Effects of Oil Exploration On Groundwater Quality in Potohar Plateau

Researcher
Mehvish Huma

219/FBAS/MSES/F14

Supervisor
Dr. Maliha Asma

Co-Supervisor
Dr. Azhar Mashiatullah

Department of Environmental Science

Faculty of Basic and Applied Sciences

International Islamic University Islamabad

SESSION 2014-2016

① Ground water — Quality

2 Water pollution

Effects of Oil Exploration On Groundwater Quality in Potohar Plateau

Researcher
Mehvish Huma
219/FBAS/MSES/F14

Supervisor
Dr. Maliha Asma

Co-Supervisor
Dr. Azhar Mashiatullah

Department of Environmental Science
Faculty of Basic and Applied Sciences
International Islamic University Islamabad
SESSION 2014-2016

بسم الله الرحمن الرحيم

In the Name of Allāh, the Most Gracious, the Most Merciful

Department of Environmental Science
Faculty of Basic and Applied Sciences
INTERNATIONAL ISLAMIC UNIVERSITY ISLAMABAD

Dated: ____________

FINAL APPROVAL

It is certified that we have evaluated the thesis report **"Effects of Oil Exploration on Groundwater Quality in Potohar Plateau"** submitted by Mehvish Huma (219-FBAS/MSES/F-14) and found the thesis of sufficient standard to warrant its acceptance to complete the course of studies of MS Degree in Environmental Science of the International Islamic University, Islamabad.

COMMITTEE

Supervisor	
Name	Dr. Maliha Asma
Designation	Assisstant Professor
Department	Department of Environmental Science
University	International Islamic University
Co-Supervisor:	
Name	Dr. Azhar Mashiatullah
Designation	Deputy Chief Scientist
Department	Radiation and Isotope and Application Division
Institute	PINSTECH
Countersigned by:	
Chairperson:	
Name	Dr. Rukhsana Tariq
Designation	Assisstant Professor
Department	Department of Environmental Science
Dean, FBAS:	Prof Dr. Arshad Zia Dean, FBAS, IIUI
Internal Examiner	
External Examiner	

DR. RUKHSANA TARIQ
A.Chairperson
Department of Environmental Science
International Islamic University, Islamabad

M. Arshad

Dr. Mushtaq Ahmad
Associate Professor
Department of Plant Sciences
Quaid-i-Azam University Islamabad
Pakistan

Effects of Oil Exploration

Effects of Oil Exploration on Groundwater Quality in Potohar Plateau

Mehvish Huma

219-FBAS/MSES/F14

A thesis submitted in partial fulfillment of the requirement for

the degree of MS in discipline of Environmental Science

at the faculty of Basic and Applied Science,

International Islamic University,

Islamabad

Supervisor

Dr. Maliha Asma **September 2016**

DECLARATION

I hereby declare that this thesis, **"Effects of Oil Exploration on Groundwater Quality in Potohar Plateau"** neither as a whole nor as a part has been copied out from any source. It is further declared that I have done this research work with the accompanied report entirely on the basis of my personal efforts under the proficient guidance of my teachers especially my supervisor **Dr. Maliha Asma** and co-supervisor **Dr. Azhar Mashiatullah**. If any part of the system is proved to be copied out from any source or found to be reproduction of any project from any of the training institute or educational institutions, I shall stand by the consequences.

Mehvish.

Mehvish Huma
219-FBAS/MSES/F14

FORWARDING SHEET

The thesis entitled, “Effects of oil exploration on groundwater quality in Potohar Plateau” submitted by Mehvish Huma in partial fulfillment of MS in Environmental Science has been completed under my guidance and supervision. I am satisfied with the quality of student’s research work and allow her to submit thesis for further processes per IIUI rules and regulations.

