iron hydroxide, Oxidation of pyrite in sediments, phosphatic fertilizers	(Baig et al., 2009)
Lahore 2007a	Semi arid, Continental	Na-HCO_3, Na-HCO_3-SO_4	32 - 1900	224 - 1984	Coal combustion,	(Farooqi et al., 2007a)
Lahore 2007b	Semi arid, Continental	Na-HCO_3	1 - 2400	256 - 2944	Coal Combustion, Application of Diammonium phosphate (DAP) fertilizer	(Farooqi et al., 2007b)
Lahore 2018	Semi arid	Na-Cl	2 - 548	307- 2572	Evaporative concentration, Alkaline conditions	(Mushtaq et al., 2018)
Muzaffargarh	Semi arid	———	1 - 906	200 - 4230	Reduction of HFO	(Nickson et al., 2005)
Sheikhupura	Semi arid	———	0 – 0.12	170 - 1023	———	(Gilani et al., 2013)
Tharparkar	Tropical desert climate	———	250 - 4120	496 - 11800	Biogeochemical, geohydrological, climatic factors, brackish under groundwater, reductive dissolution	(Brahman et al., 2013)

Kohistan Region	——	$CaHCO_3$	0.13 – 16.69	68.10 - 433	Geogenic source	(Muhammad et al., 2010)
Haripur Basin	——	——	<0.15 – 3.7	104 - 1250	Industrial effluents	(Jabeen et al., 2014)
Khairpur Sindh	Semi arid, sub tropical continental	——	9.2 – 361	153 -3350	——	(Baig et al., 2010)
Mailsi area	Semi arid	$CaMgHCO_3$	11 - 828	469 - 1911	Evaporative enrichment, Alkaline conditions	(Rasool et al., 2016)

1.5.2. Fluoride

Fluoride is another important groundwater pollutant that poses a threat to the groundwater quality of Pakistan. It serves as an essential micronutrient with dual impacts i.e., it has harmful effects both in low and excessive amounts. The safe permissible limit of fluoride set by the WHO is 1.5 mg/l. Intake of decreased amounts causes dental carries where as consumption of amounts greater than 1.5 mg/l results in various disorders particularly dental and skeletal fluorosis. Research studies have shown that fluoride contamination is known to cause impacts on muscular system, kidney, lungs, levels of erythrocytes and blood pressure. It increases the risk of heart disease, cancer and causes other diseases such as keratosis, hyperpigmentation and melanosis (Rasool et al., 2017).

Globally around 200 million people from twenty five nations of the world including Pakistan, China, India, Iran, Canada, USA, New Zealand, Thailand, Japan, Libya, Algeria, Iraq, Turkey, Scandinavia, Sri Lanka and East Africa's rift valley are suffering the alarming situation of elevated fluoride pollution. Among them the two most populous worst affected countries are India and China. Out of 85 million tons of world fluoride deposits, 12 million are present in India. China has greater than 26 million of its population suffering from chronic fluorosis whereas 16.5 million are at the threat of fluorosis due to coal burning (Brindha and Elango, 2011).

Presence of fluoride in groundwater of Pakistan is found in many areas as presented in table 1.3 which shows that fluoride contamination extends in Punjab Sindh and KPK. More than 2 million people in Pakistan are suffering from the effects of Fluoride pollution. The range of fluoride reported in different regions of Punjab including Lahore and Kasur Districts, Dera Ghazi Khan and Tehsil Mailsi is 0.11 – 29.6 mg/l. Climatic conditions in Sindh are responsible for triggering the fluoride levels in Tharparkar and Nagarparkar. Moreover, inhabitants of KPK suffer from fluorosis due to geogenic factors leading to high degree of fluoride in groundwater (Bashir et al., 2012: Brahman et al., 2013; Farooqi et al., 2007a: Farooqi et al., 2007b; Kausar et al., 2003: Naseem et al., 2010: Rafique et al., 2015; Rafique et al., 2009; Rasool et al., 2015; Siddique et al., 2006; Ullah et al., 2009).

Table 1.3: Concentration of Fluoride in ground waters of different regions of Pakistan along with their respective water types and salinity levels

Location	**Climate**	**Water type**	**F (mg/l)**	**TDS (mg/l)**	**Environmental Factors**	**References**
PCRWR (16 major cities)			1.6 - 25			(Bashir et al., 2012)
Lahore 2007 a	Semi Arid, Continental	$NaHCO_3$, $NaHCO_3$-SO_4	2.47 – 21.1	224 - 1984	Coal Combustion, Air pollution	(Farooqi et al., 2007a)
Lahore 2007 b	Semi arid, Continental	$NaHCO_3$	0.11 – 22.8	256 - 2944	Coal Combustion, Fertilizers (DAP)	(Farooqi et al., 2007b)
Tehsil Mailsi	Semi Arid	$NaHCO_3$, K-HCO_3	5.5 -29.6	418 -1326	Brick factories, Agricultural activities	(Rasool et al., 2015)
Faisalabad	Semi Arid	——	0.37 – 1.15	310 - 2330	——	(Kausar et al., 2003)
Tharparkar	Tropical Desert Climate	——	13.8 – 49.3	701 - 10218	Aridity of climate	(Brahman et al., 2013)
Nagarparkar	Arid	Na-Cl	1.13- 7.85	449–15933 564-18642	Granitic rocks, geology, soil	(Naseem et al., 2010; Rafique et al., 2009)
Karachi City	——	——	0.60 – 3.64	——	Tiles, glass and ceramic industries	(Siddique et al., 2006)
Sialkot	Semi arid and arid	——	0.41 – 0.99	135.10 -581.00	——	(Ullah et al., 2009)
Umar Kot	Arid	$NaHCO_3$	0.06 – 44.4	518 - 39067	Weathering of granite minerals, evaporation, anion exchange	(Rafique et al., 2015)

1.6. Simultaneous occurrence of Arsenic and Salinity in groundwater

Arsenic release in groundwater occurs through four basic geochemical mechanisms namely oxidative dissolution, reductive dissolution, evaporative concentration and competitive anion exchange (Rasool et al., 2015). Oxidation of pyrite (Eq i) and arsenopyrite mainly contribute to arsenic release in oxic water thereby releasing the arsenic attached to metal complexes.

$$FeS_2 - As(s) + 7/2\ O_2 + H_2O \rightarrow Fe_2^{+} + 2SO_4^{2-} + 2H^{+} + As(aq) \quad \text{.... Eq (i)}$$

In anoxic conditions microbial reduction of organic matter containing arsenic coated hydrous ferric oxides to obtain oxygen needed for their metabolism results in arsenic contamination. The mechanism proposed for arsenic release from HFO is given in equation (ii)

$$8FeOOH + CH_3COO^{-} + 15H_2CO_3 \rightarrow 8Fe^{2+} + 17HCO_3^{-} + 12H_2O \quad \text{.... Eq (ii)}$$

Arsenic is present in environment bound to hydrous ferric oxide and clay surfaces. Excessive presence of anions such as phosphates leads to competitive anion exchange. Phosphates attach themselves to the mineral surfaces at arsenic binding site thereby releasing arsenic to the groundwater (Khalequzzaman et al., 2005). Conditions in arid and semi arid regions where groundwater extraction rate is higher than its recharge rate combined with elevated evaporation can lead to enrichment of arsenic particularly in low-lying closed basins. The phenomenon is observed in Western United States in the South of San Joaquin Valley and Carson Desert (Welch et al., 2000).The groundwater of the Western transect of Meghna Basin Bangladesh has increased salinity and As concentration whereas the water at the eastern transect is found to be fresh with As concentrations less than the WHO prescribed limits (Hasan et al., 2009).Two basic triggers are mainly responsible for arsenic release; one is the development of increased pH as a result of high evaporation rate and salinity in semi arid or arid regions leading to desorption of arsenate from mineral oxides particularly iron oxide (Mladenov et al., 2014). Research studies have reported the occurrence of this type of mechanism in various arid and semi-arid countries including Argentina, Southwestern USA, Chile and Pakistan (Camacho et al., 2011; Nickson et al., 2005; Nicolli et al., 2010). Second trigger involves the development of reducing conditions at which reductive dissolution of mineral oxides leads to desorption of arsenite. SO_4^{-2} concentrations in reducing waters are less whereas Fe^{+2} and As^{+3} are found in abundance. Reducing mechanism of groundwater arsenic contamination is reported to occur in Bangladesh, West Bengal India, Northern China, Taiwan, Red River delta Vietnam, Hungary and Romania (Smedley and Kinniburgh, 2002). Groundwater arsenic contamination in semi arid and arid climate occurs through evaporative enrichment of arsenic in water. Aquifers with elevated concentrations of arsenic in Northern Chile (Atacama Desert) and Argentina (Chaco-Pampean plain) are some of the examples of climate influenced aquifers (Nicolli et al., 2010). Increased arsenic contamination is often accompanied by high salinity for instance, highly saline (TDS 11000 mg/l) Rio Lao Basin is found to be profoundly enriched with arsenic as well. Salinity might also have a considerable effect on the toxicity of arsenic (speciation) (Liu et al., 2015). Rodriguez-Lado et al. (2013) through modeling reported soil salinity as a significant factor along with other variables in predicting the occurrence of arsenic in groundwater. In semi arid region, climate through evaporation-condensation mechanism promotes soil pollution resulting in further serious groundwater contamination. Increased levels of EC may be associated with the development of pollution in water. Studies in Punjab, Pakistan (Farooqi et al., 2007b; Malana and Khosa, 2011) reported that the sampling sites having arsenic $>10\mu g/l$ displayed high concentrations of EC as well. Moreover increased evaporation and salinity might partially contribute to desorption of arsenic to groundwater from mineral surfaces. In DG Khan As showed no clear trend with physicochemical parameters of water however, a slight correlation was observed between As levels and values of EC, Na^+ and Cl^- . Furthermore, the enhanced concentrations of arsenic in shallow groundwaters of Jamshoro and Muzaffargarh may be attributed to the phenomenon of water logging and high saturation of salts in the areas (Baig et al., 2009; Nickson et al., 2005). Contamination of As along with salinity have also been found to occur in the fresh water of Manchar lake and the groundwater in its vicinity. Apart from anthropogenic causes the natural phenomenon of evaporative concentration has been accounted responsible for the buildup of salts (Baig et al., 2010).

1.7. Simultaneous occurrence of Fluoride and Salinity in groundwater

On the other hand the factors accounted responsible for the occurrence of elevated fluoride levels in groundwater are, water rock interaction, climate (evapo-transpiration), time (long residence time), mineral saturation (dissolution of fluorite/ fluorapatite) and groundwater composition (Alkaline pH, high Na^+ and HCO_3^-, low Ca^{+2}) (Edmunds and Smedley, 2005; Kim and Jeong, 2005; Saxena and Ahmed, 2001; Valenzuela-Vasquez et al., 2006). Based on these factors the mechanisms used to explain fluoride pollution in groundwater involve ion exchange, dissolution of fluoride minerals and evaporative concentration whereas condensation of soluble components in arid and semi arid areas is also considered a probable fluoride enrichment mechanism. The geochemistry of water that supports high fluoride is often based on alkaline pH with high Na, HCO_3 and low levels of Ca and Mg ions. At acidic pH fluoride adsorbs with clay particles where as it desorbs at alkaline pH with high bicarbonate ions, a condition which promotes precipitation of calcite (Rasool et al., 2017). Higher salinities due to low recharge rates and longer water mineral interaction lead to higher fluoride content in some arid regions. Evaporation is another significant factor enhancing the occurrence of fluoride in shallow groundwater. The deposited evaporative salts in arid zones act as a source of fluoride. Futhermore, salinity is one of the governing factors in the adsorption and desorption of fluoride onto clay minerals (Sivasankar et al., 2016). Elevated groundwater fluoride concentrations in North Gujrat-India overlapped with high EC are associated with evaporative enrichment along with thermal springs and dissolution of fluoride bearing minerals (Gupta et al., 2005). Elevated TDS levels increase the ionic strength of groundwater thereby further increasing the solubility of Fluoride (Su et al., 2013). Competitive ion exchange favors high fluoride concentrations in two ways i.e., base exchange, which leads to decreased Ca concentrations and anion exchange in alkaline conditions where F^- is replaced by OH in certain clay minerals and weathered micas (Brahman et al., 2013). A dominant fraction of fluoride contributed to groundwater comes from the dissolution of fluoride bearing minerals and rocks (Banerjee, 2015). Though not readily soluble but under particular environmental conditions such as alkaline pH and specific conductivity of 750 and 1750 μS/cm the dissolution rate of fluoride minerals such as fluorite and cryolite increases. The mechanism of fluorite dissolution is given below (Saxena and Ahmed, 2001).

$$CaF_2 + 2HCO_3 \rightarrow CaCO_3 + 2F + H_2O + CO_2$$

In Pakistan, dry climate has been accounted as a primary factor contributing to increased fluoride in groundwater of Tharparkar (Brahman et al., 2013). Furthermore research studies in Nagarparkar, Umarkot and Lahore have reported most of the high fluoride samples associated with elevated TDS levels (Rafique et al., 2009; 2015).The impact of salinity on the enrichment of As and fluoride has been explored by some researchers. Studies focused on this aspect are presented in table 1.4

Table 1.4: Listed are the studies focused on studying the impact of salinity on Arsenic and Fluoride enrichment in ground waters

Location	**TDS mg/l**	**Link between As and Salinity**	**Link between F and Salinity**	**Causes of Salinity**	**Reference**
Hetao Basin, China	351-6734	Positive. (SO_4 and iron oxide reduction leads to enrichment of As)	———	Non-direct evaporation (capillary evaporation and transpiration) and mineral evaporate dissolution	(Jia et al., 2017)
Datong Basin, China	451-10,000	Negative	Partial contribution	Water rock interaction, surface saline soil flushing, evapo-transpiration	(Li et al., 2016)
Yuncheng Basin, Northern China	> 4000	———	Positive	Salk lake water intrusion	(Gao et al., 2007)
Andra Pradesh India	850-3380	———	Partial	Evaporation, occurrence of clay, Salt pans and aqua cultural activities and marine sources	(Rao et al., 2017)

1.8. Problem Statement

Salinization of soil and groundwater are a known phenomenon in the arid and semi-arid Indus Basin of Pakistan. Extensive studies with reference to As and F^- have been carried in Punjab showing high levels of salinity with increased As and F^- in ground waters of some areas. However, the link between salinity and enrichment of arsenic and fluoride is still to be explored in the Basin.

Therefore, the present study aims at exploring the link that might be present between the occurrence of salinity and enrichment of arsenic and fluoride in the groundwater of Rachna Doab by incorporation of groundwater chemistry and geochemical modeling PHREEQC. As a better understanding of groundwater salinity might provide valuable information and further clarity in understanding groundwater arsenic and fluoride in the study area.

1.9. Objectives of the study

- To investigate the role of salinity in regulating the mobilization of arsenic and fluoride
- To assess the impact of changing hydrogeological conditions on the toxicity of arsenic through speciation
- To present a conceptual model of groundwater recharge sources and contribution of various factors towards salinity in Rachna Doab

1.10. Expected Outcomes

- A better understanding of groundwater salinity and its impact on the enrichment and mobilization of arsenic and fluoride
- A step towards the development of an improved remediation strategy and policy making

CHAPTER 2

MATERIALS AND METHODS

2. Methodology

2.1. Description of the Study Area

2.1.1. Location & Climate

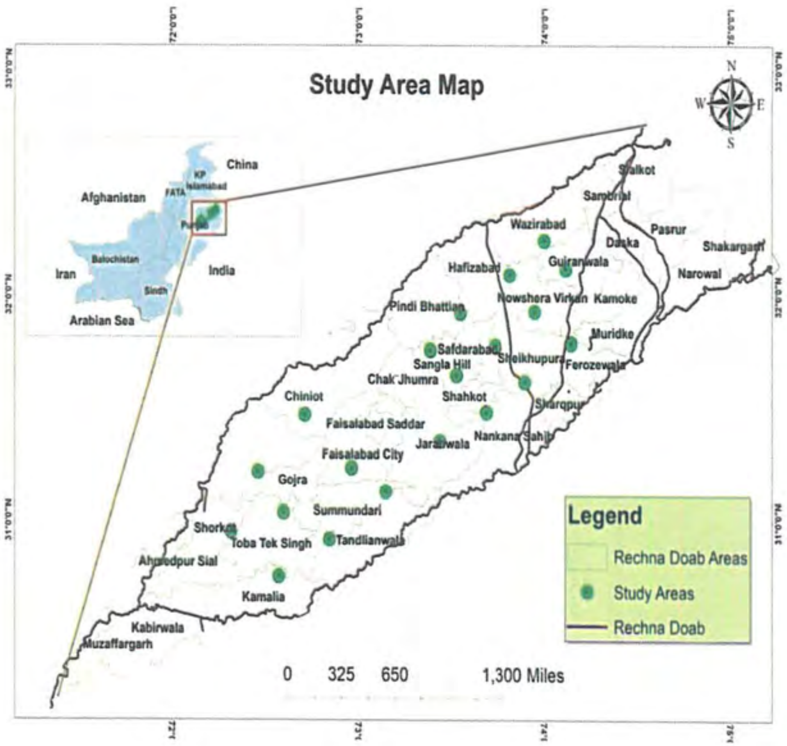
The study area, Rachna Doab is an interfluvial area between Chenab and Ravi rivers. It lies between longitudes 71°48′ E to 75°20′ E and latitude 30°to 32°51′ and is located in the core of Indus Basin. The area experiences massive seasonal variations in rainfall and temperature. It is characterized by semi-humid climate in the northeast which alters to semi arid towards the south west. Rachna Doab receives an average annual rain fall of 400mm. Maximum air temperatures in summers and winters are 21°C to 49°C and 25°C to 27°C respectively with a drop below zero at night time in winters (Bastiaanssen and Feddes, 2005).

2.1.2. Physiography

Rachna Doab is a flat terrain possessing a topographic relief difference towards the southwest. The area has an average slope of 0.37m/km which decreases by 25% in the lower part of doab. Four landforms forms namely floodplains, abandoned floodplains, bar uplands and piedmont have been identified in Rachna Doab by the Soil Survey of Pakistan. Studies report that geologically Punjab is underlain by unconsolidated alluvial deposits. Soils are composed of different proportions of sand, silt and clay. Presence of coarse sand or gravel is a rare phenomenon. Some areas contain patches of saline soils with occurrence of kankar zones in the upper sub strata (Sajjad et al., 1992).

