STUDY ON THE DETRIMENTAL EFFECTS OF WASTEWATER FROM SADQAL OIL AND GAS FIELD, FATEHJANG, PUNJAB, PAKISTAN ON WATER QUALITY AND SOIL

(PhD Thesis)

By

SAID AKBAR KHAN

Supervisor

PROF. DR. HIZBULLAH KHAN

DEPARTMENT OF ENVIRONMENTAL SCIENCES

UNIVERSITY OF PESHAWAR

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SAID AKBAR KHAN

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بسم الله الرحمن الرحيم

IN THE NAME OF

ALLAH

Most Merciful and Compassionate, the Most Gracious and Beneficent, Whose help and guidance we always solicit at every step at every moment.

APPROVAL SHEET

It is recommended that the Thesis prepared by Said Akbar Khan "Study on the detrimental effects of wastewater from Sadqal oil and gas field, Fatehjang, Punjab, Pakistan on water quality and soil" be accepted as fulfilling this part of the requirements for the degree of "DOCTOR OF PHILOSOPHY IN ENVIRONMENTAL SCIENCES"

Prof. Dr. Hizbullah Khan____________________
Research Supervisor
Department of Environmental Sciences
University of Peshawar

Prof. Dr. Imtiaz Ahmad____________________
Research Co-Supervisor
Institute of Chemical Sciences
University of Peshawar

Prof. Dr. Shahida Zakir ____________________
Chairperson
Department of Environmental Sciences
University of Peshawar

Assistant Prof. Dr. Kifayatullah Khan____________________
External Examiner
Department of Environmental Sciences &
Conservation Sciences, University of Swat

DEPARTMENT OF ENVIRONMENTAL SCIENCES
UNIVERSITY OF PESHAWAR
(SESSION 2010-11)

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“*In the name of Allah the most merciful and beneficent*”

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SAID AKBAR KHAN

DEDICATION

Dedicated to

My Beloved parents, brothers

AND

To those whom prayers enabled

me to do this job

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LIST OF ABBREVIATIONS

Abbreviation	Stands For
As	Arsenic
AAS	Atomic Absorption Spectrometer
BTEX	Benzene, Toluene, Ethyl benzene & Xylene
BOD	Biological Oxygen Demand
CRL	Centralized Recourse Laboratory
Ca	Calcium
COD	Chemical Oxygen Demand
Cd	Cadmium
Cu	Copper
CO_3	Carbonates
Cl	Chloride
Cr	Chromium
EPA	Environmental Protection Agency
Fe	Iron
F	Florid
H_2SO_4	Sulpheric acid
HCO_3^-	Bicarbonate
HNO_3	Nitric acid
HCl	Hydrochloric acid
K	Potassium
Mn	Manganese
MPL	Maximum Permissible Limits
mg/L	Mille gram per litter
Mg	Magnesium
Na	Sodium
NCEPC	National Center of Excellence in Physical Chemistry
Ni	Nickel

Abbreviation	Stands for
NEQS	National Environmental Quality Standards
NO_2	Nitrite
NPD	Naphthalene, Phenanthrene, Dibenzothiophene
OGDCL	Oil and Gas Development Company Limited
IC	Ion Chromatography
PW	Produced water
PAHs	Poly Aromatic Hydrocarbons
PPM	Part per million
Pak-EPA	Pakistan Environmental Protection Agency
PCA	Principal Component Analysis
Pb	Lead
SO_4	Sulfate
TDS	Total Dissolved Substances
WHO	World Health Organization
Zn	Zinc

PREFACE

The main objectives of present thesis were to examine the physico-chemical properties and heavy metals concentration in wastewater from oil field and their impacts on ground water and soil in the surrounding area. To achieve these objectives, the thesis research work has been divided into six chapters; each chapter is focused on specific objectives in details.

First chapter describes the general introduction of this study, the study area along with aims and objectives.

Second chapter deals with the literature review that explains related studies carried out by the environmental scientist's throughout the world.

Third chapter focuses on the physico-chemical characteristics of wastewater such as pH, temperature, conductivity, total dissolved substances (TDS), biological oxygen demand (BOD), chemical oxygen demand (COD), oil and grease, also cations including sodium (Na^{+}), potassium (K^{+}), calcium (Ca^{+2}), magnesium (Mg^{+2}) & anions including chloride (Cl^{-}), florid (F^{-}), sulfate (SO_4^{-2}), nitrate (NO_3^{-}) and nitrite (NO_2^{-}). Its second parts describes the heavy metals (HMs) concentration in wastewater including chromium (Cr), manganese (Mn), cadmium (Cd), zinc (Zn), copper (Cu), lead (Pb), nickel (Ni) and iron (Fe).

Fourth chapter describes the impact of produced water on ground water near exploration and production. Chemical properties including Na^{+}, K^{+}, Ca^{+2}, Mg^{+2}, Cl^{-}, F^{-},

SO_4^{-2}, NO_3^- & NO_2^- and HMs including Cr, Mn, Cd, Zn, Cu, Pb, Ni and Fe were discussed in this chapter.

Fifth chapter describes the impact of wastewater on soil. Anions cations including Na^+, K^+, Ca^{+2}, Mg^{+2}, Cl^-, F^-, SO_4^{-2}, NO_3^- and NO_2^-, also HMs including Cr, Mn, Cd, Zn, Cu, Pb, Ni and Fe in soil were explained in this chapter.

Sixth chapter of this dissertation includes the conclusions and recommendations based on the current study. References cited in all chapters are given at the end.

ABSTRACT

This study was conducted to investigate the characteristics of wastewater from Sadqal oil and gas field, Fateh Jang, Punjab, Pakistan and its impacts on ground water and surrounding soil. The research work was carried out in three steps.

In the first step, wastewater samples were collected from the selected sites in the study area. Physico-chemical parameters were evaluated in the months of January 2013 to January 2014 using standard analytical methods. Anions and cations were studied by Ion Chromatography (IC). The results obtained were in the following order: pH ranged from 6.7±0.4–7.5±0.20, temperature; 16.2±0.36–25.3±0.26 ˚C, conductivity; 25800±0.5–28800 µS/cm, total dissolved substances (TDS); 85000±1.90–135000±1.70 mg/L, hardness; 18000±1.30–33000±1.40 mg/L, biological oxygen demand (BOD); 550±0.29–1210±0.38 mg/L, chemical oxygen demand (COD); 1300±0.95–4200±0.75 mg/L and oil & grease; 15±0.72–400±1.20 mg/L.

Levels of cations including sodium (Na^{+}) were found to be 14739±1.20–47250±1.40 mg/L, potassium (K^{+}); 218±1.10–546±0.45 mg/L, calcium (Ca^{+2}); 3687±1.09–8314±0.65 mg/L, magnesium (Mg^{+2}); 439±0.85–1080±0.74 mg/L and anions including chloride (Cl^{-}) ranged from 8542±1.35–56890±1.60 mg/L, florid (F^{-}); 203±0.87–582±0.83 mg/L, bromide (Br^{-}); 2±0.31–9.3±0.54 mg/L, sulfate (SO_4^{-2}); 52±0.84–178±0.25 mg/L, nitrate (NO_3^{-}); 46±0.91–809±0.80 mg/L and nitrite (NO_2^{-}) 14±0.91–52±0.41 mg/L.

Heavy metals (HMs) were also assessed in the same wastewater samples by Atomic Absorption Spectrophotometry. The concentration of chromium (Cr) was found

to be 1.07±0.01–2.7±0.02 mg/L, manganese (Mn); 1.06±0.03–2.3±0.01 mg/L, cadmium (Cd); 0.02±0.02–0.04±0.01 mg/L, zinc (Zn); 1.2±0.02–2.1±0.01 mg/L), copper (Cu); 0.49±0.02–1.3±0.01 mg/L, lead (Pb); 0.51±0.07–0.91±0.41 mg/L, nickel (Ni); 0.34±0.06–0.49±0.49 mg/L and iron (Fe); 2.06±0.05–11.52±0.09 mg/L.

The results obtained were compared with the maximum permissible limits (MPL) of Pakistan Environmental Protection Agency (Pak-EPA). It was found that the wastewater from Sadqal oil and gas field are highly contaminated which is discharged on site without any prior treatment.

In the second step, representative drinking water samples were collected from different sources (wells, pressure pumps and hand pumps) in order to examine the physico-chemical properties and HMs concentrations which are effected by wastewater. pH of all samples was analyzed on the spot while Na^{+}, K^{+}, Ca^{+2}, Mg^{+2}, Cl^{-}, F^{-}, SO_4^{-2}, NO_3^{-} and NO_2^{-} were analyzed by Ion Chromatography. Among the HMs Cr, Mn, Cd, Zn, Cu, Pb, Ni and Fe were analyzed. The values of different parameters of drinking water collected from different sources indicate that their levels are above the World Health Organization (WHO) permissible limits.

In the third step, composite soil samples were collected around the wastewater ponds at various distances in east, west and south directions. To evaluate the impacts of wastewater on soil; anions, cations and HMs concentrations were investigated. Anions cations including Na^{+}, K^{+}, Ca^{+2}, Mg^{+2}, Cl^{-}, F^{-}, SO_4^{-2}, NO_3^{-} and NO_2^{-} were assessed. HMs including Cr, Mn, Cd, Zn, Cu, Pb, Ni and Fe were evaluated. The results values compared with the reference soil sample. It was found that the levels are above the reference sample values. The results inferred that soils near wastewater ponds are highly contaminated due to continuous seepages from the ponds.

On the basis of findings, it is concluded that wastewater of the area may pose serious threats to the inhabitants living near exploration and production area. So, Environmental Protection Agency (EPA) should check the illegal practices of dumping of industrial effluents on land especially in residential areas and such activities may be stopped immediately by strict imposition of National Environmental Quality Standards in order to minimize the associated environmental risks & to ensure public health.

Keywords: Wastewater, Physico-chemical properties, Heavy metals, Drinking water, Soil, Sadqal oil and gas field

CHAPTER-1

1.1. General statement

The extraction of oil in onshore and offshore deposits produces aqueous waste, called produced water (PW) (Figueredo et al., 2014). Oil and gas production sector generates large amount of PW, with water to oil ratio which increases with increasing well age. Current estimates of the average ratio of water and oil globally is 4:1 (Judd et al., 2014). PW is mostly contaminated with dissolved gases, oil, grease, sludge and heavy metals. It is considered as a highly polluted industry of the world as it holds a major potential of hazards for the environment and may have detrimental effects on water, soil and air (Fakhru'l-Razi et al., 2009; Kadafa, 2012; Sadatipour et al., 2004; Sally et al., 2011).

Petroleum is usually accumulated in reservoir rocks in association with gas and brine. Recovery of gas or oil also generates/produce a substantial quantity of waste water at the well head. As reservoir pressure declines over time, additional water is also injected into the reservoir to maintain the pressure and achieve greater recovery levels. Both formation and injected water are brought to the surface along with hydrocarbons (Ekins et al., 2007). Such water is contaminated with organic and inorganic components including mixture of hydrocarbons, anions, cations and heavy metals (Asia et al., 2007; Ekins et al., 2007; Fillo et al., 1992; Gazineu & Hazin, 2008) which is discharged carelessly in to fresh water streams thereby creating several environmental problems. Several environmental effects of such water have been reported in the literature.

Environmental pollution, biodiversity depletion, social destabilization and deforestation are some of the specific negative impacts on the region arising from the activities of oil industry (Emoyan et al., 2008; Mmom & Chukwu-Okeah, 2011). Effluent water from oil and gas industry is a major contributor of toxicity in fresh water. The high level of oil and grease contamination with electrical conductivity has been reported as major threats to all forms of life (Joel et al., 2009). Waste water from exploration and production areas, which contain high concentration of crude oil may leach into the soil creating ill effects on soil and has a highly significant effect on the seeds germination (Agbogidi & Eshegbeyi, 2006). Such polluted water often leads to lower land values and loss of land use capacities. Some metals are considered to be essential for plant growth but they can cause harmful effects when present in excess. For example, zinc (Zn) when present in high amount may retard plant growth (Asia et al., 2007). After prolonged irrigation with refinery effluent, heavy metals may accumulate in soil to toxic levels (Rajesh et al., 2009).

Environmental Protection Agency (EPA) has out lined several control measures to minimize the effects caused by the waste water in surrounding areas to ensure public health. However, there is poor compliance by the oil and gas industries in this regard. In Pakistan, many oil producing agencies / firms are engaged in drilling, exploration and production of oil. A substantial amount of waste mostly in the form of produced water highly contaminated with the dissolved gases, hydrocarbons etc. is carelessly discharged into the surrounding areas in fresh water ponds, lagoons, lacks, streams and rivers. Such illegal activity is a major threat to the surrounding environment.

The present work aimed to study the PW near exploration & production site and its detrimental effects on the drinking water & soils in the surrounding areas for safety assessment of the environment in general and public health in particular.

1.2. Introduction to study area

This study was conducted in Tehsil Fatehjang, District Attock, Sadqal oil and gas field, near Rawalpindi Islamabad (**Fig. 1.1**). The selection of areas was made on the basis of the degree of impacts of Oil and Gas Development Company Limited (OGDCL) PW. The area lies between latitude 33º- 34’ N and longitude 72º - 45'E which consists of different types of land uses. The main use is rain fed agriculture. The non-cultivated area consists of natural vegetation like forest, shrubs, grasses and the wastelands. Two major seasons exist, but the rainfall is more in summer monsoon than winter. The mean seasonal rainfall in summer and winter seasons ranges from 300 to 500 mm and 250 to 300 mm, respectively. The temperature ranges from 5-30°C (Roohi et al., 2004; Shaheen et al., 2008).

The OGDCL has started their exploration and production activities in Sadqal area. Wastewater is released one kilometer away from the plant into the ponds located in a residential area. Excess water over flows from the pond and make it way into a stream. Also excessive water seepages from the ponds occur thereby contaminating the nearby soil. Therefore, the management of oil and gas exploration companies needs constant monitoring of their effluents. No previous study about effluents physico-chemical nature and effects on ground water and nearby soil is available in literature. Therefore, this research study reports the physico- chemical analysis of OGDCL wastewater and its effects on surrounding soil and drinking water.

1.3. Aims and objectives

The overall aim of this project is to collect evidence of the pollution effects of oil and gas wastewater carelessly discharges into the ponds on the drinking water quality and also on the soil in the area. However, the physical and chemical properties of PW vary significantly depending on the geographic location of the field, the geologic formation and the type of hydrocarbon being produced. Based on the above, the main objectives of this research study were to:

- analyze the physico-chemical properties and heavy metals concentration of wastewater from Sadqal oil and gas field.
- investigate the concentration of hydrocarbons (oil and grease) in the waste water; as indicator of water pollution associated with oil and gas exploration activities.
- analyze the effects of wastewater on quality of drinking water and soil in the premises of produced water from exploration and production
- provide baseline data to adopt remedial measures and to ensure public health
- Provide sufficient data to the concerned government body like EPA and to the people living in the area to know about the actual hazards of these pollutants.

1.4. Data interpretation and significance

In this study, data was collected from PW, drinking water and soils analyses and compared with national (Environmental Protection Agency) and international (World Health Organization) standards in order to highlight and assess the risks to human life and environmental impacts. Statistical formulas and software's were used as a tool for interpretation of the data. Parts of this data were submitted for national and international journals for further dissemination and to attract the national and international researchers for best environmental solution of the PW.

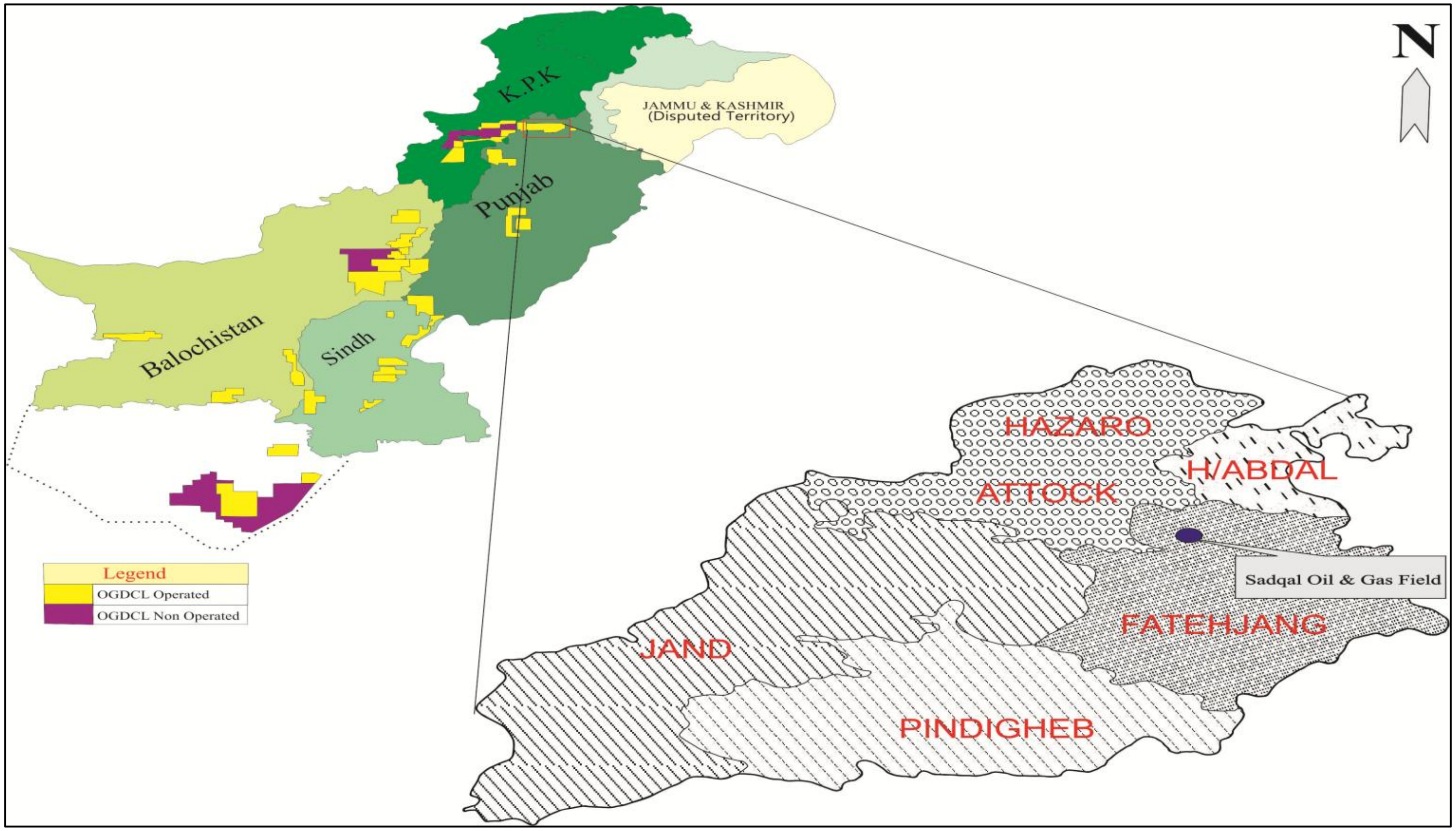

Fig. 1.1 Location map of Sadqal oil and gas field, Fatehjang, Punjab, Pakistan

CHAPTER-2

LITERATURE REVIEW

PW is water trapped in underground formations that is brought to the surface along with oil or gas. Oil and gas production sector generate largest amount of wastewater mostly contaminated with dissolved gases, oil and grease, sludge and heavy metals. It is considered as a highly polluted industry of the world as it holds a major potential of hazards for the environment and may have detrimental effects on water, soil and air.

Ekins et al. (2005) reported in their study that oil and gas reservoirs have a natural water layer (called formation water) that, being denser, lies under the hydrocarbons. At the surface, the water is separated from the hydrocarbons, treated to remove oil, and then either discharged into the sea, land or injected back into the wells. The term PW is therefore used to describe the mixture of water (formation and injected) and oil (hydrocarbons). Similarly, Clark and Veil (2009) stated that PW is not a single commodity. Physical and chemical characteristics of PW vary considerably depending on the geographic location of the field, the geological formation with which the PW has been in contact for thousands of years, and the type of hydrocarbon product being produced. PW properties and volume can even vary throughout the lifetime of a reservoir.

Fakhru'l-Razi et al. (2009) concluded that PW is the largest waste stream generated in oil and gas industries. It is a mixture of different organic and inorganic compounds. Due to the increasing volume of waste all over the world in the current decade, the outcome and effect of discharging effluents on the environment has lately become a significant issue of environmental concern. This effluent can impact on surface and underground water and soil. Globally PW production is estimated in his study at around about 250 million barrels per day, also Clark and Veil (2009) stated that on shore production in the United States, 7.6 barrels (1208 liters) of water are generated for each barrels (159 L) of oil produced.

Bader (2007) concluded from his study that physical, chemical, and biological properties of oil-fields PW depend on two factors: the geological formation and geographical location of the reservoir. These two factors prescribed the type and concentration of inorganic species in formation water as well as the type and specification of the co-existed hydrocarbons.

Stephenson (1992) investigated that PW contains many different components and has different impact on the environment when discharged. Several organizations have been studied all these components in many times for various reasons. The volume of PW can be more than 10 times the volume of hydrocarbon produced. With volumes of this extent, the disposal of PW becomes very important to the organization and the environment. In many onshore areas of the world, PW is unsuitable for human consumption; therefore it is injected into the underground formation or discharged into the environment. The release of such huge volumes of waste into the environment has caused concerns about uncontrolled, irreversible, and alarming pollution in both government agencies and nongovernment organizations. The basic source of these concerns is a lack of knowledge about the parts of PW and their effects. The basic components of PW can be grouped into the following main categories: oil, heavy metals, radionuclides, treating chemicals, salt, and dissolved oxygen.

Emoyan et al. (2008) conducted their research work on Niger Delta region which is situated in the Gulf of Guinea. They investigated the causes of environmental degradation and biodiversity depletion arising from the activities of the oil industry in the region. The authors argue that, specific negative impact on the region arising from the activities of the industries includes: environmental pollution, biodiversity depletion, and social destabilization, underdevelopment of host communities, global warming and associated elevated flood risk. Furthermore, a direct consequence of property rights structure following from existing legislature is the underdevelopment of host communities in spite of huge national earnings from oil and gas since 1970.

Asia et al. (2007) conducted their research study on Niger delta in order to analyze the impacts of exploration activities on surrounding environment. They collected the water and soil samples from four sampling points; around an oil well head, flare site, waste pit and effluent discharge point. It was analyzed for their heavy metals contents. The results indicated that the amount of Pb present in the soil ranges from 3.40-99.40 mg/kg, Cu values were in the range of 5.10-49.30 mg/kg, Ni concentration vary from 1.60-13.80 mg/kg, values for Cd, Fe, Zn and Cr were 0.04-0.95 mg/kg, 536.00-12,872.00 mg/kg, 11.1-274.00 mg/kg and 1.30-165.00 mg/kg respectively. From the results of study they concluded that exploration and production activities introduced large amount of heavy metals into the soil and groundwater where such activities are carried out.

It is therefore they suggested that remediation process to reduce the polluted soil and groundwater.

Sadatipour et al. (2004) conducted the study on kangan gas refinery which is located in Kangan city, southern part of Iran. This refinery is one of the greatest gas refineries in Iran and it is classified in highly polluted industry. The following parameters, such as oil and grease, Polycyclic aromatic hydrocarbons (PAH), BOD, total hardness (TH), turbidity, COD, Electrical Conductivity (EC), pH and Total Suspended Solids (TSS), were determined in wastewater. The results show that although pollution of the refinery wastewater is within permissible limits (EPA), but since the area is affected by the wastewater.

Ekins et al. (2005) stated in their study that PW contain oil which is made up a number of different hydrocarbons, including benzene, toluene, ethylbenzene and xylene (BTEX), naphthalene, phenanthrene, dibenzothiophene (NPD), PAHs and phenols. The hydrocarbons are largely insoluble in water, and most of the oil is therefore said to be dispersed in the PW. However, the different components of the oil dissolve partially in water to differing extents. For example, of those mentioned above, BTEX and phenols are the most soluble in water.

Farid et al. (2012) conducted the study on the ground water contamination in the third biggest city of Pakistan well known as Manchester of Pakistan that is Faisalabad. They collected water samples from hand pumps installed near sewage channels about 10 meter circumference. These samples were analyzed for pH, TDS, hardness, alkalinity,

SO_4^{-2}, Cl^-, Na^+, K^+) and heavy metals (Cd, Cr, Cu, Fe, Pb, Mn, Ni and Zn). Results showed most of the drinking water sample parameters are above the permissible limits. They concluded that in most of the developing countries due urbanization and industrialization, expanding the environmental pollution problems. Due to discharge of untreated industrial effluents in the sewage channels, the ground water quality is deteriorated to great extent. Therefore availability of healthy, clean and good quality drinking water is a matter of great concern in the urban areas.

Ahmad and Qadir (2011) investigated the impacts of sugar mill effluents on surrounding ground water and therefore they collected the water samples around the study area (Dera Ismail khan), to check the different physicochemical parameters. The samples were collected at random intervals in different villages. The physicochemical parameters such as pH, EC, TDS, TH, NO_3^-, SO_4^{-2}, Na^+, K^+, Ca^{+2}, Mg^{+2}, F^-, Fe and Pb analyzed. The results showed that values of the tested parameters for EC, TDS, TH, SO_4^{-2} and Na^+ near the sugar mill were above the permissible limits. The major source of these pollutants may be the effluent flowing from the sugar mill, the sugar mill residues that are dumped on the surface or applied as fertilizers in the nearby fields and confirms the anthropogenic activities in the sugar mill vicinity.

Jayalakshmi et al. (2011) studied the physico-chemical parameters of water and waste waters in and around Vijayawada (India) in the months of January-December 2007 for a period of one year from seven different spots. Water samples were collected and analyzed for various physical parameters like pH, temperature, turbidity, conductivity and TDS and chemical parameters like BOD, COD, SO_4^{-2}, Cl^-, hardness, alkalinity and NO_3^-. The results obtained were compared with standards of WHO. The results from the present study clearly pointed out that waters from spots II, IV, V, VI and VII are highly polluted as a result of contamination with industrial, agricultural and domestic wastes. They contain high levels of BOD, COD, TDS, NO_3^-, Cl^- and SO_4^{-2}.

Kumar and Singh (2010) conducted their study in Sanganer Tehsil, Jaipur District, Rajasthan (India) and concluded that the ground water of study area is highly deteriorated as it is polluted with high amount of F^-, NO_3^- and alkalinity. Most of the water quality parameters are above the permissible limit. Principal component analysis (PCA) of water quality data for Sanganer tehsil shows that the main variation in water quality of the study area is due to anthropogenic sources.

Jain et al. (2005) concluded from their study which was conducted in Sanganer Tehsil of Jaipur district India that EC, alkalinity, Na^+, F^- were found higher than permissible limit. They reported that due to pressure of human activity, urbanization and industrialization, the groundwater sources are degraded gradually; therefore pure, safe, healthy and odorless drinking water is a matter of deep concern.

Ite et al. (2013) conducted a study on Niger Delta region which is situated at the apex of the Gulf of Guinea on the west coast of Africa. They explore the activities associated with petroleum exploration, development and production operations have local detrimental and significant impacts on the atmosphere, soils and sediments, surface and groundwater, marine environment and terrestrial ecosystems in the Niger Delta.

Petroleum contamination and environmental degradation associated with exploitation and production of petroleum resources has clearly impacted the natural environment, human health and safety, physical and socio–economic environments in the Niger Delta. In addition, unsustainable operational practices by the multinational oil companies and the ineffective government's petroleum development policies has led to more socio–economic problems and complex environmental degradation in the Niger Delta. Although it is becoming increasingly apparent to the multinational oil companies that pollution prevention pays, petroleum exploration and production environmental issues. Environmental remediation is urgently needed in many of the aged petroleum contaminated sites, where land use may be changing from petroleum production to residential, agricultural and recreational uses in the future. Therefore, effective understanding of petroleum production and associated environmental degradation is importance for developing sustainable strategies for risks mitigation, management and remediation of environmental contamination.

Nodu and Ohimain (2014) investigated the impacts of crude oil contaminated vegetation on female rabbit's. Oil Spill is a major challenge of the petroleum industry and often occurs during routine production activities. On land spills have rodents and their vegetation. The results showed that the organs of the female rabbits including ovary size and weight, heart, liver and kidney weights decreased as the percentage of crude oil in the contaminated vegetation increased. Therefore it can be concluded that the crude oil contaminated vegetation decreased the performance of female rabbits.

Joel and Amajuoyi (2009) conducted their research work in Nigeria to analyze physicochemical characteristics of an oil Polluted Site and they collected water and soil samples from the various locations and different depths and distances. Results were obtained and indicated that the some of the physico-chemical parameters like TDS, Pb, Cu, Cr, Zn, Cd, Ni and arsenic (As) were within acceptable limits as specified by regulatory agents. However, EC, Fe, oil and grease were very high and above specified limits. The EC values ranged from 1275-3565 µS/cm with sample from crude band on soil surface. The oil and grease values ranged from 620-32040 mg/kg. The high level of oil and grease contamination poses a concern. It is therefore, confirms the concern that releases of large quantities of oil to aquatic and terrestrial environments present a long term threat to all forms of life.

Osuagwu et al. (2013) studied the adverse effect of crude oil pollution on air potato (Dioscorea bulbifera). On the basis of the results obtained from this study, it can be concluded that soil crude oil pollution has an adverse effect on growth, yield and leaf chlorophyll content of air potato. However, considering that the plant was able to grow and yield at the concentrations of crude oil pollution studied.

Obi and Okocha (2007) concluded that high level of Na^+ in drinking water is associated with disorders in heart, kidneys and complications in pregnancy, also raised levels of Na^+ in water damage domestic plumbing systems, water heaters and municipal water work equipments. So the water containing high concentration of Na^+ is not safe for drinking and other domestic use.

Sally et al. (2011) stated that extraction of natural gas from reservoirs has expanded around the world and poses multiple environmental threats to surface waters. Improved drilling and extraction technology used to access low permeability natural gas requires millions of liters of water and a suite of chemicals that may be toxic to aquatic biota. There is growing concern among the scientific community and the general public that rapid and extensive natural gas development in the United State could lead to degradation of natural resources. Gas wells are often close to surface waters that could be impacted by elevated sediment runoff from pipelines and roads, alteration of stream flow as a result of water extraction, and contamination from introduced chemicals or the resulting wastewater. However, the data required to fully understand these potential threats are currently lacking. Scientists therefore need to study the changes in ecosystem structure and function caused by natural gas extraction and to use such data to inform sound environmental policy.

Veil et al. (2004) concluded that PW from gas production have higher contents of low molecular-weight aromatic hydrocarbons such as BTEX than those from oil operations; hence they are relatively more toxic than PW from oil production. Studies indicate that the PW discharged from gas production are about 10 times more toxic than the PW discharged from oil platforms. However, for PW discharged offshore, the volumes from gas production are much lower, so the total impact may be less.

Jabeen et al. (2014) reported the high concentrations of heavy metals (Mn, Cu, Pb, Hg, and Ni) both in surface and ground water which were caused by the anthropogenic activities in Haripur basin, Pakistan.

Iram and Kanwal (2013) conducted their research study on Nullah Lai and Koh-e-Noor textile mill in the metropolitan city of Rawalpindi and Islamabad, Pakistan. They collected the water samples from selected locations of Nullah Lai and Koh-e-Noor textile mill. Physicochemical parameters including pH, temperature, Conductivity, TDS, turbidity, TH, Ca^{+2}, Cl^{-}, NO_3^{-}, SO_4^{-2}, and heavy metals Ni, Cd, Cr, pb, Zn and Cu were determined using standard analytical procedures. The highest value of physicochemical parameters (compared with Nullah Lai) was obtained in locations of Koh-e-Noor textile mill. The concentrations of metals and some anions in all the samples were higher than values set by the WHO. They concluded from his study that Nullah Lai also receives a lot of wastes from industrial, agricultural and domestic sources. With more industries discharging their effluents into the drain, the prospects of a greater pollution is high, also there is an increased risk to public health. After suitable treatment it can be used for irrigation purposes.