\-------------------------

\--- **Dr. Maliha Asma**

DEDICATION

To my parents

Whose blissful prayers enabled me to complete this uphill task

CONTENTS

ACKNOWLEDGEMENTS

All praise to **Allah Almighty** the Lord of lords who enabled and blessed me with the courage and determination to accomplish this project successfully. Countless salutations upon Holy **Prophet Hazrat Muhammad (PBUH)** for whom, this beautiful universe has been created.

I first want to express my deep sense of gratitude to my respected Supervisor **Dr. Maliha Asma**, Assistant Professor, (DES) for valuable suggestions, sincere cooperation and constant encouragement.

I am greatly indebted to my Co-Supervisor **Dr. Azhar Mashiatullah,** Deputy Chief Scientist in Radiation and Isotope Application Division (RIAD), PINSTECH for his scholastic guidance and valuable comments throughout the research project. I am wholeheartedly thankful for providing the marvelous opportunity to work in his lab. Indeed it is an honor and pleasure to work under his supervision.

While executing this research project, many people helped me and I am grateful to all of them. Among them, **Dr. Tariq**, are specially appreciated for their assistance, cooperation and guidance. I am also thankful to my friends Fatima Noor Qureshi and Quratulain for their sincere cooperation.

Last but not the least; I can`not forget the encouragement, moral and financial support from my parents and husband Muhammad Waseh Mir that led to the completion of this thesis. They kept me optimistic in the face of many hardships.

May Allah bless them all.

Mehvish Huma

SYMBOLS AND ABBREVIATIONS

Symbol/Abb.	**Description**
APHA	American Public Health Association
ATSDR	Agency for Toxic Substances and Disease Registry
$BaCl_2$	Barium Chloride
bbl/yr	Barrels per year
BDL	Below Detection Limit
BK-1	Balkassar Oilfield
BK-2	Balkassar Oilfield
C	Carbon
C-13	Isotope of Carbon
°C	Degree Centigrade
Cd	Cadmium
CO_2	Carbon Dioxide
Cu	Copper
δ	Delta
D-1	Dhurnal Oilfield
D-2	Dhurnal Oilfield
DCM	Dichloromethane
DCP	Dichlorophenol
DH-1	Dhullian Oilfield
DH-2	Dhullian Oilfield
DH-3	Dhullian Oilfield
DME	Dropping Mercury Electrode
DO	Dissolved Oxygen
EC	Electrical Conductivity

EIA	Environmental Impact Assessment
EPA	Environmental Protection Agency
EU	Eurpeon Union
ft.	Feet
FAO	Food and Agriculture Organization
GC	Gas Chromatography
GC/FID	Gas Chromatography with Flameionization Detector
GC/MS	Gas Chromatography with Mass Spectroscopy
GC/PID	Gas Chromatography with Photoionization Detector
Hg	Mercury
HMDE	Hanging Mercury Dropping Electrode
HNO_3	Nitric Acid
H_2O	Water
HPLC	High Performance Liquid Chromatography
H_3PO_4	Phosphoric Acid
H_2SO_4	Sulphuric Acid
IRMS	Isotope Ratio Mass Spectrometer
m	meter
Max.	Maximum
mg/l	Milli Gram per Liter
Min.	Minimum
ml	Milli Liter
MS	Mass Spectroscopy
MY-1	Near Meyal Oilfield
MY-2	Near Meyal Oilfield
N	Normality

NaOH	Sodium Hydro-oxide
nm	Nano Meter
NO_2	Nitrogen Dioxide
NTU	Nephelometric Turbidity Unit
O_2	Oxygen
ODEQ	Oklahoma Department of Environment Quality
O/G	Oil and Grease
OGDCL	Oil and Gas Development Company Limited
OGL	Oil and Gas Journal
PAH	Polycyclic Aromatic Hydrocarbons
PAK-EPA	Pakistan Environmental Protection Agency
Pb	Lead
pH	Hydrogen Ion Concentration
PHC	Petroleum Hydrocarbons
PINSTECH	Pakistan Institute of Nuclear Sciences and Technology
PW-1	Pari Waal Oilfield-1
PW-2	Pari Waal Oilfield-2
PW-3	Pari Waal Oilfield-3
PW-4	Pari Waal Oilfield-4
SO_2	Sulphur Dioxide
SO_4	Sulphate Ion
SPE	Solid Phase Extraction
SQ-1	Near Sadqal Oilfield
SQ-2	Near Sadqal Oilfield
SQ-3	Near Sadqal Oilfield
TCP	Trichlorophenol