2.1.3. Geological and Hydrogeological conditions

The bed rock geology is composed of igneous and metamorphic rocks of Precambrian times known as Kirana hills. The overlying unconsolidated alluvial deposits on these precambrain basements are of Pleistocene to recent age. The alluvium is nearly homogenous however reduced vertical and lateral continuity is observed indicating the diversity of depositional environments throughout the passage of time (Rehman et al., 1997b). The deep unconfined aquifer underlying the Indus plain is made up of the alluvium deposited in the late tertiary period. The aquifer is heterogenous and highly



(a)

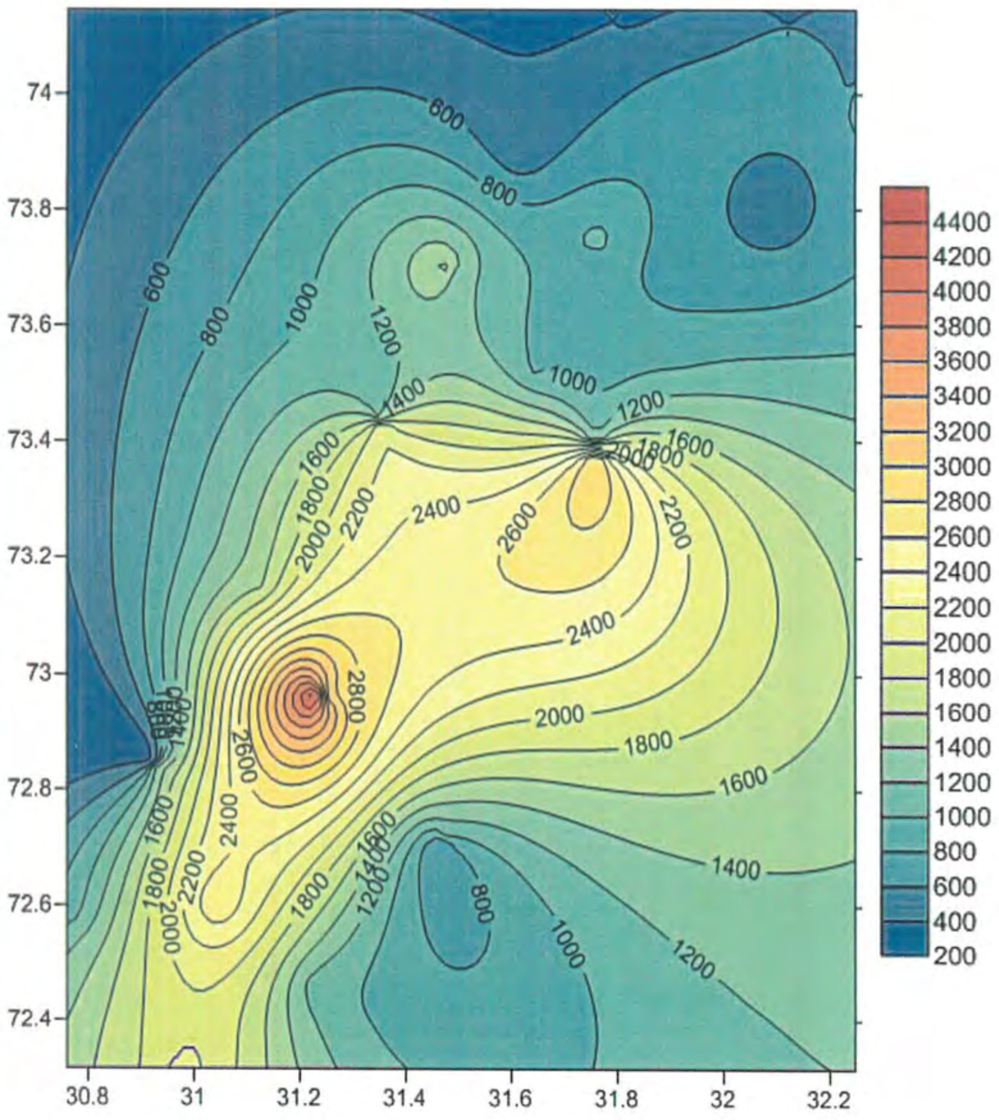


Figure 2.1: Study area map showing the sampling points with part (a) representing the contours of TDS distribution in groundwater of Rechna Doab

anisotropic with a thickness of greater than 300 meters. The region has little natural drainage. Aquifer material is highly porous capable of storing and transmitting water with relatively higher horizontal than vertical permeability (Sajjad et al., 1992).

2.1.4. Land use

The Doab covers approximately an area of 2.97 million ha with 2.3 million ha of developed land. It is an ancient most intensively developed irrigated land of Punjab. Cotton, rice, wheat, forage and sugar cane are the major crops cultivated in the area. Owing to erratic and scanty precipitation canal irrigation system was introduced in 1892 to achieve successful agricultural practices. Groundwater salinity is a major issue found in most regions of Rachna doab (Sikandar et al., 2010).

2.2.Ground Water sampling

Blanket sampling of groundwater was carried out in the month of September 2016-2017 for the screening of Rachna doab to test the occurrence of salinity, arsenic and fluoride. 1179 wells were sampled with depth ranging from 5 ft to 600 ft. Groundwater in-situ parameters were measured on field using portable multiprobe meter Oaktron® pH meter (Vista, CA, USA) along with As and F^- through Arsenic Econo Quick II kit and Hanna Instrument HI96739 Fluoride High Range portable photometer respectively. The results of blanket sampling revealed that 55.6%, 40.7% and 4.6% of the samples had TDS<1000 mg/l (fresh water/ non-saline), 1000-3000 mg/l (slightly saline) and >3000 mg/l (moderately saline) respectively. Samples from wells with depth greater than 100 ft were found to fall in fresh category i.e., TDS< 1000 mg/l. Based on the results of blanket sampling a total of 54 representative groundwater samples with depth ranging from 35ft to 250ft were collected from all villages throughout doab.

2.2.1. Sample Collection

Groundwater samples were collected in duplicates. Collection was carried out in 100 ml polypropylene bottles in accordance with the protocols defined by (APHA, 2005). One subsample was left untreated for anion analysis whereas the other subsample was acidified by the addition of HCL to lower the pH<2 for major cation analysis. For the

2.3. Groundwater Quality Analysis

Water samples were analyzed for their physicochemical parameters, pH, EC, anions, cations, bromide and arsenic. The standard protocols followed for the determination of various physicochemical parameters are described below.

2.3.1. In-situ parameters

pH, EC and TDS measurement

Electrical conductivity and pH of the groundwater samples were measured on field using multiprobe meter i.e., Oaktron® pH meter (Vista, CA, USA) whereas TDS was calculated indirectly through electrical conductivity using the relationship given by (Shainberg and Levy, 2005) for a mixture of salts.

$$\text{TDS (mg/l)} = 640 * \text{EC(mS/cm)} \text{ ....Eq (1)}$$

2.3.2. Laboratory analysis – Determination of Anions

Alkalinity and chlorides were measured using titrimetric method while other major anions including sulphates, phosphates and nitrates in the groundwater samples were determined via UV visible spectrophotometer HACH DR-5000 following the standard methods (APHA, 2005).

2.3.2.1. Alkalinity

The determination of bicarbonates and carbonates in the groundwater samples was carried out by performing simple acid-base titration. Standardization of 0.1 N H_2SO_4 against 0.1 N NaOH was carried out before titration whereas phenolphthalein and methyl orange were the indicators used for analysis of total alkalinity (APHA, 2005). Alkalinity was then calculated by using the following equation:

$$Alkalinity\ (mg/l) = \frac{Acid\ used\ (ml) * N * 50 * 1000}{volume\ of\ sample\ (ml)} \qquad \text{Eq(2)}$$

2.3.2.2. Chlorides

The concentration of chlorides in the groundwater samples was determined through argentometric titration. Potassium chromate was added in the samples as indicator and the samples were titrated against silver nitrate. The development of red color indicated

2.3.2.2. Chlorides

The concentration of chlorides in the groundwater samples was determined through argentometric titration. Potassium chromate was added in the samples as indicator and the samples were titrated against silver nitrate. The development of red color indicated the end point of titration (APHA, 2005). The equation used for the calculation of chloride concentration in the groundwater samples is as follows:

$$Chlorides\ (mg/l) = \frac{volume\ of\ AgNO3\ used(ml)*N*35.45*1000}{volume\ of\ sample\ (ml)} \quad \text{........Eq (vi)}$$

2.3.2.3. Sulphates, Nitrates and Phosphates

Sulphates, phosphates and nitrates in groundwater samples were determined using UV visible spectrophotometer HACH DR-5000 model. For sulphates the sample was precipitated as barium sulphate by the addition of conditioning reagent and a pinch of barium chloride crystals. The resultant solution was analyzed spectrophotometrically at 420nm wavelength. The sample preparation for nitrates was carried out by heating the sample to dryness and dissolving the content in phenol di-sulphonic acid. The addition of phenol di-sulphonic acid results in the formation of a nitro derivative which in alkaline condition i.e., upon the addition of ammonia develops a yellow color. The developed color was analyzed at 410nm wavelength. Furthermore, the measurement of phosphates was performed by the addition of ammonium molybdate to the sample along with a reducing agent ie., stannous chloride. The addition of stannous chloride produces blue color as an indication of the presence of phosphates in the sample. The resulting solution was then analyzed at 690nm wavelength (APHA, 1985; Trivedy and Goel, 1984).

Prior to analysis the instrument was calibrated using working standards. The calibration curves were plotted according to the Beer's Lambert Law by plotting the concentration of the working standard against the absorbance measured. These calibration curves were then used for the calculation of the concentration of sulphates, phosphates and nitrates in the ground water samples.

2.3.3. Determination of Cations, and Arsenic

Major Cations (Na^+, K^+, Ca^{+2}, Mg^{+2}) and arsenic was analyzed using Atomic absorption spectrophotometer (APHA, 2005). The instruments were calibrated prior to analyses.

2.3.4. Stable Isotopic ($\delta\ ^{18}O$ and $\delta\ ^{2}H$ relative to VSMOW) Analysis

Stable isotopic compositions ($\delta\ ^{18}O$ and $\delta\ ^{2}H$ relative to VSMOW) of groundwater samples were determined using Liquid Water Isotope Analyzer, LWIA-24-EP at laboratory of Isotope Application Division, Pakistan Institute of Nuclear Science and Technology (IAD, PINSTECH).

2.3.5. Arsenic Speciation

The speciation of arsenic was carried out using column speciation method. The method is used only for the removal of inorganic species of arsenic. The adsorbent in the column (cartridge) retains As^{+5} whereas $As^{+3}$is allowed to pass through in the filtered water. The concentration of As^{+5}in water was determined by the following equation:

As_T = Total As in raw or 0.4μm filtered water

As^{+3} concentration = Total As in column filtered water

As^{+5}concentration= As_T - As^{+3}

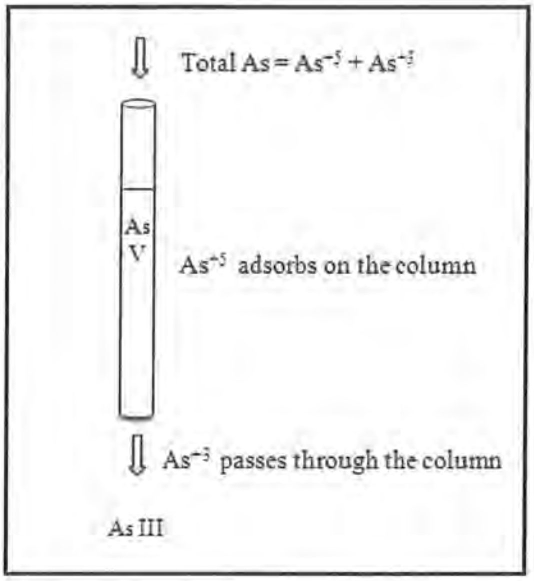


Figure 2.2: Onsite Column speciation method for inorganic arsenic species

taking place in the study area. Saturation indices were calculated through PHREEQC software whereas graphical representation of results was presented using Microsoft Excel 2013. Basic statistical analysis was performed on SPSS-20 whereas assessment and interpretation of results by applying Principle Component Analysis (PCA) was carried out using Multivariate Statistical Packages software (MVSP).

CHAPTER 3

RESULTS AND DISCUSSIONS

3. Results and Discussions

Current research was based on studying the sources of groundwater salinity and its possible impact on the enrichment of groundwater As and F^- levels. Groundwater samples understudy were classified into three groups based on their TDS levels (salinity). The quality of groundwater was assessed against various physicochemical parameters. The analytical results of all physicochemical parameters measured in groundwater samples are presented in table 3.1 whereas the detailed analysis is mentioned in Annexure I.

3.1. Groundwater Chemistry of the study area

Groundwater samples of the study area were analyzed for the physicochemical parameters (pH, EC, TDS, As, F, major cations and anions). Results of physical analysis stated that groundwater is slightly acidic to alkaline in nature having a pH ranging between 6.18 and 8.48. The samples showed great variation in EC (μS/cm) and TDS (mg/l) ranging between 365 to 7120 μS/cm with a mean of 2980.9 μS/cm and 233.6 to 4556.8 mg/l with a mean of 1907.8 respectively. Further the groundwater samples understudy were grouped on the basis of their TDS levels following the Rabinove et al. (1958) classification i.e.,

- TDS <1000 mg/l – Fresh water
- TDS 1000-3000 mg/l – slightly saline
- TDS 3000-10,000 mg/l – moderately saline
- TDS >10,000 mg/l – very saline

The samples of the current study however lie in the first three classes (table 3.1). Very saline water is not found in the study area. The TDS calculated in the present study through the relationship given by (Shainberg and Levy, 2005) showed a good correlation (R^2= 0.937) with TDS calculated based on major ion compositions Annexure II.

In general the order of major cationic abundance in groundwater of the study area was Na>Ca>Mg>K. Na was found to be the major cation with concentration ranges between

10.8 and 1381.7mg/l. Out of the total, 72% of the groundwater samples exceeded the WHO permissible level of Na i.e., 200mg/l with highest concentration in moderately saline water. The content of Ca and Mg was found to be above WHO permissible limit in 10 and 15 groundwater samples respectively. Furthermore, 59% of the groundwater samples were found to have enhanced K levels.

However, in case of anions sulphate were found to be the major anion with concentrations varying between 2.1 and 2134.2 mg/l with a mean of 501.3 mg/l. Among 54 groundwater samples, 31 samples of slightly and moderately saline water were found to have SO_4 levels higher than WHO standards. The Alkalinity of groundwater samples ranged from 200 to 700 mg/l with an average of 405.6 mg/l. Chloride appeared as the third dominant anion with 43% of samples possessing enhanced groundwater chloride levels. Elevated levels of PO_5 were identified in 22 samples ranging from 0.6 to 2.2 mg/l. NO3 however were below detection limit in almost all samples apart from 3 slightly saline samples with concentrations 62.5, 81.7 and 143.6 mg/l respectively. Therefore the major anions in the study area followed the following sequence $SO_4 > HCO_3 > Cl > NO_3 > PO_4$.

According to the TDS classification followed in the current study the hydrochemical facies in different categories of groundwater followed the following order, Freshwater Na>Ca>K>Mg: $HCO_3 > SO_4 > Cl$, Slightly saline water Na>Ca>K>Mg: $HCO_3 > SO_4 > Cl$ and Moderately saline water Na>Ca>Mg>K: $SO_4 > Cl > HCO_3$. The trend was almost similar to the findings of Rao et al. (2017) with Na as the major cation. An increased Na represents anthropogenic influence and mineral dissolution whereas dominating Cl level indicates domestic input and leaching from soil. More over Na and Cl possess high solubility potential. Fertilizers, domestic wastes and evaporites are sources of sulphates and nitrates. Dissolution of minerals is responsible for enhanced HCO_3 (Rao et al., 2017) whereas higher Mg and Ca levels may be attributed to natural weathering of minerals (Mukherjee et al., 2006).

Table 3.1: Descriptive Statistical parameters of groundwater samples

Parameters	Units	WHO	Group 1			Group 2			Group 3		
			TDS<1000			TDS 1000-3000			TDS>3000		
			Min	Max	Mean	Min	Max	Mean	Min	Max	Mean
Depth	Ft	-	35	250	89	30	90	61	35	100	65
pH	-	6.5-9.2	6.27	8.06	7.4	6.72	8.43	8	6.18	8.48	7.05
EC	µS/cm	1500	365	1541	1035	1618	4340	2479.4	4710	7120	5687.1
TDS	mg/l	1000	233.6	986.2	662.1	1035.5	2777.6	1586.4	3014.4	4556.8	3640
Na^+	mg/l	200	10.8	312.4	116.03	205.6	887.4	484.01	828.2	1381.7	1119.1
K^+	mg/l	12	20.3	81.7	38	2.3	115.2	31	Bdl	93.7	16.1
Ca^{+2}	mg/l	100	10	93	51.4	7.2	203.2	50	10.5	411	130
Mg^{+2}	mg/l	50	4.4	59.2	25	3.1	93.9	24.2	5.7	63.4	47
Cl^-	mg/l	250	1.3	165.1	53	31.2	595.6	240.4	300.3	1730	971
HCO_3^-	mg/l	-	200	600	347.4	200	700	472	200	700	400
SO_4^{-2}	mg/l	250	2.4	208.9	105	178.8	1161.2	425.2	483.1	2134.2	1025
NO_3^-	mg/l	50	Bdl	41.4	9	Bdl	143.6	23.1	Bdl	35.9	4
PO_4^{-3}	mg/l	0.1	Bdl	2.1	0.3	Bdl	2.2	0.6	Bdl	1.7	0.5
Fe	mg/l	0.3	Bdl	1.0	0.17	Bdl	6.4	0.66	Bdl	0.5	0.06
Mn	mg/l	0.5	Bdl	0.2	0.04	Bdl	0.4	0.07	Bdl	1.4	0.13

Bdl=below detection limit, Detection limits for NO_3=0.1 to 1mg/l, As = 2µg/L, PO4-3 = 0.01 mg/L, Fe = 0.01 mg/L, Mn = 0.025 mg/L

3.1.1. Hydro-chemical Facies

In the field of hydrological studies, water quality analysis holds a significant position. The chemical analysis of major cations and anions allow in assessing the quality of water and the influential parameters responsible for the change in its quality. Piper plot is a tool for representing the relative abundance of these major ions by plotting multiple samples on the same trilinear diagram.

Based on the analytical results obtained through the chemical analysis of groundwater samples piper plot (Figure 3.1) identifies NaCl (68.5%) as the dominant water type in the study area similar to the ones reported by (Li et al., 2016; Mushtaq et al., 2018; Rafique et al., 2009; 2015). Other water types identified includes $CaHCO_3$ (16.7%) and $NaCaHCO_3$ (9.2) where as 5.6% of the samples fell in $NaHCO_3$ type water. Generally the level of salinity in water types follows the following order: NaCl>SO_4 type>$CaHCO_3$ (Kumar et al., 2015). In the present study almost all of the slightly and moderately saline samples are found to be present in NaCl type water confirming the influence of evaporation (Rafique et al., 2015). The occurrence of increased Na^+ ion however indicates mineral dissolution and anthropogenic influence in the area (Rao et al., 2017). Exceptionally two of the slightly saline samples occurred in $NaHCO_3$ and $NaCaHCO_3$ type water, one in each representing slow recharge and ion exchange taking place. In case of non-saline water samples out of 19 samples 9 fell in $CaHCO_3$ type water representing frequent recharge in the area (Rafique et al., 2015). Eight of the fresh water samples occurred in $NaCaHCO_3$ and NaCl type water, 4 in each whereas the remaining 2 were found to be associated with $NaHCO_3$ type water. These results are also supported by the aid of Chadha diagram (Figure 3.2), that is another tool to assess the groundwater facies in an area by plotting the difference between the alkali and alkaline earth metals on X axis whereas difference between weakly acidic and strongly acidic anions are plotted on Yaxis.