Kaur et al. (2010) conducted their study on sugar and textile industry effluents. In this study they have analyzed the effluents and their harmful effects on the soil microflora. They concluded from his research work that industrial effluents releasing into the water streams are one of the key sources of environmental toxicity. It not only affects the quality of drinking water but also has toxic impact on the soil microflora and aquatic ecosystems. For a wide range of microorganisms that includes bacteria, fungi, algae, viruses and protozoa, soil is the most favorable habitat. Industrial effluents releasing into environment without treatment is quite toxic whether its sugar mill or fertilizer industries, causes problems for the survival of the soil micro flora.

Azizullah et al. (2011) reported in their study that improper disposal of municipal, industrial effluents and indiscriminate applications of agrochemicals in agriculture are the main factors contributing to the deterioration of drinking water quality. Therefore Pakistan ranks at number 80 among 122 nations regarding drinking water quality.

Gulshan and Dasti (2012) conducted their study on Pak-Arab Oil Refinery Muzzafar Garh, Pakistan and their research work was focused on oil refinery effluents effects on physicochemical properties of soil. They concluded from his study that effluents are not suitable for arable land, plants and animals also surrounding environments. Effluents contain many different chemicals at different concentrations including SO_4^{-2}, Cl^- and hydrocarbons and Na^+ etc. and it is continuously releasing it into the River Indus that may be harmful to vegetation of down flow areas. Further they tested the effluents effects on seeds germination and found that concentrated effluent of oil refinery highly impacts on seed germination of three tested plants species.

Rajesh et al. (2009) conducted their study on the effluent of Panipat oil refinery India and they collected the effluent samples and analyzed for different physico-chemical properties. They stated that treated oil refinery effluent has no adverse effects on physicochemical properties of soil and can also be used as an alternate source for irrigating crops as it increases the nutrient content of the soil which is essential for the proper growth and maintenance of crop plants. It is good example for the management of industrials effluents if we treated effluents and use it irrigation, fertilizer and other suitable proposes.

The studies carried out previously indicate the concern of research with respect to produced water. Exploration of oil and gas in Pakistan is one of the largest industries. However, in Pakistan there is a general lack of data on the chemical composition of PW from oil fields. The chemical composition of PW is field-dependent. So, the field-specific detailed chemical characterization of PW from each oilfield or platform is necessary in order to predict the composition and effects of the PW discharged to the environment. Taking into account the above considerations and inferring that, to date, no data on chemical composition of the oilfield PW in Pakistan have been reported in the literature, this study provides a preliminary evaluation of the levels of physicochemical properties and heavy metals concentration in PW from the Sadqal oil and gas field, Fateh jang, Punjab, Pakistan and also their impacts on ground water and surrounding soil.

CHAPTER-3 (Part A)

ASSESSMENT OF PHYSICO-CHEMICAL CHARACTERISTICS OF PRODUCED WATER OF SADQAL OIL AND GAS FIELD

Abstract

Wastewater samples were collected from selected sites of Sadqal oil and gas field, tehsil Fatehjang, district Attock, near Rawalpindi. Physicochemical parameters were assessed in the months of January 2013 to January 2014 using standard methods. Results were obtained in the order: pH (6.7±0.40–7.5±0.20), temperature (16.20±0.36–25.30±0.26˚C), conductivity (25800±0.50–28800±0.22 µS/cm), TDS (85000±1.90–135000±1.70 mg/L), hardness (18000±1.30–33000±1.40 mg/L), BOD (550±0.29–1210±0.38 mg/L), COD (1300±0.95–4200±0.75 mg/L), oil & grease (15±0.72–400±1.20 mg/L), Na^{+} (14739±1.20–47250±1.4 mg/L), K^{+} (218±1.10–546±0.45 mg/L), Ca^{+2} (3687±1.09–8314±0.65 mg/L), Mg^{+2} (439±0.85–1080±0.74 mg/L), Cl^{-} (8542±1.35–56890±1.60 mg/L), F^{-} (203±0.87–582±0.83 mg/L), Br^{-} (2±0.31–9.3±0.54mg/L), SO_4^{-2} (52±0.84–178±0.25 mg/L), NO_3^{-} (46±0.91–809±0.80 mg/L) and NO_2^{-} (14±0.91–52±0.41 mg/L). The results obtained were compared with maximum Permissible Limits (MPL) of Pakistan Environmental Protection Agency (Pak-EPA). It was found that the wastewater from Sadqal oil and gas field are highly polluted, released without any pretreatment and may cause impacts on surrounding environment. It is, therefore, recommended that wastewater should be treated to reduce the inputs of pollutants into the surrounding.

3.1. Introduction

Oil and gas production sector generates large amount of waste “PW”. This water is a mixture of formation water present in the reservoir and various amounts of injection water (used to maintain the pressure and achieve greater recovery levels of oil) mostly highly contaminated. Generally, in the early stages of production, volumes of hydrocarbons are greater relative to the PW, but with time the volume of PW increases to exceed hydrocarbon production (Ekins et al., 2007). Such water is contaminated with organic and inorganic components including mixture of hydrocarbons, anions, cations, and heavy metals (Asia, 2006; Ekins et al., 2007; Fillo et al., 1992; Gazineu & Hazin, 2008) which if discharged carelessly in to fresh water streams will create several environmental problems. Global PW production is estimated at around 250 million barrels per day compared with around 80 million barrels per day of oil. As a result, water to oil ratio is around 3:1 that is to say water cut is 70%. The global water cut has risen since a decade ago and continues to rise (Ferro & Smith, 2007; Khatib et al., 2002).

Characteristics of the PW depend on the nature of the producing well, the operational conditions, and chemicals used in process facilities. PW composition may vary and strongly dependent on the source and prevailing conditions (Fillo et al., 1992). pH and temperature increase the concentration of soluble organics in PW. PW chemistry is also affected by cations such as Na^{+}, K^{+}, Ca^{+2}, Mg^{+2}, and anions such as Cl^{-}, SO_4^{-2} , CO_3^{-2}, HCO_3^{-} (Hansen, 1994). Salt concentration of produced water may vary from a few parts per million (ppm) to about 300,000 mg/L and 1000–250,000 mg/L. SO_4^{-2} concentration is lower than seawater (Jacobs et al., 1992). In some sites that use seawater for oil enhancing recovery, sulfate concentration is high (Neff, 2002). In gas fields, water injection is not utilized; therefore, the PW are mixture of formation water and condensed water. Their Cl^- content varies from almost those of fresh water to salty formation water with Cl^- concentration about 14 times that of seawater. Its acidity is greater than that of PW from oilfields. The volume of PW from gas field is less than in oilfields (Faksness et al., 2004).

It is considered that oil and gas is highly polluted industry of the world as it holds a major potential of hazards for the environment and may have detrimental effects on water, soil and air (Fakhru'l-Razi et al., 2009; Kadafa, 2012; Sadatipour et al., 2004; Sally et al., 2011). Several environmental effects of such water salts have been reported in the literature. Environmental pollution, biodiversity depletion, social destabilization and deforestation are some of the specific negative impacts on the region arising from the activities of oil industry (Emoyan et al., 2008; Mmom & Chukwu-Okeah, 2011).

Effluent water from oil and gas industry is a major contributor of toxicity in fresh water. The high level of oil and grease contamination with electrical conductivity has been reported as major threats to all forms of life (Joel et al., 2009). Oil contaminated soil has a highly negative effect on crop yields (Agbogidi, 2006). Turbidity levels of water bodies will be high, if total dissolved solids are released largely in the effluents (Fakhru'l-Razi et al., 2009).

In Pakistan, due to several reasons there is no check on the pollutants released into the environment and the environmental protection activities are ignored. However, the recent stringent rules and regulations have necessitated strict compliance. As per spirit of the new rules and regulations, the industries are required to adopt several control measures to mitigate the effects caused by the pollutants in surrounding areas to ensure public health.

OGDCL has started exploration and production activities in Sadqal area. PW is released carelessly and without any pretreatment into the ponds located at residential area. Excess water over flows from the pond and also seepages occur thereby contaminating the nearby soil and water. This has created health risks exposure of not only of inhabitants in the neighboring population but also resulted in disturbances of aquatic life. There is lack of data on the chemical composition of PW from the oil field. The present work provides a preliminary evaluation of the waste water in term of several contaminants.

3.2. Materials and methods

3.2.1 Study area

This study was conducted in Fatehjang Sadqal oil and gas field, near Rawalpindi, Pakistan (**Fig.3.1**). The selection of area was made on the basis of the degree of impacts. The area lies between latitude 33º- 34’ N and longitude 72º - 45'E. Study area details are given in chapter 1 in section 1.2.

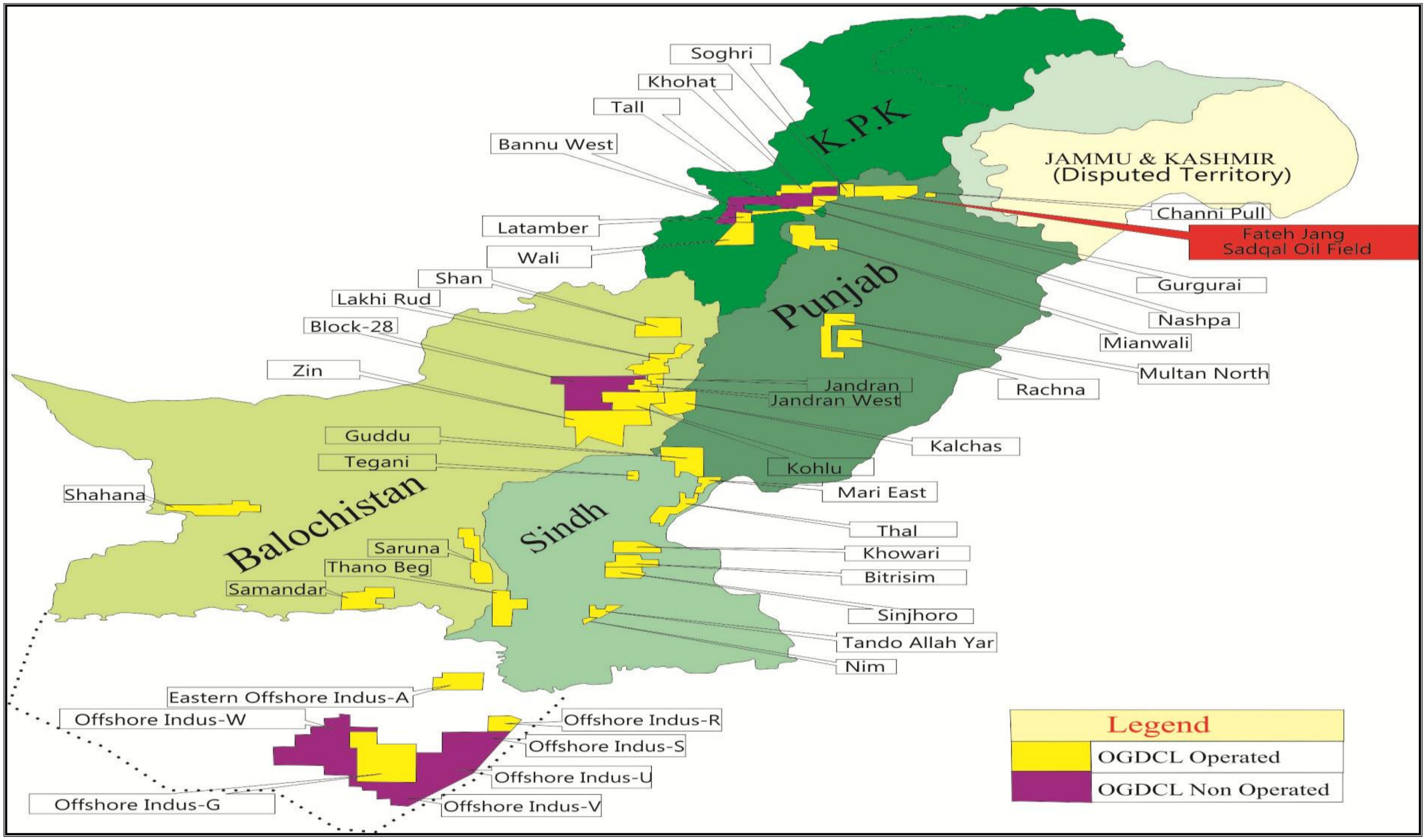

Fig.3.1. Location map of the study area, Sadqal oil and gas field

3.2.2 Samples collection

PW composite samples were collected from Inlet, pond-A, pond-B, seepage pond-C and out-let, in the study area. Total of two samples were collected from each of five sampling points in 1.5 liter sampling containers that has been rinsed with 1:1 concentrated HNO_3 acid and double distilled water and fixed with identification labels. pH, temperature and conductivity of the samples were determined using hand potable pH and conductivity meters, respectively. One sample was used for the physico-chemical analysis and the second one for the analysis of oil and grease. In the laboratory, samples were stored in the refrigerator at 4°C for further analysis (APHA, 1998).

3.3. Physico-chemical and anions cations procedures for analysis

The Physico-chemicals parameters including, Hardness, TDS, Conductivity, BOD, COD, oil and grease concentrations in waste water samples were determined by using standard methods (APHA, 1998), in the Environmental Sciences Laboratory, University of Peshawar, KPK, Pakistan. The concentrations of cations and anions including Na^+, K^+, Ca^{+2}, Mg^{+2}, Cl^-, F^-, Br^-, SO_4^{-2}, NO_3^- and NO_2^- in the samples were determined using the Ion chromatography in National Center of Excellence in Physical Chemistry (NCEPC), University of Peshawar, KPK, Pakistan.

3.3.1. A brief introduction of ion chromatography

The ions were analyzed using Ion Chromatograph (Metrohm, 800 series) equipped with anion self-regenerating suppressor, a dual-piston pump, a DS6 conductivity detector and Metrosep A Supp5-250 separating column (4 x 250 mm). 3.2 mM sodium carbonate and 1 mM sodium bicarbonate solution was used as eluents for detecting of anion, while 50 mM sulfuric acid was added as a regenerating agent. The flow rate was 0.70 mL/ minute, temperature was 30˚C and pressure was 11.9 Mpa and the injection volume was 500 µL. Similarly, for cations, column Metrosep C 2-250 (4.0 x 250 mm) was used. 4mM tartaric acid, 0.75 mM/L Dipicolinic acid solution was used as eluents and also 50 mM sulfuric acid was added as a regenerating agent. The flow rate was 1mL/minute temperature was 40˚C, pressure was 8.2 Mpa and the injection volume was 10 µL. The eluents were sonicated for 15 min and filtered through 0.45 µm cellulose acetate filters (Sartorius, Ministar) before use, to prevent the entrance of air bubbles and other impurities. For calibration different standards solutions including 0.5, 1, 5, 10, 15, 20 mg/L for cations and 0.1, 0.5, 0.7, 1.5 mg/L for anions were prepared.

3.4. Results and discussion

The mean results of physico-chemical properties of produced water samples from the study area are given in **Table 3.1**. The data indicated that pH and temperature, of the produced water were ranged from 6.7±0.40-7.5±0.20 and 16.2±0.36-25.3±0.26°C with mean values of 7.08 and 18.32°C, respectively. These values fall in line with MPL of Pak-EPA acceptable guideline values, so it does not pose any hazard to the homeostatic balance of the receiving water bodies, in conformity with the early report (Jaji et al., 2007).

Total hardness is defined as the sum of calcium and magnesium concentration in mg/L. High conductivity, TDS and hardness values were recorded, these values were ranged from 25800±0.50-28800±0.22 µS/cm, 85000±1.90–135000±1.70 mg/L, and 18000-33000 mg/L with mean values of 27620 µS/cm, 117400 mg/L and 24600 mg/L, respectively. Conductivity which is the ability of water to conduct electric current, so high conductivity values recorded in this study means that there is high amount of cations and anions in the water samples (Abdullah & Musta, 1999), also impacts the electric conductivity of soil. TDS was recorded higher than MPL of Pak-EPA of 1000 mg/L shown in (**Fig.3.2)**. These TDS concentrations automatically influenced the quality of the received water body. Higher TDS can be toxic to freshwater animals by causing osmotic stress and affecting the capability of the organisms (Mcculloch et al., 1993). pH has no direct effects on aquatic life yet it has some indirect effects, by bringing changes in water quality parameters such as metal ion solubility and aquatic life survival.

COD and BOD were determined in the range of 1300±0.95–4200±0.75 mg/L and 550±0.29–1210±0.38 mg/L with mean values of 2940 mg/L and 952 mg/L, respectively. High levels of BOD and COD indicate depletion of the dissolved oxygen in the water systems. These values are higher than MPL of Pak-EPA 80 mg/L and 150 mg/L, respectively shown in (**Fig.3.3)**. This is undesirable since continuous discharge of effluent may have negative effects on the quality of the freshwater and subsequently cause harm to the aquatic life especially fish, downstream (Igbinosa & Okoh, 2009; Morrison et al., 2001).

Oil and grease content in the samples were used as a measure of oil pollution. Oil and grease level were determined and found to be in the range of 15±0.72–400±1.20 mg/L with a mean value of 137 mg/L. It is higher than MPL of Pak-EPA of 10 mg/L as shown in (**Fig.3.4)**.

Refinery effluent containing oil when discharged into water body can cause depletion of dissolved oxygen due to transformation of organic component into inorganic compounds, loss of biodiversity through a decrease in amphipod population that is important in food chain and eutrophication. Short term toxicity in fishes includes lymphocytosis and epidermal hyperplasia (Beeby, 1993).

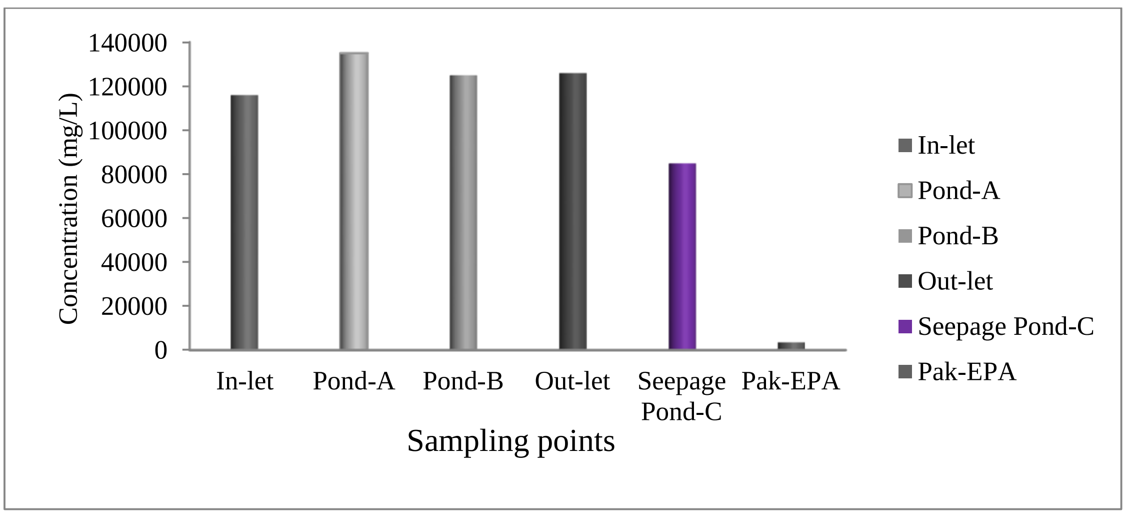

Fig.3.2 Concentration of TDS in wastewater at various points of the study area

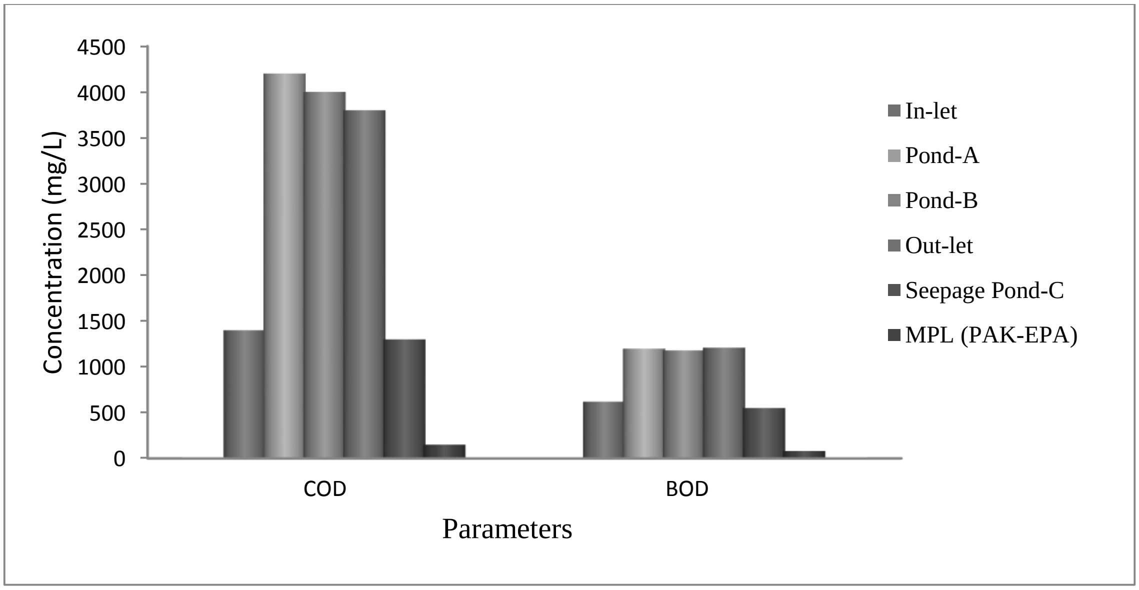

Fig.3.3 Concentration of COD and BOD in wastewater at various points of the study area

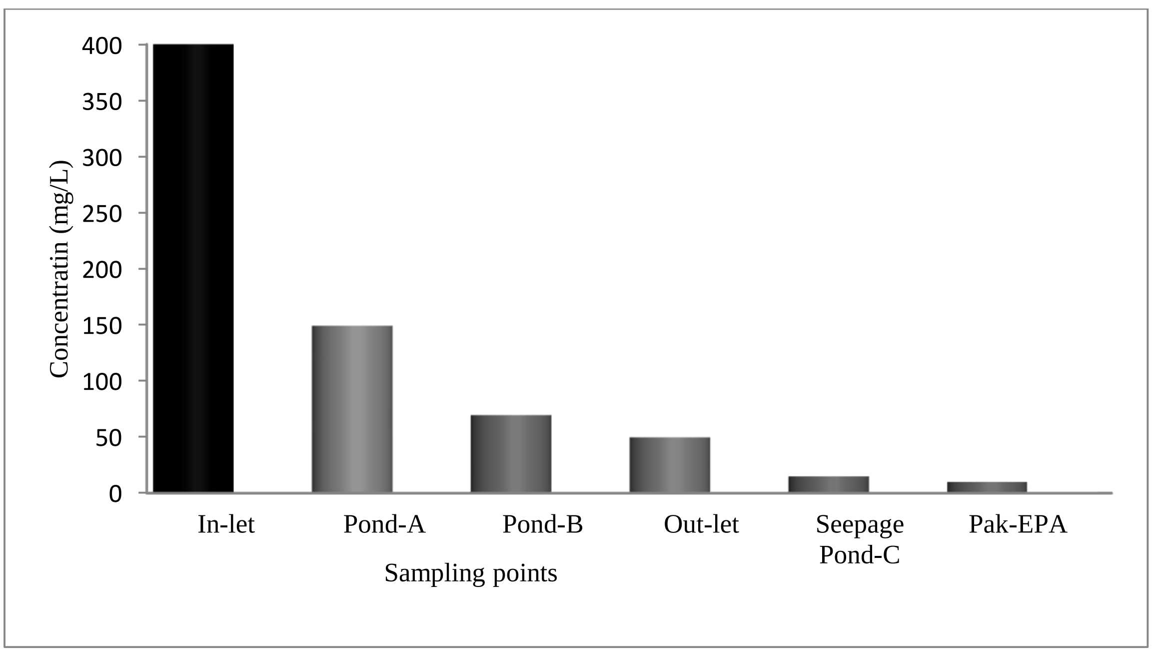

Fig.3.4 Concentration of oil & grease in wastewater at various points of the study area

The mean results concentrations of anions and cations are given in **Table 3.2**. The data indicated that Na^{+}, K^{+}, Ca^{+2} and Mg^{+2} values were found in the range of 14739±1.20–47250±1.40 mg/L, 218±1.10–546±0.45 mg/L, 3687±1.09–8314±0.65 mg/L and 439±0.85–1080±0.74 mg/L with mean values of 35254 mg/L, 355.5 mg/L, 6625 mg/L and 856 mg/L, respectively.

Na^{+} is the most commonly occurring dominant cation in PW. High Na^{+} levels compete with Ca^{+2}, Mg^{+2}, and K^{+} for uptake by plant roots; therefore, excess Na^{+} can prompt deficiencies of other cations. High levels of Na^{+} also can cause poor soil structure and inhibit water infiltration in soils. Chromatogram (**Annexure-I**) shows the concentration of cations in wastewater sample of the study area. In anions, Cl^{-} value ranged from 8542±1.35–56890±1.60 mg/L with a mean value of 32350 mg/L, which is above the MPL of Pak-EPA 1000 mg/L as shown in (**Fig.3.5**). Cl^{-} existence in the aquatic systems is regarded as pollution because it is not utilized directly and indirectly for aquatic plant growth and causes eutrophication. Both Na^{+} and Cl^{-} high concentration indicate that it will create problems for soil salinization (Hentati et al., 2013).

Table 3.1

Mean concentrations of physico-chemical properties of produced water of Sadqal oil and gas field

	Basic Characteristics							
Area	pH	Temperature (˚C)	TDS (mg/L)	Hardness (mg/L)	Conductivity (µS/cm)	COD (mg/L)	BOD (mg/L)	Oil &Grease (mg/L)
In-let	6.7±0.40	25.3±0.26	116000±1.30	23000±1.20	25800±0.50	1400±0.50	620±0.50	400±1.20
Pond-A	7.01±0.30	16.3±0.20	135000±1.70	33000±1.40	27400±0.64	4200±0.75	1200±0.70	150±0.95
Pond-B	7.08±0.20	16.3±0.23	125000±1.60	25000±1.60	28700±0.40	4000±1.00	1180±0.45	70±0.61
Out-let	7.5±0.20	17.5±0.15	126000±1.30	24000±1.10	28800±0.22	3800±0.75	1210±0.38	50±0.31
Seepages Pond-C	7.1±0.36	16.2±0.36	85000±1.90	18000±1.30	27400±0.12	1300±0.95	550±0.29	15±0.72
*MPL(Pak EPA)	6-9	40.00	3500.00	ND**	ND	150.00	80.00	10.00

*MPL (Pak EPA) = Maximum Permissible Limits of Pakistan Environmental Protection Agency
**ND = not defined in Pak-EPA
±= Standard deviation

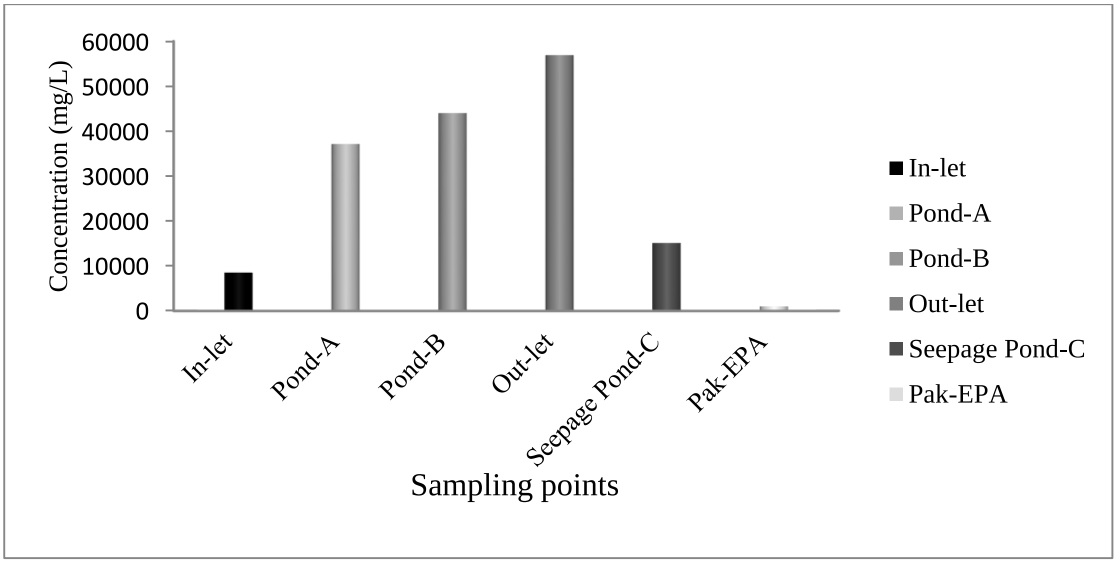

Fig.3.5 concentration of Cl in wastewater at various points of the study area

F^- ranged from 203±0.87–582±0.83 mg/L with a mean value of 388.6 mg/L, higher than MPL of Pak-EPA 20 mg/L. Br^- value ranged from 2±0.31–9.3±0.54 mg/L with a mean value of 5.14 mg/L as shown in (**Fig.3.6**).

SO_4^{-2} value ranged from 52±0.84–178±0.25 mg/L with a mean value of 114.8 mg/L. SO_4^{-2} values is lower than MPL of Pak-EPA of 600 mg/L. NO_3^- and NO_2^- values were ranged from 46±0.91–809±0.80 mg/L and 14±0.91–52±0.41 mg/L with mean values of 444.8 mg/L and 28.6 mg/L, respectively.

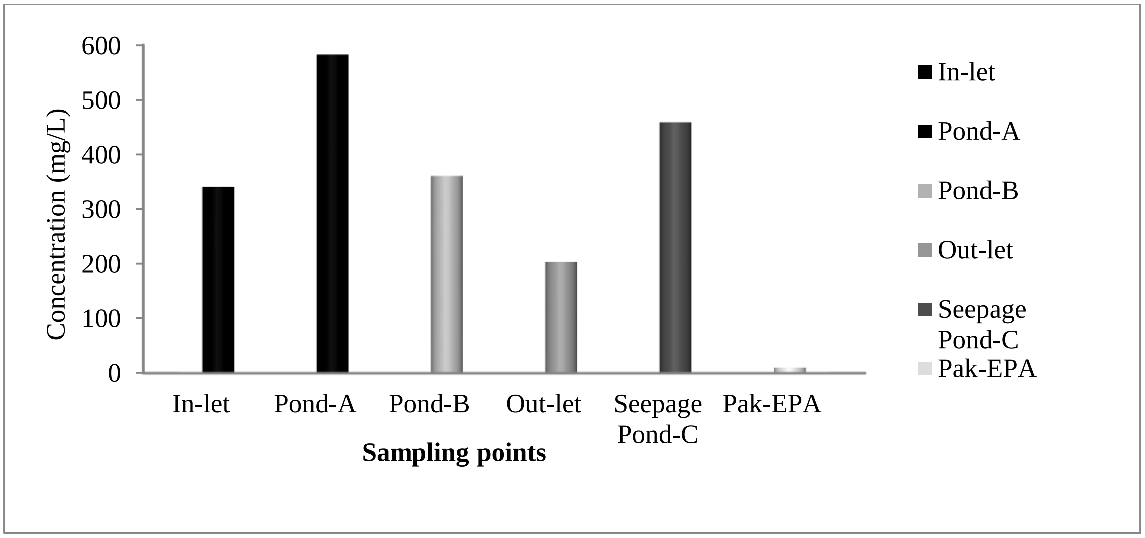

Fig.3.6 concentration of F in wastewater at various points of the study area

NO_3^- is the essential nutrient to plant life, but when found in excessive quantities; they can stimulate excessive and undesirable plant growth such as algal blooms. Eutrophication could adversely affect the use of rivers and dams for recreation purposes (Holdsworth, 1991). Unpolluted natural waters usually contain only minute amounts of nitrate (Jaji et al., 2007). Chromatogram (**Annexure-II**) shows the concentration of anions in wastewater sample of the study area.