TDIC	Total Dissolved Inorganic Carbon
TDS	Total Dissolved Solids
TPH	Total Petroleum Hydrocarbons
USEPA	United States Environmental Protection Agency
µg	Micro Gram
µm	Micro Meter
µs/cm	Micro Siemens per Centi Meter
UV	Ultra Violet
WHO	World Health Organization
Zn	Zinc

LIST OF FIGURES

LIST OF TABLES

ABSTRACT

Oil contamination in groundwater poses a major threat to the environment. In the present investigation samples were collected from the areas near oil and gas exploration in Potohar Plateau to assess impacts of oil exploration activities on groundwater quality. Samples were analyzed for physiochemical parameters, stable carbon isotope, TPH and oil and grease content. Statistical equation of linear correlation evaluated via E Views 8 was applied between the physicochemical and organic parameters. pH values indicated that water is alkaline in nature. The correlation analysis showed a positive correlation of 0.623345 between EC and sulphate concentration. A positive correlation of 0.699214 was computed between TDS and sulphate concentration. The correlation coefficient value for EC and TDS was 0.632447 which means that the variables are positively correlated. As the pH of the samples ranged from neutral to slightly alkaline ranges so the correlation between pH and sulphate concentration was 0.06421 which indicates a weak correlation. Contamination of groundwater with organics was shown by high values of total hydrocarbons. UV-absorption spectrum for groundwater showed absorption peak around 190 nm in samples which may show presence of hydrocarbons. Depleted C-13 is observed for the samples indicated possible mixing of petroleum hydrocarbon in these samples. The values of linear correlation coefficient, 'R' between Ph and Pb, Cd, Cu and Zn were 0.096735, 0.214673, 0.550338 and 0.572571. These values of regression analysis of Ph with pB and Cd indicate the weak correlation whereas the R values of pH with Cu and Zn show a slight positive correlation. The correlation coefficient depicted that the pH and C13 values are negatively correlated. The correlation analysis between oil and grease and TPH was 0.319461 which showed that the two variables have a weak positive correlation. The results of the study confirm impact of oil exploration on nearby groundwater which may affect local population consuming groundwater.

INTRODUCTION

1. Introduction

1.1. Background

Mineral deposits are being discovered from beneath the earth and the sea surfaces with the aid of latest technical instruments. Fuel minerals, metallic minerals and industrial minerals are the three types of mineral resources that are being explored differently. Petroleum, natural gas, coal, lignite and uranium are the examples of fuel minerals (Bayode et.al, 2011). It takes hundreds of thousands of years for the formation of crude oil through the decaying process of corpses of animals and plants (Smith, 1972).

The interstices in the geologic rocks that are close to the shale oil sandstones were once constituted of water before the intervention of crude oil (Amyx et al. 1960). As the organic compounds are non-polar and are immiscible in water so they occupied a portion of interspaces between rocks. Hence organic fuels and water are both the components of the oil deposits. The term of connate water or formation water is used to describe this water and this water is referred to as produced water if it is extracted during the petroleum exploration process (Cadwallaer, 1993; Smith,N., 1972; Anoliefo, 1991).