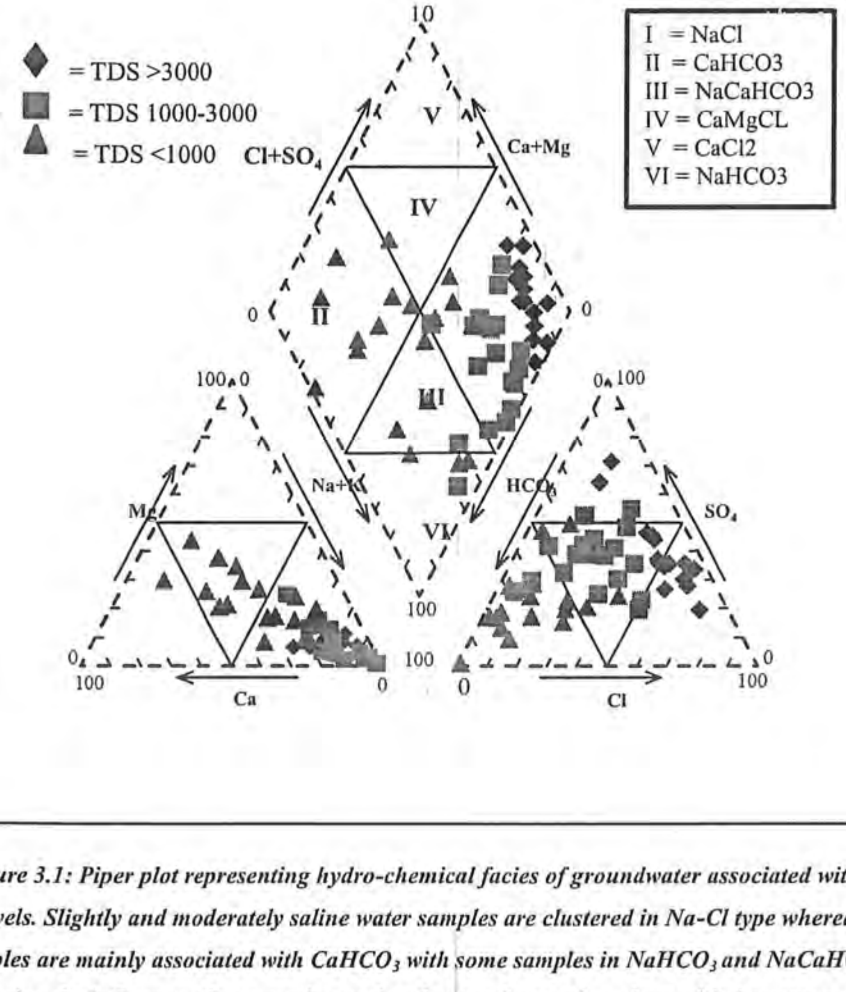


***Figure 3.1:** Piper plot representing hydro-chemical facies of groundwater associated with varying TDS levels. Slightly and moderately saline water samples are clustered in Na-Cl type whereas non-saline samples are mainly associated with $CaHCO_3$ with some samples in $NaHCO_3$ and $NaCaHCO_3$ type waters showing the influence of evaporation and rock water interaction along with frequent recharge in non-saline samples.*

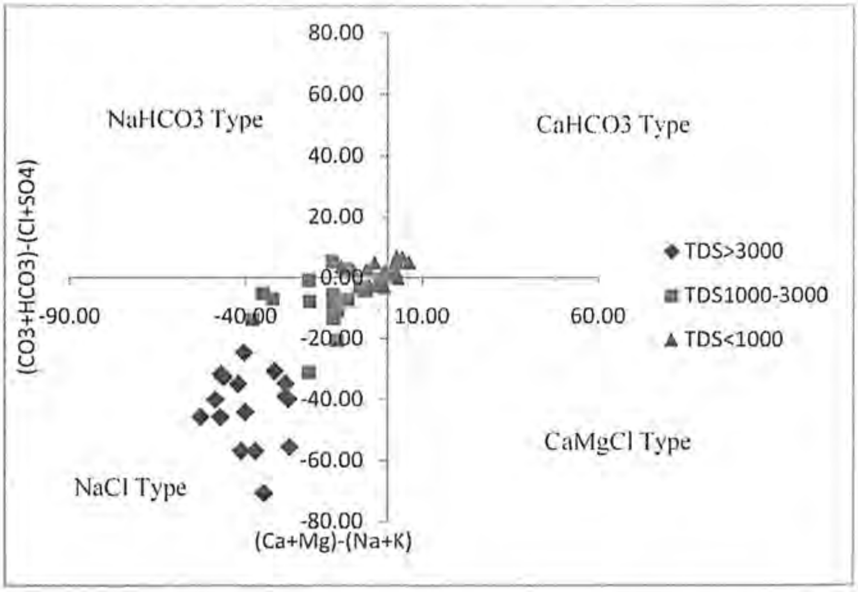


Figure 3.2: Classification of groundwater types in Rachna Doab

(i) NaCl type waters showing evaporation or sea water mixing, (ii) NaHCO3 type waters reflecting base ion exchange, (iii) CaHCO3 type waters indicating weathering and recharge processes and (iv)CaMgCl identifying reverse ion exchange phenomenon taking place.

3.2. Sources of solutes in groundwater

The interactions between the aquifer minerals and groundwater are the major controlling factors determining its quality (Srinivasamoorthy et al., 2014). The analyzed data is subjected to graphical biplots in order to understand groundwater genesis and hydrogeochemical processes taking place in the aquifer region of Rachna doab. Some of the possibly determined processes prevailing in the region such as evapotranspiration, mineral dissolution and ion exchange are discussed below.

3.2.1. Mineral Dissolution

The molar ratios of Ca/Mg allow the identification of groundwater calcium and magnesium source. The ratio if equals to 1 represents dolomite rock dissolution whereas >1 indicates an enhanced contribution of calcite rocks which release great amounts of bicarbonate and calcium ions in water. However, when this ratio approaches >2 it indicates dissolution of silicate minerals in the groundwater (Sheikhy Narany et al., 2014;

Srinivasamoorthy et al., 2014). In the study area 42.6% of samples had Ca/Mg ratio near and equals to 1 indicating dissolution of dolomite, 28% of samples lie in > 1 zone showing the dissolution of calcite rocks which may be attributed to presence of Kankar zones in upper sub strata (Sajjad et al., 1992) whereas 30% of the samples reflected the contribution of silicate minerals to the groundwater (Figure3.3a). In (Figure 3.3 b) Ca+Mg and SO_4+HCO_3 plot the samples are clustered near to 1:1 line and towards SO_4+HCO_3 suggesting silicate weathering and ion exchange processes dominating in the region. This plot eases in identification of ion exchange processes. In case of reverse ion exchange processes the samples tend to shift to left side of 1:1 equiline whereas if ion exchange is the dominating process the samples move to the right side of the plot as observed by (Mushtaq et al., 2018).

In Figure 3.3e, bivariate plot between Ca+Mg and HCO_3 illustrates deficiency of Ca+Mg relative to HCO_3 as observed by (Tiwari and Singh, 2014). The data points lying on right side of 1:1 equiline represent contribution of silicate weathering towards alkaline earth metals and on the left side represent calcite and dolomite dissolution towards bicarbonate in the groundwater.

3.2.2. Evaporation and Evapotranspiration

In semi arid and arid areas Na- Cl plot is used as a tool to identify the process controlling salinity. Na/Cl ratio if >1 indicates non-halite dissolution as the Na ion source particularly referring to silicate weathering. Whilst the ratio if equals to 1 represents halite dissolution whereas <1 is due to ion exchange and agricultural return flow (Srinivasamoorthy et al., 2014). The average Na/Cl ratio in ground water is 4.5 showing higher Na then Cl (Annexure III). Figure 3.3c represents silicate weathering as the source of sodium along with partly contribution of evaporation to some extent. As Na and Cl are positively correlated with R^2=0.721 reflecting the dissolution of evaporite minerals that are particularly formed due to evaporation in arid and semi arid areas (Taheri et al., 2017). Figure 3.3d, a plot between Na/Cl molar ratio and TDS further confirms the evaporation input. An inverse relationship has been observed between Na/Cl and TDS with higher Na/Cl ratio in non saline samples representing silicate weathering. However most of the slightly and moderately saline samples have been plotted parallel to TDS identifying the contribution of evapotranspiration towards increased sodium concentration.

3.2.3. Ion Exchange

The slope of plot between (Ca+Mg) – (HCO_3+SO_4) and Na-Cl equals -1 if cation exchange reactions are contributing actively in aquifers. As evident from Figure 3.3f, slope is found to be -0.78 in the current study falling closer to -1 indicating cation exchange reactions to be significant contributors to the aquifer chemistry. Same trend has been observed by Mushtaq et al. (2018) in a study carried out in Lahore.

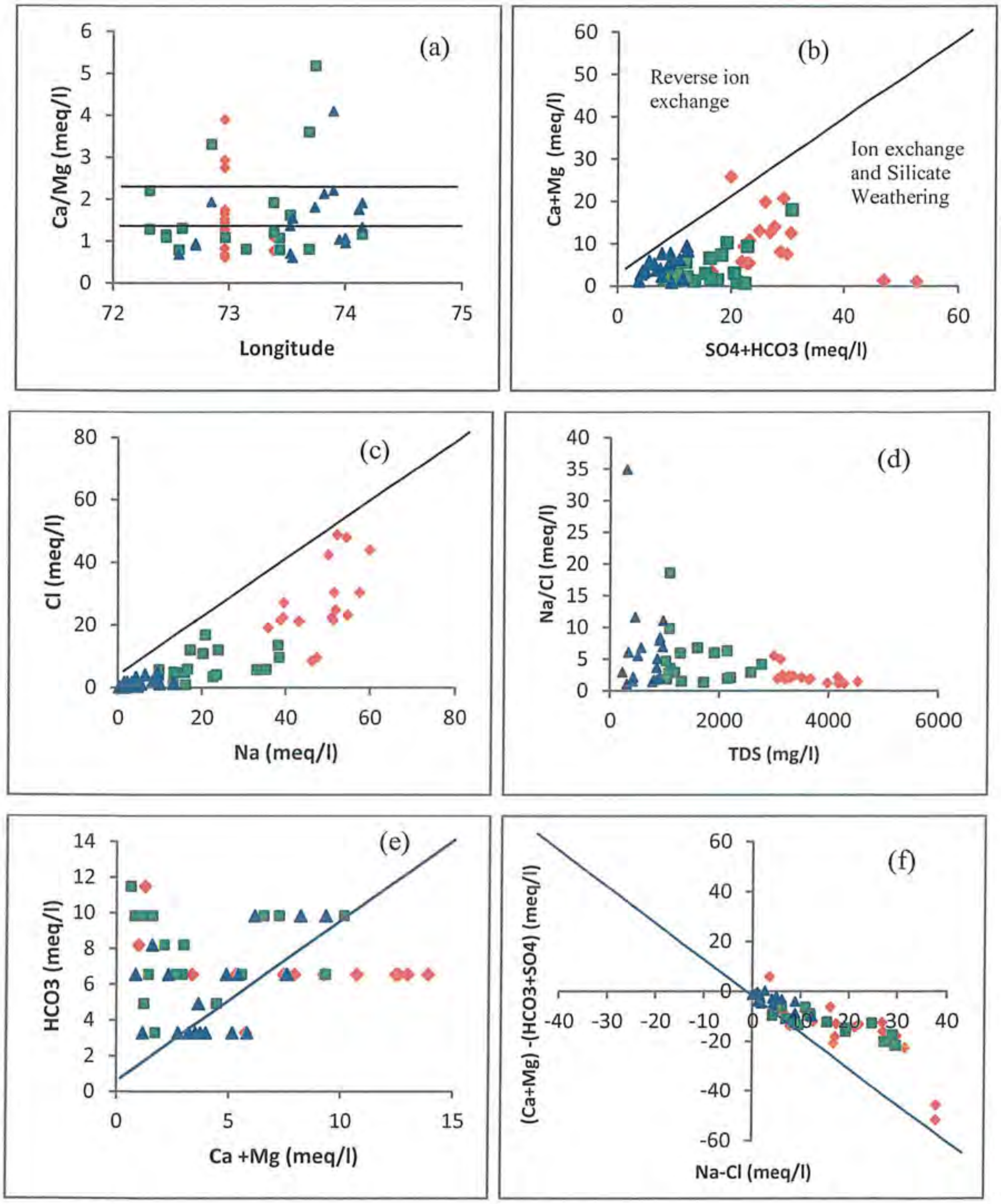


Figure 3.3: Bivariate plots showing relationship between (a) Molar ratios of Ca and Mg (b) (Ca+Mg) vs (SO_4+HCO_3) (c) Na and Cl (d) Na/Cl vs TDS (e) (Ca+Mg) vs HCO_3 and (f) (Ca+Mg)-(HCO_3+SO_4) vs Na-Cl

Note: Legends are same as piper and Chaddah diagrams

3.3. Groundwater salinization in Rachna Doab

The maximum permissible limit of TDS for drinking water given by WHO is 1000 mg/l (Srinivas et al., 2017). Samples containing TDS above this prescribed limit are considered saline. Groundwater samples of the study area showed a large variation in the TDS levels i.e., 233-4556.8 mg/l with a mean of 1907.8 mg/l. Higher TDS levels are mainly found to be associated with ground waters from shallow depth i.e., 30 to 100 feet (Figure 3.4). Various hydro-chemical processes might be attributed to this trend, one of which is the presence of saline soil (soil with elevated TDS level) in the region as shallow aquifers are more vulnerable towards leached contamination (Kumar et al., 2015). As approximately 77% of the area is developed therefore, soil might contribute to shallow groundwater salinity through rainfall or irrigation leaching as discussed by Li et al. (2016) in a study carried out in Datong Basin, China. The particle size analysis (Annexure IV) of soil of the study area revealed soil texture as Sandy loam with sand contents of 38.5-84.5% (mean 67.7%) and silt contents of 9.3-48.9% (mean 25.5%). Clay content of soil however is low ranging from 1.8 to 15.9%. The permeable nature of soil therefore tends to transmit (leach) salts through to groundwater with relative ease (Cleveland and Soleri, 1991). The study area generally possesses an irregular salinity pattern however mainly an increase in salinity is observed in the flow through region down the slope (central part) with decreasing elevation (as shown in fig 2.1(a)). Groundwater TDS levels showed a good positive correlation with Na (R^2=0.922), Cl (R^2=0.812) and SO_4 (R^2=0.644) whereas poor correlation is observed with Ca (R^2=0.351) and Mg (R^2=0.307). Anion and cation equivalents vs TDS plots in figure 3.5 further confirm that Na and Cl ions increase with increasing salinity. SO_4 is also found to have a moderate correlation with salinity

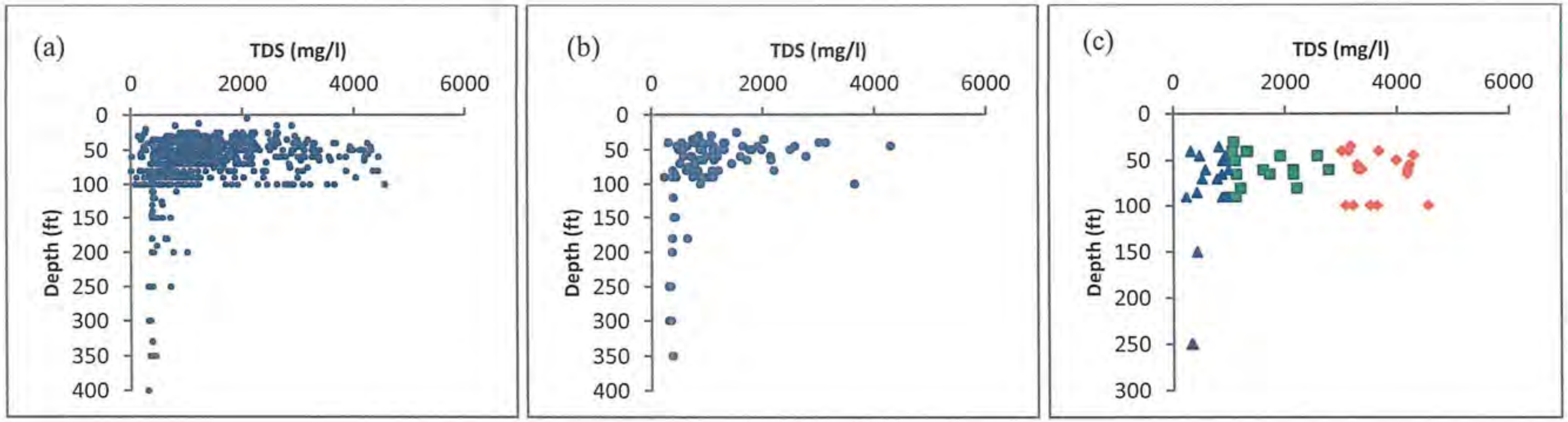


Figure 3.4: Variation of groundwater salinity with depth (a). Depth vs TDS plot of all the groundwater samples tested under the blanket sampling strategy on the field in Rachna Doab (b). Depth vs TDS plot of the Quality control samples collected from the field (c). Depth vs TDS plot of the selected samples of current study

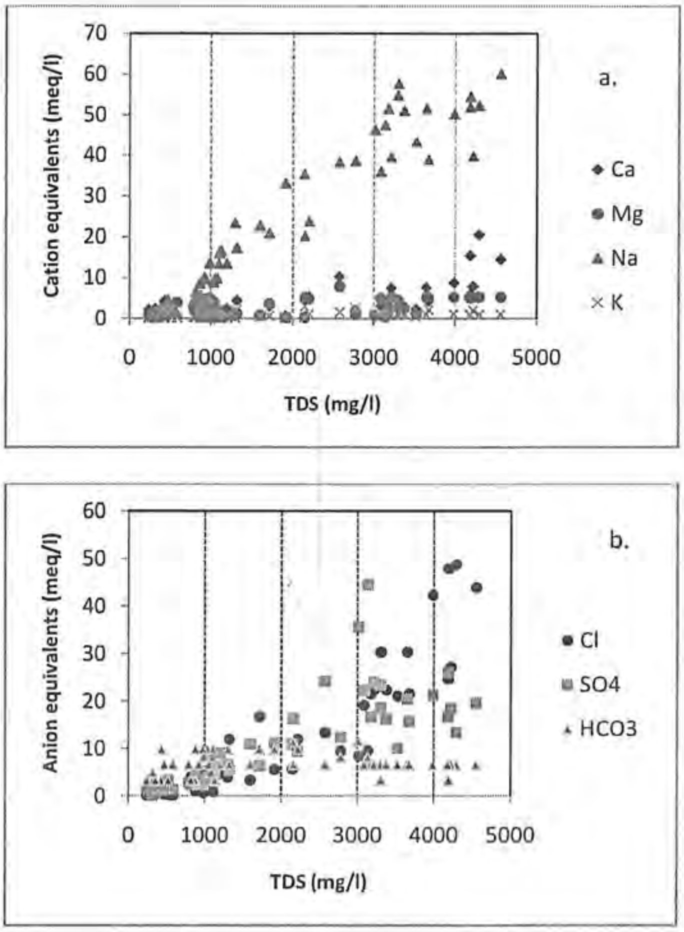


Figure 3.5: Plot of Salinity (as TDS) vs (a) Cations and (b) Anion equivalents showing variation of different ions with increasing TDS

3.4. Sources of salinity

The salts present in groundwater depend on the source, movement and geologic environment in which the water resides. A direct input of salts in groundwater is the weathering of primary minerals (Carreira et al., 2014). Salinity of groundwater is also associated with the relief of an area. Topographically high areas usually possess fresh ground water whereas movement down to low regions (discharge areas) leads to saline water due to increased contact time, mineralization of groundwater and ion exchange (Hiteshkumar, 2014). Irrigation is another factor which itself adds salts not only to the soil but also to groundwater. Moreover, evapotranspiration also contributes towards concentrating salts in ground water (Carreira et al., 2014).