Table 3.2

Mean concentration of cations and anions in produced water of Sadqal oil and gas field

Area	Cations (mg/L)				Anions (mg/L)					
	Na^{+}	K^{+}	Ca^{+2}	Mg^{+2}	F^{-}	Cl^{-}	Br^{-}	SO_4^{-2}	NO_3^{-}	NO_2^{-}
In-let	28746±1.70	218±1.10	5595±0.76	794±1.01	340±0.61	8542±1.35	9.3±0.54	122±0.13	466±0.50	52±0.41
Pond-A	40401±1.50	319±0.19	7704±0.95	969±0.74	582±0.83	37160±1.75	6±0.71	178±0.25	809±0.80	36±0.91
Pond-B	45135±1.80	409.5±0.20	7826±0.73	999±0.85	360±0.93	44016±1.07	4.4±0.45	115±0.18	550±0.08	22±0.74
Out-let	47250±1.40	546±0.45	8314±0.65	1080±0.74	203±0.87	56890±1.60	2±0.31	52±0.84	46±0.91	14±0.91
Seepages Pond-C	14739±1.20	285±0.55	3687±1.09	439±0.85	458±0.29	15140±1.01	4±0.12	107±0.91	350±0.13	19±0.89
*MPL(Pak EPA)	**ND	ND	ND	ND	20.00	1000.00	ND	600.00	ND	ND

*MPL= Maximum permissible limits of Pakistan Environmental Protection Agency
**ND= not defined in Pak-EPA
±=Standard deviation

The correlations among the physicochemical properties were studied and the results are presented in **Table 3.3**. It is also suggested that mean concentration of physico-chemical properties results is changed at five different points some of the measured pollutants due to the fact that some have localized factor which impacts may get dilute and weaken the effects of ponds pollution. Surface area of ponds is so large and evaporation occurred than released outside. The mean seasonal rainfall of Fatehjang area in summer and winter seasons ranges from 300-500 mm and 250-300 mm, respectively, also effects on ponds water. There was significant positive correlation observed between pH-K (r= 0.920), Temperature-oil and grease (r= 0.931), TDS-Na^{+} (r= 0.902), TDS-Ca^{+2} (r= 0.926), TDS-Mg^{+2} (r= 0.942), Conductivity-K^{+} (r= 0.989), conductivity-Cl^{-} (r= 0.890), COD-Na^{+} (r= 0.899), COD-Ca^{+2} (r= 0.924), COD-Cl^{-} (r= 0.888), BOD-Na^{+} (r= 0.937), BOD-Ca^{+2} (r= 0.955), BOD-Mg^{+2} (r= 0.893), BOD-Cl^{-} (r= 0.923), Oil & grease-Br^{-} (r= 0.926), Oil & grease-NO_2^{-} (r= 0.954), K^{+}-Cl^{-} (r= 0.940) and F-SO_4^{-2} (r= 0.906) at $p< 0.05$. Also, a significant correlation was observed in case of COD-BOD (r= 0.993), Na^{+}-Ca^{+2} (r= 0.994), Na^{+}-Mg^{+2} (r= 0.987), Ca^{+2}-Mg^{+2} (r= 0.986), Br^{-}- NO_3^{-} (r= 0.983) and SO_4^{-2} - NO_3^{-} (r= 0.977) at $p< 0.01$. There was also significant negative correlation observed between pH-Br^{-} (r= -0.958), pH- NO_2^{-} (r= -0.893), conductivity-Br^{-} (r= -0.902) and conductivity-NO_3^{-} (r= -0.882) at $p< 0.05$.

Table 3.3

Correlation of Physico-chemical parameters of produced water of Sadqal oil and gas field

	pH	Temp	TDS	Hard.	Cond.	COD	BOD	O&G	Na^+	K^+	Ca^{+2}	Mg^{+2}	F^-	Cl^-	Br^-	SO_4^{-2}	NO_3^-	NO_2^-
pH	1																	
Temp	-0.644	1																
TDS	-0.566	0.089	1															
Hard	-0.059	-0.17	0.768	1														
Cond.	0.859	-0.776	-0.204	0.085	1													
COD	0.495	-0.551	0.433	0.753	0.708	1												
BOD	0.545	-0.498	0.366	0.715	0.724	0.993**	1											
O&G	-0.789	0.931*	0.419	0.155	-0.831	-0.369	-0.349	1										
Na^+	0.437	-0.198	0.366	0.635	0.606	0.899*	0.937*	-0.101	1									
K^+	0.920*	-0.501	-0.328	0.104	0.898*	0.679	0.741	-0.612	0.724	1								
Ca^{+2}	0.435	-0.227	0.393	0.702	0.586	0.924*	0.955*	-0.104	0.994**	0.704	1							
Mg^{+2}	0.347	-0.062	0.402	0.673	0.479	0.849	0.893*	0.044	0.987**	0.649	0.986**	1						
F^-	-0.444	-0.3	0.532	0.439	-0.318	0.018	-0.096	-0.008	-0.343	-0.588	-0.266	-0.344	1					
Cl^-	0.811	-0.577	-0.01	0.417	0.890*	0.888*	0.923*	-0.561	0.865	0.940*	0.865	0.794	-0.351	1				
Br^-	-0.958*	0.786	0.558	0.164	-.902*	-0.436	-0.46	0.926*	-0.3	-0.839	-0.292	-0.177	0.317	-0.732	1			
SO_4^{-2}	-0.658	-0.014	0.812	0.627	-0.452	0.105	0.004	0.327	-0.129	-0.645	-0.063	-0.089	0.906*	-0.352	0.593	1		
NO_3^-	-0.636	-0.062	0.894*	0.65	-0.333	0.215	0.113	0.286	-0.004	-0.563	0.047	0.018	0.848	-0.252	0.553	0.977**	1	
NO_2^-	-0.893*	0.799	0.575	0.282	-0.882*	-0.339	-0.354	0.954*	-0.189	-0.76	-0.171	-0.052	0.29	-0.637	0.983**	0.588	0.536	1

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

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

Hard.= Hardness

Cond= conductivity

O&G= Oil and Grease.

3.5. Conclusion

It was concluded that all the physico-chemical parameters of PW are highly contaminated. They are entering into the surrounding environment without any treatment. The concentration of metals and some anions which were monitored in Nullah Lai and sites of Koh-e-Noor textile mill, were higher than values set by the WHO, it increased risk to public health (Iram & Kanwal, 2013). The PW from Sadqal oil and gas is released into the residential area, percolates and may have changed the ground water quality. PW should be treated before releasing into the surrounding environment and Environmental Protection Agency should have continuous pollution monitoring program to monitor PW regularly.

CHAPTER-3 (Part B)

ASSESSMENT OF HEAVY METAL CONCENTRATIONS IN PRODUCED WATER OF SADQAL OIL AND GAS FIELD

Abstract

PW samples were collected from selected sites of Sadqal oil and gas field, Fatehjang, Punjab, Pakistan. Heavy metals were assessed in the months of January 2013 to January 2014 using standard methods through flame atomic absorption spectrophotometer (Perkin Elmer AAS 700). The concentrations of heavy metals were obtained as; Cr (1.07±0.03–2.7±0.05 mg/L), Mn (1.06±0.03–2.3±0.08 mg/L), Cd (0.02±0.01–0.04±0.01 mg/L), Zn (1.2±0.06–2.1±0.10 mg/L), Cu (0.49±0.02–1.3±0.08 mg/L), Pb (0.51±0.1–0.91±0.10 mg/L), Ni (0.34±0.06–0.49±0.09 mg/L) and Fe (2.06±0.10–11.52±3.00 mg/L). The results obtained were compared with MPL of Pakistan Environmental Protection Agency (Pak-EPA). It was found that the concentrations of Cr, Mn, Pb, Ni and Fe were found above the permissible limits. It is released without any treatment and may cause impacts on surrounding environment. There is a need for the intervention of appropriate regulatory agencies to ensure the treatment of PW before releasing into the environment.

3.6 Introduction

Industries and municipal sewage system are the main sources of toxic metals such as Cr, Cu, Pb, Cd, Zn and Ni which cause environmental pollution problems and ecosystem damage. Heavy metals presence in the wastewater of several industrial processes, such as, electroplating, metal finishing, metallurgical work, tanning, chemical manufacturing exploration and production been reported to have environmental concerns due to their toxicity even at low concentrations.

Heavy metal concentrations in PW depend on age of the wells and formation geology. Produced water contains trace quantities of various heavy metals such as Cd, Cr, Cu, Pb, Ni, and Zn (Hansen, 1994). It is considered that oil and gas is highly polluted industry of the world as it holds a major potential of hazards for the environment and may have detrimental effects on water, soil and air (Fakhru'l-Razi et al., 2009; Kadafa, 2012; Sadatipour et al., 2004; Sally et al., 2011). Globally PW production is estimated to be at around 250 million barrels per day compared with around 80 million barrels per day of oil. As a result, water to oil ratio is around 3:1 that is to say water cut is 70%. The global water cut has risen since a decade ago and continues to rise (Ferro & Smith, 2007; Khatib et al., 2002).

Characteristics of the PW depend on the nature of the producing well, the operational conditions, and chemicals used in process facilities. PW composition from different sources can vary; however, qualitatively similar to oil and/or gas production

(Fillo et al., 1992). Several environmental effects of such water salts have been reported in the literature. Environmental pollution, biodiversity depletion, social destabilization and deforestation are some of the specific negative impacts on the region arising from the activities of oil industry (Emoyan et al., 2008; Mmom & Chukwu-Okeah, 2011). In Pakistan, nowadays government sector and also industrial sector, trying to protect the environment by imposing the environmental impact assessment but in past mostly ignored the environmental protection activities. The OGDCL has started their exploration and production activities in Sadqal area. PW is released into the ponds located at residential area. Excess water over flows from the pond and also excessive water seepages occur thereby contaminating the soil and water. This has created health risks exposure of not only of inhabitants of the neighboring population but also resulted in disturbances of aquatic life.

However, in Pakistan there is a general lack of data on the chemical composition of PW from oil fields. The chemical composition of PW is field-dependent. So, the field-specific detailed chemical characterization of PW from each oilfield or platform is necessary in order to predict the composition and effects of the PW discharged to the environment. Taking into account the above considerations and considering that, to date, no data on chemical composition of the oil field PW in Pakistan have been reported in the literature, this part of the work provides a preliminary evaluation. This study was proposed with the following objectives.

1. To analyze the heavy metals concentration in produced water which is released from Sadqal Oil and Gas field in residential area.

2. To provide the base line data for Government bodies like EPA and also for research orientation.

3.7 Materials and methods

3.7.1 Study area

Figure 3.7 shows the location site of the study area Sadqal oil and gas field, Fatehjang, Punjab, Pakistan. This site is located near Rawalpindi, Islamabad Pakistan. The details are given in chapter 1 section 1.2.

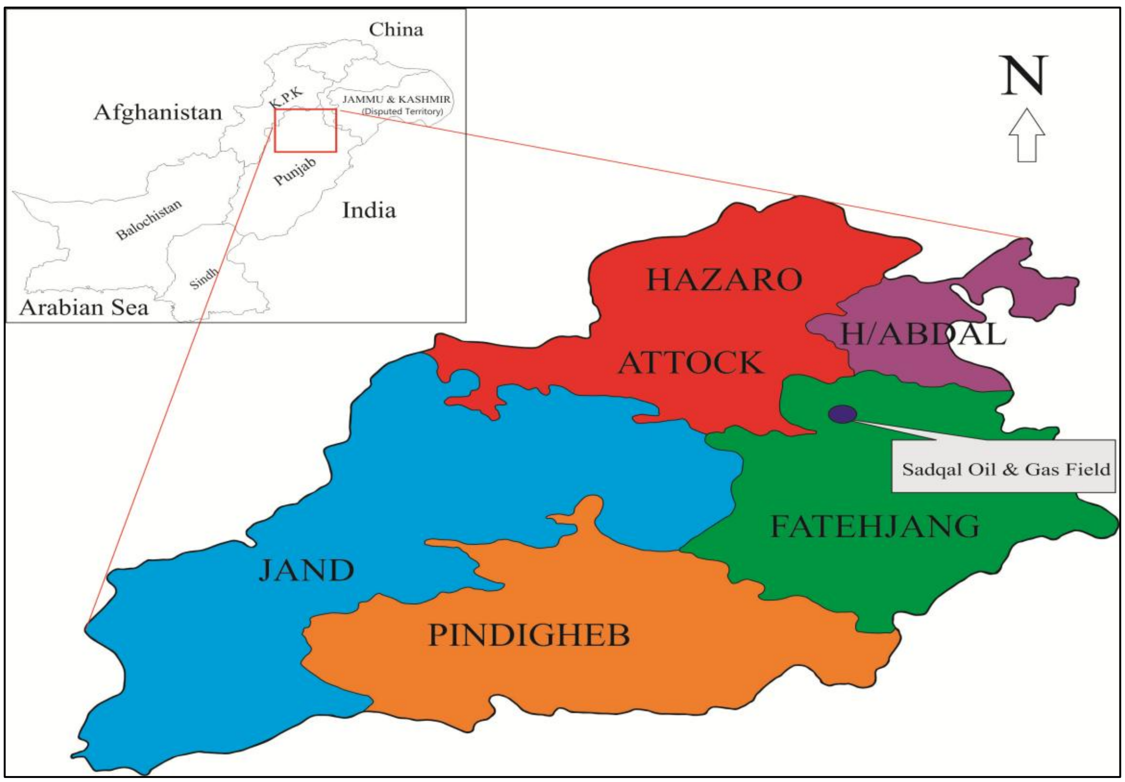

Fig.3.7 Map shows the location of the study area

3.7.2 Samples collection

PW composite samples were collected from In-let, pond-A, pond-B, seepage pond-C and out-let, in the study area. Samples were acidified with 10% nitric acid for the analysis of heavy metals. In the laboratory, the acidified samples were filtered using Whatman's no. 0.45µm filter paper. Samples were stored in a refrigerator at 4°C for further analysis.

3.7.3 Chemical analysis procedures for heavy metals

100 ml acidified water sample was mixed with 5ml concentrated HNO_3 and 5ml concentrated H_2SO_4. This mixture was then heated until the volume was reduced to about 15-20 ml. The digested sample was allowed to cool to room temperature. It was then filtered through Whatman's 0.45µm filter paper. The final volume was adjusted to 100 ml with double distilled water and stored for analysis. Filtered and acidified water samples of the area were analyzed for heavy metals (Cd, Cr, Cu, Mn, Ni, Pb, Zn and Fe) by using flame atomic absorption spectrophotometer (Perkin Elmer AAS 700 Perkin Elmer, USA), under standard operating conditions at the Centralized Resource Laboratory, University of Peshawar, KPK, Pakistan. Analytical grade chemicals with 99.9% spectroscopic purity (Merck Darmstadt, Germany) were used for sample preparation and analysis. Double distilled water was used throughout the analysis. Standard solutions of all eight elements were prepared by diluting 1000 mg/L certified standard solutions (Fluka Kamica, Buchs, Switzerland) of corresponding metal ions. The integration and delay time of AAS was 5

sec. The instrumental detection limits of Cd, Cr, Cu, Mn, Ni, Pb, Zn and Fe were 0.0008, 0.0030, 0.0015, 0.0015, 0.0060, 0.0150, 0.0015 and 0.005 mg/L, respectively.

3.8 Results and discussion

The mean concentrations of heavy metal are given in **Table 3.4**. The data indicate that Cr level ranged from 1.07±0.03-2.7±0.05 mg/L with a mean value of 1.93 mg/L. Cr concentration at In-let, pond-A, pond-B, Out-let and seepage pond-C are higher as compare to MPL of Pak-EPA of 1 mg/L. Mn level ranged from 1.06±0.03-2.3±0.08 mg/L with a mean value of 1.61 mg/L, which is also higher above the MPL of Pak-EPA of 1.5 mg/L at Inlet, pond-A and pond-B except for samples out-let and seepage pond-C. Cd level ranged from 0.02±0.01-0.04±0.01 mg/L with a mean value of 0.03mg/L and Zn ranged from 1.2±0.06-2.1±0.10 mg/L with a mean value of 1.8 mg/L, their values is lower as compare to MPL of Pak-EPA of 0.1 mg/L and 5 mg/L, respectively. Cr, Mn, Cd and Zn are shown in **Fig.3.8**. (a, b, c & d).

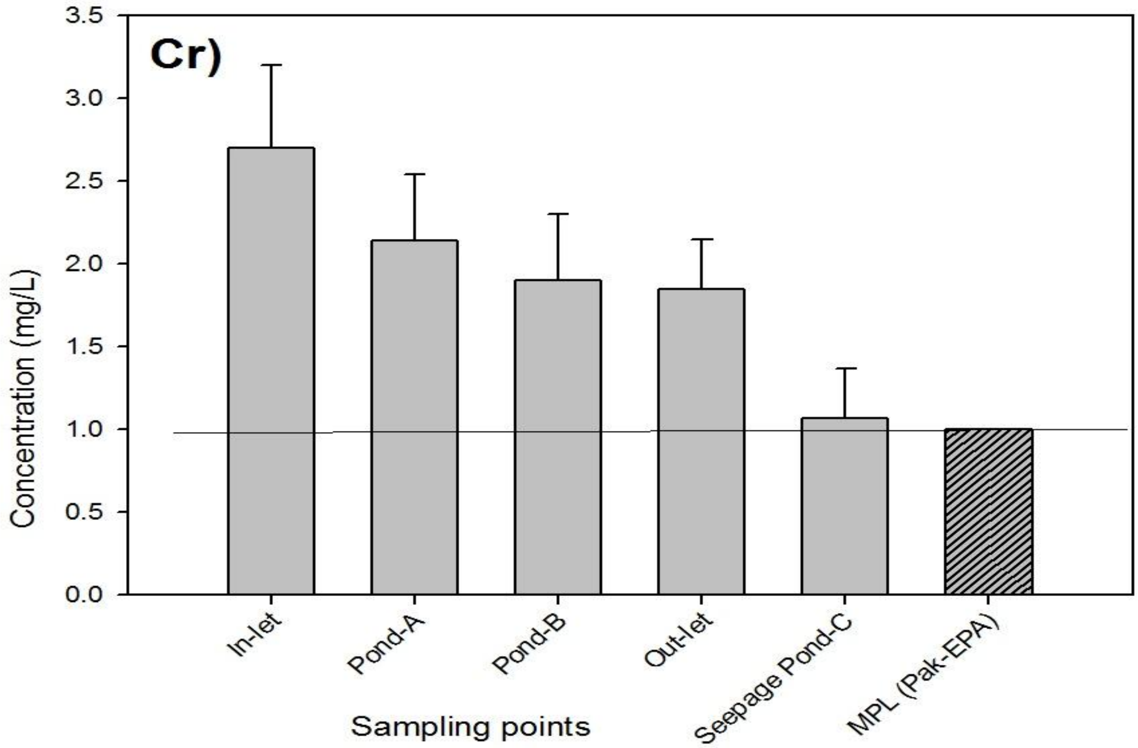

Fig.3.8(a) Mean concentrations of Cr in produced water of Sadqal oil and gas field

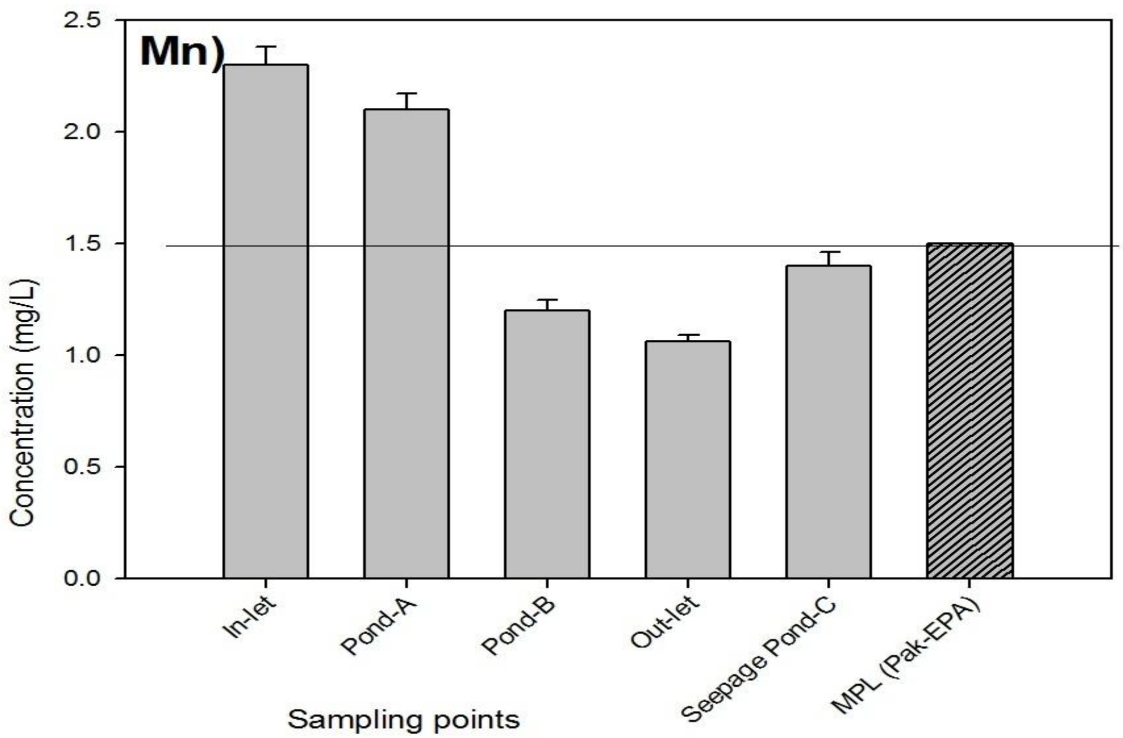

Fig.3.8(b) Mean concentrations of Mn in produced water of Sadqal oil and gas field

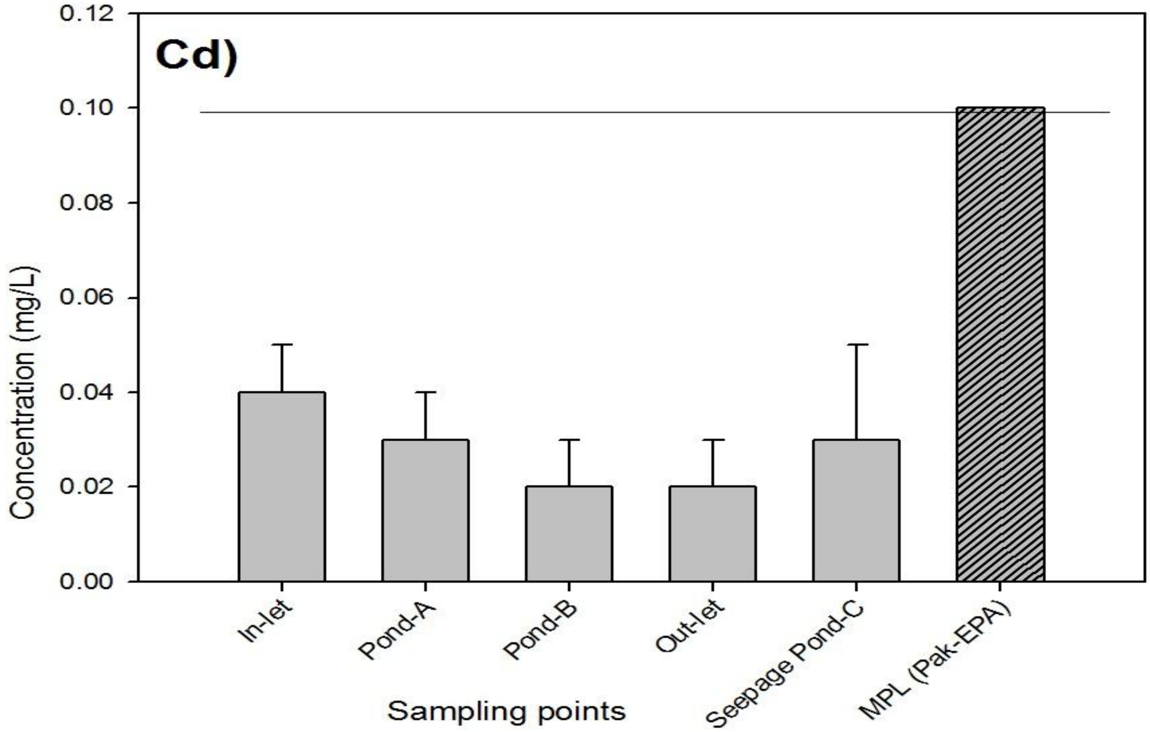

Fig.3.8(c) Mean concentrations of Cd in produced water of Sadqal oil and gas field

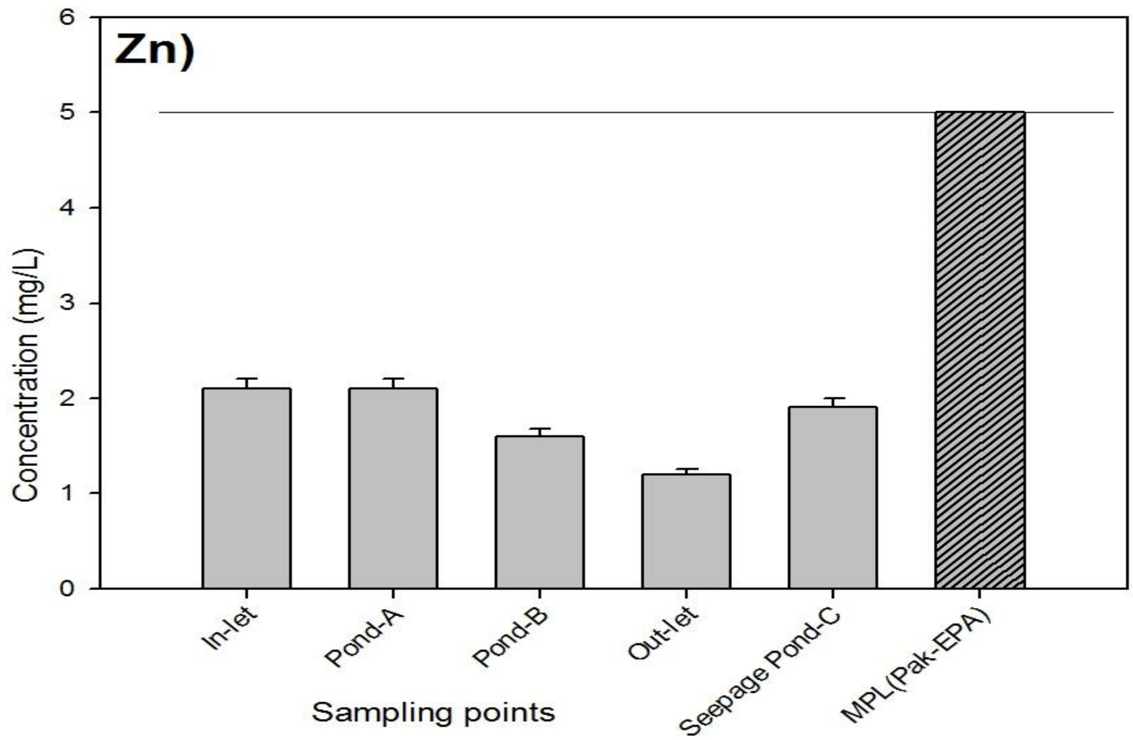

Fig.3.8(d) Mean concentrations of Zn in produced water of Sadqal oil and gas field

Cu level ranged from 0.49±0.02-1.3±0.08 with a mean value of 0.9 mg/L, which is also higher at In-let point then MPL of Pak-EPA of 1.3 mg/L. Pb level ranged from 0.51±0.10-0.91±0.20 mg/L with a mean value of 0.71 mg/L, which is above the MPL of Pak-EPA of 0.5 mg/L. Ni level ranged from 0.34±0.06-0.49±0.09 mg/L with a mean value of 0.43 mg/L, their values is lower than Pak-EPA. Fe level ranged from 2.06±0.10-11.52±3.00 mg/L with a mean value of 6.34 mg/L, its concentration at all points is higher than MPL of Pak-EPA 2 mg/L. Cu, Pb, Ni and Fe are shown in **Fig 3.9**. (a, b, c, & d).