1.2. Composition of Crude Oil

During oil exploration process crude oil is extracted via rocks and appears like a mixture of dispersed particles of hydrocarbons, non-hydrocarbon or inorganic compounds and a definite proportion of water which differs in its composites on the basis of its location (Cadwallaer, 1993; SmitH, 1972; Anoliefo, 1991). A major portion i.e. approximately ninety percent of rock oil is composed of hydrocarbons. Hydrocarbons are classified into four types on the basis of the chemical bonds present between the atoms of carbon and include alkanes (paraffins), alkenes (olefins), alkynes and aromatic compounds (ATSDR, 1999; Odu, 1981). Alkanes, alkenes and alkynes have single, double and triple bonds respectively existing between their respective carbon atoms. Whereas, aromatic hydrocarbons have carbon atoms arranged in a cyclic structure with resonant chemical bonds. Since organic compounds of any category are all hazardous to some extent (Levy, J.M., 2005; Odu, 1981). The remaining one percent of the unrefined oil is constituted of oxygen, nitrogen, sulphur and few metals are found in crude oils. The unrefined oil which is extracted from different geologic formations serves as the primary source of all petrochemicals (Odu, 1981).

1.3. Concept of Total Petroleum Hydrocarbons

It is not possible to quantify all the components of the raw oil so to determine the concentration TPH is a better approach (ATSDR, 1999). All the types of the chemical compounds that are derived from the rock oil are referred to as the Total Petroleum hydrocarbons (TPH) (Gustafson, 2007). The term TPH encompasses the chemicals like fluorine, naphthalene, hexane, compounds of gasoline etc. Whenever, TPH concentration is to be determined in a water body, then although not all but a few of these composites may be present in it. In the present era, no one can deny the contribution of fuel reservoirs in the economic development (Bayode et.al, 2011). Oil and natural gas have served as the major sinks of energy to both the developing and the developed countries (USEIA, 2013). Despite of the important role of petroleum industry in the development of a state, the negative impacts posed on the ecological system during the exploitation and exploration process cannot be overlooked (Nwachukwu and Osuagwu, 2014).

1.4. Environmental Contamination by Oil

The advantages of utilization of natural oil reserves cannot be denied but the associated exploration, exploitation and refining activities lead to the effects on the state level like leakages from transporting ships, and ruptures in the supplying pipelines result in spillage of the petroleum; air pollution and unexpected changes in the climatic conditions. The negative impacts on the air quality, groundwater pollution and increased temperature levels worldwide are all the problems due to increased consumption of coal and petrochemicals (Kharaka and Dorsey, 2005).

All forms of life weather they are aquatic, wild or microscopic are all effected due to oil exploration operations. The incidents of oil spillage not only contaminate the surface water and soil layers but the oil also percolates down and pollutes the nearby groundwater resources (Nwachukwu and Osuagwu, 2014). When anthropogenic causes result in the release of oil in the environment directly or indirectly and this ultimately poses negative impacts on the wellbeing of the surrounding biota, then the phenomenon is termed as oil pollution (Muller, 1987).In the areas where fuel exploitation activities are conducted, the land and specifically groundwater pollution becomes a major issue (Gustafson, 2007).

Unfortunately due to anthropogenic activities, the water beneath the earth surface is continuously being polluted and this problem is now amongst the highly consequential environmental agendas (Vodela, et.al., 1997). The severity of the issue can be well explained by the phenomenon of balance existing between the gravitational field of earth and the network of interaction between the surface and groundwater (Otokunefor and Obiukwu, 2005; Riccardi, et.al, 2008). Nevertheless the process of exploitation used for fuel minerals badly deteriorates groundwater quality of the region (Kharaka and Otton, 2007).

1.5. Sources of Oil Pollution

During the oil exploitation process the ecosystem is adversely affected due to broken bits of solid materials produced during drilling and because of frequent usage of drilling fluids, fluids used for enhancing the exploitation process and chemicals added to segregate oil from water (Nwankwo and Ifeadi, 1988). The primary sources of groundwater pollution as a result of oil exploration activities include saline water extracted with oil and gas and huge quantity of produced water generated during fuel exploitation operations (Kharaka et al., 1995; Veil et al., 2004) due to inappropriate discarding method, improper handling of equipment and unintentional spillage (Kharaka and Otton, 2007).