The possible sources responsible for groundwater salinity in Rachna Doab are identified and discussed through isotopic analysis, hydrogeo-chemical modeling and Gibbs plot as follows:

3.4.1. Isotopic Evidence of Groundwater Recharge and Salinization

$\delta^{18}O$ and $\delta^{2}H$ isotopes in water share a significant bond. Various Researchers involved in investigation of this relationship saved it the status of a complete discipline in hydrological Science. Their conservative nature makes them effective tracers for the determination of atmospheric moisture and circulation patterns. Some studies also highlight their role in the identification of sources of salinity and origin of groundwater (recharge sources) (Gaye, 2001; Hao et al., 2000; Hussain et al., 2013; Phillips et al., 2003).

The isotopic composition ($\delta\ ^{18}O$ and $\delta\ ^{2}H$ relative to VSMOW) of groundwater samples are given in table 3.2. In order to identify the sources of salinity and recharge in Rachna Doab isotopic analysis ($\delta\ ^{18}O$ and $\delta^{2}H$ relative to VSMOW) of groundwater samples was carried out. Representative groundwater samples from each village were analyzed for their isotopic signatures. The variation in $\delta\ ^{18}O$ and $\delta\ ^{2}H$ of the groundwater samples relative to VSMOW are plotted in comparison with the local meteoric Water line (LMWL) and Global meteoric water line (GMWL) as shown in Figure 3.6. The variation ranged from -5.83 to -10.09‰ for $\delta\ ^{18}O$ and from -39.81 to -64.18‰ for $\delta\ ^{2}H$ respectively. For the current study the LMWL of Sargodha (station lying close to the study area) was used given by Hussain et al. (1993).

Table 3.2: The isotopic composition ($\delta\ ^{18}O$ and $\delta\ ^{2}H$) of groundwater samples along with their d-excess

Sample IDs	**$d^{18}O$ ‰**	**d D ‰**	**D-excess**	**TDS**
T3bk6	-7.59	-48.79	11.93	278.4
T3GL6	-6.08	-41.49	7.15	878.72
T3ay2	-5.83	-39.81	6.83	654.72
T3c241-2	-9.23	-55.17	18.67	567.68
T3NO8	-7.48	-48.1	11.74	919.68
T3CS5	-6.85	-43.95	10.85	1100.16
T3KS7	-6.42	-42.75	8.61	905.6
T3AS2	-8.2	-50.77	14.83	875.52
T3PR2	-7.96	-50.65	13.03	346.24
T3SP5	-8.05	-54.46	9.94	378.24
T3C80-6	-7.96	-50.86	12.82	1108.48
T3C445-7	-10.09	-64.18	16.54	1117.44
T3C238-4	-8.52	-55.46	12.7	1081.6
T3ls5	-8.38	-52.64	14.4	1644.8
T3c171-3	-5.84	-40.37	6.35	2496
T3C487-6	-9.61	-61.91	14.97	2144
T3c288-2	-8.35	-50.36	16.44	2579.2

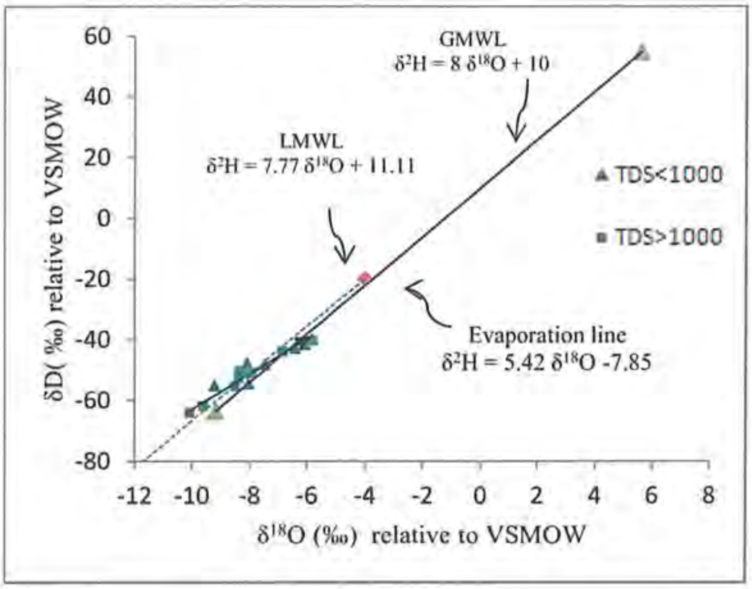


Figure 3.6: Isotopic variations (δ ^{18}O and δ ^{2}H relative to VSMOW) in groundwater samples of Rachna Doab

The LMWL has a slope of 7.77 close to the slope of GMWL i.e., 8 showing that before aquifer replenishment the recharging waters do not experience significant evaporation (Akram et al., 2014). Ground waters that have undergone the phenomenon of evaporation deviate away from the LMWL with slopes ranging usually from 4 to 6 (Gibson et al., 1993). Figure 1 reveals the evaporation line of ground waters in the current study with a slope of 5.42. The possible sources of groundwater recharge in Rachna Doab are rainfall and surface waters such as rivers and canals. Based on the spatial variation of $\delta^{18}O$ the groundwater of Rachna Doab can be divided into two categories i.e., $\delta^{18}O$= -7.5 to -5.5‰ (intermediate isotopic composition) and $\delta^{18}O$< -7.5‰ (depleted isotopic composition) (Akram et al., 2014). In general the groundwaters in the upper part of the Doab (T3GL-6, T3AY-2, T3CS-5 and T3KS-7) possess isotopic compositions that reflect mixed sources of recharge. Ground waters with $\delta^{18}O$ composition between -5.5‰ and -6.5‰ reveal a dominant portion of recharge through rain and very low contribution through surface water. In contrast the sampling point with $\delta^{18}O$ value of -6.85‰ shows a relatively depleted composition revealing a dominant recharge from surface waters as compared to precipitation. However, as we move laterally and vertically away from the upper part of Doab the values of $\delta^{18}O$ composition of ground waters were found to be < -10.09‰.

These highly negative values signify pure depleted surface water recharge in this zone (Akram et al., 2014).

Figure 3.7 presents a plot of $\delta^{18}O$ vs Cl which assists in understanding the mechanisms (phenomenon) contributing to groundwater salinization in the area. The waters showing comparatively constant $\delta^{18}O$ values with increasing chloride concentration corresponds to dissolution of soluble salts however, the waters presenting a gradual increase in $\delta^{18}O$ composition along with increasing chloride concentrations are affected by evaporation (Saka et al., 2013). Two varying trends were observed in the groundwater samples of the current study, with one group of samples lying close to the x-axis which represent the dissolution of soluble salts where as the samples lying towards y-axis shows the contribution of evaporation to the salinization of groundwater. Similar results were observed by Saka et al. (2013) in the groundwaters of Ga West Municipal area Ghana.

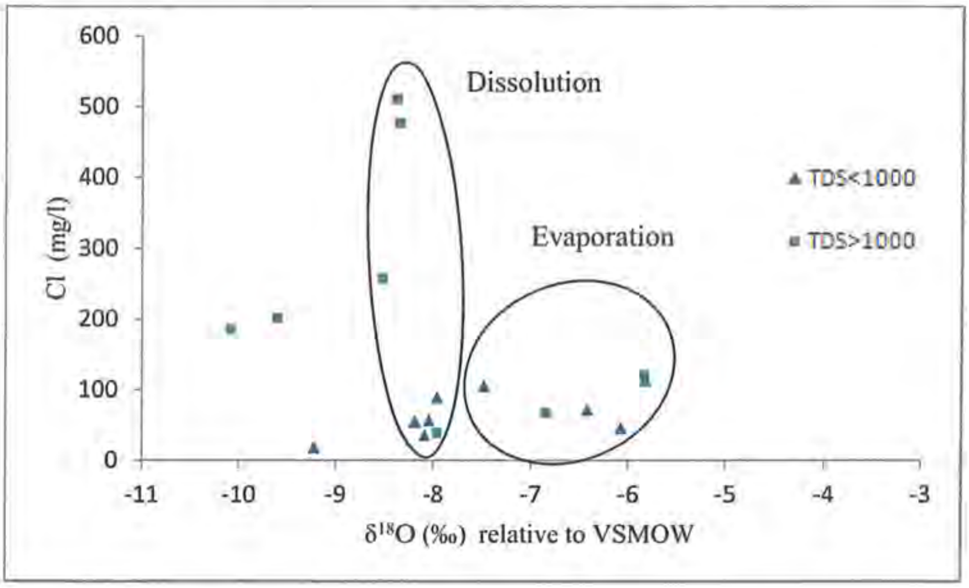


Figure 3.7: Plot representing the relationship between Cl^- concentrations and isotopic composition of $\delta^{18}O$ in the groundwater of Rachna Doab

Table 3.2 shows the isotopic composition ($\delta\ ^{18}O$ and $\delta\ ^{2}H$ in ‰ relative to VSMOW), TDS and d- excess values of groundwater samples of Rachna Doab. Dansgaard. (1964) for the first time proposed the calculation of d-excess in global precipitation and defined it as Equation vii.

$$d\ (‰) = \delta\,^{2}H - 8\,\delta\,^{18}O \qquad ....Eq\ (vii)$$

The d-excess value for GMWL is approximately 10 depicting evaporative effects at 85% relative humidity. Deviation from this value can be used to determine the extent of evaporation in a region. The local precipitation in an area occurring at low humidity can have a d-excess >10 (Saka et al., 2013). 29% of the groundwater samples of the current study are found to have a d-excess< 10.

A bivariate plot between TDS and d-excess is useful to evaluate the role of evaporation and mineral dissolution in the groundwater chemistry of an area. According to this plot an increase in TDS with decreasing d-excess is expected to occur in an evaporation dominant area whereas a slight or constant increase in d-excess with increasing TDS is observed in areas experiencing mineral dissolution (Guo et al., 2014). A plot of TDS vs d-excess is shown in Figure 3.8 suggesting that the groundwater chemistry of Rachna Doab is influenced by both mineral dissolution and evaporation processes with a dominant contribution from mineral dissolution.

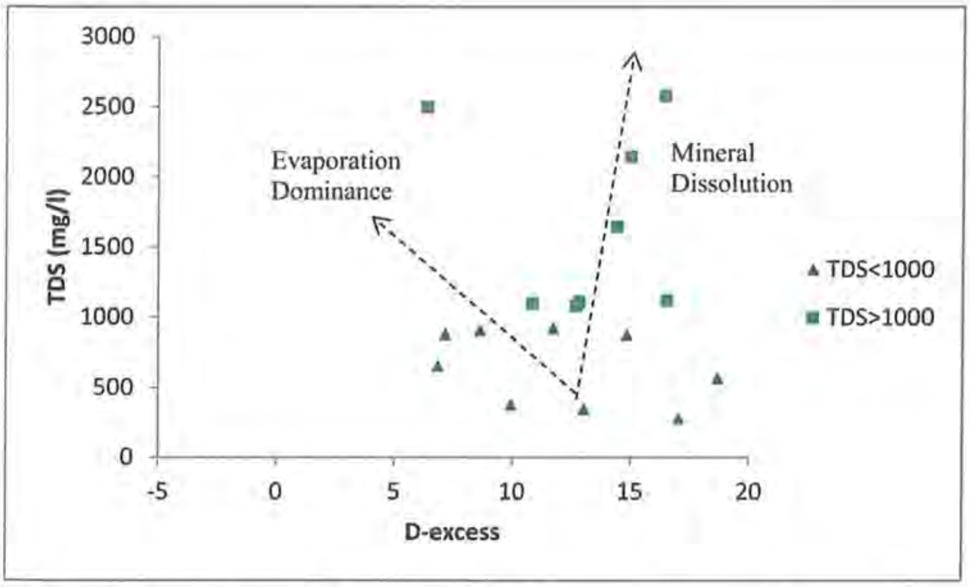


Figure 3.8: Plot showing relationship between TDS and d-excess in the groundwater samples of Rachna Doab

3.4.2. Hydro-geochemical modeling- Saturation Indices

Saturation Indices were calculated using hydrological data to estimate the presence of minerals and state of their reactivity in the subsurface water without analyzing mineralogy by collection of solid phase samples. PHREEQC, a USGS Program was used for this purpose (Parkhurst and Appelo, 1999). It allows predicting the deviation of water from equilibrium conditions i.e., whether the groundwater will tend to precipitate or dissolve a particular mineral. The positive value of saturation Index (SI>0) indicates the oversaturation of minerals in water. In such a condition the water is incapable of dissolving more of that particular mineral and under favorable conditions precipitation of that mineral occurs from equilibrium phase. On the other hand, a negative saturation index (SI<0) suggests the under saturation of water with respect to a certain mineral and its possible dissolution. However, SI= 0 reflects a neutral (saturated) state i.e., a condition in which the water is in equilibrium with the mineral phase (Tiwari and Singh, 2014). The saturation indices of gypsum, dolomite, halite and anhydrite in the understudy groundwater samples are plotted against TDS (Figure 3.9). All of the samples show under saturation with respect to gypsum, anhydrite and halite. A positive correlation is observed among the SI of gypsum and anhydrite with TDS. Therefore, the dissolution of these minerals is contributing towards an increase in the TDS level of water. Hence the sulfate content in groundwater is attributed to the dissolution of gypsum and anhydrite (Chenini et al., 2010). In case of dolomite most of the samples were under saturated although 9 samples were found to be super saturated. The dominating trend of under saturation in groundwater explains the increased TDS levels and may be accredited to water logging in the study area leading to extensive mineral dissolution (Baig et al., 2009; Brahman et al., 2013).

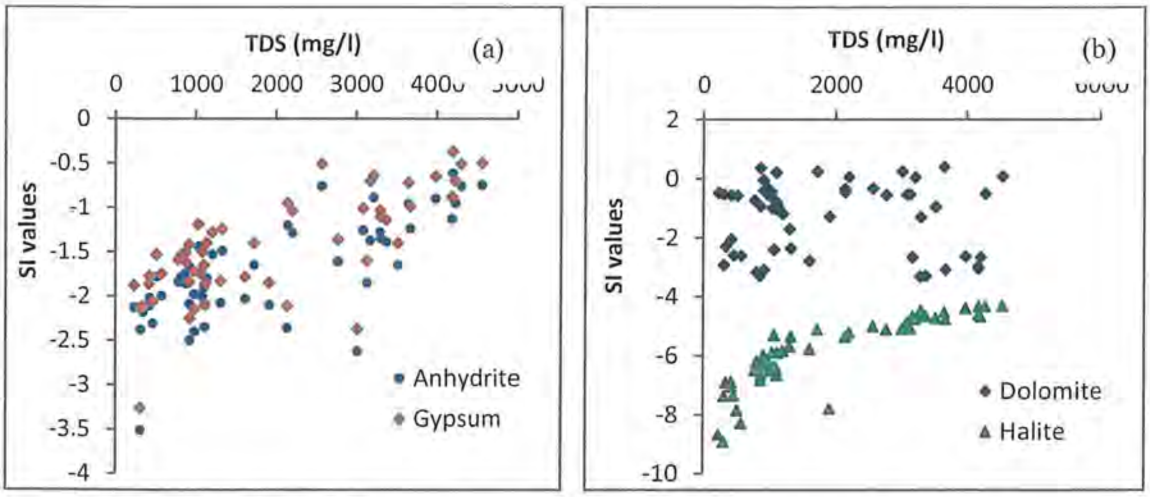


Figure 3.9: Saturation indices of (a) Anhydrite and gypsum, (b) Dolomite and halite plotted against TDS levels of groundwater

Calcite and fluorite are the two main minerals controlling the fluoride ion contamination in groundwater. The solubilities of these two minerals are interdependent (Brahman et al., 2013; Rafique et al., 2009). In the current study the saturation indices of fluorite and calcite are plotted as shown in Figure 3.10. The plot shows that groundwater of the study area is capable of further dissolution of both the minerals. All but eighteen of the samples are found to be under saturated with respect to calcite and fluorite. However, the saturation indices of calcite and fluorite follow an inverse trend. The rest of the eighteen samples have reached to a state of supersaturation with respect to calcite which should favor the precipitation of calcium and elevation of fluoride in groundwater. Similarly, the occurrences of both these saturation states of calcite and fluorite have been reported by Rafique et al. (2015) in a study carried out in Tharparkar, Pakistan.