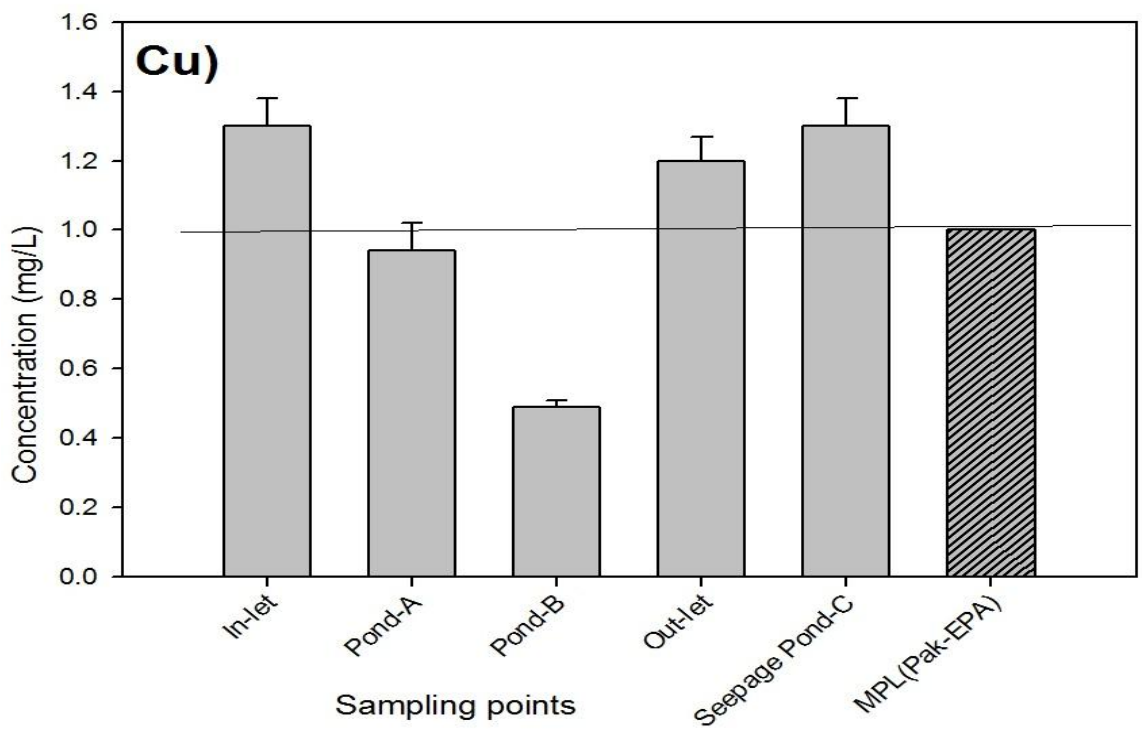

Fig.3.9(a) Mean concentrations of Cu in produced water of Sadqal oil and gas field

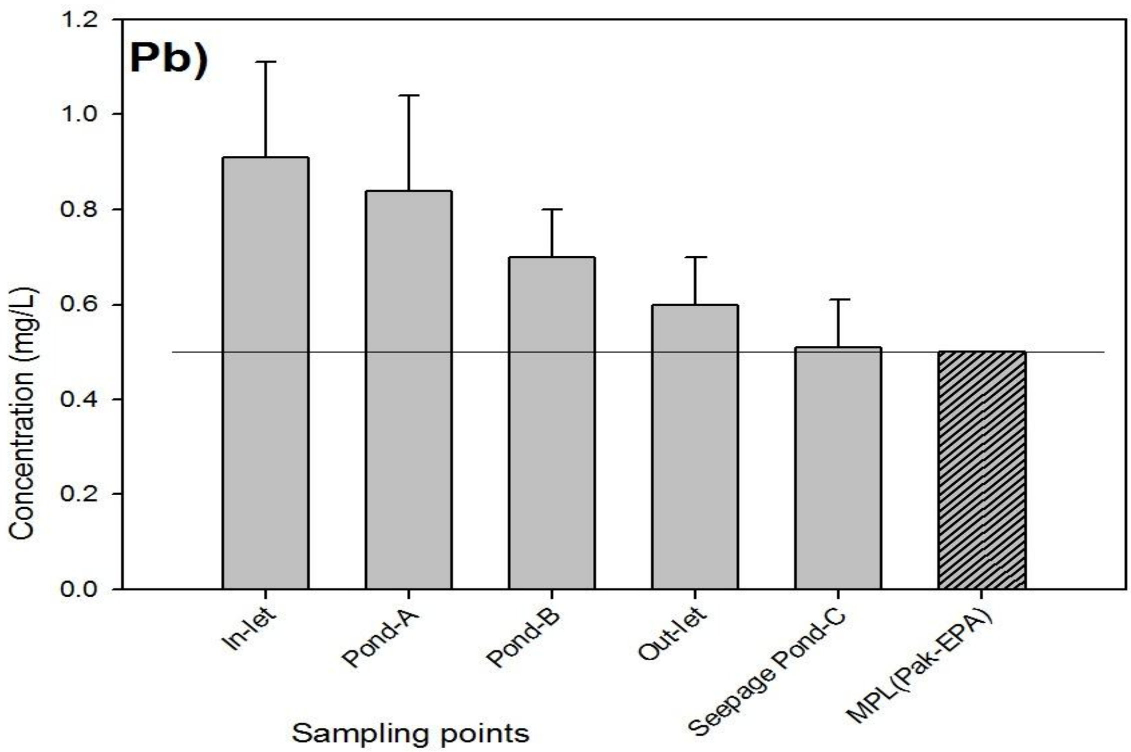

Fig.3.9(b) Mean concentrations of Pb in produced water of Sadqal oil and gas field

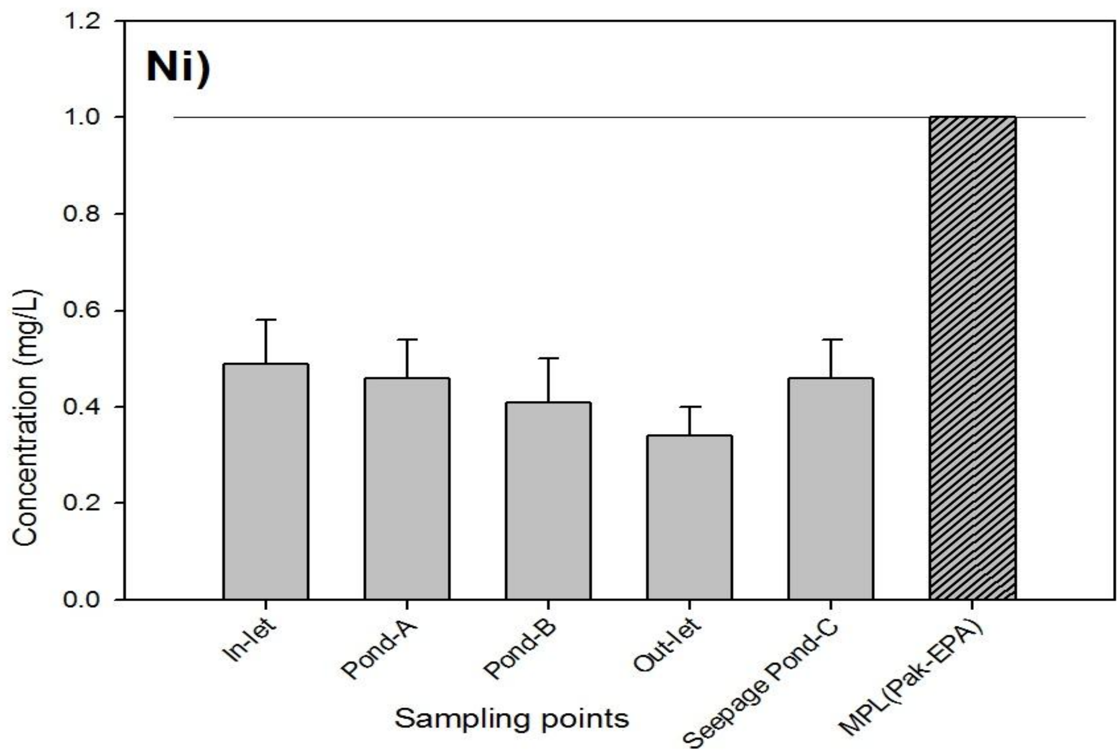

Fig.3.9(c) Mean concentrations of Ni in produced water of Sadqal oil and gas field

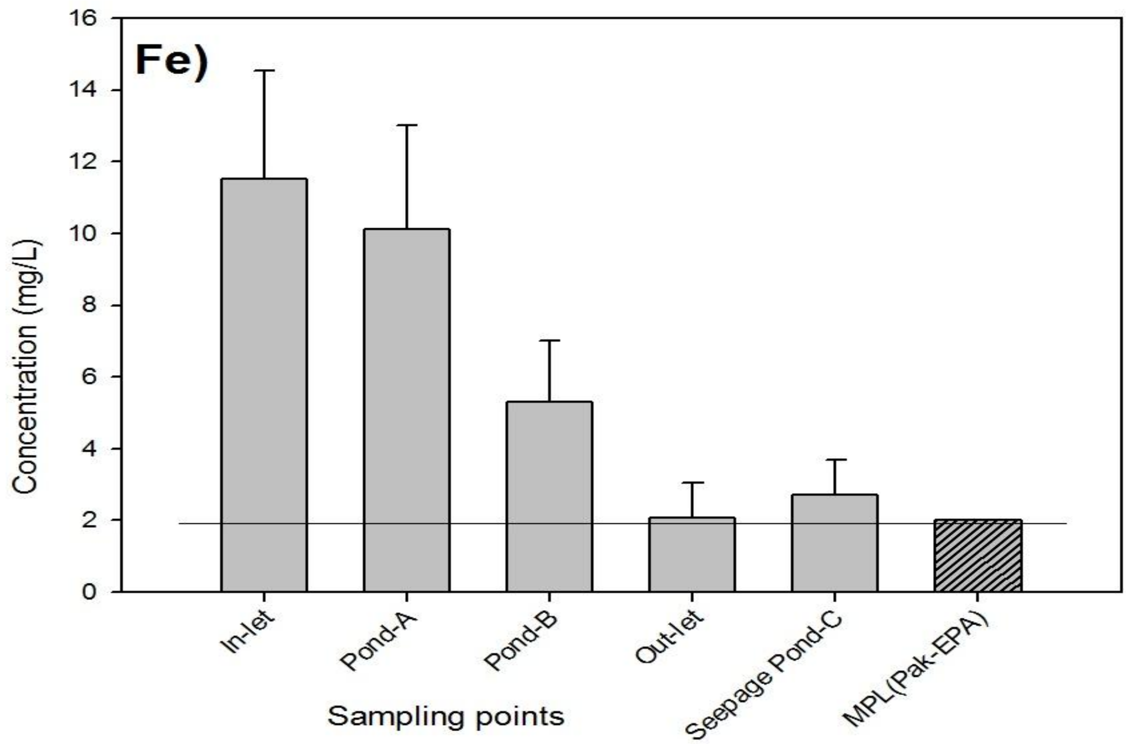

Fig.3.9(d) Mean concentrations of Fe in produced water of Sadqal oil and gas field

These metals are continuously adding into waste water ponds and released without any treatment and can accumulate in soil to toxic level (Sharma et al., 2007). Further, it can harm living things even at low concentrations and can bio accumulate in organisms and food webs (Rattan et al., 2005). Long-term use of industrial wastewater in irrigation is known to have significant contribution to trace elements such as Cd, Cu, Zn, Cr, Ni, Pb, and Mn in surface soil (Mapanda et al., 2005). Excessive accumulation of trace elements in agricultural soils through wastewater irrigation may not only result in soil contamination but also affect food quality and safety (Muchuweti et al., 2006; Sharma et al., 2007). Long term addition of wastewater to soil accumulated heavy metals to a level which is toxic to some plant (Jarausch-Wehrheim et al., 2000).

Heavy metals in soils not only cause the toxicity of plants and animals but also have impact on the balancing of biochemical process (Baath, 1989). For the uses of plants, many process like assimilation, nitrogen fixation and degradation of organic matter presence of microorganisms is very important (Brookes, 1995), also adversely affected by heavy metals in soil (Nwnche & Ugoji, 2008; Stuczynskiel et al., 2003).

Table 3.4

Mean concentration of heavy metals in produced water of Sadqal oil and gas field

Area/parameters	Concentration (mg/L)							
	Cr	Mn	Cd	Zn	Cu	Pb	Ni	Fe
In-let	2.7±0.05	2.3±0.08	0.04±0.01	2.1±0.10	1.3±0.08	0.91±0.20	0.49±0.09	11.52±3.00
Pond-A	2.14±0.04	2.1±0.07	0.03±0.01	2.1±0.10	0.94±0.08	0.84±0.20	0.46±0.08	10.12±2.90
Pond-B	1.9±0.04	1.2±0.05	0.02±0.01	1.6±0.08	0.49±0.02	0.7±0.10	0.41±0.09	5.3±1.70
Out-let	1.85±0.04	1.06±0.03	0.02±0.01	1.2±0.06	1.2±0.07	0.6±0.10	0.34±0.06	2.06±0.10
Seepage Pond-C	1.07±0.03	1.4±0.06	0.03±0.02	1.91±0.09	1.3±0.08	0.51±0.10	0.46±0.08	2.7±1.00
*MPL (Pak-EPA)	1.00	1.50	0.10	5.00	1.00	0.50	1.00	2.00

*MPL= Maximum Permissible Limits of Pakistan Environmental Protection Agency

The correlations among the heavy metals were studied and the results are presented in **Table 3.5**. It is also suggested that mean concentration of heavy metals is changed at five different points some of the measured pollutants due to the fact that some have localized factor which impacts may get dilute and weaken the effects of ponds pollution. Surface area of ponds is so large and evaporation occurred than released outside. The mean seasonal rainfall of Fatehjang area in summer and winter seasons ranges from 300 to 500 mm and 250 to 300 mm, respectively, effects on ponds water.

There was positive correlation observed between Cr and Pb (Cr= 0.933), Mn-Cd (r=0.890), Mn-Fe (r= 0.941) and Cu-Ni (r= 0.914) at $p < 0.05$. Also, highly significant positive correlation was observed in case of Zn-Ni (0.976) and Pb-Fe (r= 0.965) at $p < 0.01$.

Table 3.5
Correlation among the heavy metals of produced water of Sadqal oil and gas field

Heavy metals	Cr	Mn	Cd	Zn	Cu	Pb	Ni	Fe
Cr	1							
Mn	0.667	1						
Cd	0.448	0.890*	1					
Zn	0.281	0.872	0.841	1				
Cu	0.116	0.747	0.937*	0.865	1			
Pb	0.933*	0.841	0.583	0.572	0.313	1		
Ni	0.251	0.823	0.877	0.976**	0.914*	0.513	1	
Fe	0.820	0.941*	0.731	0.767	0.526	0.965**	0.712	1

* Correlation is significant at the 0.05 level (2-tailed)
** Correlation is significant at the 0.01 level (2-tailed).

3.9 Conclusion

It was concluded that heavy metals concentrations of Cr, Mn, Pb, Cu and Fe were found to be above the permissible limits prescribed by Pak-EPA; and thus entering into the surrounding environment. The concentration of metals and some anions which were monitored in Nullah Lai and sites of Koh-e-Noor textile mill, were higher than value set by the WHO, with increased risk to public health (Iram & Kanwal, 2013). The effluents from oil and gas are released into the ground, percolates and may change the ground water quality. PW should be treated before releasing into streams or other location where infiltration may occur. Also, ponds walls should be cemented and covered with high density polyethylene, to prevent the seepages outside in order to decrease the impacts of wastewater on the surrounding environment.

CHAPTER-4

IMPACT ASSESSMENT OF WASTEWATER ON GROUND WATER NEAR EXPLORATION AND PRODUCTION ACTIVITIES

Abstract

This study was conducted to find out the quality of drinking water in the premises of PW ponds and exploration and production area. The main sources of drinking water are wells, pressure pumps and hand pumps in the study area, Sadqal oil and gas field, Fatehjang, Punjab, Pakistan. Representative water samples were collected from different sources in order to determine the physico-chemical properties and heavy metal concentrations which are effected by produced water. pH of all samples was determined on the spot. Among the cations & anions Na^+, K^+, Ca^{+2}, Mg^{+2}, Cl^-, F^-, SO_4^{-2}, NO_3^- and NO_2^- were determined. Heavy metals Cr, Mn, Cd, Zn, Cu, Pb, Ni and Fe were also analyzed. The values of different parameters of drinking water from different sources indicate that maximum physico-chemical and heavy metal levels are above the WHO permissible limits. On the basis of findings, it is concluded that drinking water of the study area may pose a serious threat to the health of the users near exploration and production activities. So, the EPA should check the illegal practice of dumping of industrial effluents on land especially in residential areas and such activities must be stopped immediately by strict imposition of national environmental quality standards.

4.1. Introduction

The quality of drinking water for human being is vital importance. Water supports the life processes (Javid et al., 2012; Parveen et al., 2007) especially ground water which decides its suitability for domestic, agriculture and industrial purposes (Raju et al., 2009). Water is among the most abundant substances and a universal solvent in the world. About 70% of the earth is covered with water and most drinking fluid by living things, therefore, often a potential source of causing toxicities (Joyce et al., 1996; Prasad & Narayana, 2004).To meet our requirements, less than 1% water is present in ground resources and in rivers (Qadeer, 2004). These water resources are highly contaminated with toxic substances, which is a big hazard to living beings (Ghoochani et al., 2011).

Generally, poor management of the domestic, industrial and commercial wastes, it pollutes the natural water supplies, mostly streams and rivers. A huge amount of used water is disposed off generally by returning it to a natural body of water in the surrounding area, making it hazardous as it carries toxic chemicals (Jain et al., 2005; Leoni et al., 2005). Ground and surface water can be contaminated by discharge from sewage treatment plant and industrial effluent, uncontrolled discharge from land fill sites and from chemical accidents and disaster, refuse dumping sites, excess use of fertilizers and anthropogenic activities causing ground water pollution. Therefore, availability of healthy, clean and good quality drinking water is a matter of great concern in the urban areas (Farid et al., 2012), because condition or composition or both of the drinking water are changed.

Many investigators have analyzed the water samples and the results were compared with standard values. Jabeen et al. (2014) concluded in a study about the high concentrations of heavy metals (Mn, Cu, Pb, Hg, and Ni) both in surface and ground water which were caused by the anthropogenic activities in Haripur basin, Pakistan. Analysis of drinking water samples in Faisalabad city showed the results are above the permissible limits, which might be due to seepage of domestic sewage and industrial effluents (Farid et al., 2012). In another study conducted in the Pettaivaithalai area India, it was observed that sugar mill effluents have high impacts on the physico-chemical parameters (TDS, Na^+, K^+, Cl^-, NO_3^- and SO_4^{-2}) of the ground water (Jameel & Sirajudeen, 2006).

Intake of excessive heavy metals in drinking water and contaminated food causes shortness of breath, liver and kidney related disorders, cancers, immune dysfunction, hypertension, cardiovascular diseases and cancer (Muhammad et al., 2011; Pınar et al., 2009) Analysis of drinking water near oil exploration and production sites is important for safety assessment of the environment in general and human health in particular. Effluents from various sources when contaminated water resources is associated with heavy disease burden (Okoh et al., 2007) and this could impact the current shorter life expectancy in the developing countries as compared with developed nations (WHO, 2002).

To protect the public health and the environment, assessment of water is very essential (Okoh et al., 2005; Okoh et al., 2007). However, in Pakistan, water quality data are still scarce and in uncoordinated form. Therefore, this study is aimed to analyze the impact of oil exploration and production activities on ground water which is used as a major source for drinking and other domestic purposes in the study area.

4.2. Materials and methods

4.2.1. Study area

Fateh Jang is a town and the tehsil headquarters of Attock district in the Punjab province Pakistan. Sadqal (Darwazi) village is located less than 100 meters from Sadqal oil and gas field (**Fig.4.1**). Area selection was made on the basis of the degree of impacts of OGDC activities and the effluents that contaminants the available water. About one kilometer away from the field, PW is released into the ponds from several years. Ponds walls are neither secured nor covered with high density polyethylene, so continuous seepages occur. Further details are given in chapter 1, in section 1.2.

4.2.2. Samples collection

Drinking water samples were collected from Sadqal village and near ponds area of produced water including, bore well, hand pumps and wells, in 1.5L sampling containers. Before samples collection, containers were rinsed with 1:1 concentrated HNO_3 acid and triple distilled water of Milli Q. pH of the samples was determined using hand potable pH meter and it was properly checked and calibrated by using standard method (APHA, 1998). One sample from each point was acidified with 10% nitric acid for the analysis of heavy metals whilst the other was used for the physico-chemical

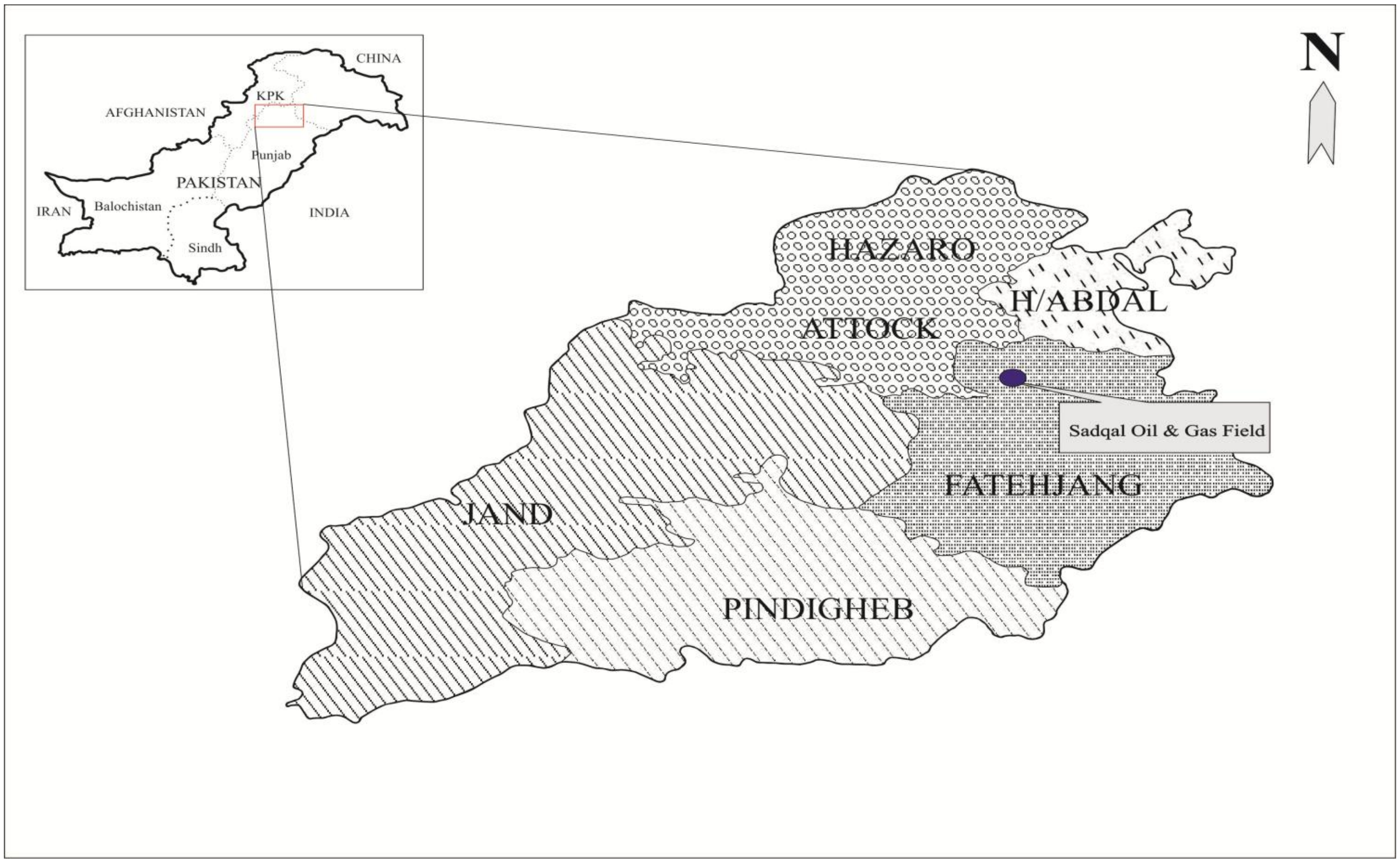

Fig.4.1 Location map of the study area

analysis. In the laboratory, these samples were stored in a refrigerator at 4°C for further analysis (APHA, 1998).

4.3. Analysis of anions and cations

According to the standards methods of American Wastewater Associations (APHA, 1998), the concentrations of cations and anions i.e. Na^{+}, K^{+}, Ca^{+2}, Mg^{+2}, Cl^{-}, F^{-}, SO_4^{-2}, NO_3^{-} and NO_2^{-} in the drinking water samples were determined. Further details are given in chapter 3 and section 3.3.1.

4.4. Analysis of heavy metals

100 ml acidified water sample were filtered through Whatman's 0.45µm filter paper. Selected Heavy metals (Cd, Cr, Cu, Mn, Ni, Pb, Zn and Fe) concentrations in drinking water were determined by using flame atomic absorption spectrophotometer (Perkin Elmer AAS 700). Further details are given in chapter 3 and section 3.8.3.

4.5. Results and discussion

4.5.1 Physicochemical properties of the drinking water

The pH value is given in **Table 4.1**, ranged from 6.8±0.01 to 9.1±0.05. All samples show values with in WHO permissible limits of 6.6-9.2 for drinking water. pH has no direct effects on human health yet it has some indirect effects, by bringing changes in water quality parameters such as metal ion solubility and aquatic life survival.

Na^+ and K^+ were present in all the samples of water. The values of Na^+ and K^+ are given in **Table-4.1**, indicating a range of 68±3.00 to 708±4.00 mg/L and 0.21±0.10 to 15.5±1.00 mg/L, respectively. In samples D.15, D.16 & D.17 and **Fig.4.2**(a) value of Na^+ is above the WHO maximum permissible level of 200 mg/L for drinking water. Singh et al. (2008) reported that high Na^+ intake might cause hypertension, heart diseases and kidney problems. In sample D.16 and **Fig.4.2** (b) value of K^+ was above the WHO maximum permissible limit of 12 mg/L for drinking water. Na^+ and K^+ are the most important minerals occurring naturally. The major source of both of the cations may be weathering of rocking (Singh et al., 1999) besides the sewage and industrial effluents.

Ca^{+2} and Mg^{+2} were found to in the range from 10.2±2.00 to 490±7.00 mg/L and 19.6±2.00 to 116.5±4.00 mg/L, as displayed in **Table-4.1**, respectively. The result shows that Ca^{+2} values in case of samples D.14, D.15, D.16 & D.17 and **Fig.4.2** (c) are above the WHO maximum permissible level which is 75 mg/L for drinking water.

Mg^{+2} values in case all the samples were above the WHO maximum permissible level of 30 mg/L as shown in **Fig.4.2**(d). Ca^{+2} and Mg^{+2} ions cause hardness and hence they are interrelated. Chromatogram (**annexure-iii**) shows the concentration of cations in drinking water.

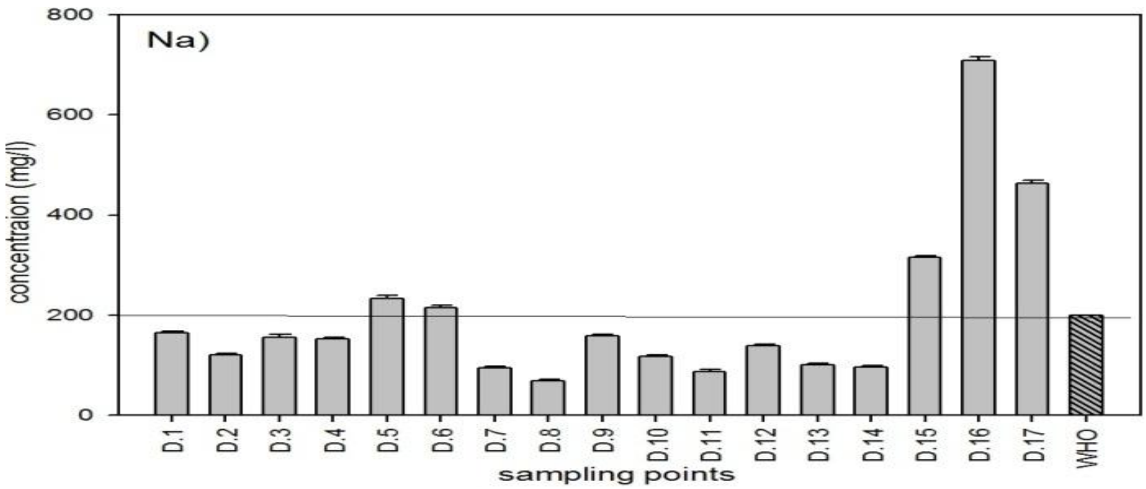

Fig.4.2(a) Mean concetration of Na in drinking water of the study area

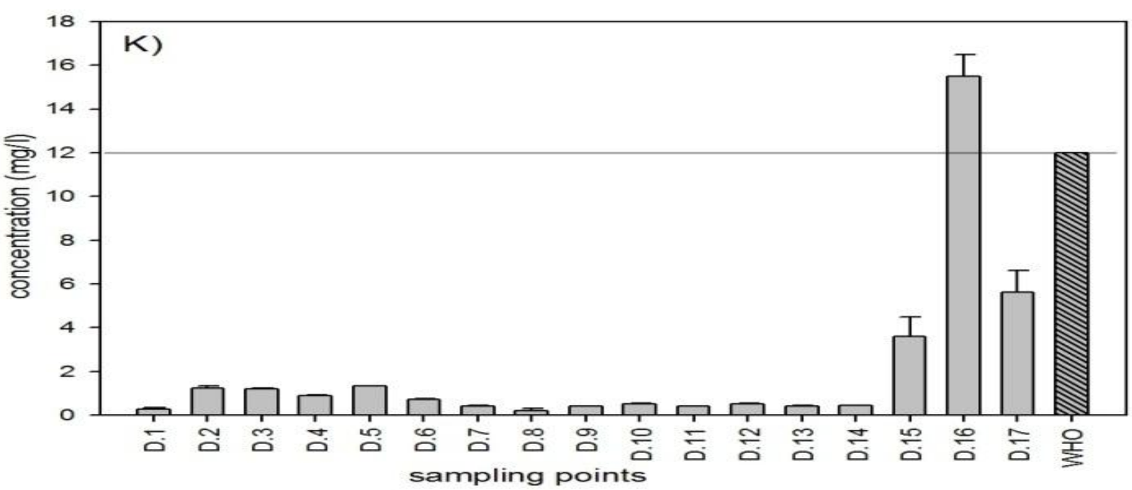

Fig.4.2(b) Mean concetration of K in drinking water of the study area

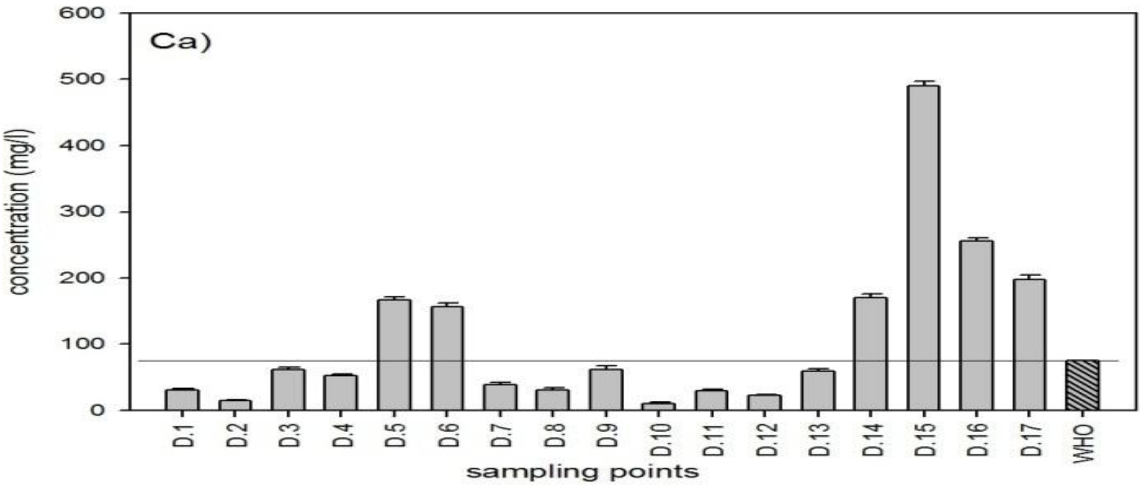

Fig.4.2(c) Mean concetration of Ca in drinking water of the study area

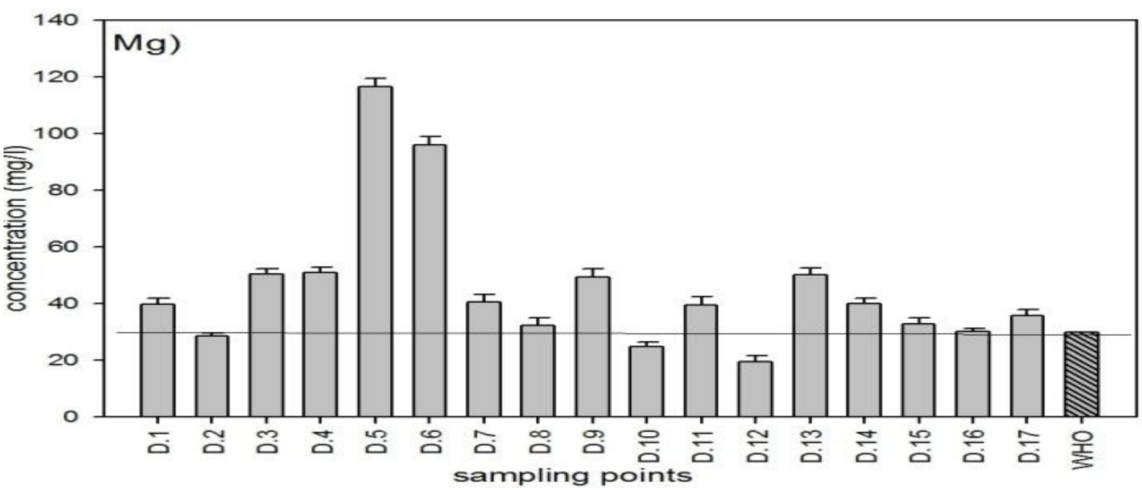

Fig.4.2(d) Mean concetration of Mg in drinking water of the study area

Cl^- were present in all samples of water understudy. The value for Cl^- ranged from 75±4.00 to 2441±8.00 mg/L as displayed in **Table-4.1**. The values are high than WHO maximum permissible limit of 250 mg/L for drinking water except in case of samples D.4, D.7 & D.8 as shown in **Fig.4.3**(a). Cl^- occurs naturally in all types of water and mostly enter from agricultural activities, industries and chloride rich rocks. This high values shows high contamination due to percolation of produced water from ponds to ground water. The result is coherent with earlier studies (Jameel & Sirajudeen, 2006; Mariappan et al., 2000).