The main causes of spillage of petroleum hydrocarbons into the surrounding area of exploration include drilling of an oil well, unsuitable closure of a shaft in the rock which has ceased to produce oil, processes of transport and storage, purification process, supplying to the industries and other anthropogenic causes (Oberdorster and Cheek, 2000; USEPA, 1987; Richter and Kreitler, 1993; Kharaka et al., 1995; Kharaka and Hanor, 2003). Another significant source of hydrocarbons introduction into the environment is the instance of bursting of underground oil pipes which ultimately affects the groundwater quality. Due to progress in business of fuel products between countries, the underground supplying channels of oil and gas extend millions of miles and hence the incidences of leaking in these oil and gas supplying pipes are increasing (Beller, et al., 1996). As a result of sudden damages in the petrochemicals pipes, the different types of fuel liquids like diesel, gasoline etc. often adversely affect soil and the nearby underground waterways (Odu, 1981). When raw oil is purified then it becomes more hazardous as the toxic metals, antioxidants, dyes, anticorrosion agents and other organic compounds are added to improve its quality (Anoliefo, 1991).

During the process of mining for petrochemicals the lots of waste containing toxic metal elements, nitrogen, phosphorous, viruses and bacteria is also generated (Botkin and Keller, 1998). Severe incidents of toxic metals pollution although on local scales have been reported even during the earlier roman era (FAO, 1993). Further, formation water or produced water if released into the environment is the massive pollutant of exploration activity (Frost et al. 1998). To protect the environment from the contamination of produced water, it is essential to have information about its composition. The total dissolved solids is the main indicator of the polluting components present in it (Tibbetts et al., 1992), besides organic compounds, potentially hazardous elements (Davis, Waskom et al., 2007) for e.g. boron, bromide, fluorine and Radium may be found in high concentrations (Guerra, et. Al., 2007), besides oil and grease may also be present (Tibbetts et al., 1992).

The biological community and the physical components of the environment are all badly impacted due to the cases of accidental oil spills. It is reported by the Agency for Toxic Substances and Disease Registry (ATSDR) that after an oil pipeline leaks into an aquifer then the organic layer of the oil will rest on the surface of the water and the denser hydrocarbon components will sink and will add up to the portion of the bottom sediments(ATSDR, 1991). Since many years, the oil extraction techniques being employed, significantly affect the native people of that area, unexpectedly when no recent incidence of spillage of oil is reported in the area, a clear layer of oil has been observed on the water surface being used for drinking and other household purposes (Ekpenyong and Udofia, 2015).

1.6. Impacts of Oil Exploration on Water Quality

After the occurrence of an oil spillage the different components present in the spilled product isolate from one another on the basis of their structural compositions, a few from these would vaporize into atmosphere and remaining with more solubility would reach the underground water (Olatunji and Abimbola, 2010). In Potohar Plateau, the main source of water that is available throughout the year is groundwater. The oil exploration and exploitation activities are conducted at different regions of the plateau (Majeed, et al., 2010). If the oil contaminated water is consumed for a long period of time then it may result in serious health issues (Nwachukwu and Osuagwu, 2014).

Due to petrochemicals pollution in the palatable water all the physiological functions of a human body are badly disturbed which include respiratory system, nervous system, including the brain, liver, reproductive/ urogenital system, kidneys, endocrine system, circulatory system, gastrointestinal system, immune system, hematopoietic system (blood forming), skin and integumentary system metabolism. Consequently different health disorders develop like interruptions in the normal functioning of endocrine system and impairment in fetus on cellular level or tissue level. Besides malignant cell growth and cancer develops in different body organs due to disrupted DNA structure caused by hydrocarbon polluted water ingestion (Chinedu and Lovette, 2014). Further, diseases related to kidneys and liver, high blood pressure, reduced levels of platelets in the blood, anemia and poor reproductive ability are the symptoms associated with hydrocarbon polluted water intake (Nwachukwu and Osuagwu, 2014)