Geochemical modeling also presents the evidence of partly contribution of evapotranspiration towards salinity. The positive SI values of calcite for some samples indicate the precipitation of carbonate minerals. The bicarbonate ions present in groundwater precipitates as carbonates during evapotranspiration-based ion concentration. Furthermore, the evaporation processes lead to Cl^- ion enrichment in groundwater (Li et al., 2016). The saline groundwaters of the study area mostly have Cl^- concentrations higher than WHO as presented in Table 3.1

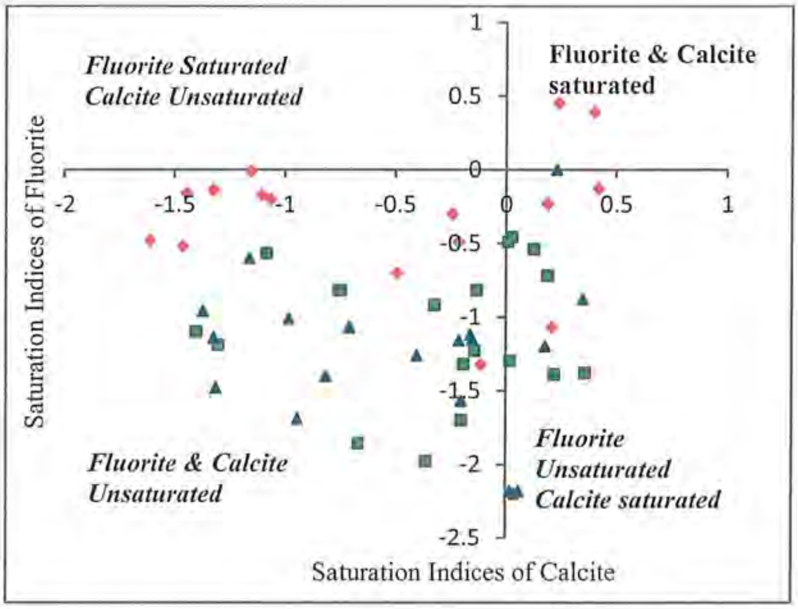


Figure 3.10: Plot of saturation indices of calcite vs fluorite

Note: Legends are same as piper and Chaddah diagrams

3.4.3. Hydro-geochemical processes controlling salinity in groundwater

Different mechanisms and hydrogeochemical processes contribute to the chemistry of groundwater in a region. Gibbs plot is a useful tool to identify the dominant controls operative in an area and their impact on the water quality. According to Gibbs (1970) the three major natural processes responsible for influencing the hydrogeochemistry of groundwater include rain fall, rock weathering and evaporation. They either individually or mutually contribute to the hydrogeochemical scenario of groundwater depending on the climatic, geological and lithological conditions in a particular region. The Gibbs diagram for the current study is presented in Figure 3.11. The plot illustrates that two-phenomenon prevailing in the region are mineral dissolution and to some extent evaporation dominance. The slightly and moderately saline samples suggest a clear influence of evaporation on the groundwater chemistry. Therefore the occurrence of sodium chloride type water in these samples could be credited to the enhanced evaporation rates as shown earlier in (Figure 3.1). Non-saline samples however are clustered in the zone of rock weathering influenced by evaporation. The average ratio of Chloride with reference to other anions (0.372) (Annexure III) indicates the influence of weathering in the study area (Naseem et al., 2010). Moreover, TDS increases as a result of evaporation influenced by anthropogenic activities or chemical weathering bending the samples from rock dissolution to evaporation dominance zone (Subba Rao, 1998)

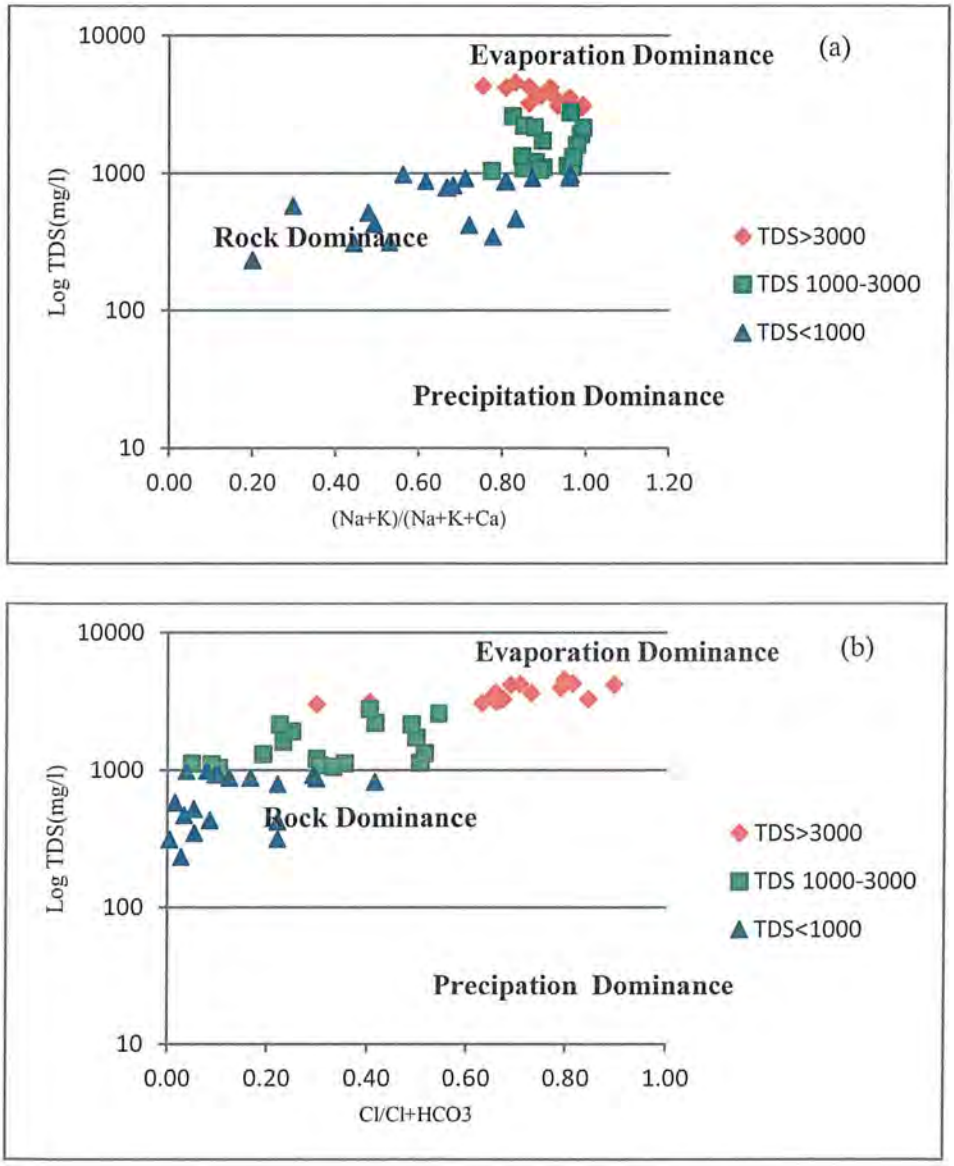


***Figure 3.11:** Gibbs (a) Cationic and (b) anionic plots illustrating major hydrogeochemical processes defining groundwater chemistry*

3.4.4. Conceptual model

Based on the secondary data available in the literature, a conceptual model of groundwater recharge sources and chemical processes responsible for progression of saline groundwater in the region has been made as shown in Figure 3.12 which corresponds to the findings of current study. According to the study carried out by Sajjad et al. (1992) the isotopic signatures of the water samples of Rachna Doab revealed that the North East of the study area is mainly recharged by rainfall whereas the North Western part is directly recharged by River Chenab. Groundwater was found to be a blend of different sources with major contribution from canals. The study area had an average slope of 0.37m/km (decreases 25% in the lower parts) (Rehman et al., 1997b). Such a gentle slope leads to slow groundwater movement as identified by (Sajjad et al., 1992) through tritium analysis. Furthermore, the slow movement of groundwater provides enough time for rock water interaction and solubility.

Sajjad et al. (1993) further reports that the salinity in Indus Basin is mainly attributed to the dissolution of sediment salts with partial role of evaporation and fertilizers.

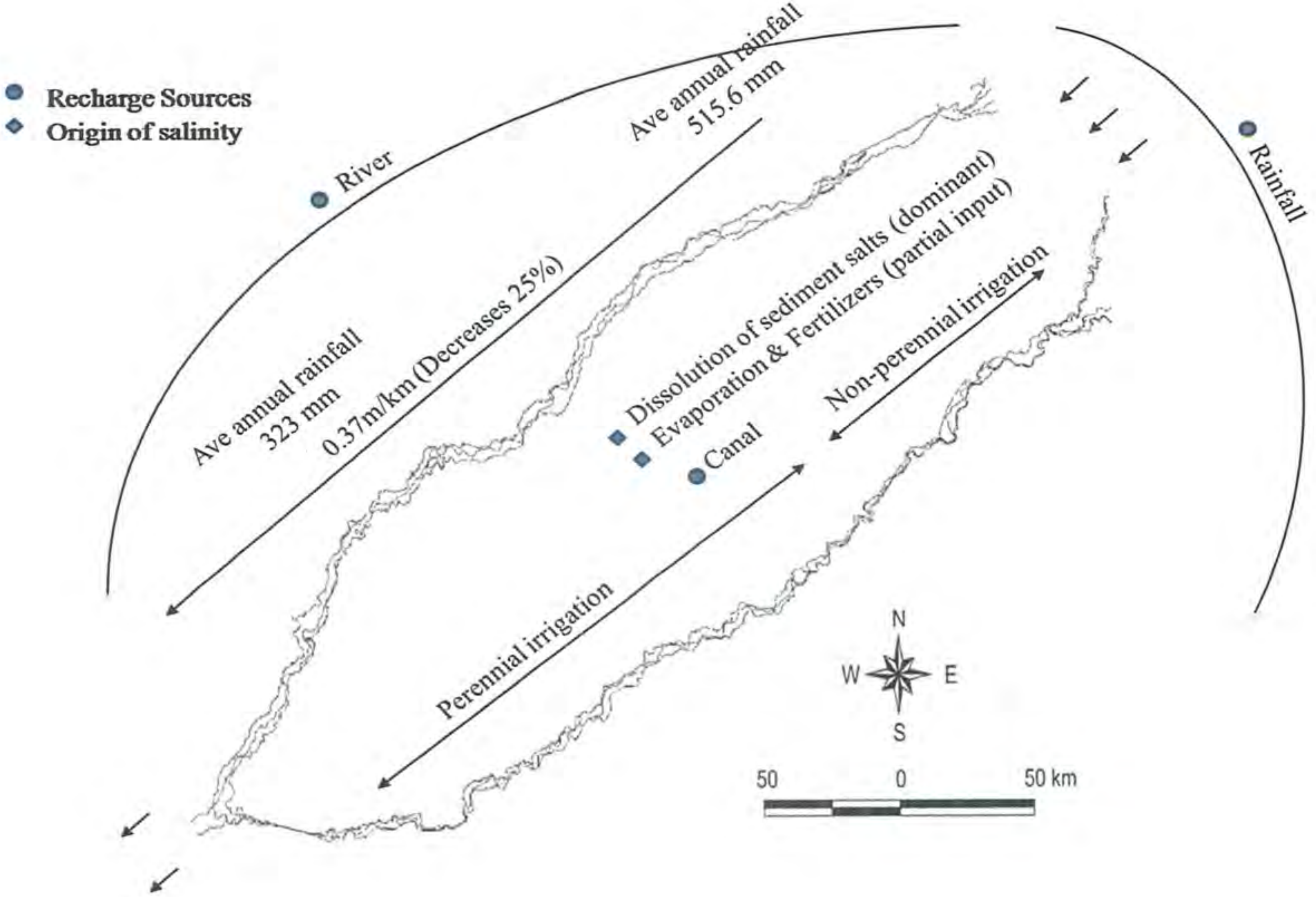


Figure 3.12: Conceptual model of groundwater recharge and salinity sources in Rachna Doab

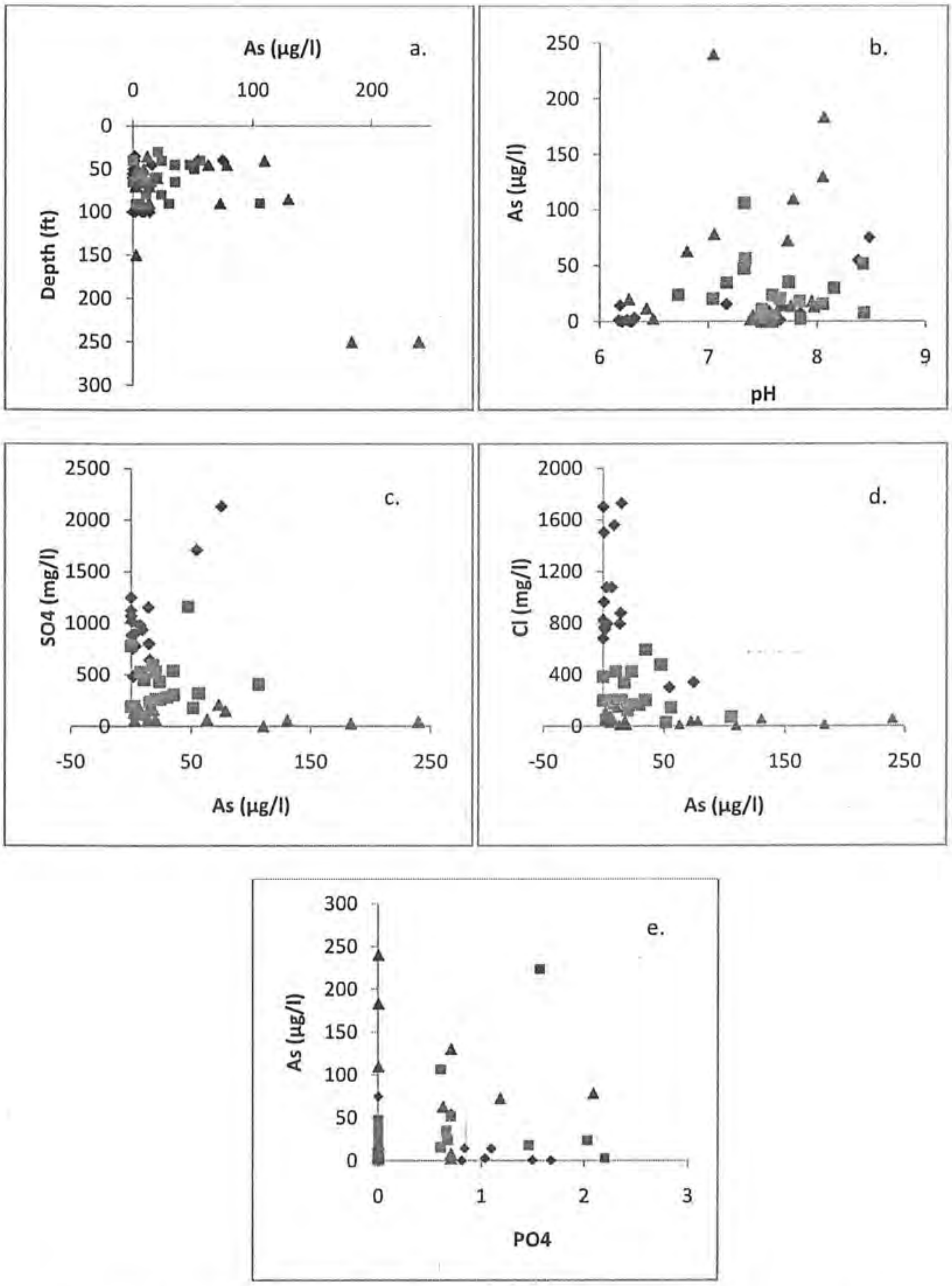


Figure 3.11: Relationship of Arsenic with (a) depth (b) pH (c) SO_4 (d) Cl and (e) PO_4

Note: Legends are same as piper and chaddah diagrams

3.5. Variation of fluoride in groundwater and possible impact of salinity

Fluoride concentrations in groundwater of the study area ranged from below detection limit to 3.9 mg/l (Annexure I). All non-saline samples have fluoride concentrations below detection limit. 28% of slightly saline samples were found to have Fluoride levels above WHO prescribed limit whereas all samples with TDS >3000mg/l possessed higher Fluoride concentrations with the exception of one sample. The Fluoride concentrations in groundwater showed a slight dependence on depth with maximum concentrations found to occur in shallow groundwater within a depth of 30 to 100 ft as shown in Figure 3.13 a. This trend was similar to the ones observed in the previous studies by (Farooqi et al., 2007a,b).

The three possible mechanisms for fluoride release in the ground water of an area are ion exchange, dissolution of fluoride minerals and evaporation. According to the studies carried out in Lahore and Kasur Districts high fluoride ground waters possessed increased Na with decreased Mg and Ca levels (Sarma and Rao, 1997). Acidic pH is favorable for adsorption of fluoride on clays whereas in alkaline pH it desorbs and dissolves in groundwater (Saxena and Ahmed, 2003). The Ca level lowers in fluoride bearing waters as a result of ion exchange between Na and Ca. Moreover, alkaline pH also aids in precipitation of Ca as calcite and Mg as dolomite. The relationship of fluoride with Ca, Na, Cl, ions and pH in the current study is given in Figure 3.13. A poor correlation of fluoride is observed with Ca and Mg. Whilst Na and Cl were found to be positively correlated with fluoride having R^2 values of 0.46 and 0.3 respectively. Low Ca levels might be attributed to cation exchange between Ca and Na consistent with the findings of (Farooqi et al., 2007a,b ; Rasool et al., 2015). As the samples were selected from blanket sampling therefore due to lack of variation the groundwater samples showed no significant correlation with pH. However when plotted with variation a significant correlation (R^2 =0.41) was observed between F and pH as shown in Figure 3.13.