The F^- in water come from fluoride bearing rocks or from the water treatment processes. The data for F^- concentration ranged from 0.16±0.10 to 5.75±1.00 mg/L as provided in **Table-4.1**, indicating that only in case of samples D.7, D.8, D.14 & D.16 as shown in **Fig.4.3**(b), the concentration is high than maximum permissible limit set by WHO (1.30 mg/L for drinking water). F^- offers protection against dental caries at low concentrations, but at higher levels causes serious problems such as dental and skeletal fluorosis (Schafer et al., 2010). Bhosle et al. (2001) reported that the percolation of wastes from fertilizers, discharge of domestic wastes and other industries are responsible for high contamination of the F^- in underground water.

The values of SO_4^{-2} ranged from 4±1to 280±7.00 mg/L; the data for SO_4^{-2} in the samples are given in **Table-4.1**. The values of all samples are within WHO maximum permissible limits of 250 mg/L except sample D.16 **Fig.4.3**(c).

NO_3^- is a contaminant that has significant health risks associated with excess NO_3^- consumption in the human diet. These include methemoglobinemia in infants (‘‘blue baby syndrome’’) (Fewtrell, 2004). The value of nitrate (NO_3^-) ranged from 4.6±1 to 576±4 mg/L as given in **Table-4.1**, this high values indicating that the ground water contamination is due to the leaching of NO_3^- present on the surface with percolating water. All samples having high concentration of NO_3^- values than permissible limit of WHO (50 mg/L for drinking water) except D.8, D.9 and D.15 as shown in **Fig.4.3**(d). This may be due to the infiltration from produced water effluents which are released into the ponds.

The value of NO_2^- ranged from 0.14±0.01 to 4±0.70 mg/L as reported in **Table-4.1**, shows that all values are within the limits except D.6, D.16 and D.17, having high concentration than WHO maximum permissible limits of 3 mg/L. Chromatogram (**annexure-iv**) shows the concentration of various anions in drinking water samples.

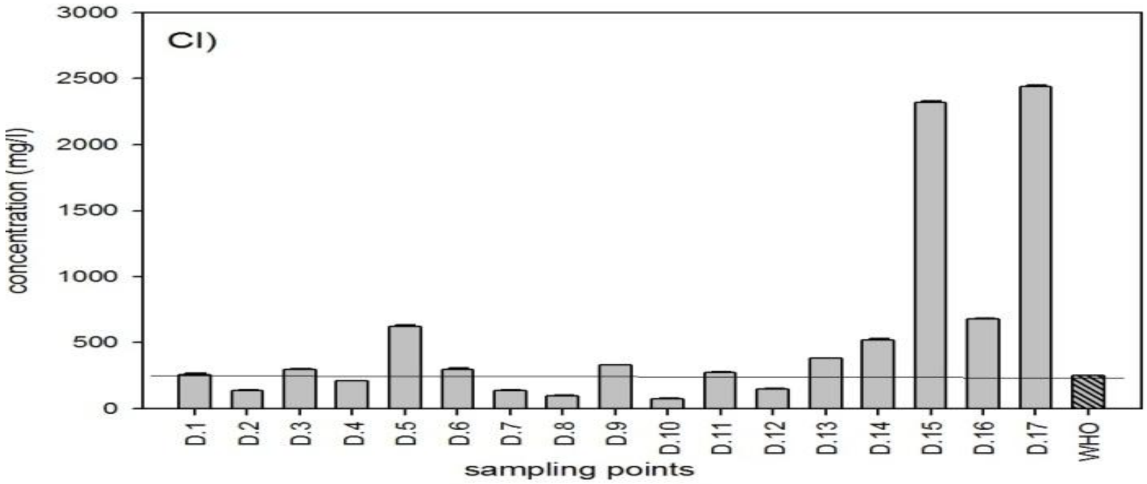

Fig.4.3(a), Mean concetration of Cl in drinking water of the study area

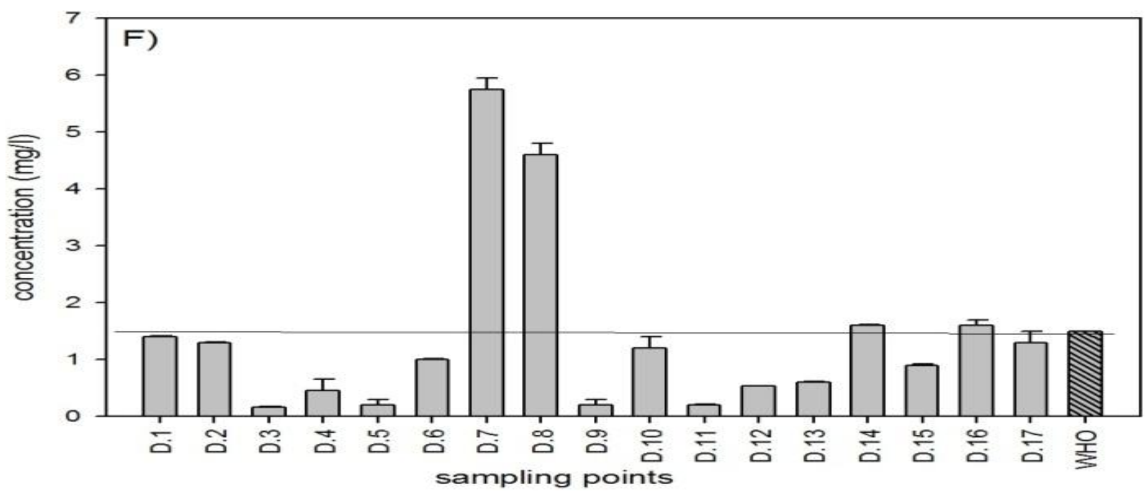

Fig.4.3(b), Mean concetration of F in drinking water of the study area

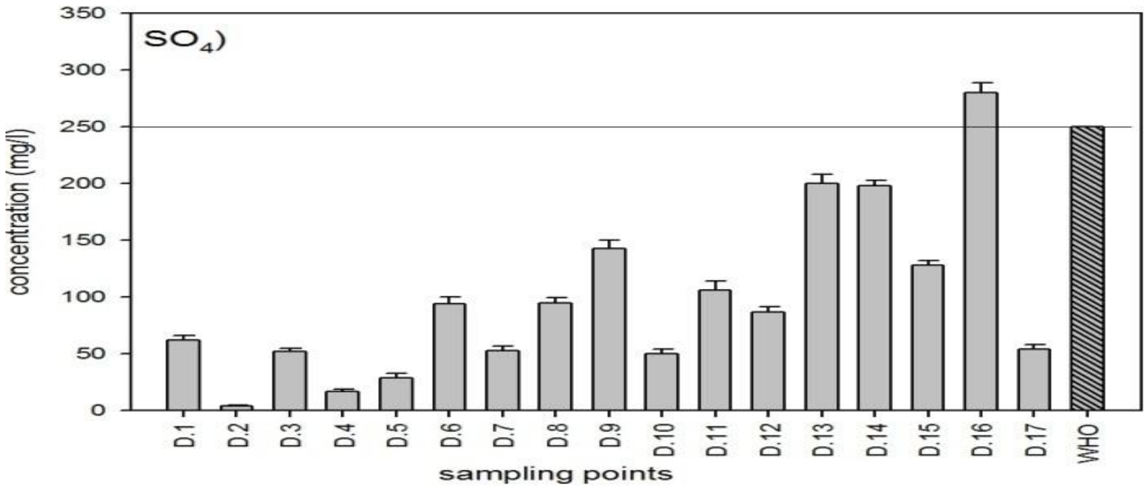

Fig.4.3(c), Mean concetration of SO_4 in drinking water of the study area

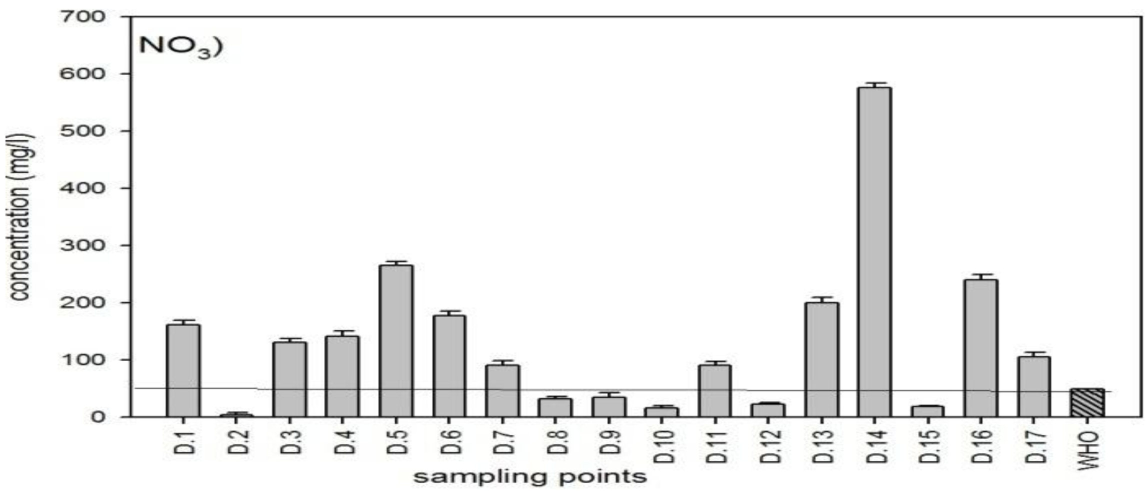

Fig.4.3(d), Mean concetration of NO_3 in drinking water of the study area

Table 4.1
Mean concentration of physico-chemical properties of drinking water near Sadqal oil field

S.No	pH	Concentration (mg/L)								
		Na^{+}	K^{+}	Ca^{+2}	Mg^{+2}	Cl^{-}	F^{-}	SO_4^{-2}	NO_3^{-}	NO_2^{-}
D.1	6.9±0.02	164±2.00	0.26±0.10	31±2.00	39.8±2.00	258±3.00	1.4±0.50	62±4.00	161±2.00	1.2±0.10
D.2	6.8±0.01	121±3.00	1.24±0.10	14.7±1.00	28.6±2.00	137±4.00	1.3±0.80	4±1.00	4.6±1.00	1.1±0.02
D.3	7.2±0.03	156±3.00	1.2±0.02	61.7±3.00	50.4±3.00	298±3.00	0.16±0.10	52±3.00	131±2.00	1.6±0.10
D.4	7.5±0.05	152±2.00	0.9±0.01	53±2.00	50.9±2.00	209±4.00	0.46±0.20	17±2.00	142±2.00	1.5±0.02
D.5	7.8±0.01	233±3.00	1.34±0.01	167±4.00	116.5±4.00	624±5.00	0.2±0.10	29±4.00	266±2.00	0.5±0.01
D.6	8.1±0.03	215±2.00	0.73±0.01	157±2.00	95.9±3.00	300±2.00	1±0.50	94.3±6.00	177±3.00	4±0.70
D.7	8.5±0.01	94±3.00	0.42±0.01	39±3.00	40.6±2.00	138±4.00	5.75±1.00	52.5±4.00	91±2.00	0.14±0.01
D.8	7.5±0.05	68±3.00	0.21±0.10	30.3±4.00	32.3±3.00	98±2.00	4.6±1.00	94.5±5.00	32.13±2.00	0.34±0.06
D.9	8.05±0.01	158±4.00	0.4±0.01	61±4.00	49.4±2.00	330±3.00	0.2±0.10	143±7.00	34.3±3.00	0.4±0.03
D.10	7.8±0.07	117±3.00	0.52±0.02	10.2±2.00	24.8±2.00	75±4.00	1.2±.20	49.9±4.00	15.4±1.00	0.13±0.05
D.11	8.5±0.01	87±4.00	0.41±0.01	29.3±3.00	39.4±2.00	276±3.00	0.2±0.01	106±8.00	90.8±2.00	0.4±0.08
D.12	7.9±0.04	139±3.00	0.51±0.02	22.5±2.00	19.6±2.00	147±4.00	0.53±0.01	86.6±5.00	22.4±3.00	0.7±0.03
D.13	8.2±0.01	100±4.00	0.4±0.03	60±3.00	50.1±3.00	380±3.00	0.6±0.02	200±8.00	200±2.00	0.34±0.01
D.14	8.5±0.03	96±3.00	0.43±0.02	170±5.00	40±2.00	522±4.00	1.6±0.01	198±5.00	576±4.00	1.5±0.10
D.15	8.4±0.03	315±4.00	3.6±0.09	490±7.00	32.9±2.00	2321±5.00	0.9±02.00	128±4.00	18.6±2.00	1±0.01
D.16	9.1±0.05	708±4.00	15.5±1.00	256±4.00	30.2±1.00	682±6.00	1.6±0.10	280±7.00	240±3.00	3.5±0.50
D.17	8.3±0.02	463±3.00	5.61±1.00	198±7.00	35.8±2.00	2441±8.00	1.3±0.20	54±3.00	105.6±3.00	4±0.70
WHO	6.50-9.20	200.00	12.00	75.00	30.00	250.00	1.50	250.00	50.00	3.00

WHO=World Health Organization

4.5.2 Heavy metals concentration in drinking water

Cr ranged from 0.006±0.01 to 0.97±0.05 mg/L as reported in **Table-4.2**, indicating that the samples D.6, D.12, D.15, D.16 & D.17 and in **Fig.4.4.**(a) show high concentration than WHO maximum permissible limits of 0.05 mg/L. In the earth crust and water, Cr is one of the most common elements. Cr itself is not toxic but in its hexavalent status cause cancers, digestive, excretory, respiratory reproductive system and skin diseases (Feroz, 2008).

Mn ranged from 0.01±0.001 to 1.7±0.10 mg/L as given in **Table-4.2**. The data shows that samples D.2, D.4, D.8, D.9, D.12, D.15, D.16 & D.17 and **Fig.4.4**.(b) have high concentration than WHO described permissible limit of 0.5 mg/L. Mn is an essential trace nutrient for all forms of life. However, exposure to excessive doses of Mn causes severe disorders in the body.

Cd is an element of great concern from a toxicity point of view. The samples analyzed have Cd concentration ranges from 0.001±0.001 to 0.3±0.01 mg/L. The data is given in **Table-4.2**. All samples show high concentration than WHO maximum permissible limits of 0.003 mg/L except D.5, D.6, D.7, D.8, D.9 & D.10 as shown in **Fig.4.4**.(c). In the study area, more than ten years PW is continuously released into the ponds and further through seepages and percolation it contaminates the ground water. PW was also examined for Cd but their concentration is less as compare to in drinking water, because exploration and production PW chemistry changes with the passage of time as discussed in literature. In humans, Cd causes both acute and chronic toxicity and may cause acute gastrointestinal problems, such as vomiting and diarrhea (Nordberg, 2004) while chronic exposure to cadmium for a long time may cause kidney damage (Barbier et al., 2005; Qadeer, 2004).

In **Table-4.2**, Zn values ranged from 0.32±0.20 to 4±0.80 mg/L where samples D.3, D.6, D.16 & D.17 and **Fig.4.4**.(d), show high concentration than WHO maximum permissible limit of 3 mg/L.

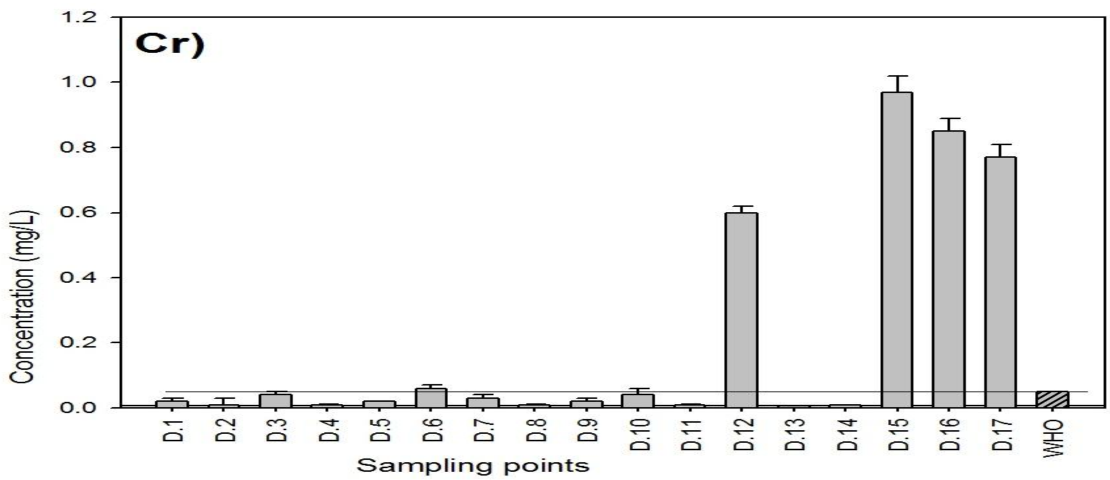

Fig.4.4(a), Mean concentration of Cr in drinking water of the study area

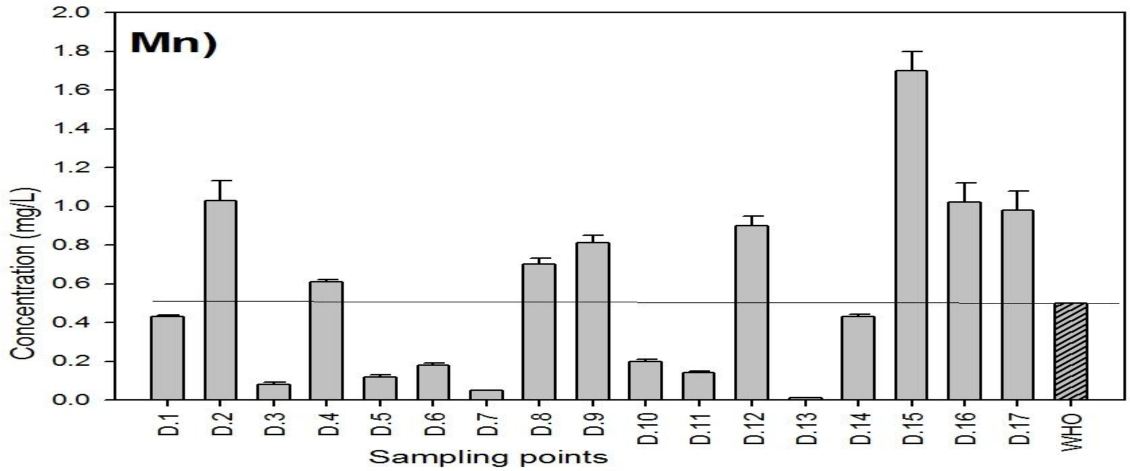

Fig.4.4(b), Mean concentration of Mn in drinking water of the study area

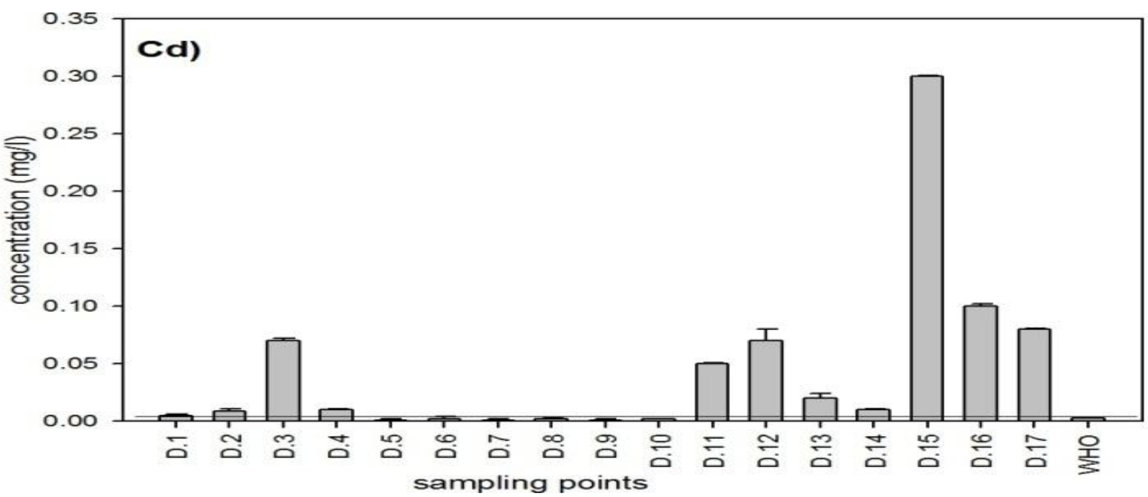

Fig.4.4(c), Mean concentration of Cd in drinking water of the study area

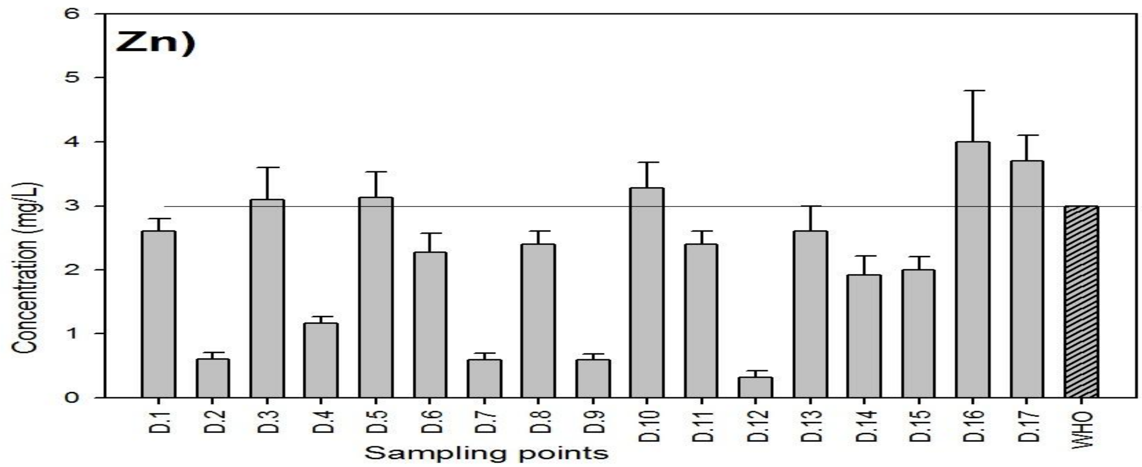

Fig.4.4 Fig.4.3(b), Mean concentration of Zn in drinking water of the study area

Cu values ranged from 0.08±0.01 to 3.1±0.01 mg/L as given in **Table-4.2**. Cu values in samples D.5, D.9, D.12, D.14, D.15, D.16 & D.17 and **Fig.4.5** (a), indicate high concentration than WHO values of 2 mg/L. Both Zn and Cu are essential elements for human health, but their excess amount can lead to adverse health problems (Singh et al., 2006).

Pb value ranged from 0.003±0.001 to 0.6±0.01 mg/L as given in **Table-4.2,** indicating that samples D.2, D.4, D.6, D.8, D.11, D.15, D.16 & D.17 and **Fig.4.5** (b), show high values than WHO permissible level of 0.01 mg/L. Pb enters into the drinking water from different sources like vehicle exhausts, paints and industrial wastes (Nadeem-ul-Haq et al., 2009). Their higher concentration affects adversely the major organs and system of body like nervous, digestive system and kidneys (Qadeer, 2004).

Table-4.2, shows that Ni level ranged 0.001±0.003 to 1.48±0.001 mg/L. Maximum samples as shown in **Fig.4.5(c),** high concentration than WHO permissible limits of 0.02 mg/L. High concentration may cause different diseases like, allergic dermatitis, lung fibrosis and cancer in respiratory tract (Ifegwu & Anyakora, 2012), vomiting, nausea, abdominal discomfort, headache, cough and shortness of breath (Ifegwu & Anyakora, 2012).

Table 4.2
Mean concentration of heavy metal in drinking water near Sadqal oil field

S.No	Concentration (mg/L)							
	Cr	Mn	Cd	Zn	Cu	Pb	Ni	Fe
D.1	0.02±0.010	0.43±0.010	0.005±0.001	2.6±0.020	0.14±0.010	0.005±0.004	0.001±0.003	0.04±0.010
D.2	0.01±0.020	1.03±0.100	0.009±0.002	0.61±0.100	0.39±0.020	0.02±0.001	0.01±0.001	0.1±0.020
D.3	0.04±0.010	0.08±0.010	0.07±0.002	3.1±0.500	0.41±0.020	0.003±0.001	0.07±0.002	0.28±0.020
D.4	0.01±0.001	0.61±0.010	0.01±0.001	1.17±0.100	0.51±0.100	0.1±0.0001	0.01±0.001	0.77±0.050
D.5	0.02±0.001	0.12±0.010	0.001±0.001	3.13±0.400	2.03±0.010	0.01±0.003	0.04±0.001	0.54±0.050
D.6	0.06±0.010	0.18±0.010	0.002±0.002	2.27±0.300	0.08±0.001	0.2±0.001	0.01±0.001	0.08±0.010
D.7	0.03±0.010	0.05±0.001	0.001±0.001	0.6±0.100	1.5±0.030	0.009±0.002	0.002±0.001	0.43±0.030
D.8	0.01±0.001	0.7±0.003	0.002±0.005	2.4±0.200	0.35±0.020	0.12±0.004	0.006±0.001	1.3±0.060
D.9	0.02±0.010	0.81±0.040	0.001±0.001	0.59±0.100	2.1±0.100	0.003±0.001	0.01±0.001	0.1±0.010
D.10	0.04±0.020	0.2±0.010	0.002±0.002	3.28±0.400	0.43±0.010	0.01±0.003	0.06±0.005	0.6±0.030
D.11	0.01±0.001	0.14±0.010	0.05±0.001	2.4±0.200	0.29±0.020	0.1±0.001	0.3±0.001	1.5±0.200
D.12	0.6±0.020	0.9±0.050	0.07±0.010	0.32±0.200	2.5±0.010	0.008±0.002	0.001±0.001	0.4±0.040
D.13	0.006±0.001	0.01±0.001	0.02±0.004	2.6±0.400	0.39±0.010	0.006±0.001	0.1±0.001	0.21±0.030
D.14	0.009±0.001	0.431±0.001	0.01±0.001	1.92±0.300	3.1±0.010	0.004±0.001	0.13±0.002	0.82±0.100
D.15	0.97±0.050	1.7±0.100	0.3±0.001	2±0.200	2.8±0.400	0.3±0.002	1.48±0.001	1.08±0.300
D.16	0.85±0.040	1.02±0.100	0.1±0.002	4±0.800	3.1±0.010	0.6±0.010	0.5±0.003	0.92±0.200
D.17	0.77±0.040	0.98±0.100	0.08±0.001	3.7±0.400	2.3±0.200	0.09±0.002	0.8±0.001	1.3±0.300
WHO	0.050	0.500	0.003	3.00	2.000	0.010	0.020	0.300

WHO=World Health Organization

Fe values ranged from 0.04±0.01 to 1.5±0.200 mg/L compared to WHO permissible limit of 0.30 mg/L as displayed in **Table-4.2** and shown in **Fig.4.5** (d). In Pakistan, iron is one of the major pollutants of both ground and surface water. Iron deficiency and overload can be harmful both for animals and plants (Feroz, 2008).