1.7. Oil Exploration in Pakistan

The requirement for fuel resources has expanded to a great extent since World War II (Kakulu and Osibanjo, 1998). In Pakistan approximately 150 million barrel oil and 1.6 trillion cubic feet gas are utilized on yearly basis (Tirmizi, 2011) and about 47% and 30% of the electricity is produced with the aid of gas and oil respectively (Hussain, 2013) and the term of oil province if frequently used for the state now. The earliest successful oil exploitation operation in Pakistan was conducted in 1866 at Kundal, in the Upper Indus Basin. Afterwards in 1886, at Khattan, Balochistan oil reserves were exploited but were not so deep. In Potohar Plateau, Punjab Province the oil was discovered in 1915. After a year, in 1916, the Pakistan's Government laid the foundation of Oil and Gas Development Company Limited (OGDCL) and the firm played a vital role in the oil and gas exploration operations. Public sector organizations and OGDCL unearthed huge oil deposits followed by the energy crisis of 1973 (EIA, 2006).

Oil deposits of 300 million barrels were reported in Oil and Gas Journal (OGJ), in 2006. The three oilfields in south of the Indus Basin, besides at upper and lower Indus Basin, some fuel deposits are discovered. From the nineteenth century up till now, many oil firms have searched for oil in the country and at locations close to a petroleum seep were exploited for oil reservoirs. Massive quantities for oil were explored in Khattan, Balochistan Province and in Fateh Jang, Punjab Province; but the after some years, oil supply stopped abruptly. Followed by the successful oil search activities in Khaur and Dhullian in Potowar Plateau, the oil exploitation activities were conducted in the area and it revealed the presence of folded layers of an arch of non-porous rocks overlying the porous strata or reservoir rock in which mineral resources get trapped. After 1947, more than hundred wells were dug and hundred thousand kilometers of sediment were drilled in other areas also but no successful results were achieved (Day, 1962).

1.8. Significance of the Study

Globally, groundwater is the most vital and commonly exploited resource (Dami, et al., 2013). Particularly in areas that receive little or no rainfall and in areas that receive less than 20 inches of rainfall, because of the unexpected changes in the monsoon patterns and limited surface water resources, the groundwater is the only source for meeting the daily needs of water supply. The similar circumstances are being experienced in Pakistan as it is an arid country (Ullah, et al., 2009).

Since precipitation, streams and groundwater are the main water sinks in Potohar Plateau (Majeed, et al., 2010). In Pakistan, the surface water resources are deteriorated due to overexploitation behavior of industrial and domestic sector and the issues of water deficiency are predicted in the future (Majeed, et al., 2010; Ullah, R., et al., 2009). The petroleum geologists and geophysicists in the Potohar region remain engaged in the search for oil reservoirs (Khan, 2011). The most consequential environmental issue in all the continents particularly in industrialized states is the pollution of groundwater with oil contamination (Egila and Terhemen, 2004). Devastating effects that endure for a long duration of time are produced in groundwater due to organic pollution (Okoye and Lovette, 2014). Hence to keep a check on oil pollution incidents is a more secure and sensible approach (Nwachukwu and Osuagwu, 2014). The current research aims to analyze the groundwater resources in the vicinity of the oil exploration and exploitation areas in Potohar Plateau so that it would be fruitful in planning about the sustainable use of the groundwater resources to retrieve declining quality of the groundwater resources of the plateau. This study would also be imperative as providing a database for future research work.