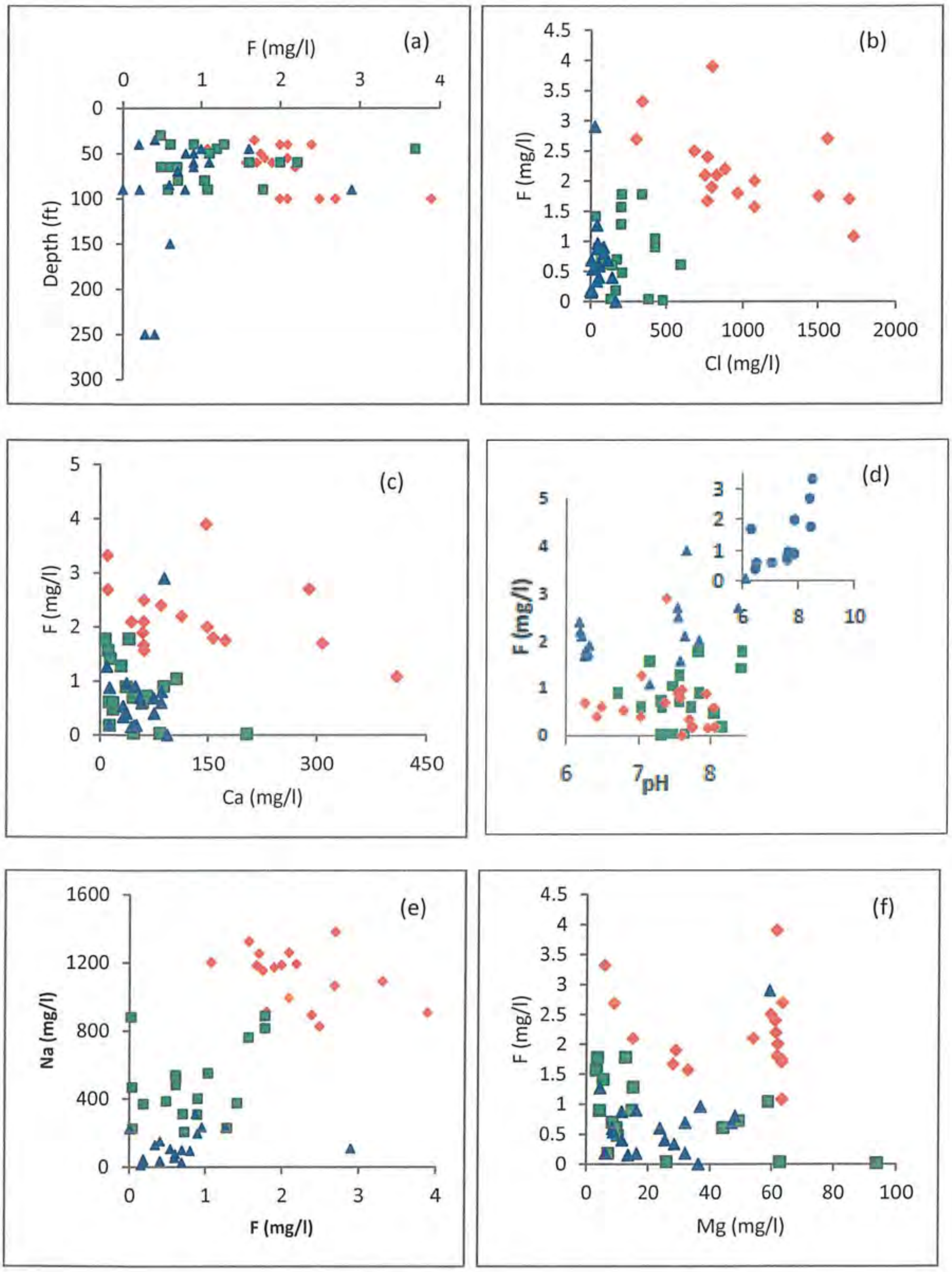


Figure 3.13: Relationship of Fluoride with (a) depth (b) Cl (c) Ca (d) Ca (e) Na and (f) Mg

High fluoride concentrations are found in shallow groundwater samples showing similar trend with depth as observed by TDS (Figure 3.4, 3.13 a). Ground water Fluoride content shows a good correlation with salinity i.e., $R^2=0.478$ as shown in Figure 3.15 c. Figure 3.15 a, b represents the cationic and anionic abundance of groundwater samples with increasing fluoride levels. An increase in Na ion is observed with increasing fluoride concentrations. Elevated Na levels increase the ionic strength and solubility of fluoride in groundwater (Gao et al., 2007; Gao et al., 2013; Singaraja et al., 2013; Surya Rao et al., 2015). The waters however are characterized by low Ca and Mg levels due to cation exchange reactions with sodium (Farooqi et al., 2007a). Most of the groundwater samples with high fluoride levels are found to have increased Cl concentrations indicating the contribution of evapotranspiration towards high fluoride in groundwater (Jacks et al., 2005). Similarly Rao et al. (2017) has reported evaporation and saline water to play a significant role for increased F content in groundwater along with ion exchange. In moderately saline groundwater the fluoride content ranges from 1.08 to 3.9 mg/l. However at TDS 4294 mg/l the fluoride level decreases to 1.08 mg/l. This decrease may be attributed to high Ca level (410 mg/l). Similar trend is observed by Li et al. (2016) suggesting that increased evaporation might restrict fluoride enrichment in groundwater due to increased Ca levels as increased Ca results in precipitation of Fluorite.

3.6. Variation of Arsenic in groundwater and possible impact of salinity

The concentration of arsenic in the study area ranges from below detection limit to 105.96 μg/l. Out of the total, 35% of the samples have As >10μg/l (WHO limit) whereas 22% of the samples have As>50μg/l (EPA-NEQS) (WHO, 2011). Increased As levels are found in saline ground waters however, overall a decreasing trend in the concentration of As is observed with increasing salinity as shown in Figure 3.15 d. The bivariate plots of As with depth, pH, SO_4, PO_4 and Cl^- are given in figure 3.14. High arsenic samples are mainly found in the depth of 30 to 100ft with the exception of two samples at a depth of 250 ft. The positive correlation between As and SO_4 ($R^2=0.684$) in moderately saline samples reflect the existence of an oxic behavior (Baig et al., 2010). However the conditions are not enough oxidizing as NO_3 in some samples show a comparatively reducing trend. NO_3 is among one of the easily available electron acceptor compared to sulphates in groundwater (Ohio EPA, 2014). Overall the moderately saline samples of groundwater (TDS>3000) with high sulphate (R^2 =0.648) and nitrate ranging from below detection limit to 35.9 mg/l show a mixed redox pattern.

If we compare our results with respect to salinity, 73% of the moderately saline samples showed As levels below WHO limit (Annexure I). Results of the Saturation Indices indicate the presence of Fe minerals, goethite, Hematite and Siderite mostly in supersaturated state (Annexure V). Flocculation of iron oxides initiate with increasing salinity resulting in decreased As concentrations (Cullen and Reimer, 1989). Under aerobic conditions As mostly adsorbs on Fe oxide minerals whereas an elevated pH >8.5 leads to desorption of As from mineral surfaces due to weathering and cation exchange reactions (Mukherjee and Fryar, 2008; Smedley and Kinniburgh, 2002). Arsenic may be adsorbed on Fe minerals due to varying redox conditions in moderately saline samples. Similar to the study area, the fluctuation in redox conditions due to periodic irrigation in Datong Basin could not favor As enrichment in relatively oxidizing conditions (Li et al., 2016). As per reported in the study, Fe oxyhydroxides due to their high affinity for As adsorbs As under relatively oxidizing conditions (Roberts et al., 2004).

The occurrence of HCO_3^- and PO_4 further aids in desorption of As from metal oxide surfaces due to competitive ion exchange. Under alkaline conditions, PO_4 being an anion with similar behavior and chemical properties as As^{+5} competes for sorption on metal oxides replacing As (Eiche et al., 2008; Jain and Loeppert, 2000; Smedley, 2005). Among the slightly saline samples 74% of the samples possessed As concentrations above WHO levels. Detection of PO_4 was observed in 53% of these samples ranging from 0.6 to 2.2mg/l with a pH (6.72 – 8.43) suggesting a competitive ion exchange control on these samples. Similar competitive ion exchange between PO_4 ion and As has been found to occur at some sites in a study carried out by Mushtaq et al. (2018) on the Eastern alkaline aquifers of Punjab. The non-saline samples however show a slightly reducing behavior with low sulphates compared to saline samples and a slight positive correlation with Fe and Mn, R^2= 0.2 respectively. This trend might be attributed to the reductive dissolution of As containing Iron hydroxides as discussed by (Baig et al., 2009; Haque et al., 2008)

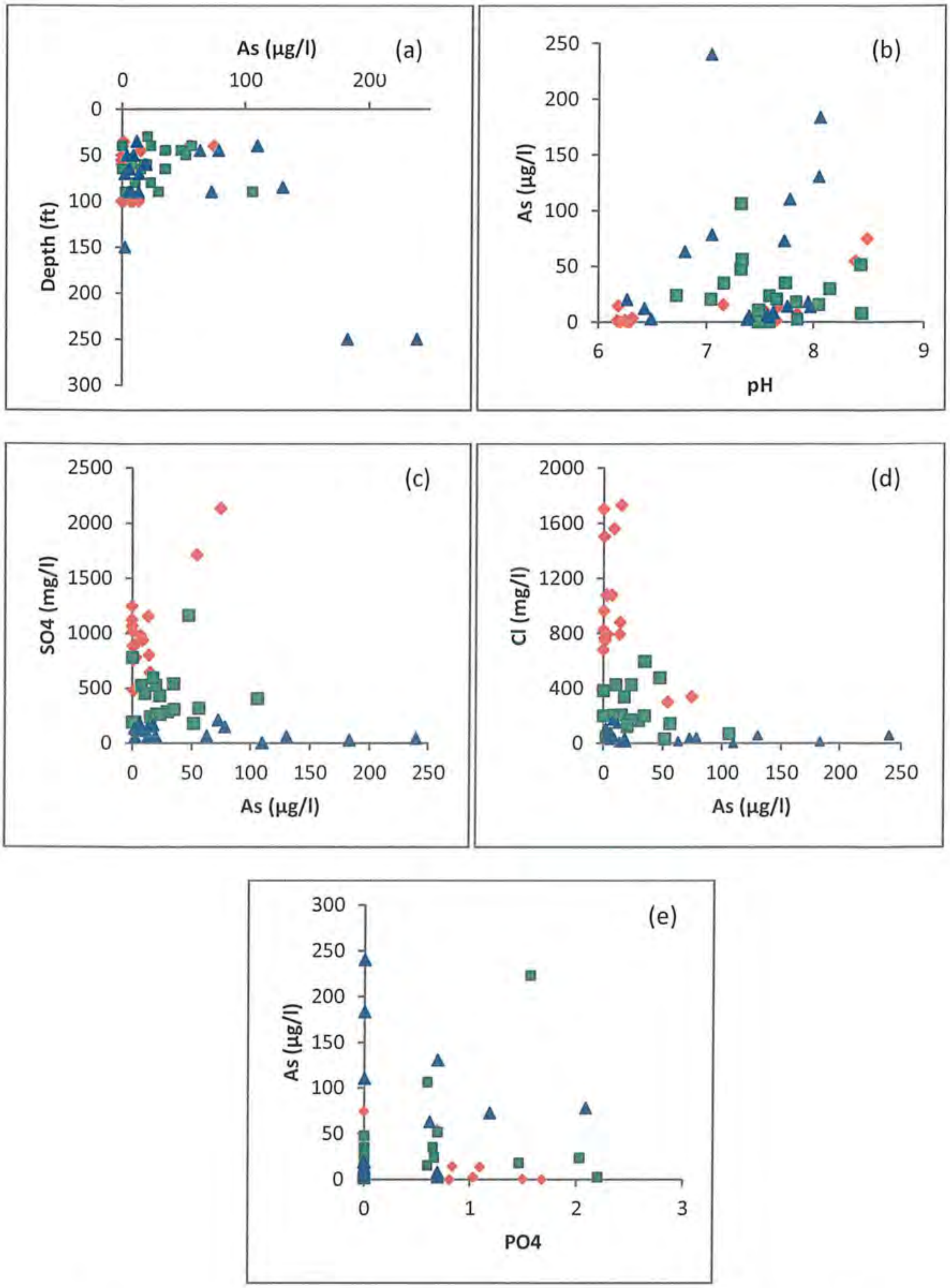


Figure 3.14: Relationship of Arsenic with (a) depth (b) pH (c) SO_4 (d) Cl and (e) PO_4

Note: Legends are same as piper and chaddah diagrams

Prevalence of both views i.e., positive and negative effect of TDS on arsenic is found in literature as discussed above. In the current study, the correlation of As with TDS in (Figure3.15 d) reflects that samples with relatively higher As concentrations are commonly found to have lower TDS levels, similar to the findings of Li et al. (2016) in a study carried out in Datong Basin, China. The plots of cationic and anionic abundance of groundwater (Figure 3.15. c, f) with arsenic generally indicate a decrease in almost all cations and anions with increasing arsenic concentrations in groundwater suggesting that increased salinity might limit As enrichment in groundwater. The moderately saline samples (TDS>3000) in the study area mainly have arsenic levels within WHO limit. These samples depict relatively oxidizing conditions with good correlation amid As and SO_4 (R^2= 0.684) (as discussed in section 3.6). According to Jia et al. (2017) the less reducing conditions in highly saline waters are responsible for a patchy relation between As and TDS. Groundwater arsenic enrichment occurs simultaneously as the reduction of sulfate prevails (Jia et al., 2014; 2017). Therefore the relatively oxidizing conditions of moderately saline waters fail to favor arsenic enrichment in the groundwater. The irrigation processes in the area may be responsible for the fluctuating redox conditions.

On contrary evaporative concentration tends to elevate arsenic concentrations, the phenomenon is observed in closed low lying basins in Western United States (Welch et al., 2000). The increased pH of saline groundwaters seems to be a contributor affecting As by limiting its adsorption. Due to minimum incorporation of As in most evaporite minerals the groundwater associated with such minerals have elevated arsenic levels (Levy et al., 1999). The groundwaters of Meghna Basin, Bangladesh possess a positive correlation between groundwater salinity and As levels with insignificant evaporation inputs in the area (Hasan et al., 2009). Low Eh values are observed in groundwater with high arsenic levels whereas oxidizing conditions are found in groundwaters with low As levels (Hasan et al., 2009). Therefore, high salinity may affect arsenic levels in groundwater depending on which ions and hydrogeochemical processes are responsible for occurrence of high TDS.

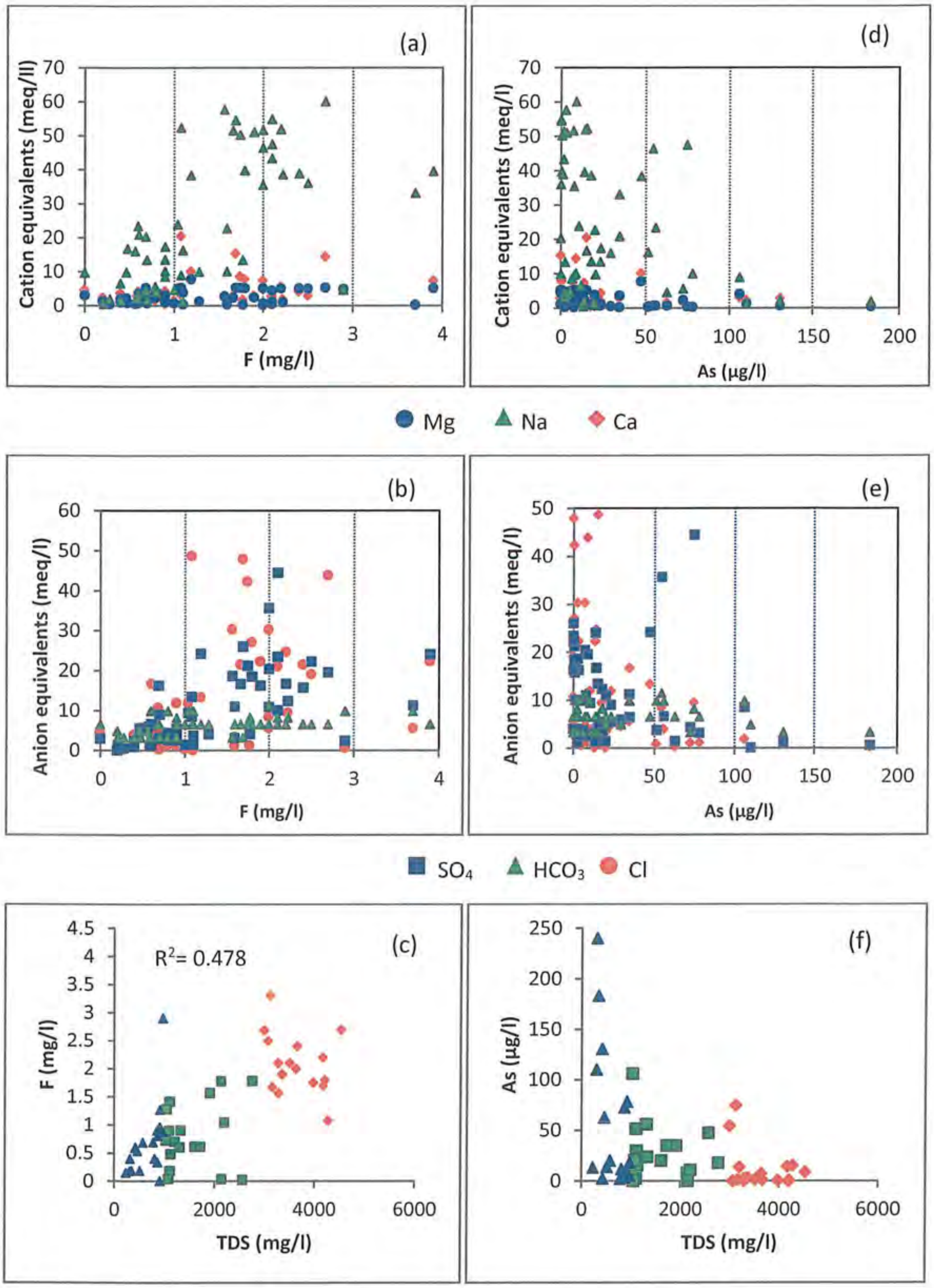


Figure 3.15: (a) Cationic and (anionic) abundance of groundwater samples with varying Fluoride levels and arsenic levels, (c) TDS vs F and As plot

3.6.1. Speciation of Arsenic

The speciation of arsenic is an important aspect to be covered in arsenic focused research studies. This parameter identifies the dominating specie distributed in an area thereby indicating the degree of toxicity. On field speciation of nine samples was carried out using column speciation method as shown in table 3.3. Speciation analysis revealed the presence of both As^{+5} and As^{+3} in the area confirming the presence of partial redox conditions. On contrary a study conducted in Lahore by Farooqi et al. (2007b) reported the occurrence of As mainly as arsenate in the groundwater with positive Eh values, high SO_4 and HCO_3 (oxidizing conditions). Arsenate is released in groundwater with increasing alkaline conditions whereas it adsorbs on iron oxyhydroxides under reducing conditions. However, in the current study the moderately saline samples present a mixed redox pattern. The conditions are neither enough oxidizing nor enough reducing with high sulphates but low nitrates in groundwater as discussed in section 3.6. Whereas the non-saline samples show a slightly reducing behavior with low sulphates and slight positive correlation with Fe and Mn ($R^2=0.2$) respectively thereby permitting the occurrence of both species (As^{+5}, As^{+3}) in groundwater.

Table 3.3: On site Speciation of Arsenic

Sample IDs	As^{+5}	As^{+3}
T1 C80 1	40	60
T4 As 8	25	75
T2 PR 3	200	0
T2 C113 1	100	0
T3 PR 2	200	0
T3 As 2	25	75
T4 BK 5	0	100
T2 Ks11	100	0
T1 BK 9	50	50

3.7. Statistical Verification

Correlation analysis and Principal Component Analysis were the multivariate tools used for statistical verification of data. PCA is one of the most often used techniques for water quality analysis in the last decade (Ali et al., 2015).