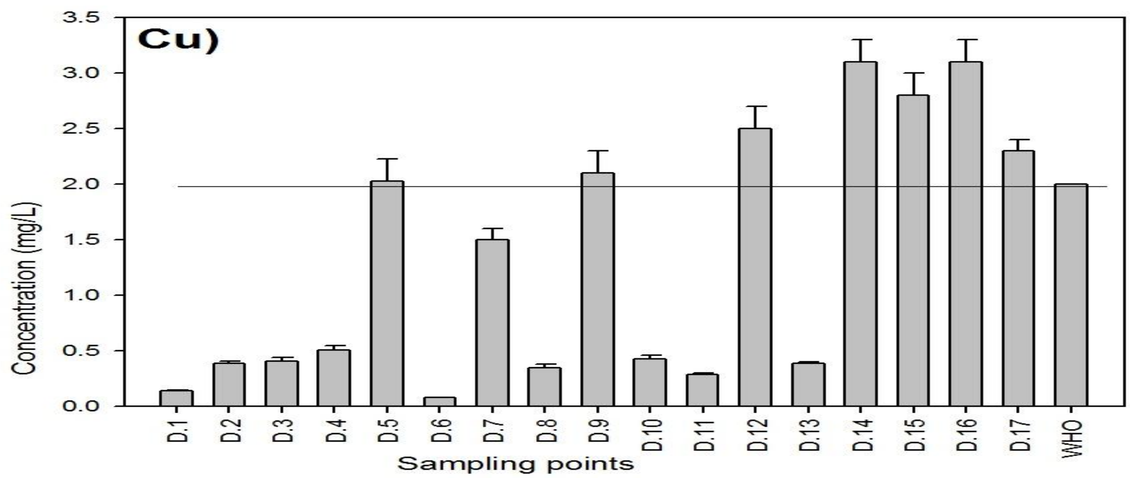

Fig.4.5(a), Mean concentration of Cu in drinking water of the study area

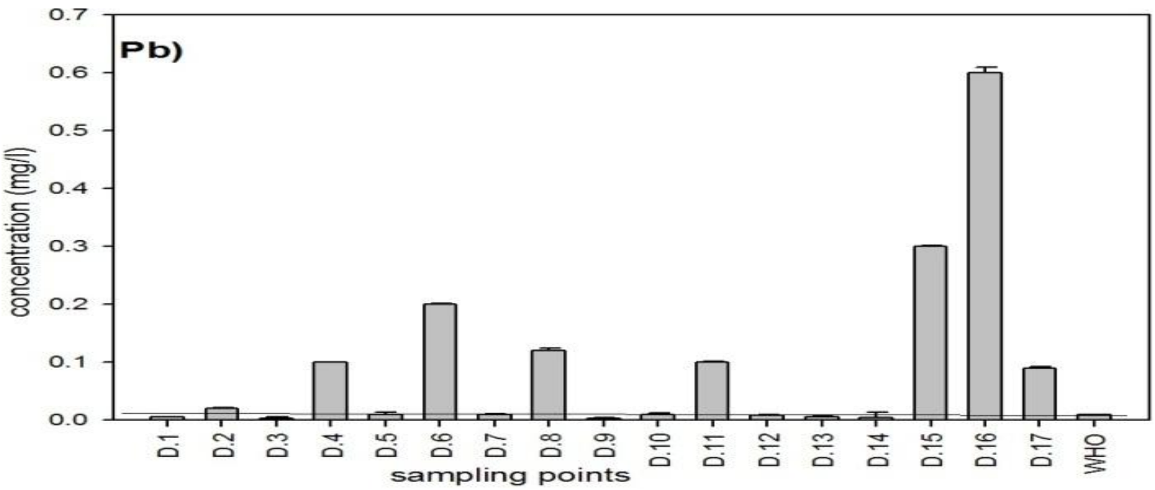

Fig.4.5(b), Mean concentration of Pb in drinking water of the study area

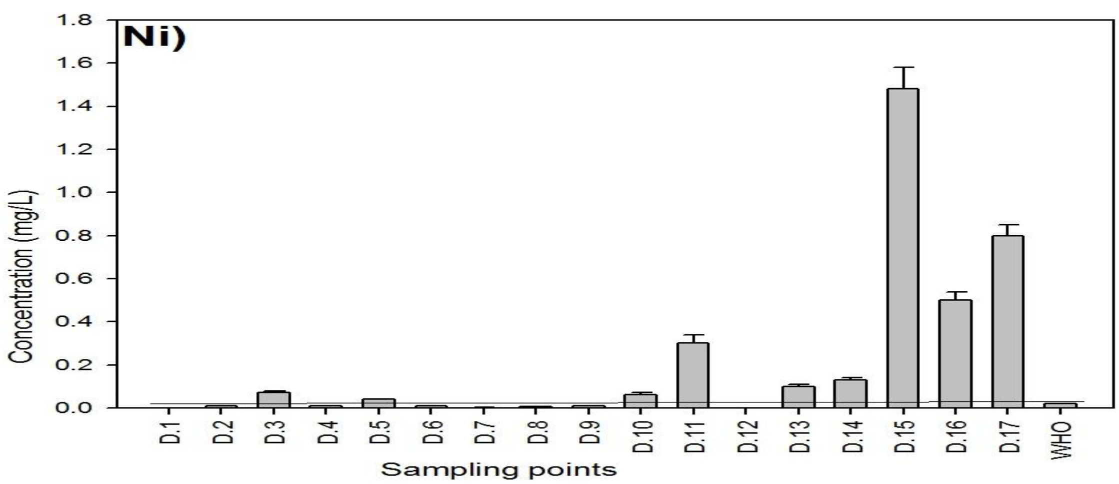

Fig.4.5(c), Mean concentration of Ni in drinking water of the study area

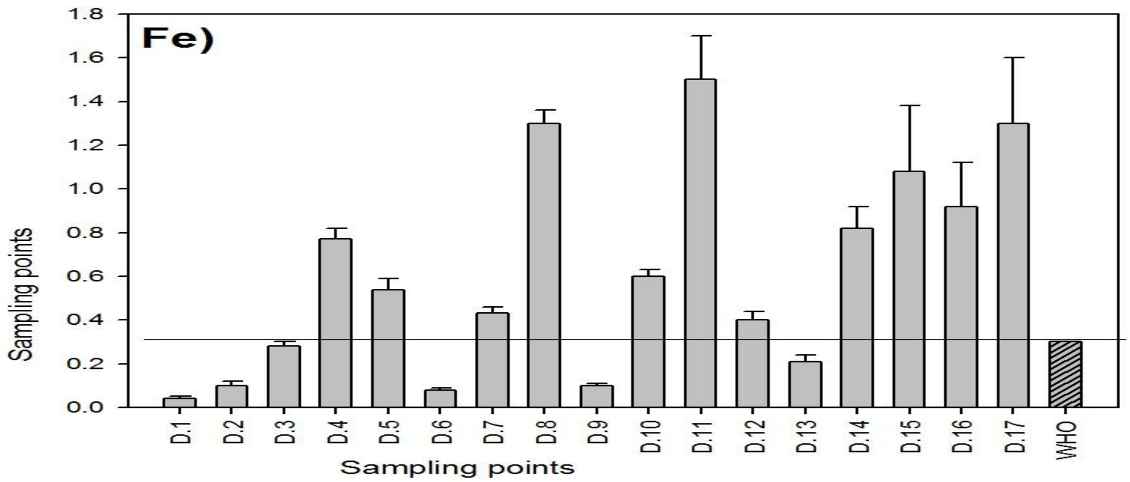

Fig.4.5(d), Mean concentration of Fe in drinking water of the study area

There was positive correlation observed between Na-Cl (r= 0.570), Na-Zn (r= 0.501), K-Ca (r= 0.517), K-SO_4 (r= 0.547), K-NO_2 (r= 0.593), K-Cu (r= 0.582), Ca-Fe (r= 0.485), Mg-Zn (r= 0.593), Cl-Fe (r= 0.597), SO_4-Pb (r=0.597), NO_2-Pb (r= 0.590), Cr-Fe (r=0.514), Mn-Fe (r=0.581), Cd-Pb (r= 0.552), Cd-Fe (r= 0.504), Cu-Pb (r= 0.578) and Cu-Fe (r= 0.590) at $p < 0.05$. Also, highly significant positive correlation were observed between Na-K (r= 0.951), Na-Ca (r= 0.620), Na-NO_2 (r= 0.708), Na-Cr (r= 0.771), Na-Mn (r= 0.683), Na-Cu (r=0.693), Na-Pb (r= 0.869), K-Cr (r= 0.703), K-Mn (r= 0.617), K-Pb (r= 0.899), Ca-Cl (r=0.804), Ca-Cr (r= 0.735), Ca-Mn (r= 0.911), Ca-Cd (r= 0.823), Ca-Cu (r= 0.833), Ca-Pb (r= 0.686), Ca-Ni (r= 0.810) Cl-Cr (r= 0.756), Cl-Mn (r= 0.855), Cl-Cd (r= 0.740), Cl-Cu (r= 0.935), Cl-Ni (r= 0.915), Cr-Mn (r=0.847), Cr-Cd (r= 0.814), Cr-Cu (r= 0.842), Cr-Pb (r= 0.713), Cr-Ni (r= 0.715), Mn-Cd (r= 0.850), Mn-Cu (r= 0.922), Mn-Pb (r= 0.701), Mn-Ni (r= 0.850), Cd-Cu (r= 0.824), Cd-Ni (r= 0.869) and Cu-Ni (r= 8.97) at $p < 0.01$ as shown in **Table 4.3**.

Table 4.3

Correlation among the physico-chemical and heavy metals of drinking water samples of the study area

Parameters	Na^{+}	K^{+}	Ca^{+2}	Mg^{+2}	Cl^{-}	F^{-}	SO_4^{-2}	NO_3^{-}	NO_2^{-}	Cr	Mn	Cd	Zn	Cu	Pb	Ni	Fe
Na^{+}	1																
K^{+}	**0.951**	1															
Ca^{+2}	**0.620**	*0.517*	1														
Mg^{+2}	-0.022	-0.171	0.113	1													
Cl^{-}	*0.570*	0.396	**0.804**	-0.056	1												
F^{-}	-0.122	-0.014	-0.130	-0.245	-0.139	1											
SO_4^{-2}	0.432	*0.547*	0.385	-0.174	0.112	-0.035	1										
NO_3^{-}	0.105	0.127	0.192	0.331	-0.016	-0.078	0.450	1									
NO_2^{-}	**0.708**	*0.593*	0.403	0.164	0.433	-0.148	0.199	0.253	1								
Cr	**0.771**	**0.703**	**0.735**	-0.333	**0.756**	-0.087	0.342	-0.152	0.457	1							
Mn	**0.683**	**0.617**	**0.911**	-0.223	**0.855**	-0.012	0.407	-0.006	0.393	**0.847**	1						
Cd	0.459	0.406	**0.823**	-0.273	**0.740**	-0.179	0.251	-0.201	0.162	**0.814**	**0.850**	1					
Zn	*0.501*	0.377	0.394	*0.593*	0.338	-0.225	-0.009	0.359	0.290	0.200	0.250	0.053	1				
Cu	**0.693**	*0.582*	**0.833**	-0.160	**0.935**	-0.095	0.166	-0.150	0.377	**0.842**	**0.922**	**0.824**	0.328	1			
Pb	**0.869**	**0.899**	**0.686**	-0.067	0.392	-0.010	*0.597*	0.085	*0.590*	**0.713**	**0.701**	*0.552*	0.297	*0.578*	1		
Ni	0.362	0.219	**0.810**	-0.165	**0.915**	-0.083	0.047	-0.213	0.197	**0.715**	**0.850**	**0.869**	0.108	**0.897**	0.339	1	
Fe	0.409	0.399	*0.485*	-0.159	*0.597*	0-.086	0.224	0.170	0.238	0.*514*	*0.581*	*0.504*	0.341	*0.590*	0.307	0.479	1

Bold correlation is significant at the 0.05 level (2-tailed)

Italic correlation is significant at the 0.01 level (2-tailed)

4.6. Conclusion

Continuous discharge of effluents has the potential of causing deterioration of the soil and groundwater quality. Normally, during the preliminary period, the pollutants will settle in the soil and then progressively percolate to the groundwater especially in the rainy season. The groundwater flows and other hydro-geological characteristics effect the migration of pollutants in the aquifer. The values of different parameters of water which were obtained from different sources indicated that maximum parameters were above the WHO permissible limits. This indicates that the ground water of the area is highly affected by various pollutants. The major source of these pollutants is produced water which is released into the study area without treatment. High rate of contamination is observed in the down slope homes that are closed to the produced water ponds area. This shows that water sources are not protected properly in the study area. The slope nature of the land also plays a major role in the percolations of contaminants into the ground. From all the results which have been discussed above, the situation is very discouraging. If the same activity continuous in the area, ground water will be polluted and will become unfit for drinking and other purposes. Therefore, EPA should check the illegal practice of dumping of industrial effluent on land especially in residential areas; effluents must be stopped immediately and strict adherence to national environmental quality standards must be ensured.

CHAPTER-5

IMPACT ASSESSMENT OF PRODUCED WATER ON SOIL NEAR PONDS AREA OF SADQAL OIL AND GAS FIELD

Abstract

Composite soil samples were collected from east west and south different around the produced water ponds of Sadqal oil and gas field to assess the anions cations and heavy metal concentrations. Ions including Na^{+}, K^{+}, Ca^{+2}, Mg^{+2}, Cl^{-}, F^{-}, SO_4^{-2}, NO_3^{-} and NO_2^{-} were determined with the help of Ion chromatography (Metrohm, 800 series). Heavy metals concentrations like Cr, Mn, Cd, Zn, Cu, Pb, Ni and Fe were analyzed through Atomic absorption spectrophotometer (Perkin-Elmer model 700, USA). The Results were compared with reference soil sample of the study area. It was found that maximum parameters of soil samples are above the reference soil sample values. On the basis of findings, it is concluded that implementing authority should check the illegal practice of discarding industrial wastes on agriculture lands or in residential area and strictly impose national environmental quality standards.

5.1. Introduction

Soil, an important environmental medium, is exposed to a number of pollutants including toxic heavy metals by various natural and anthropogenic activities. Consequently, heavy metal contaminated soil has the potential to pose severe health risks and hazards to humans as well as other living creatures of the ecosystem through various routes of exposure such as direct ingestion, contaminated water, food crops, contact with contaminated soil and through food chain (Soodan et al., 2014). Soil pollution with heavy metals is a major threat to ecological integrity and human well-being due to discharge of untreated urban and industrial wastewater (Mahmood & Malik, 2014). Toxic metals can enter the human body by consumption of contaminated food crops, water or inhalation of dust (Cambra et al., 1999). Heavy metal accumulation in soil is one of the most serious environmental concerns of the present day. Toxic heavy metal concentrations have potential effects on human, animals and plants life. Metals are non-biodegradable and are considered major environmental pollutants resulting in cytotoxic, mutagenic and carcinogenic effects in animals (AL-Othman et al., 2011; More et al., 2003). Soils irrigated by wastewater accumulate heavy metals (Cd, Zn, Cr, Ni, Pb, and Mn) in surface soil. When the capacity of the soil to retain heavy metals is reduced due to repeated use of wastewater, soil can release heavy metals into ground water or soil solution available for plant uptake. Wastewater irrigation is known to contribute significantly to the heavy metal content of soils (Mapanda et al., 2005; Singh et al., 2004) and is causing a major potential environmental risk (Chary et al., 2008). Uncontrolled heavy metal input to soils is undesirable, because once accumulated, it is extremely difficult to remove these metals. This situation may subsequently lead to i) toxicity to plants grown on contaminated soils, ii) absorption by crops resulting in heavy metals in plant tissues which may be harmful to the health of humans or animals, and iii) transport from soils to groundwater or surface water (Murtaza et al., 2010). Heavy metal contamination of soil resulting from wastewater irrigation is a cause of serious concern due to the potential health impacts of consuming contaminated produce. Sharma et al. (2007) concluded that the use of treated and untreated wastewater for irrigation has increased the contamination of Cd, Pb, and Ni in edible portion of vegetables causing potential health risk in the long term from this practice. Industrialization and poor environmental management in developing countries like Pakistan have increased the environmental problems. Industrial wastes and chemicals in the terrestrial environment clearly pose a significant risk to the quality of soils, plants, natural waters and human health. The main objective of the study was to assess the levels of soil contamination in produced water ponds area of Sadqal oil and gas field.

5.2. Materials and methods

5.2.1. Study area

In the Punjab, Fateh Jang is a town and the tehsil headquarters of Attock district, study area shown in **Fig.5**.1. The detail is given in chapter 1 section 1.2.

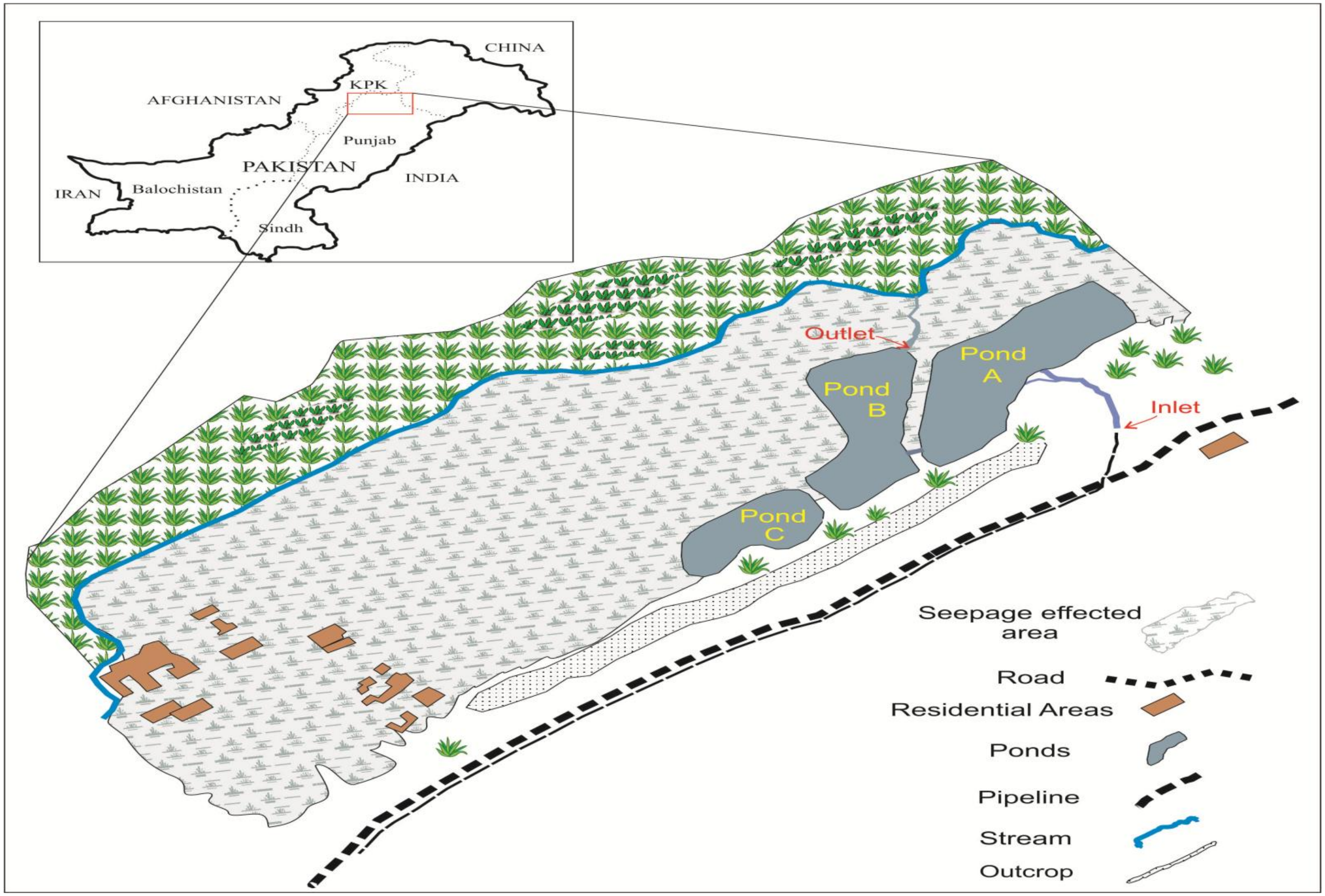

Fig.5.1 Location map of the study area

5.2.2. Soil samples collection

About one kilogram from each point, sixteen (16) composite soil samples were collected in self-locking polythene bags from produced water ponds area at various distances i.e. 0, 30, 60, 90, 120-meters in different directions (East, West and South) from the top soil i.e. 0-20 cm depth in order to analyze the impacts of wastewater effluents on surrounding land. A monolith of 10 ×10 × 20 cm was dug for the collection of soil.

Metal tools were avoided and a plastic spatula was used for sample collection to prevent from further contamination. Soil samples were air-dried and organic matter was removed. Each sample was homogenized and then representative portion was selected by quartering and coning. This portion was then used for further analysis, the dried soil samples were mechanically ground to obtain less than 2mm particle size. The powered samples were stored in air tight bottles and kept in an oven at 1100 °C for two hours to remove the moisture.

5.3. Analysis of anions and cations

Soil samples (0.5 g) were mixed with 100 mL of deionized water. This mixture was shaken vigorously and then filtered through a 0.45µm Millipore filter paper. Further, these soil samples were analyzed by Ion chromatography, their specification and other details are given in section chapter 3 and section 3.3.1.

5.4. Analysis of heavy metals

By using standard method, a known amount (0.5g) of well-mixed soil sample (representative) was taken in a glass tube for digestion with HCl and HNO_3 and was heated so that a transparent solution was obtained. The solution was filtered through Whatman's 0.45μm filter paper and the solution was diluted to 50 mL with distilled water. The concentrations of heavy metals (Cd, Cr, Cu, Mn, Ni, Pb, Zn and Fe) in filtrate of soil samples were determined with an atomic absorption spectrophotometer (Perkin-Elmer model 700, USA). Instrument specification and their details study are given in chapter 3 and section 3.8.3.

5.5. Results and discussion

5.5.1 Anions cations properties of soil

In **Table 5.1**, it is shown that concentration of cations and anions in soils samples at various distance (0, 30, 60, 90, 120 meters) from ponds to southern side i.e. Na^+ ranged from 4020±3 to 7870±5 mg/kg, the concentration is found to be very high as compared to the reference soil. In **Table 5.1,** concentration of K^+ ranged from 115±2.00 to 255±2.00 mg/kg, which is found to be above from the reference soil. Ca^{+2} concentrations, ranged from 6727±5.00 to 11122±9.00 mg/kg and Mg^{+2} from 170±1.00 to 234±1.00 mg/kg. Concentration of Cl^- ranged from 5980±5.00 to 6397±5.00 mg/kg, F^- from 0.5±0.01 to 0.88±0.01 mg/kg, SO_4^{-2} from 5.9±0.50 to 11.36±1.20 mg/kg, NO_3^- 78±1.00 to 115±1.00 mg/kg and NO_2^- from 1±0.01 to 3±0.50 mg/kg.

Similarly, the same distance to eastern side, concentration of Na^+ ranged from 5690±5.00 to 6714±3.00 mg/kg, K^+ from 211±1.00 to 277±1.00 mg/kg and Ca^{+2} from 5783±3.00 to 9293±2.00 mg/kg. Concentration of Mg^{+2} ranged from 223±1.00 to 280±2.00 mg/kg. Compare to the reference soil concentration of Cl^- are very high which indicate the impacts of produced water on soil. The concentration of Cl^-, are ranged from 4585±5.00 to 5304±5.00 mg/kg. Similarly, concentration of F^- ranged from 0.37±0.02 to 2.4±0.02 mg/kg. SO_4^{-2} ranged from 6±0.40 to 15±0.70 mg/kg, NO_3^- from 179±3.00 to 220±1.00 mg/kg and NO_2^- from 2.6±0.02 to 4±0.50 mg/kg.

To western side, concentration of cations and anions in soils samples at distance (0, 30, 60, 90, 120 meter) from ponds to western side i.e. Na^+ ranged from 4130±4.00 to 7100±4.00 mg/kg, K^+ from 243±1.00 to 312±1.00 mg/kg, Ca^{+2} from 6200±2.00 to 11045±7.00 mg/kg, Mg^{+2} from 296±1.00 to 3.2±0.20 mg/kg, Cl^- from 5020±4.00 to 7350±5.00 mg/kg, F^- from 0.42±0.02 to 3.2±0.1 mg/kg, SO_4^{-2} from 7.4±0.30 to 18±1.00 mg/kg, NO_3^- from 311±2.00 to 345±1.00 mg/kg and NO_2^- from 2.8±0.01 to 5±0.30 mg/kg as displayed in **Table 5.1**. Chromatogram (**Annexure-v)** shows the concentration of cations in soil sample of the study area**.**

Table 5.1

Mean concentration of Cations and anions in soil near ponds area, Sadqal oil and gas field Fateh jang, Punjab Pakistan

Sampling Area	Depth (cm)	Distance	**Concentration (mg/L)**								
			Na^+	K^+	Ca^{+2}	Mg^{+2}	Cl^-	F^-	SO_4^{-2}	NO_3^-	NO_2^-
Southern side	0-20	0-Meter	7870±2.00	255±1.00	11122±9.00	234±1.00	6397±5.00	0.88±0.01	11 ±1.20	115±1.00	3±0.50
		30-M	7200±3.00	235±1.00	9623±3.00	220±2.00	6289±5.00	0.52±0.02	6.9±0.50	118±2.00	2±0.10
		60-M	5800±2.00	213±2.00	8345±4.00	212±1.00	6191±4.00	0.41±0.01	5.9±0.50	105±1.00	1.5±0.05
		90-M	4780±2.00	141±1.00	7453±3.00	203±2.00	6075±3.00	0.5±0.01	7.4±0.80	95±2.00	1±0.01
		120-M	4020±3.00	115±2.00	6727±5.00	170±1.00	5980±5.00	0.5±0.01	7.7±0.50	78±1.00	1.6±0.04
Eastern side	0-20	0-Meter	6714±3.00	277±1.00	9293±2.00	280±2.00	5304±5.00	2.4±0.02	15±0.70	220±1.00	4±0.50
		30-M	6500±2.70	244±2.00	7654±1.00	250±1.00	5194±5.00	0.5±0.01	6±0.40	212±3.00	2.6±0.02
		60-M	5428±4.00	235±1.00	6402±3.00	245±1.00	4980±3.00	1.8±0.02	8.8±0.50	215±1.00	2.9±0.10
		90-M	5750±3.00	224±1.00	6237±2.00	233±2.00	4773±4.00	1.8±0.01	8.6±0.80	201±2.00	3±0.20
		120-M	5690±5.00	211±1.00	5783±3.00	223±1.00	4585±5.00	0.37±0.02	8.4±0.50	179±3.00	2.8±0.50
Western side	0-20	0-Meter	7100±4.00	312±1.00	11045±2.00	342±2.00	7350±5.00	3.2±0.01	18±1.00	345±1.00	5±0.30
		30-M	6800±4.00	286±2.00	8454±5.00	321±2.00	7145±4.00	0.61±0.02	7.8±0.50	326±1.00	3±0.20
		60-M	6245±3.00	261±1.00	7894±2.00	318±2.00	6930±5.00	1.3±0.01	9.1±0.50	311±2.00	3.4±0.10
		90-M	4500±3.00	274±1.00	6890±3.00	302±1.00	5505±3.00	0.42±0.02	7.5±0.50	315±3.00	2.8±0.01
		120-M	4130±4.00	243±1.00	6200±2.00	296±1.00	5020±4.00	0.71±0.01	7.4±0.30	316±2.00	3.2±0.05
Reference Soil	0-20	5 km	700±3.00	115±2.00	850±1.00	120±1.00	250±3.00	0.4±0.01	2.7±0.20	90±1.00	1.8±0.05

Reference soil samples, which were collected five (5) kilo meter away from the PW ponds, were analysed and the results were compared. It was found that the values of contaminated soils were higher than reference soil, as shown in **Fig.5.2** (**a, b, c, d, e, f, g & h**).