3.7.1. Degree of interdependence between different groundwater parameters

Pearsons correlation matrix was calculated for the data set to analyze the interdependence of various physicochemical parameters and their relation with As and F. As the correlation is applied on the complete data set therefore it provides a generally observed trend among the whole data set (table 3.4). TDS exhibits positive correlation with all ions except nitrate. A significant positive correlation is however observed between TDS-Na (r=0.960), TDS-Cl (r=0.902) and TDS-SO_4 (r=0.803). As is generally found to be negatively correlated with groundwater TDS levels (r=0.379) (as discussed in section 3.7.2) and all ions except PO_4 supporting the occurrence of competitive ion exchange.

On the other hand Fluoride has a strong positive correlation with TDS (r=0.647). Fluoride is found to be positively correlated with Na (r=0.644) and poorly correlated with Ca (r=0.188). Furthermore the negative correlation between As and F (r=0.323) suggest that their contamination in groundwater do not share a same source opposite to the trend observed in Tehsil Mailsi where they were found to be positively linked sharing same anthropogenic source of contamination (Rasool et al., 2015).

3.7.2. Principal Component Analysis (PCA)

The correlation matrix was further supported by Principal Component Analysis (PCA). PCA is statistical tool used to reduce a large data set into more precise information that elaborate the results based on the degree of variance or similarity (Qin et al., 2013). The application of PCA to the data set identified first three factors explaining 64.5 % variability in the data. Table 3.5 presents the factor loadings for respective principal components along with their variance and eigen values. The first principal component (PC-1) explains 41.6% variability in the data set. High positive loadings have been observed by PC-1 for EC, TDS, F^-, Na^+, Cl^- and SO_4. The factor explains the chemistry of shallow groundwater of the study area. The high values of Na^+, Cl^-, SO_4^{-2} represent the contribution of evaporation combined with the rock weathering leading to mineralization and enhanced TDS of groundwater as discussed in section 3.4.3. Furthermore high positive F loading shows that high F substantiates increased TDS and various geochemical factors namely mineral dissolution and evaporation (Krishan et al., 2017).

PC-2 corresponds to 12.7% of the total data variance. Higher loadings are observed for Ca and Mg reflecting the mechanism of F in deep groundwater. With the increase of depth F decreases where as Ca and Mg posses' higher values. The factor loadings of PO_4 and As are found to complement each other supporting competitive ion exchange process (Mushtaq et al., 2018).

The third component shows high factor loadings for NO_3 and K explaining 10% of the data variability. This component corresponds to the anthropogenic input in the study area. Mainly the anthropogenic sources of nitrates are fertilizers and domestic animals (Liu et al., 2005).

Table 3.3: Pearsons correlation matrix of physicochemical parameters, As and F in the study area (significance level, p=0.05)

Variables	Depth (m)	pH	EC (µS/cm)	TDS (mg/l)	F	As (µg/l)	Na	K	Ca	Mg	Cl	HCO3	SO4	NO3	PO4
Depth	**1**														
pH	0.139	**1**													
EC	-0.229	-0.310	**1**												
TDS	-0.229	-0.310	1.000	**1**											
F	-0.152	-0.154	**0.647**	**0.647**	**1**										
As (µg/l)	0.465	0.190	-0.379	-0.379	-0.323	**1**									
Na	-0.251	-0.238	**0.960**	**0.960**	**0.644**	-0.321	**1**								
K	-0.243	-0.204	0.414	0.414	0.163	-0.167	0.337	**1**							
Ca	-0.059	-0.343	0.593	0.593	0.188	-0.261	0.479	0.291	**1**						
Mg	-0.088	-0.418	0.554	0.554	0.274	-0.360	0.415	0.365	0.719	**1**					
Cl	-0.133	-0.384	**0.902**	**0.902**	0.442	-0.344	**0.849**	0.340	0.791	0.610	**1**				
HCO3	-0.236	0.116	0.125	0.125	0.349	-0.099	0.153	0.037	-0.103	0.018	-0.079	**1**			
SO4	-0.236	-0.065	**0.803**	**0.803**	0.589	-0.211	**0.831**	0.332	0.328	0.384	0.618	0.182	**1**		
NO3	-0.177	0.219	-0.047	-0.047	0.003	-0.064	-0.052	0.518	-0.136	-0.017	-0.185	0.145	0.101	**1**	
PO4	-0.030	0.013	0.001	0.001	0.180	0.109	0.044	-0.012	-0.170	-0.194	-0.041	0.122	0.043	0.025	**1**

Table 3.4: Factor loadings of, physicochemical parameters, As and F

(Factor loadings >0.5 are in bold)

	F1	F2	F3
Depth (m)	-0.190	0.055	-0.596
pH	-0.236	-0.537	0.018
EC (µS/cm)	**0.937**	0.243	0.163
TDS (mg/l)	**0.937**	0.243	0.163
F	**0.779**	-0.237	0.103
As (µg/l)	-0.311	-0.225	-0.431
Na	**0.943**	0.104	0.123
K	0.218	0.266	**0.718**
Ca	0.478	**0.710**	0.035
Mg	0.436	0.655	0.215
Cl	**0.814**	0.501	0.009
HCO3	0.264	-0.515	0.286
SO4	**0.829**	-0.048	0.215
NO3	-0.173	-0.179	**0.802**
PO4	0.185	-0.492	-0.093
Eigenvalue	6.237	1.914	1.527
Variability (%)	41.582	12.762	10.182
Cumulative %	41.582	54.344	64.526

Table 3.5: Factor loadings of , physicochemical parameters, As and F

(Factor loadings >0.5 are in bold)

	F1	F2	F3
Depth (m)	-0.190	0.055	-0.596
pH	-0.236	-0.537	0.018
EC (µS/cm)	**0.937**	0.243	0.163
TDS (mg/l)	**0.937**	0.243	0.163
F	**0.779**	-0.237	0.103
As (µg/l)	-0.311	-0.225	-0.431
Na	**0.943**	0.104	0.123
K	0.218	0.266	**0.718**
Ca	0.478	**0.710**	0.035
Mg	0.436	0.655	0.215
Cl	**0.814**	0.501	0.009
HCO3	0.264	-0.515	0.286
SO4	**0.829**	-0.048	0.215
NO3	-0.173	-0.179	**0.802**
PO4	0.185	-0.492	-0.093
Eigenvalue	6.237	1.914	1.527
Variability (%)	41.582	12.762	10.182
Cumulative %	41.582	54.344	64.526

4. Conclusion

The groundwater of Rachna Doab possesses TDS concentrations ranging from 233.6 to 4556.8 mg/l. The dominant water type observed for saline waters was NaCl whereas it was $CaHCO_3$ for non-saline waters. Various complex hydrogeochemical processes were found to contribute to groundwater chemistry in the region.

As the original Gibbs plot (1970) was proposed for the evolution of surface water chemistry (using ionic ratios and TDS of water) that considerably differs from the components important for groundwater environments, therefore although aids in understanding of hydrochemical processes it also leads to slight confusion in some cases. Hence to obtain an improved understanding Gibbs plot was followed by isotopic analysis. Graphical biplots, Stable isotopic analysis ($\delta\ ^{18}O$ and $\delta\ ^{2}H$ relative to VSMOW) and geochemical modeling identified ion exchange, mineral dissolution (mainly carbonate and silicate minerals) and partial input of evaporation towards groundwater salinity.

Fluoride concentration varied from below detection limit to 3.9 mg/l whereas As ranged from below detection limit to 183.42µg/l with prevalence of both arsenate and arsenite in the Doab. Groundwater TDS levels and evapotranspiration were found to play a part in the enrichment of groundwater fluoride. Na was the major cation and Cl was the major anion responsible for increased salinity in the region. Increased TDS and fluoride levels were found to be concentrated in shallow depths. Arsenic however, showed a decreasing trend with increasing salinity. The redox mechanism is the major factor regulating As enrichment. Saline ground waters had relatively oxidizing conditions which restricted As enrichment. Salinity of groundwater is attributed to various hydrogeochemical factors and major ions. Therefore whether salinity contributes as a factor affecting As and F enrichment depends on which of the factors and ions are mainly responsible for causing increased groundwater TDS levels.

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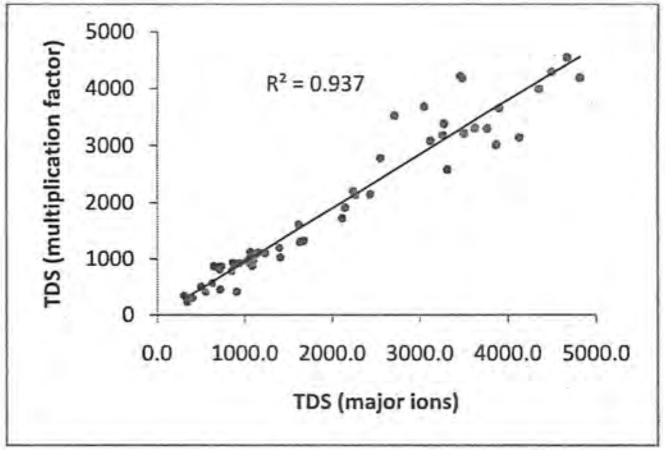
Annexure ***I: Physicochemical analysis of groundwater samples of Rachna Doab***

Sample ID	Depth (ft)	pH	EC (µS/cm)	TDS	F	As µg/l	Na	K	Ca	Mg	Cl	HCO_3	SO_4	NO_3	PO_4	Fe	Mn
T2c260-1	100	7.84	5700	3648	2.0	7.3	1187.5	40.9	149.5	61.9	1077.7	400	980.0	BDL	BDL	0.52	1.44
T3c260-2	45	7.16	6710	4294.4	1.1	15.4	1203.7	38.9	411.0	63.3	1730.0	400	643.9	BDL	BDL	BDL	0.08
T3C113-3	40	8.38	4710	3014.4	2.7	54.4	1067.6	36.1	11.4	8.9	300.3	700	1710.7	35.9	0.7	BDL	BDL
T2c113-1	40	8.48	4900	3136	3.3	74.7	1092.3	20.3	10.5	5.7	340.1	500	2134.2	26.2	BDL	BDL	BDL
T1C260-1	60	6.29	6550	4192	1.7	BDL	1254.0	35.7	308.5	63.2	1701.6	200	1249.4	BDL	BDL	BDL	0.14
T1C260-11	55	6.21	5150	3296	2.1	BDL	1261.2	40.7	60.5	53.8	822.4	400	1123.8	BDL	0.8	BDL	BDL
T1C260-12	60	6.32	5270	3372.8	1.9	3.3	1173.3	36.1	58.9	29.1	794.1	400	780.6	BDL	BDL	BDL	BDL
T1C260-13	35	6.25	4960	3174.4	1.7	1.4	1184.1	26.6	60.4	28.1	765.7	400	798.1	BDL	BDL	BDL	BDL
T1C260-3	55	6.27	6600	4224	1.8	0.5	914.1	74.7	157.3	61.8	964.2	400	885.6	BDL	BDL	BDL	BDL
T1C260-4	65	6.19	6540	4185.6	2.2	14.4	1194.2	31.7	113.2	61.3	879.2	400	801.3	BDL	0.8	0.02	0.10
T1C260-6	50	6.3	6230	3987.2	1.8	0.5	1156.0	34.9	173.6	63.0	1503.1	400	1016.9	BDL	1.5	BDL	BDL
T1C260-7	40	6.18	5740	3673.6	2.4	1.1	895.7	81.7	84.7	61.1	765.7	400	755.6	BDL	BDL	BDL	BDL
T2c260-2	100	7.55	7120	4556.8	2.7	9.0	1381.7	34.0	290.3	63.4	1559.8	400	937.5	BDL	BDL	0.49	0.41
T2c260-3	100	7.67	5020	3212.8	3.9	13.9	909.2	31.6	147.8	61.5	794.1	400	1155.6	BDL	1.1	0.06	BDL
T2c260-7	100	7.56	4820	3084.8	2.5	BDL	828.2	23.1	60.8	59.6	680.6	400	1068.8	BDL	1.7	BDL	BDL
T2c260-10	100	7.65	5500	3520	2.1	1.4	996.0	21.1	43.7	15.0	750.0	400	483.1	BDL	BDL	BDL	0.08
T3c260-9	60	7.59	5160	3302.4	1.6	2.7	1326.0	30.8	61.2	33.0	1077.7	200	893.8	BDL	1.0	BDL	BDL
T3C445-7	90	8.15	1746	1117.4	0.2	29.7	369.2	6.3	13.2	6.9	164.6	300	285.2	8.8	BDL	BDL	BDL

T4c445-3	65	8.05	1765	1129.6	0.5	15.3	385.3	2.3	18.2	10.0	205.3	200	238.9	BDL	0.6	BDL	BDL
T3c288-2	45	7.32	4030	2579.2	0.0	47.3	881.5	61.0	203.2	93.9	476.2	400	1161.2	33.3	BDL	6.41	0.30
T1C487-1	45	7.16	2990	1913.6	1.6	34.8	761.9	6.9	11.3	3.1	199.5	600	538.9	26.1	0.7	BDL	BDL
T3C487-6	60	8.43	3350	2144	1.8	7.8	815.5	7.1	7.2	3.4	202.7	700	524.5	5.5	BDL	BDL	BDL
T4AS8	90	7.32	1618	1035.5	0.7	106.0	205.6	12.2	64.2	49.0	68.9	600	405.1	0.9	0.6	2.74	0.35
T2c488-2	80	7.58	1880	1203.2	0.7	23.4	310.5	23.2	45.7	8.3	170.2	400	431.9	BDL	2.0	BDL	BDL
T4-c260-13	80	7.48	3450	2208	1.0	10.6	548.9	46.8	105.8	58.7	425.4	600	451.6	BDL	BDL	2.00	BDL
T1C171-5	60	7.04	2510	1606.4	0.6	20.2	523.1	18.7	12.8	9.6	120.5	400	527.3	5.8	BDL	0.42	BDL
T3C238-4	30	7.65	1690	1081.6	0.0	20.6	225.9	31.5	46.2	26.0	132.1	300	263.5	62.5	BDL	BDL	BDL
T1LS-9	40	6.72	2072	1326.1	0.9	23.7	399.8	81.9	87.8	14.6	425.4	400	262.0	BDL	0.7	0.04	BDL
T4ls-17	65	7.73	2690	1721.6	0.6	35.0	480.9	22.0	58.7	44.0	595.6	600	308.4	BDL	BDL	BDL	BDL
T3C80-6	50	8.42	1732	1108.5	1.4	51.4	373.7	6.1	14.2	5.3	31.2	600	178.8	16.6	0.7	BDL	BDL
T3CS5	90	7.84	1719	1100.2	0.9	2.4	308.2	8.9	36.2	4.2	48.8	500	193.0	30.5	2.2	BDL	BDL
T4pr-21	40	7.58	1648	1054.7	1.3	BDL	229.1	4.1	28.8	15.0	198.5	400	193.4	BDL	BDL	0.27	0.43
T1C113-6	40	7.33	2040	1305.6	0.6	56.0	538.8	5.9	17.8	8.9	141.8	600	317.5	BDL	1.6	BDL	BDL
T4-c113-10	60	7.83	4340	2777.6	1.8	17.8	887.4	96.0	39.8	12.5	337.9	500	592.0	81.7	1.5	BDL	0.04
T4-238-5	65	7.48	3360	2150.4	0.0	BDL	467.0	115.2	82.5	62.6	382.5	400	781.1	143.6	BDL	BDL	0.09
T3AS2	90	7.72	1368	875.5	0.3	72.5	129.2	7.7	32.5	28.5	40.0	200	208.9	0.1	1.2	0.52	0.09
T4-c488-6	90	7.97	365	233.6	0.2	13.5	10.8	BDL	43.2	13.4	5.8	200	64.4	2.4	BDL	BDL	BDL
T4-c241-7	90	7.4	1530	979.2	2.9	5.3	108.3	5.4	88.7	59.2	24.3	600	116.6	19.4	BDL	0.99	BDL
T2c80-2	60	7.95	1541	986.2	0.9	18.2	312.4	27.3	13.4	11.4	43.8	500	165.2	21.8	BDL	BDL	BDL

T1C80-1	45	7.05	1450	928	1.3	78.2	231.0	6.9	10.0	4.4	42.8	400	150.0	14.4	2.1	BDL	BDL
T3NO8	90	7.62	1437	919.7	0.0	7.8	221.7	4.4	93.0	36.3	165.1	400	139.3	BDL	0.7	BDL	0.03
T2cs-2	65	7.56	1356	867.8	0.9	6.3	197.6	2.1	48.5	16.1	85.1	200	178.0	BDL	BDL	0.24	BDL
T4-bk-5	85	8.05	658	421.1	0.6	130.2	52.6	93.7	57.3	8.4	56.7	200	58.8	19.8	0.7	BDL	BDL
T1Bk-9	45	6.8	731	467.8	0.5	62.9	105.6	52.9	32.2	8.8	14.1	400	67.4	35.8	0.6	BDL	BDL
T2PR-3	250	7.04	492	314.9	0.4	240.0	36.7	4.3	36.6	11.5	56.7	200	43.1	BDL	BDL	1.00	0.18
T3PR2	250	8.06	541	346.2	0.2	183.4	45.7	1.1	13.5	6.1	11.8	200	27.0	BDL	BDL	0.26	0.05
T2ks11	40	7.77	486	311	0.2	109.9	29.8	7.4	47.0	16.2	1.3	300	2.4	BDL	BDL	BDL	0.02
T1KS-4	35	6.43	1275	816	0.4	11.9	150.9	7.9	74.7	25.5	141.8	200	113.0	BDL	BDL	BDL	0.06
T4-ay-7	70	7.38	1228	785.9	0.7	2.2	99.4	11.3	55.4	32.1	113.4	400	136.9	BDL	BDL	BDL	BDL
T1SP-3	150	6.49	670	428.8	0.6	2.6	76.6	5.0	84.5	23.8	56.7	600	58.0	BDL	0.7	BDL	0.00
T1GL-5	60	6.27	903	577.9	0.7	20.0	27.6	3.9	74.3	46.8	6.3	400	66.8	0.1	BDL	0.13	0.12
T3GL6	50	7.59	1373	878.7	0.8	3.9	95.0	41.5	85.3	47.9	85.1	600	123.4	6.4	BDL	BDL	0.09
T2c241-2	70	7.75	808	517.1	0.2	13.9	40.7	5.1	50.3	32.1	11.5	200	154.6	0.2	BDL	BDL	0.07
T2no-2	50	7.62	1445	924.8	1.0	9.0	233.1	17.1	36.9	36.9	45.7	400	120.9	41.4	BDL	BDL	BDL

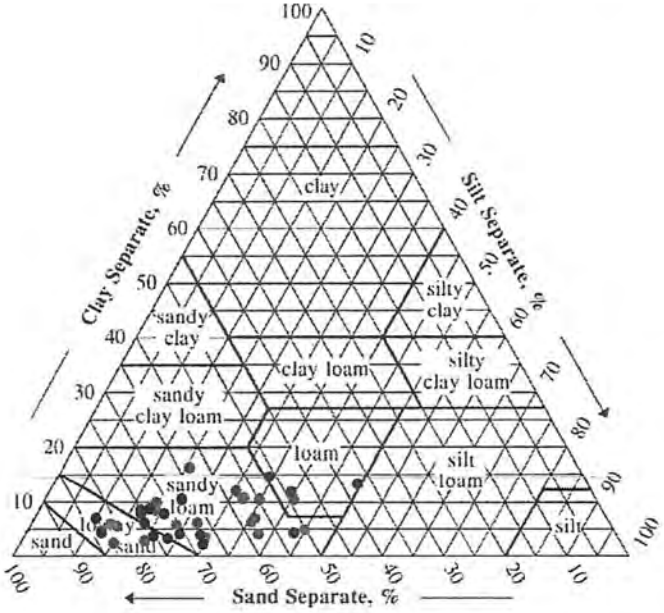
Note: All units are in mg/l, if otherwise they are mentioned



Annexure II: Plot between TDS calculated in the current study through the relationship given by (Shainberg and Levy, 2005) and TDS calculated based on major ion composition and

Annexure III: Ratios of Na-Cl and Cl-∑Anions

Statistic	Cl/∑Anions	Na/Cl
Minimum	0.004	0.998
Maximum	1.657	34.856
Mean	0.372	4.500



Annexure IV: Texture Analysis of soil identifying soil texture mainly as Sandy Loam

Annexure V: Saturation Indices calculated through PHREEQC (USGS software)

Sample ID	Anhydrite	Aragonite	Calcite	Dolomite	Fluorite	Goethite	Gypsum	Halite	Siderite	Manganite	Hematite
T2c260-1	-0.96	0.25	0.42	0.39	-0.13	4.3	-0.72	-4.52	0.07	-6.99	10.49
T3c260-2	-0.76	0.02	0.19	-0.51	-0.23	–	-0.51	-4.32	–	-10.23	–
T3C113-3	-2.62	0.05	0.21	0.24	-1.07	–	-2.37	-5.08	–	–	–
T2c113-1	-1.85	-0.28	-0.11	-0.53	-1.32	–	-1.6	-5.07	–	–	–
T1C260-1	-0.62	-1.31	-1.15	-3.05	-0.01	–	-0.37	-4.31	–	-12.58	–
T1C260-11	-1.28	-1.77	-1.61	-3.32	-0.48	–	-1.03	-4.61	–	–	–
T1C260-12	-1.39	-1.63	-1.46	-3.3	-0.52	–	-1.14	-4.65	–	–	–
T1C260-13	-1.37	-1.27	-1.1	-2.67	-0.17	–	-0.7	-4.67	–	–	–
T1C260-3	-0.95	-1.27	-1.1	-2.67	-0.17	–	-0.7	-4.67	–	–	–
T1C260-4	-1.13	-1.49	-1.32	-2.98	-0.14	-2.32	-0.88	-4.6	-3.24	-13.01	-2.75
T1C260-6	-0.9	-1.23	-1.06	-2.63	-0.2	–	-0.65	-4.39	–	–	–
T1C260-7	-1.24	-1.6	-1.44	-3.08	-0.16	–	-0.99	-4.77	–	–	–
T2c260-2	-0.75	0.24	0.4	0.08	0.39	3.42	-0.5	-4.31	-0.25	-8.39	8.71
T2c260-3	-0.89	0.08	0.24	0.04	0.45	2.79	-0.64	-4.76	-1.1	–	7.45
T2c260-7	-1.26	-0.4	-0.24	-0.54	-0.3	–	-1.01	-4.86	–	–	–
T2c260-10	-1.65	-0.37	-0.21	-0.96	-0.49	–	-1.4	-4.73	–	-8.81	–
T3c260-9	-1.35	-0.66	-0.49	-1.31	-0.7	–	-1.1	-4.47	–	0	–
T3C445-7	-2.1	-0.52	-0.36	-1.05	-1.98	–	-1.85	-6.65	–	0	–
T4c445-3	-1.8	-0.34	-0.2	-0.9	-1.7	–	-1.4	-5.9	–	0	–
T3c288-2	-0.76	-0.14	0.03	-0.34	-0.46	3.86	-0.51	-5	0.67	-9.18	9.62

T1C487-1	-2.1	-1.24	-1.08	-1.3	-0.57	_	-1.85	-7.79	_	_	_
T3C487-6	-2.36	-0.14	0.02	-0.35	-1.3	_	-2.11	-5.37	_	_	_
T4AS8	-1.44	-0.29	-0.13	-0.45	-0.82	3.53	-1.19	-6.42	0.55	-9.07	8.95
T2c488-2	-1.53	-0.35	-0.19	-1.19	-1.32	_	-1.28	-5.84	_	_	_
T4-c260-13	-1.29	0.03	0.19	0.06	-0.72	3.84	-1.04	-5.22	9.57	_	9.57
T1C171-5	-2.03	-1.47	-1.3	-2.79	-1.19	1.9	-1.78	-5.77	-0.69	_	5.69
T3C238-4	-2.01	-1.3	-1.4	-2.4	-1.1	1.4	-1.5	-5.3	-0.5	_	
T1LS-9	-1.49	-0.92	-0.75	-2.36	-0.82	_	-1.24	-5.34	-1.96	_	1.88
T4ls-17	-1.65	0.06	0.22	0.24	-1.39	_	-1.4	-5.12	_	_	_
T3C80-6	-2.35	0.2	0.36	0.21	-1.38	_	-2.1	-6.48	_	_	_
T3CS5	-1.9	-0.04	0.13	-0.76	-0.54	_	-1.65	-6.37	_	_	_
T4pr-21	-1.99	-0.48	-0.32	-1	-0.92	3.38	-1.74	-5.89	-0.29	-8.15	8.64
T1C113-6	-2.08	-0.83	-0.67	-1.71	-1.86	_	-1.83	-5.68	_	_	_
T4-c113-10	-1.61	-0.15	0.01	-0.55	-0.49	_	-1.36	-5.12	_	-8.61	_
T4-238-5	-1.2	-0.3	-0.14	-0.46	-1.23	_	-0.95	-5.35	_	-9.22	10.23
T3AS2	-1.86	-0.56	-0.4	-0.93	-1.26	4.18	-1.61	-6.82	-0.07	-8.34	_
T4-c488-6	-2.13	-0.1	0.06	-0.48	-2.18	_	-1.88	-8.68	_	_	_
T4-c241-7	-1.98	-0.2	0.04	-0.32	-2.2	_	-1.72	-6.5	_	_	_
T2c80-2	-2.4	-0.36	-0.2	-0.55	-1.57	_	-2.15	-6.14	_	_	_
T1C80-1	-2.5	-1.49	-1.32	-3.09	-1.14	_	-2.25	-6.35	_	_	_
T3NO8	-1.67	0.06	0.23	-0.04	0	_	-1.42	-5.99	_	-9.2	_
T2cs-2	-1.75	-1.54	-1.37	-3.3	-0.96	3.44	-1.5	-6.3	8.77	_	_

T4-bk-5	-2.11	0.02	0.18	-0.56	-1.2	–	-1.86	-7.04	–	–	–
T1Bk-9	-2.31	-1.15	-0.98	-2.6	-1.01	–	-2.06	-7.35	–	–	–
T2PR-3	-2.38	-1.1	-0.94	-2.93	-1.69	2.48	-2.13	-7.37	-0.39	-9.96	6.84
T3PR2	-2.18	-0.9	-0.81	-2.3	-1.4	2.14	-2.11	-6.9	-0.23	-8.67	–
T2ks11	-3.51	-0.15	0.02	-0.53	-2.18	–	-3.26	-8.91	–	-9.33	–
T1KS-4	-1.79	-1.48	-1.31	-3.17	-1.48	–	-1.54	-6.2	–	-12.38	–
T4-ay-7	-1.84	-0.37	-0.21	-0.74	-1.16	–	-1.59	-6.49	–	–	–
T1SP-3	-2.02	-0.88	-0.71	-2.06	-1.07	–	-1.77	-6.89	–	-13.38	
T1GL-5	-2	-1.32	-1.16	-2.61	-0.6	-0.81	-1.75	-8.29	-1.85	-12.56	0.27
T3GL6	-1.76	0.18	0.35	0.36	-0.88	–	-1.51	-6.64	–	-8.83	–
T2c241-2	-1.78	-0.32	-0.15	-0.58	-1.15	–	-1.53	-7.85	–	-8.34	–
T2no-2	-2.09	-0.32	-0.16	-0.4	-1.12	–	-1.84	-6.52	–	–	–

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Sources of salinity and its impact on mobilization of arsenic and fluoride in groundwater of Rachna Doab by Ambreen Parvaiz

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Arsenic speciation: Sources of salinity and its impact on mobilization of arsenic and fluoride in groundwater of Rachna Doab

Department of Environmental Sciences, Quaid-i-Azam University, Islamabad 45320, Pakistan

Abstract

The current research was based on studying the sources of groundwater salinity in Rachna Doab, Pakistan and its possible impact on the enrichment of arsenic and fluoride levels. For this purpose blanket sampling was conducted throughout Rachna Doab to test the occurrence of salinity, As and F-. The groundwater was found to have varied TDS concentrations i.e., 233.6 to 4556.8mg/l. Based on the results of blanket sampling representative groundwater samples from all villages were selected. The samples were classified into three groups based on their TDS levels and analyzed for As, F- and other physicochemical parameters. As and F- concentrations in the study area ranged from below detection limits to 183.42µg/l and 3.9mg/l respectively with the prevalence of both arsenate and arsenite in the area. Graphical biplots, stable isotopic analysis (δ 18O and δ 2H relative to VSMOW), Gibbs plot and hydrogeochemical modeling of the groundwater samples revealed mineral dissolution, ion exchange processes and partial input of evaporation towards groundwater salinity in the region. The results were in accordance with the conceptual model developed based on secondary data. Groundwater salinization was found to have a positive influence on the enrichment of fluoride whereas groundwater As levels showed an overall decreasing trend with increasing salinity identifying a negative effect of salinization on enrichment of arsenic in groundwater.

Introduction

The continuous increase in the world population is leading towards an expanding demand for water. Over extraction of water to meet the demands cause various serious water crises in terms of its quality as well as quantity. According to an estimate 884 million people in the world do not have access to clean drinking water. Increasing groundwater salinity is informed to be one of the many reasons of this crisis (Vineis et al., 2011). More than hundred countries in the world including India, China and US are affected by aquifer and land salinization. Many parts of India and China are found to be suffering from severe inland groundwater salinity (Shahid, 2013;Krishan et al., 2017; Lorenzen et al., 2012; Misra and Mishra, 2007; Rao, 2008; Rao et al., 2017; Gao et al., 2007; 2013; Sun et al., 2016). Investigations of groundwater quality of Pakistan through British Geological Survey have identified increased salinization of groundwater as a major concern prompting towards the confinement in the availability of precious resource (Smedley, 2001). Moreover, events of excessive arsenic and fluoride contamination in some ground water sources within Indus Plain are reported to be additional water quality concerns faced by Pakistan. Previous Studies in Punjab, Pakistan (Farooqi et al., 2007b; Malana and Khosa, 2011) reported that the sampling sites having arsenic >10µg/l displayed high concentrations of EC as well. Moreover increased evaporation and salinity might partially contribute to desorption of arsenic to groundwater from mineral surfaces. Furthermore, the enhanced concentrations of arsenic in shallow groundwaters of Jamshoro and Muzaffargarh may be attributed to the phenomenon of water logging and high saturation of salts in the areas (Baig et al., 2009; Nickson et al., 2005). Contamination of As along with salinity have also been found to occur in the fresh water of Manchar lake and the groundwater in its vicinity. Apart from anthropogenic causes the natural phenomenon of evaporative concentration has been accounted responsible for the buildup of salts (Baig et al., 2010). In Tharparkar, dry climate has been accounted as a primary factor contributing to increased fluoride in groundwater (Brahman et al., 2013). Furthermore research studies in Nagarparkar, Umarkot and Lahore have reported most of the high fluoride samples associated with elevated TDS levels (Rafique et al., 2009; 2015).

Aims and Objectives

- To determine and present a conceptual model of groundwater recharge sources and factors controlling groundwater salinity in Rachna Doab
- To investigate the extent to which salinity plays a role in regulating the enrichment of Arsenic and Fluoride in groundwater of Rachna Doab
- To assess the impact of changing hydrogeological conditions on the toxicity of arsenic through speciation

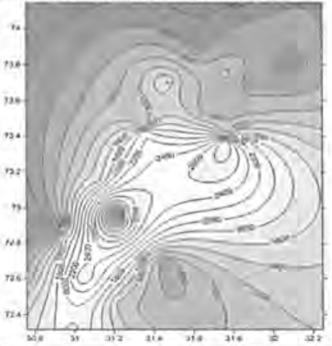
Methodology

Study area: The study area, Rachna Doab is an interfluvial area between Chenab and Ravi rivers. It lies between longitudes 71 48' E to 752°0' E and latitude 30 to 32 51' and is located in the core of Indus Basin. It is characterized by semi-humid climate in the northeast which alters to semi arid towards the south west (Bastiaanssen and Feddes, 2005). The bed rock geology is composed of igneous and metamorphic rocks of Precambrian times known as Kirana hills. The overlying unconsolidated alluvial deposits on these precambrain basements are of Pleistocene to recent age. The alluvium is nearly homogenous however reduced vertical and lateral continuity is observed indicating the diversity of depositional environments throughout the passage of time (Rehman et al., 1997b).

The deep unconfined aquifer underlying the Indus plain is made up of the alluvium deposited in the late tertiary period. The aquifer is heterogenous and highly anisotropic with a thickness of greater than 300 meters. The region has little natural drainage. Aquifer material is highly porous capable of storing and transmitting water with relatively higher horizontal than vertical permeability (Sajjad et al., 1992). The Doab covers approximately an area of 2.97 million ha with 2.3 million ha of developed land. It is an ancient most intensively developed irrigated land of Punjab (Sikandar et al., 2010).

Groundwater sampling: Blanket sampling of groundwater was carried out in the month of September 2016-2017 for the screening of Rachna doab to test the occurrence of salinity, arsenic and fluoride. Based on the results of blanket sampling a total of 54 representative groundwater samples with depth ranging from 35ft to 250ft were collected from all villages throughout doab.

Groundwater samples were collected in duplicates. Collection was carried out in 100 ml polypropylene bottles in accordance with the protocols defined by (APHA, 2005). One subsample was left untreated for anion analysis whereas the other subsample was acidified by the addition of HCL to lower the pH<2 for major cation analysis. For the analysis of Stable isotopes δ2H and δ18O samples were collected in 15ml glass bottles devoid of any headspace and tightly sealed using paraffin film. Water samples were analyzed for their physicochemical parameters, pH, EC, anions, cations and arsenic. The speciation of arsenic was carried out using column speciation method. Soil sampling was carried out from the same village sites as the groundwater samples from 15cm depth. Soil samples were air dried and texture analysis of the samples was performed using sieve machine.

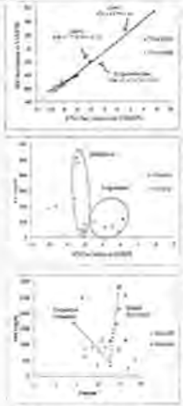


Results

Groundwater Chemistry: Results of physical analysis stated that groundwater is slightly acidic to alkaline in nature having a pH ranging between 6.18 and 8.48. The samples showed great variation in EC (µS/cm) and TDS (mg/l). Alkalinity ranged from 200 – 700 mg/l. Na was found to be the major cation whereas SO_4^{-2} as the major anion. NaCl and $CaHCO_3$ were identified as dominant water types in saline and non-saline groundwaters respectively.

Sources of salinity

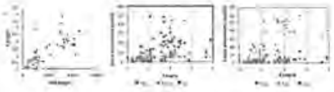
The isotopic composition of the groundwaters of Rachna Doab represent elevated rain, mixed and pure depleted surface water recharge in the area. Two varying trends were observed in the groundwater



samples of the current study, with one group of samples lying close to the x-axis which represent the dissolution of soluble salts where as the samples lying towards y-axis shows the contribution of evaporation to the salinization of groundwater. A plot of TDS vs d-excess is shown in Figure 3.8 suggesting that the groundwater chemistry of Rachna Doab is influenced by both mineral dissolution and evaporation processes with a dominant contribution from mineral dissolution.

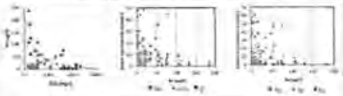
Saturation indices calculated using PHREEQC, a USGS program suggested a dominating trend of undersaturation which explains that the increased TDS levels and may be accredited to water logging in the study area leading to extensive mineral dissolution. However partial contribution of evaporation towards salinity was presented by the positive SI of calcite indicating the precipitation of carbonate minerals.

Variation of fluoride in groundwater and possible impact of salinity



- High fluoride concentrations are found in shallow groundwater samples showing similar trend with depth as observed by TDS. Groundwater fluoride content shows a good correlation with salinity i.e., $R^2=0.478$. Anionic and cationic abundance of groundwater samples with fluoride showed an increase in Na ion with increasing fluoride concentrations whereas low Ca and Mg levels are observed due to cation exchange reactions with sodium. Elevated Na levels increase the ionic strength and solubility of fluoride in groundwater. Most of the groundwater samples with high fluoride levels are found to have increased Cl concentrations indicating the contribution of evapotranspiration towards high fluoride in groundwater.

Variation of arsenic in groundwater and possible impact of salinity



Out of the total, 35% of the samples have As >10µg/l (WHO limit) whereas 22% of the samples have As>50µg/l (EPA-NEQS) (WHO, 2011). Samples with relatively higher As concentrations are commonly found to have lower TDS levels. Flocculation of iron oxides initiate with increasing salinity resulting in decreased As concentrations. Speciation analysis revealed the presence of both As^{+5} and As^{+3} in the area confirming the presence of partial redox conditions.

Conclusions

- Graphical biplots, Stable isotopic analysis (δ 18O and δ 2H relative to VSMOW) and geochemical modeling identified mineral dissolution (mainly carbonate and silicate minerals) and partial input of evaporation towards groundwater salinity.
- Furthermore the groundwater of Rachna Doab has found to be recharged by rainfall mainly in the upper region of Doab followed by mixed and solely surface (canal and river) recharge as we move laterally and vertically away from upper part of Doab
- Groundwater TDS levels and evapotranspiration were found to play a part in the enrichment of groundwater fluoride. Increased TDS and fluoride levels were found to be concentrated in shallow depths.
- Arsenic however, showed a decreasing trend with increasing salinity. The redox mechanism is the major factor regulating As enrichment.

Acknowledgements

Add your information, graphs and images to this section.