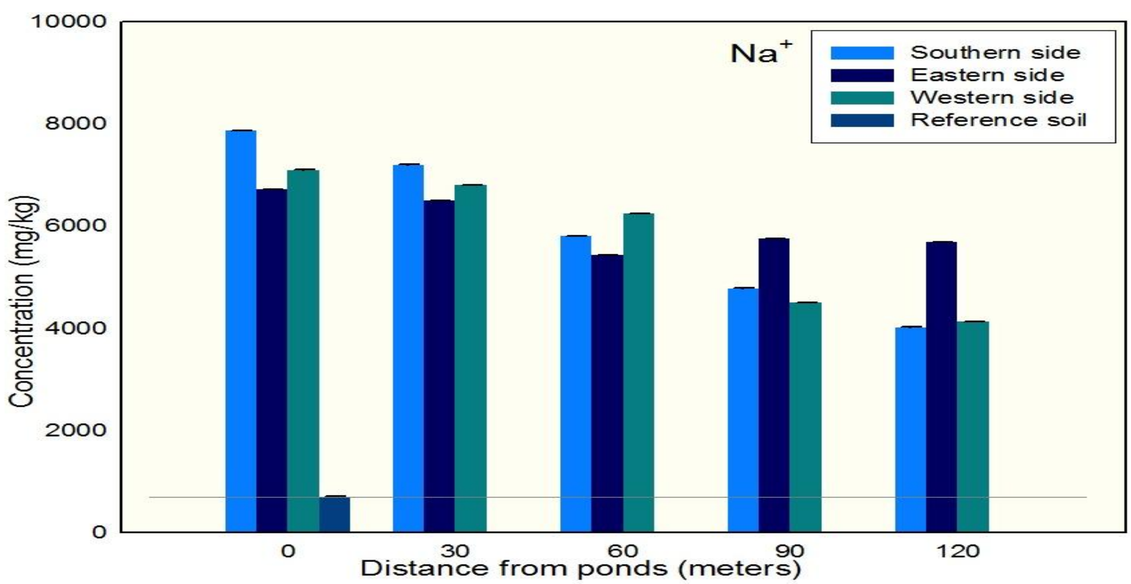

Fig.5.2 (a), Mean concentration of Na in soil samples of the study area

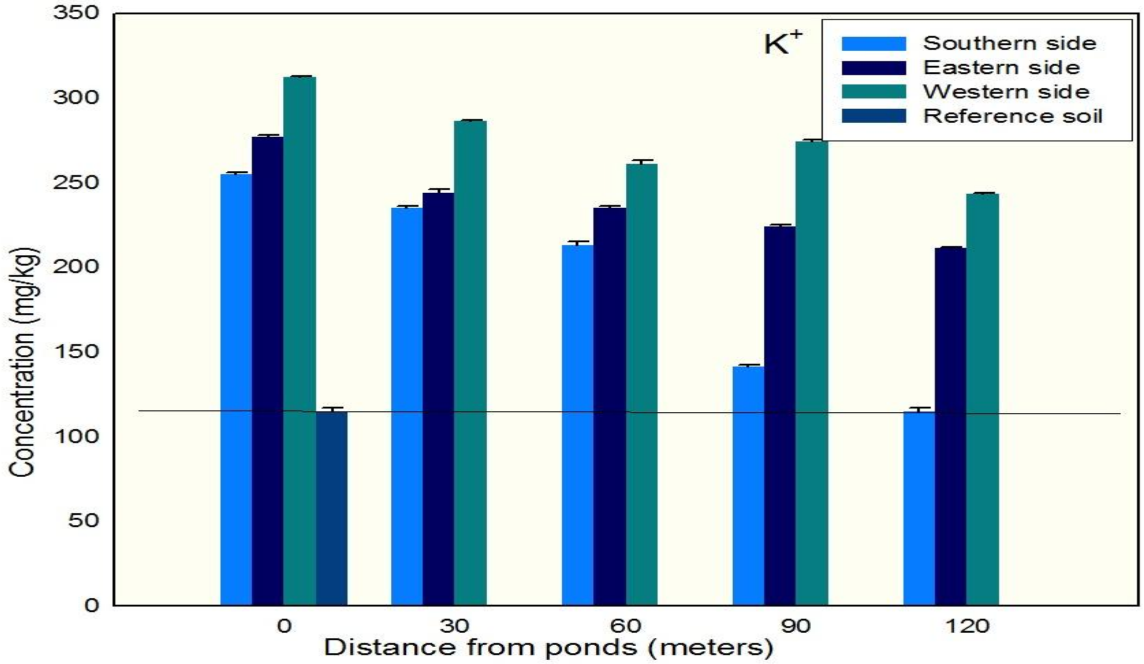

Fig.5.2 (b), Mean concentration of K in soil samples of the study area

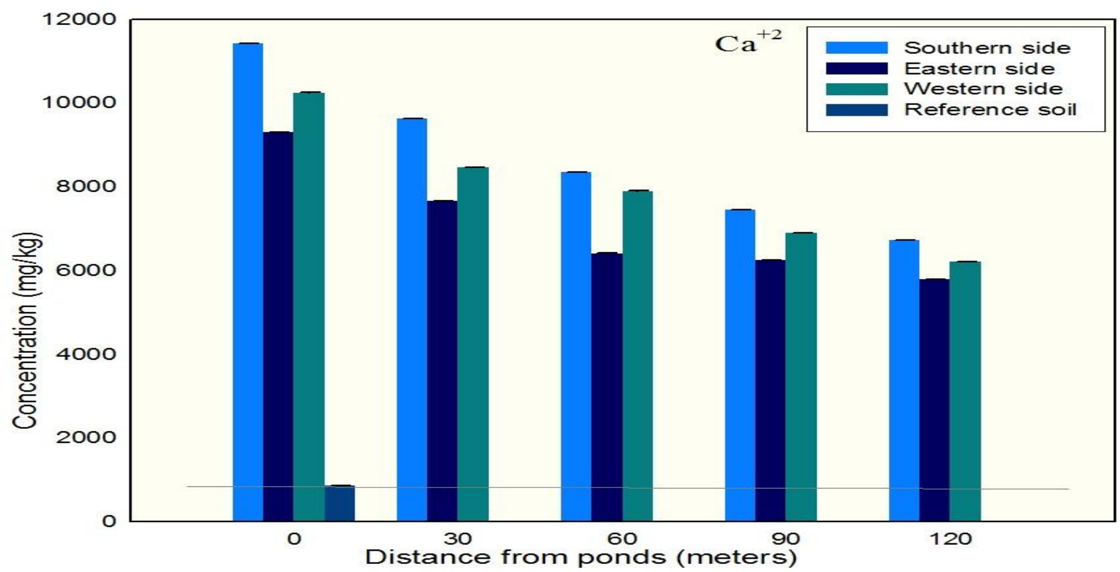

Fig.5.2 (c), Mean concentration of Ca in soil samples of the study area

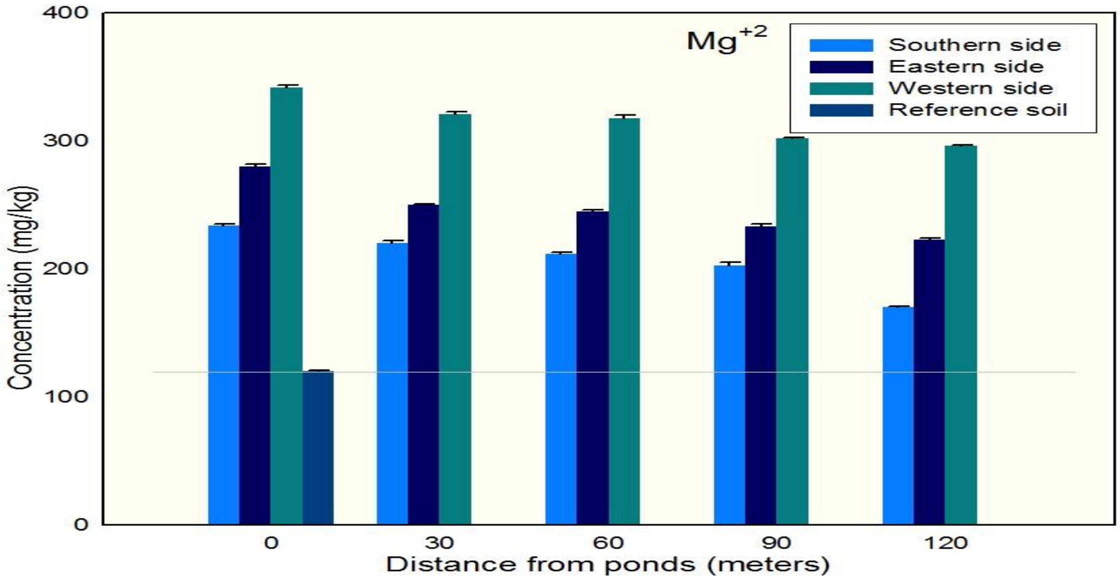

Fig.5.2 (d), Mean concentration of Mg in soil samples of the study area

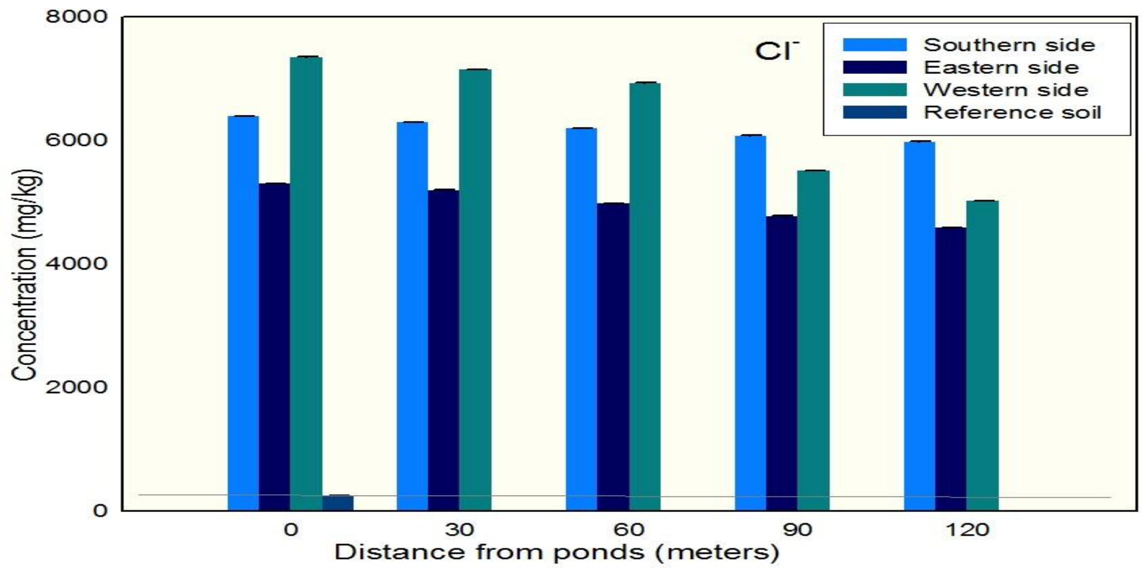

Fig.5.2 (e), Mean concentration of Cl in soil samples of the study area

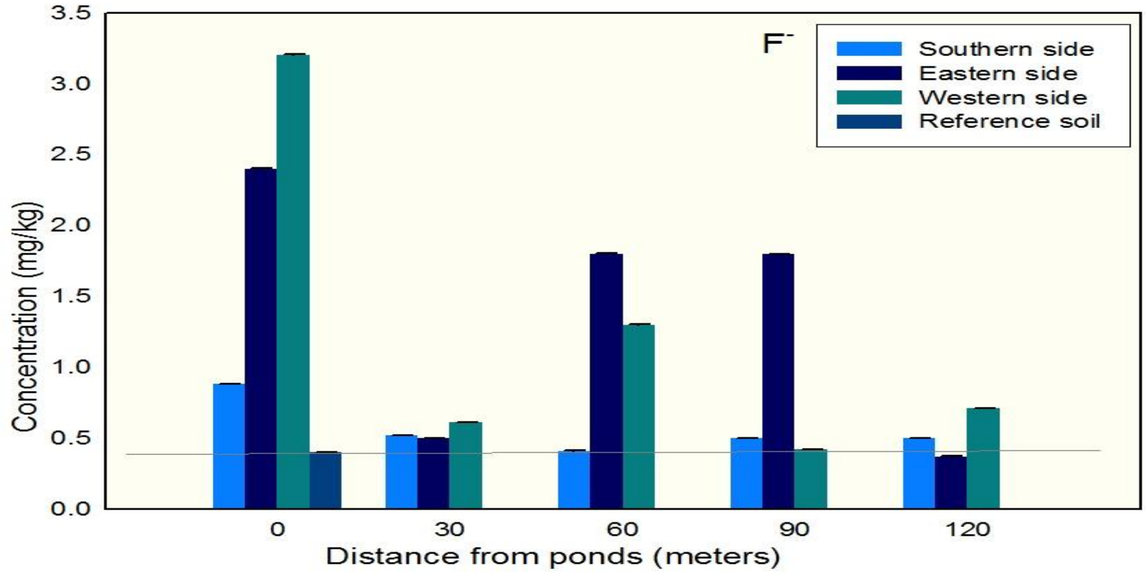

Fig.5.2 (f), Mean concentration of F in soil samples of the study area

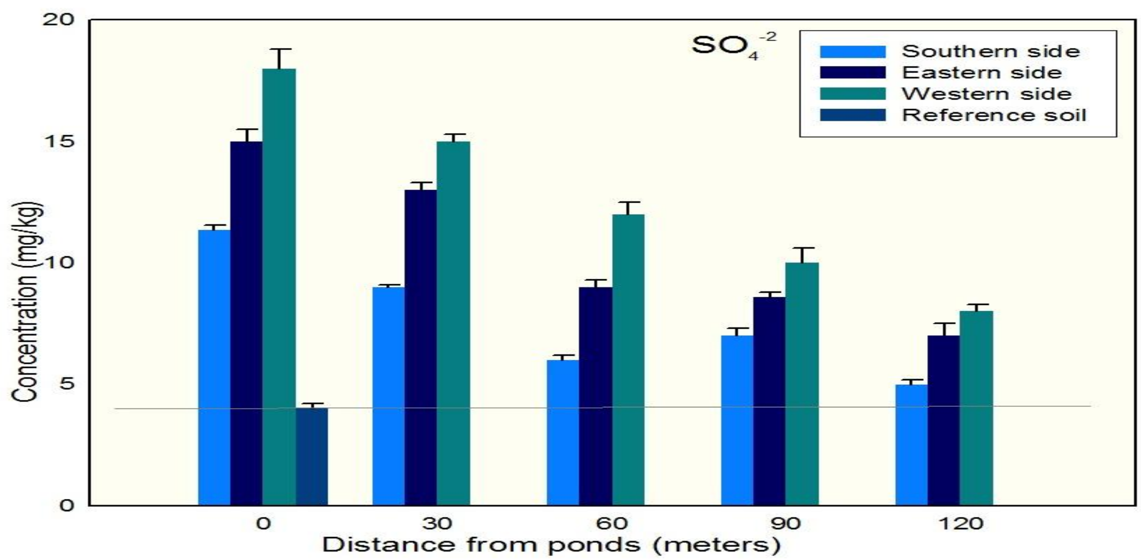

Fig.5.2 (g), Mean concentration of SO_4 in soil samples of the study area

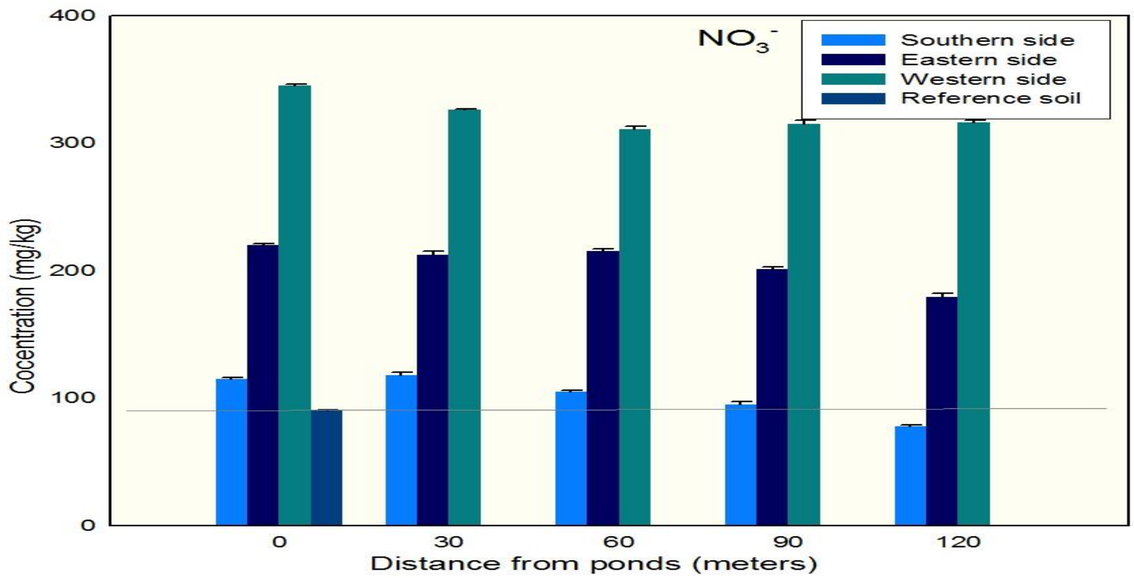

Fig.5.2 (h), Mean concentration of NO_3 in soil samples of the study area

5.5.2 Heavy metals concentration in soil

The results of heavy metal contents in soil are displayed in **Table 5.2**. The results showed that heavy metals are present in considerable amount in the soil. This is due to the wide range of chemicals containing heavy metals being discharged into the environment as a result of petroleum exploration and production activities.

It is shown that concentration of heavy metals in soils samples at distance (0, 30, 60, 90, 120 meter) from ponds to southern side vary greatly. Cr concentrations ranged from 4±1.8 to 6.8±2.2 mg/k. Mn from 17±3 to 27±6 mg/kg, Cd from 0.01±0.001 to 0.05±0.001 mg/kg, Zn from 7±1.5 to 24±3 mg/kg, Cu from 1.8±.5 to 12±1.8 mg/kg, Pb from 2.9±0.5 to 19±3 mg/kg, Ni from 2.2±0.5 to 4.2±1 mg/kg and Fe from 59±12 to 78±14 mg/kg as displayed in **Table 5.2.**

To eastern side, concentration of Cr ranged from 2.9±1 to 5.1±2.5 mg/kg, Mn from 18±3 to 30±5 mg/kg, Cd from 0.01±0.001 to 0.08±0.002 mg/kg and Zn from 5±1 to 17±2 mg/kg. Concentration of Cu ranged from 1.5±0.01 to 13±1.3 mg/kg, Pb from 4.2±0.8 to 16±1.4 mg/kg, Ni from 3.1±0.5 to 6.2±1 mg/kg and Fe from 50±8 to 75±12 mg/kg as displayed in **Table 5.2.**

Similarly, the same distance to western side, Cr ranged from 3±1 to 4±1.4 mg/kg, Mn from 14±3 to 41±11 mg/kg, Cd from 0.01±0.001 to 0.07±0.001 mg/kg, Zn from 4±0. 6 to 14±1.2 mg/kg, Cu from 1.8±0.1 to 16±1.6 mg/kg, Pb from 2.2±0.04 to 3.7±0.7 mg/kg, Ni from 2.2±0.4 to 4.8±0.7 mg/kg and Fe ranged from 43±8 to 83±15 mg/kg as displayed in **Table 5.2.**

The results of the contaminated soils collected from different direction were compared with the reference soil, which were collected five (5) kilo meter away from the study area. It was found that most of the heavy metals concentrations are above the limits of the reference soil, shown in **Fig.5.3** (**a, b, c, d, e, f, g & h**).

Chromatogram (**Annexure-vi**) shows the concentration of anions in soil sample of the study area.

Table 5.2

Mean concentration of heavy metals in soil near ponds area, Sadqal oil and gas field Fateh jang, Punjab Pakistan

Sampling Area	Depth (cm)	Concentration (mg/L)								
		Distance	**Cr**	**Mn**	**Cd**	**Zn**	**Cu**	**Pb**	**Ni**	**Fe**
Southern side	0-20	0-Meter	6.8±2.200	21±5. 000	0.05±0.001	24±3.000	12±1.800	19±3.000	4.2±1.000	78±14.000
		30-M	6±2.100	27±6. 000	0.03±0.002	18±3.000	11±1.500	12±1.500	3.2±0.500	74±13.000
		60-M	5.6±2.000	20±4.000	0.02±0.001	12±2.000	5±1.000	15±1.600	2.2±0.500	72±12.000
		90-M	4±1.800	17±3.000	0.01±0.001	7±1.500	1.8±0.500	2.9±0.500	3.7±0.700	59±12.000
		120-M	4.1±1.900	23±4.000	0.01±0.001	9±1.200	2±0.500	3.1±0.500	3.5±0.600	61±11.000
Eastern side	0-20	0-Meter	5±3.000	30±5.000	0.08±0.002	17±2.000	13±1.300	16±1.400	6.2±1.000	75±12.000
		30-M	5.1±2.500	23±4.000	0.04±0.001	9±1.200	12±1.200	11±1.500	5.4±0.800	65±11.000
		60-M	3.2±2.000	25±4.000	0.025±0.001	6±1.000	6±1.000	4.2±0.800	3.2±0.600	67±11.000
		90-M	2.9±1.000	18±3.000	0.01±0.001	5±1.000	1.5±0.010	4.9±0.800	3.1±0.500	50±8.000
		120-M	2.4±1.000	16±2.000	0.01±0.002	5±1.000	1.5±0.010	5.6±1.000	2.8±0.500	60±9.000
Western side	0-20	0-Meter	3.7±1.200	41±11.000	0.07±0.001	14±1.200	16±1.600	3±0.500	4.8±0.700	83±15.000
		30-M	3.6±1.200	30±6.000	0.03±0.001	10±1.200	15±1.000	3.7±0.700	3.3±0.500	77±12.000
		60-M	4±1.400	24±4.000	0.01±0.002	7±1.000	11±1.300	3±0.400	3.4±0.500	73±11.000
		90-M	3.2±1.000	14±3.000	0.02±0.001	5±1.000	5±1.000	2.8±0.400	2.2±0.400	71±11.000
		120-M	3±1.000	15±3.000	0.01±0.001	4±0.600	1.8±0.100	2.2±0.300	4±0.900	43±8.000
Reference Soil	0-20	5 km	2.2±0.800	13±2.500	0.001±0.001	13±1.000	8.5±1.000	2.1±0.300	2.9±0.800	23±3.000

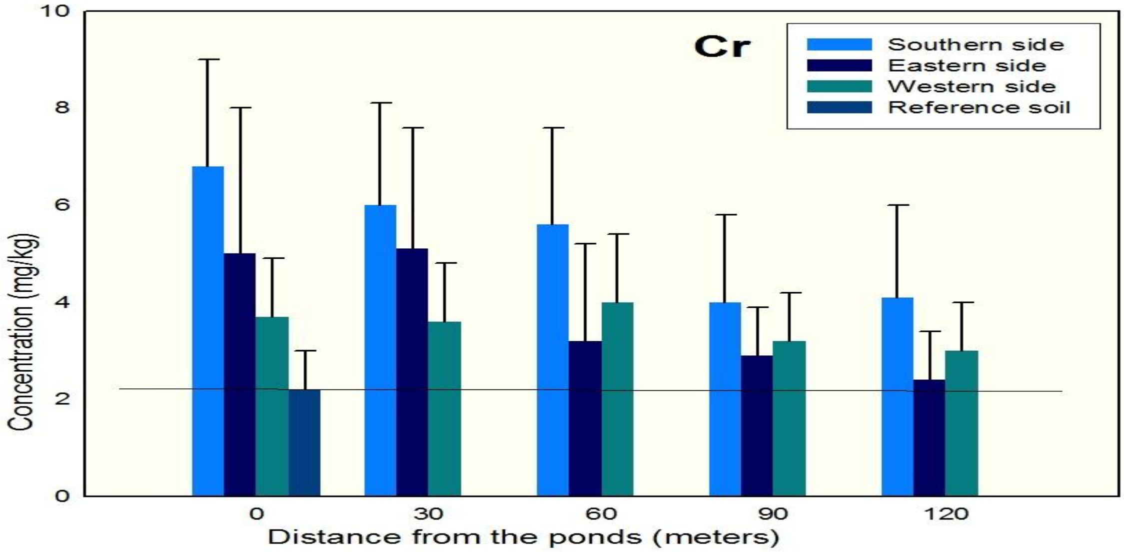

Fig.5.3 (a), Mean concentration of Cr in soil samples of the study area

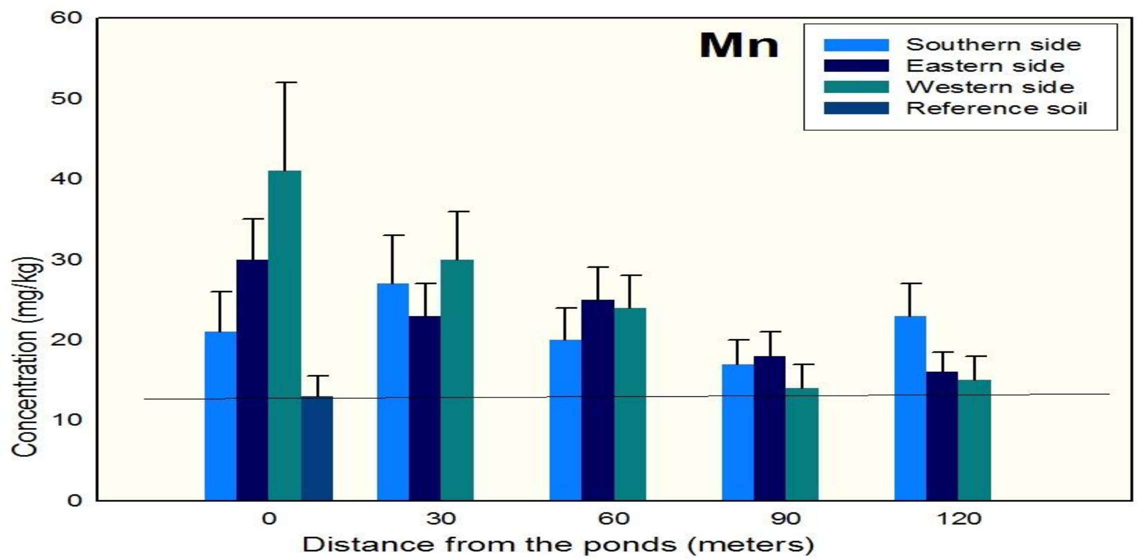

Fig.5.3 (b), Mean concentration of Mn in soil samples of the study area

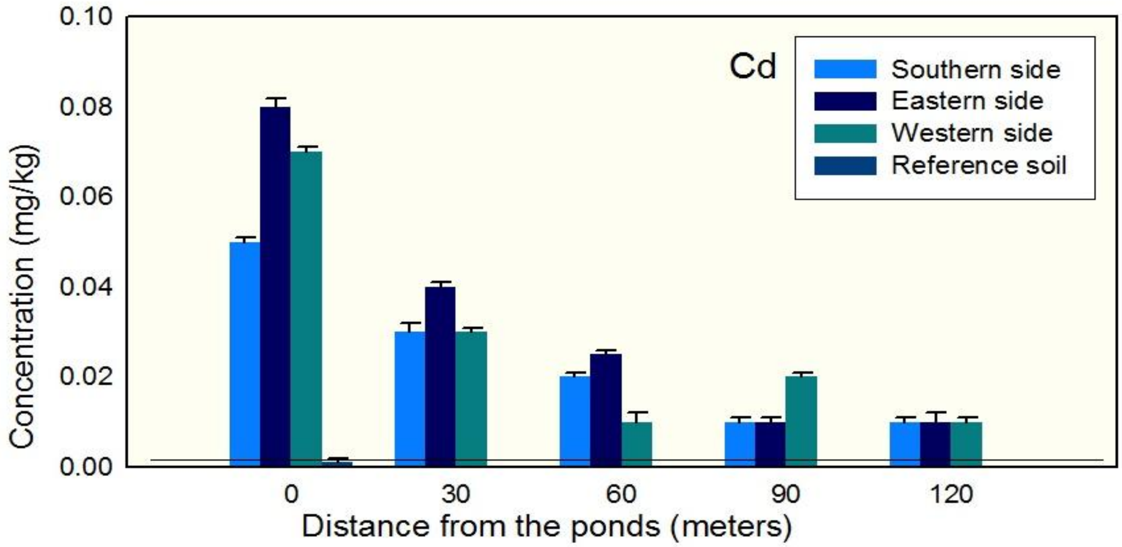

Fig.5.3 (c), Mean concentration of Cd in soil samples of the study area

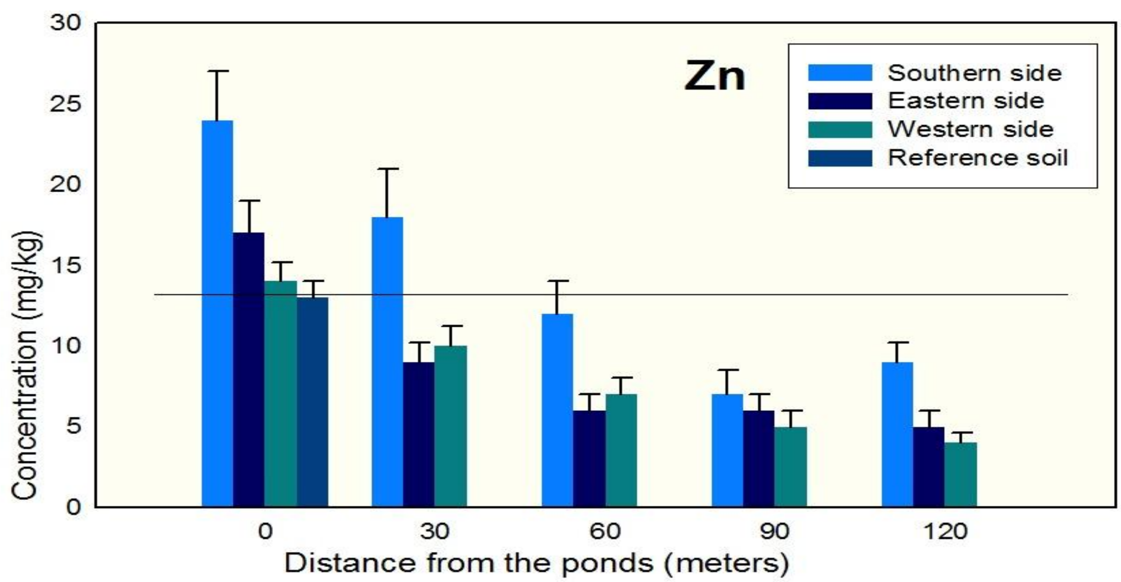

Fig.5.3 (d), Mean concentration of Zn in soil samples of the study area

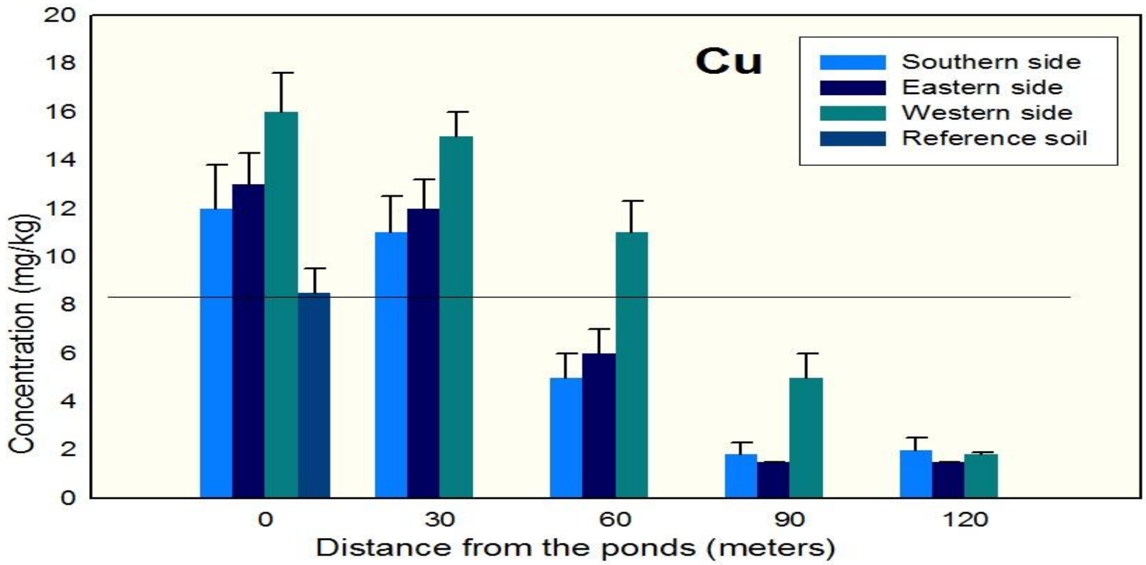

Fig.5.3 (e), Mean concentration of Cu in soil samples of the study area

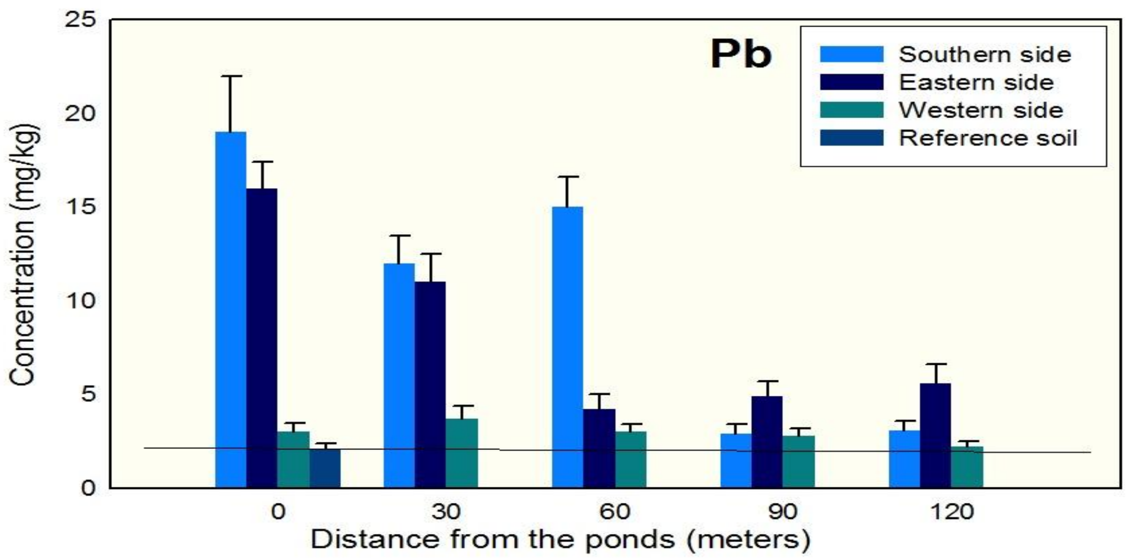

Fig.5.3 (f), Mean concentration of Pb in soil samples of the study area

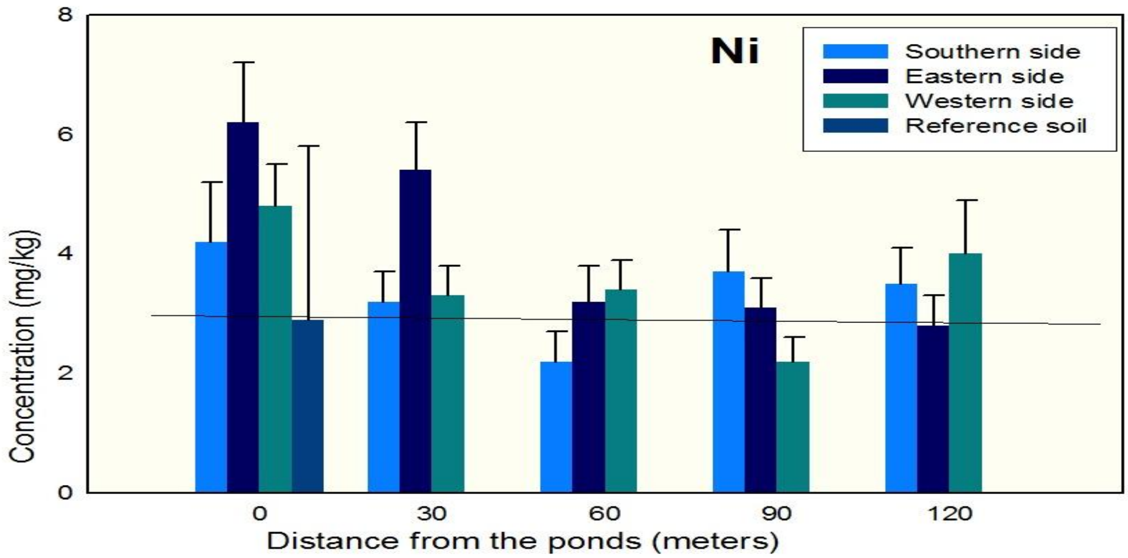

Fig.5.3 (g), Mean concentration of Ni in soil samples of the study area

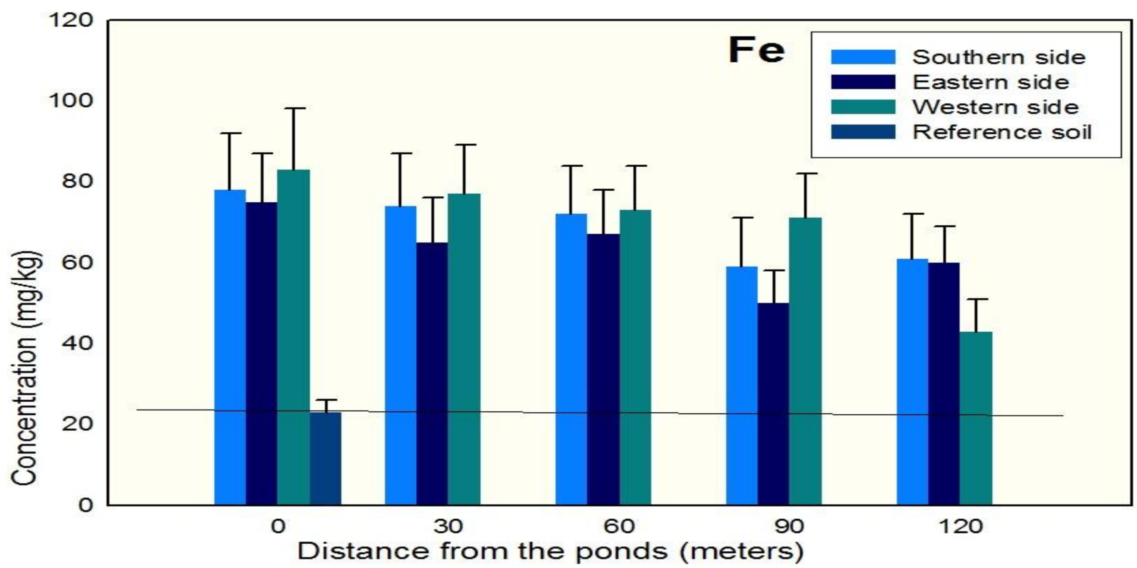

Fig.5.3 (i), Mean concentration of Fe in soil samples of the study area

5.6 Significance of the results

Data collected from the soils samples analyses were compare with the reference soil. This indicated that anions, cations and some HMs present above the reference soil sample result. While, for different parts of the plant growth, some metals are considered to be of vital importance but if there concentration increase their toxicity is also increased and cause harmful effects. For example if Zn concentration levels in the soil become higher the crops production on such lands may be suffer from leaves and slow down their growth. Similarly increased concentration of Cu affected grey node symptoms on plant grown on cultivated lands. Other ions like Na, if the amount is increases in soil it can causes different problems in cultivation lands, particularly disturb the soil structure and damage to plants. After land structures degradation, further it decrease the infiltration and hydraulic conductivity of the soil (Bagarello et al., 2006; Tarchitzky et al., 1999). It disturbs the movement of water through a soil profile and across the landscape. (Coppola et al., 2004). The concentration of anions, cations and heavy metals in produced water are high, long-term seepage from the ponds often results in the build-up of the raised levels in soils, as reported in (Rattan et al., 2002).

Soil is not only a medium for plants to grow or a place to dispose of unwanted constituents, but also a receiver of many pollutants to water, groundwater, atmosphere and food. Therefore, accumulate pollutants in surface soils can be transported to different environmental components. The Pak-EPA is not able to implement the National Environmental Quality Standards (NEQS) successfully for various reasons, due to absence of implementation capacity, conflict from industrial and other business activities. A strong environmental policy is essential for mitigating the potential adverse consequences of industrialization.

5.7 Conclusions

There is a strong need to treat wastewater at the source. Moreover it is possible that there is some modern method to make the waste water reusable for alternate activities, which is commonly practiced in Europe and America. Being a developing and third world country such practices are valuable to reduce the harmful effects of such a valued activity. Thus appropriate measures regarding waste water are needed like effect of wastewater and heavy metals on human beings should be taken through media, printing of posters, calendars, newsletters and leaflets. A well-coordinated program seems necessary to create awareness among different sections of the society like the general public, industrialist and farmers, because one of the major challenges in safeguarding the natural environment is the lack of interest in the subject in communities, where activities that have a detrimental impact.

CHAPTER-6

CONCLUSIONS AND RECOMMENDATIONS

The physico-chemical parameters of wastewater of Sadqal oil and gas field were studied and found that pH and temperature are with in maximum permissible limits of Pak-EPA. TDS, BOD, COD, F^-, Cl^-, SO_4^{-2}, oil and grease were noted above maximum permissible limits of Pak-EPA. Conductivity, hardness, Na^+, K^+, Ca^{+2}, Mg^{+2}, and NO_3^- values were found to be very high but permissible limits are not mentioned in Pak-EPA. Similarly, heavy metals concentration were also studied in wastewater and noted that levels of Cr, Mn, Pb, Ni and Fe were above the permissible limits of Pak-EPA. It is concluded that the wastewater which are released in Sadqal residential area without any treatment is high polluted and may have an impact on surrounding environment.

In Sadqal oil and gas field area, drinking water samples were collected and studied for various parameters. Anions cations including Na^+, K^+, Ca^{+2}, Mg^{+2}, Cl^-, F^-, SO_4^{-2}, NO_3^- and NO_2^- also HMs including Cr, Mn, Cd, Zn, Cu, Pb, Ni and Fe were analyzed. The values of different parameters indicated that maximum parameters of anions, cations and HMs concentration were above the WHO permissible limits. This indicated that the ground water of the area, where wastewater is released into the ponds is highly affected by various pollutants. High rate of contamination is observed in the down slope homes that are closed to the wastewater ponds area. This showed that water source is not protected properly from wastewaters. The slope nature of the land also plays a major role in the percolations of contaminants into the ground. From all the results it is concluded that the ground water in exploration and production area, especially near ponds is high impacted by wastewater because continuously seepages occurs to due mismanagement.

Soil samples around the ponds area at different locations were collected and analysed. Anions cations including Na^+, K^+, Ca^{+2}, Mg^{+2}, Cl^-, F^-, SO_4^{-2}, NO_3^-, NO_2^- also HMs including Cr, Mn, Cd, Zn, Cu, Pb, Ni and Fe were investigated. The values were compared with reference soil sample. It was found that maximum parameters of soil samples of the study area were above the reference soil which showed the impacts of wastewater on nearby soils.

For the improvement of existing situations, the following are recommendations.

1. Wastewater of the exploration and production should be treated before releasing into streams or other location where infiltration may occur.
2. Ponds walls should be cemented and covered with high density polyethylene, to prevent the seepages outside in order to decrease the impacts of wastewater on surrounding environment.
3. The study exposed that EPA should have continuous pollution monitoring program to monitor the exploration and production wastewater regularly.
4. EPA should check the illegal practice of dumping of industrial effluent on land especially in residential area, effluents must be stopped immediately and strictly impose national environmental quality standards.

5. A further research should be conducted on wastewater of exploration and production in Pakistan to analyze the evidence of impacts on surrounding environment.

6. The OGDCL may be inquired to establish better wastewater treatment plants and water storage ponds, so that the level of anions cations and heavy metals wastewater could be minimized before its discharge in to surrounding environment.
7. To protect human health and the environment, Public should be made aware of the dangers of wastewater pollution through media, printing of posters, calendars, newsletters and leaflets, Otherwise, the petroleum industry will continue to dispose of oil field waste that can pollute soils and groundwater.
8. Environmentalist and people generally give blame to the oil companies so Federal Government should provide the laws, legislations and proper licensing, which the oil companies must obey too.

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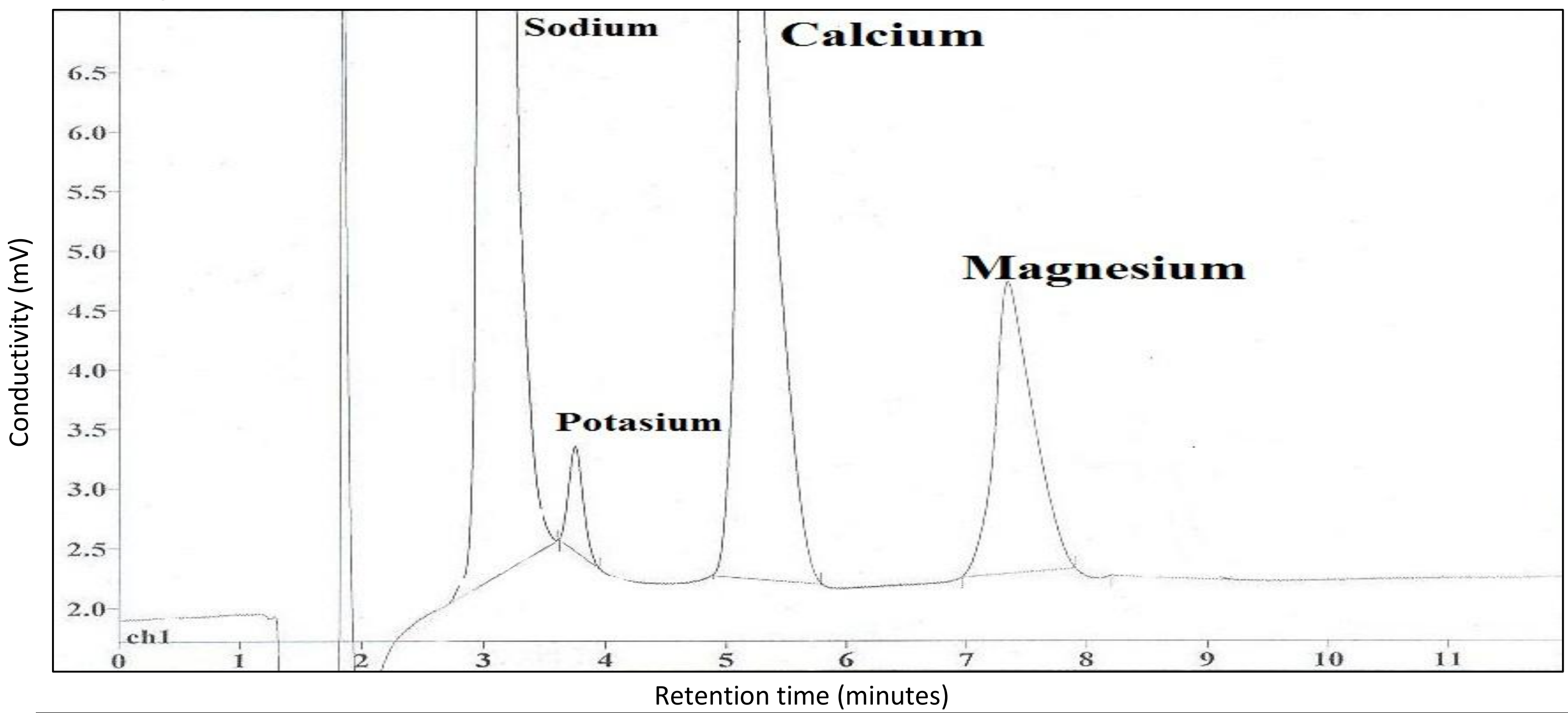
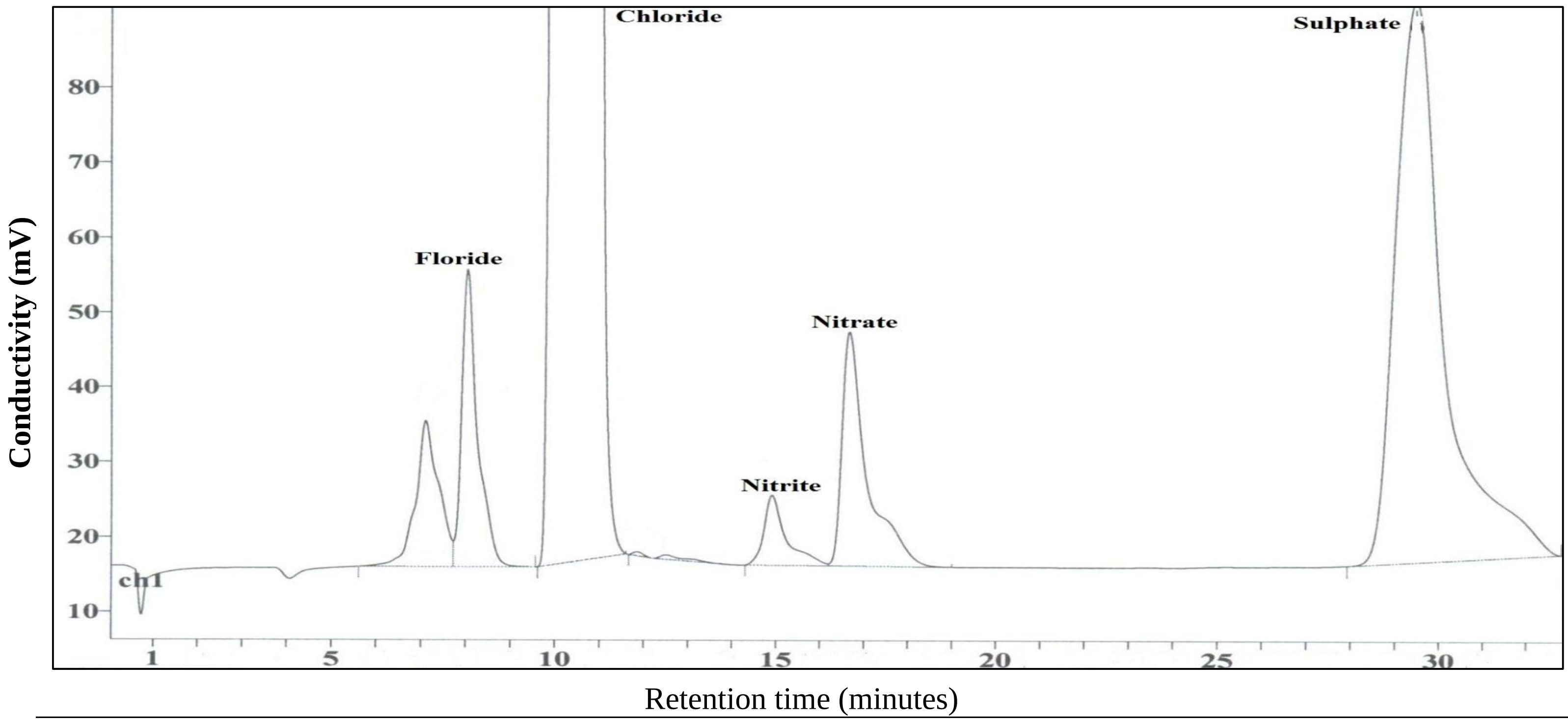
ANNEXURE-I



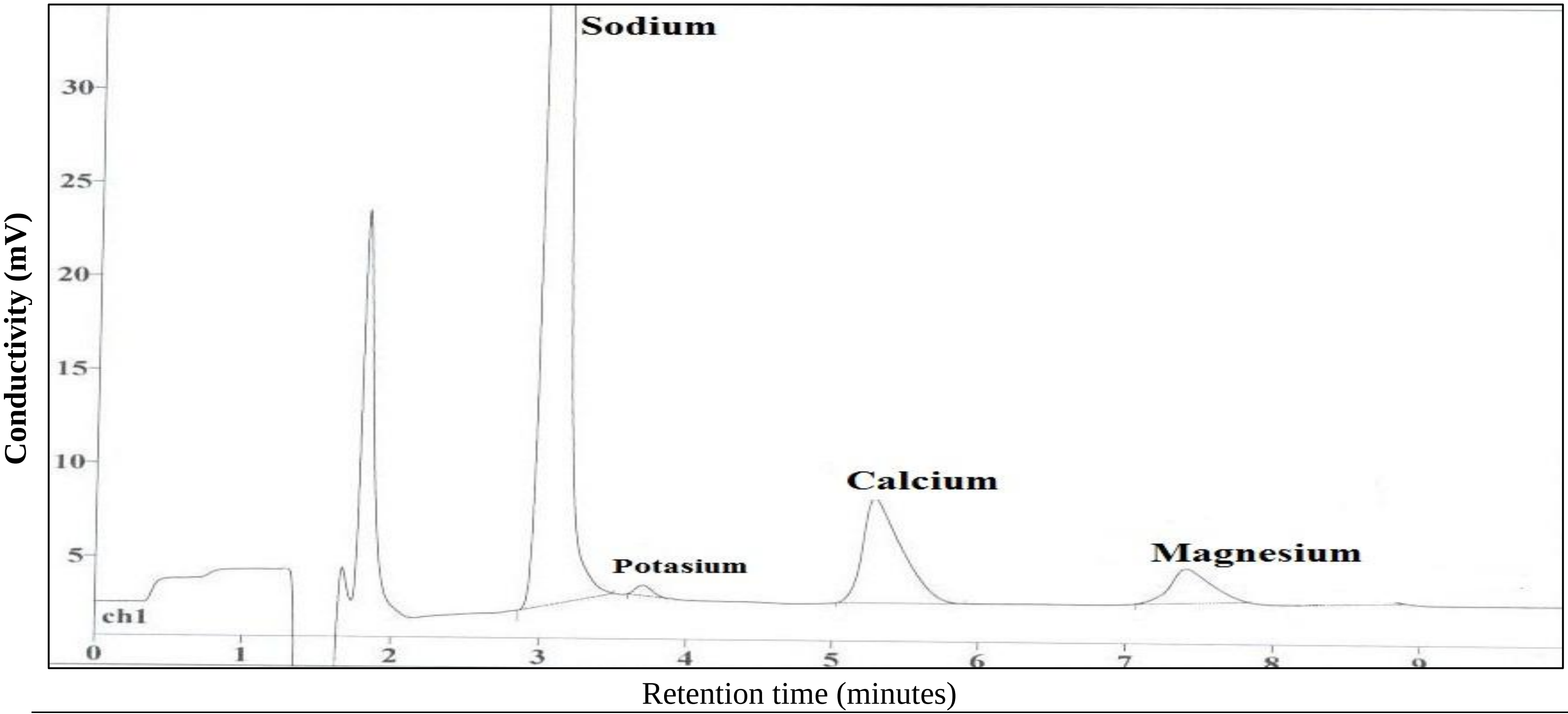
Chromatogram shows the concentration of cations in wastewater sample of the study area.

ANNEXURE-II



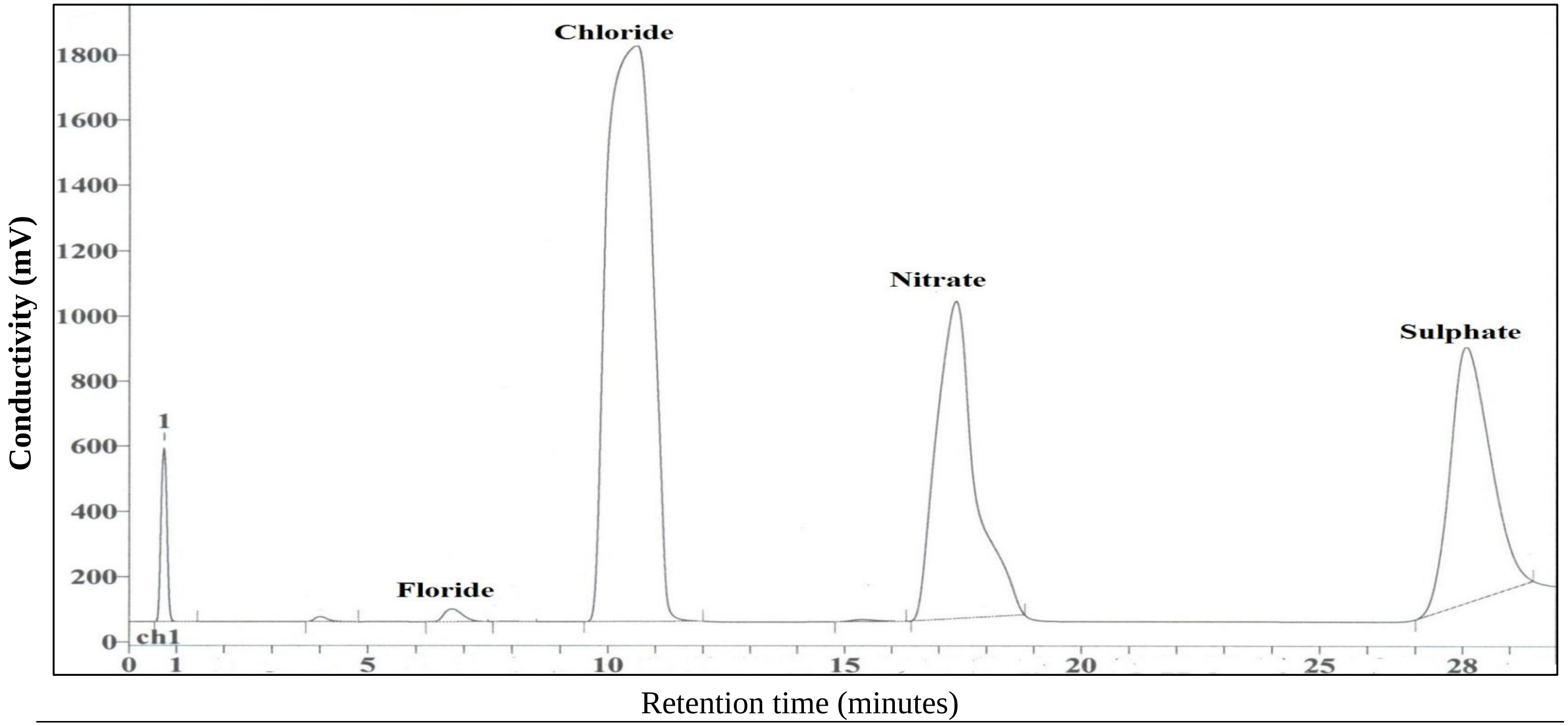
Chromatogram shows the concentration of anions in wastewater sample of the study area.

ANNEXURE-III



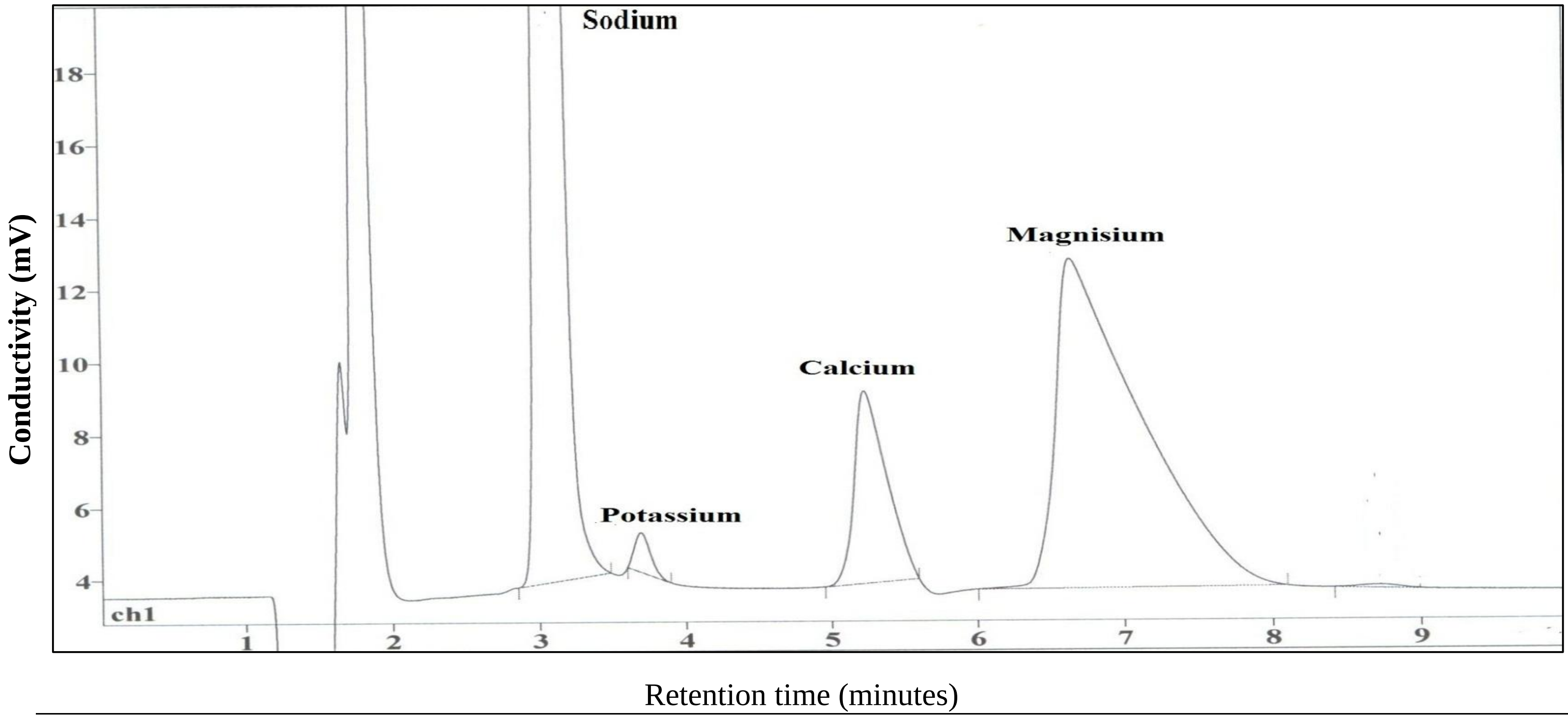
Chromatogram shows the concentration of cations in drinking water sample of the study area.

ANNEXURE-IV



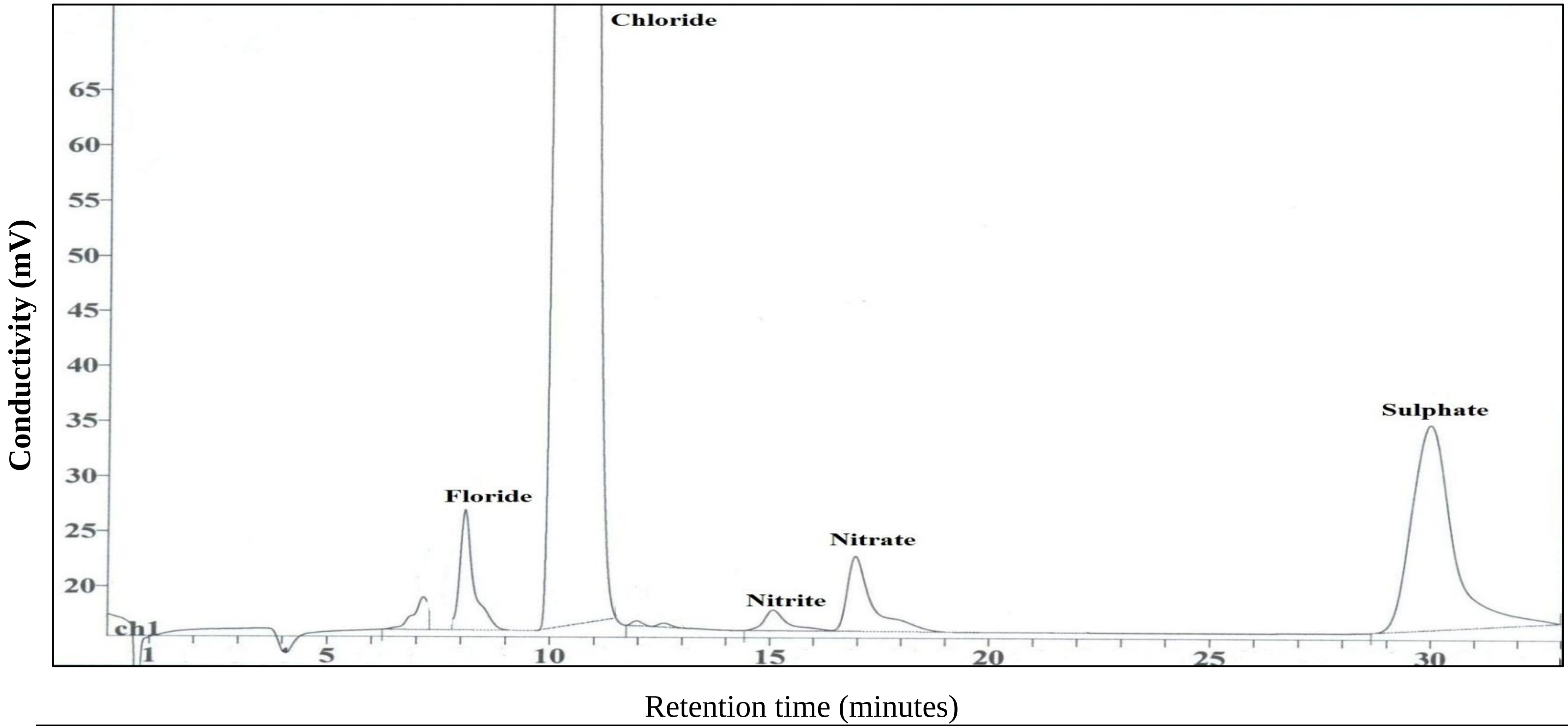
Chromatogram shows the concentration of anions in drinking water sample of the study area.

ANNEXURE-V



Chromatogram shows the concentration of cations in soil sample of the study area.

ANNEXURE-VI

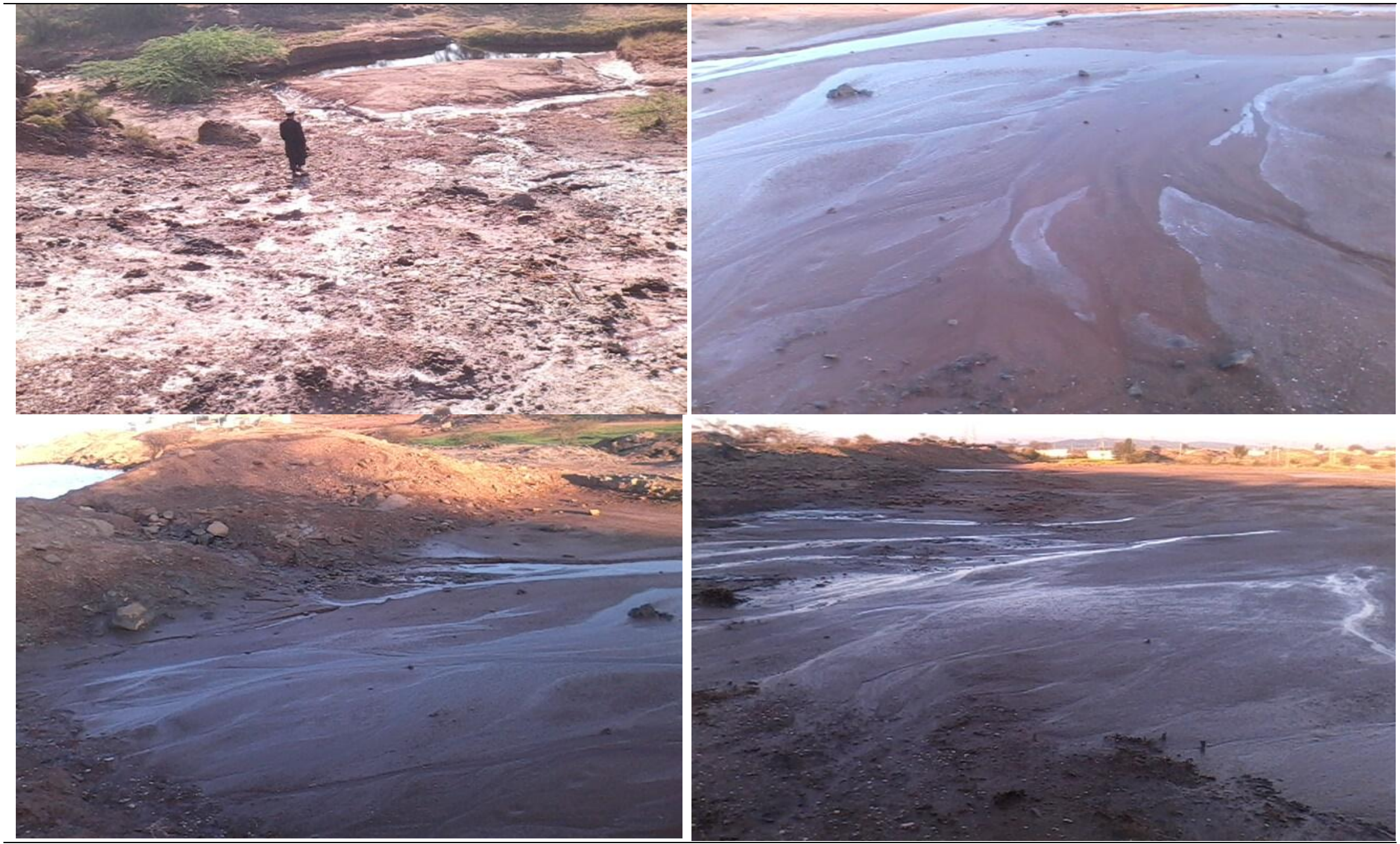


Chromatogram shows the concentration of anions in soil sample of the study area.

ANNEXURE.VII

In-let, out-let points & wastewater ponds of the Sadqal oil and gas field Fateh Jang, Punjab, Pakistan

ANNEXURE.VIII



Seepages from wastewater ponds into the surrounding environment of the Sadqal oil and gas field Fateh Jang, Punjab, Pakistan

ANNEXURE.IX

Soil surface near wastewater ponds and residential area of the Sadqal oil & gas field Fateh Jang, Punjab, Pakistan