1.9. Objectives of the Study

The specific objectives of this research work are:

a) To identify and characterize the groundwater samples on the basis of their physico-chemical characteristics

b) To evaluate the concentrations of heavy metals (Pb, Zn, Cd and Cu) in the groundwater samples

c) To assess and determine the concentration of hydrocarbons in the nearby groundwater of oil exploration areas environment.

d) To perform the stable carbon isotope analysis of total dissolved inorganic carbon (TDIC)

LITERATURE SURVEY

2. Literature Survey

Petroleum is a very complicated mixture constituted of different types of low and high weight hydrocarbons (Costello, 1979). Besides some non-hydrocarbon constituents exist in the crude oil for example nitrogen, sulphur or oxygen and these constituents are referred to as hetero-atoms (Zemo and Foote, 2003).Oil exploration and exploitation activities, production, refining and storage processes are responsible for degrading the environmental components. Oil spills that occur accidently and residues from oil refineries are accelerating their concentrations in the surroundings. Unintentional releases from the oil supplying vehicles and ships occur so frequently. Petroleum transport to different locations for the purposes of purification or petrochemicals synthesis is performed via underground oil supplying channels, which mostly get burst at certain locations and huge fractions of oil are released into the surrounding soil and groundwater resources. According to Kvenvolden and Cooper (2003) 600,000 metric tons with an uncertainty range of 200,000 metric tons are estimated as annual oil discharged into the environment. As a result of these accidental spills cases of sudden fires, groundwater quality deterioration and air pollution are experienced. In recent era, petrochemicals serve as the primary energy sources for industrial and transport sector but petrochemicals pollution is among the main environmental agendas being faced worldwide. Nevertheless, the byproducts from oil purification processes are even more harmful as they contain increased levels of cancer causing elements and cannot be easily biodegradable (Jain and Bajpai, 2012).

Anthropogenic causes have resulted in increased levels of heavy metals in the soil that once existed only in trace quantities. The researches have proved that bioremediation does not produces satisfactory results if areas polluted with oil residues also contain huge amounts of heavy metals. This is because metals hinder in process of microbial degradation. Heavy metals are also present in crude oil. Plants and animals are adversely affected due to oil pollution. The residues of the petrochemicals that are discharged into the surrounding environment from refineries are highly toxic. Different components of petrochemicals have different molecular weights and boiling points and hence vary in their toxicological properties (Costello, 1979).

To meet the increasing energy demands of the state, the oil and gas resources contribute a lot so Pakistan can be referred to as a petroleum province as the production ratios of different energy resources are depicted in the table 2.1. The greater amount of crude oil comes from the oil deposits in Southern Indus Basin, middle and upper Indus Basins (Ahmad and Jha, 2008)

Table 2.1 Energy Reserves of Pakistan

Fuel	Annual Production	Reserve to Production Ratio
Oil	23.94 Mbbl	14
Gas	1.40 Tcf	21
Coal	4.59 M tons	678
Hydro	16% realized	

The other routes of hydrocarbon contamination include the oil wells that are abandoned because they do not produce significant quantities of oil or they have ceased to produce oil, indiscriminate release of petrochemical containing waste products or byproducts into the environment, oil refineries that are no more functional and partial burning of coal or oil. Among these contamination sources, processes involved in oil exploration and exploitation activities and deserted oil wells particularly pose serious threats to the soil, surface water and groundwater resources (US Environmental Protection Agency (USEPA), 1987; Richter and Kreitler, 1993; Kharaka et al., 1995; Kharaka and Hanor, 2003). Hydrocarbons flow slowly through porous particles of soil and result in pollution of groundwater resources. Streams receiving polluted water from petroleum refining industries and from oil exploration sites also lead to pollution of ground and surface water resources present in their vicinity (Malik and Ahmad, 2012).

Nwachukwu and Osuagwu (2014) conducted research to ascertain the effects of oil spillage on groundwater quality in the oil producing region. The samples were analyzed for pH, turbidity, electrical conductivity, TDS, DO, Mg, and P and total hydrocarbon constituents. It was discovered pH which exceeds WHO standards, low dissolved oxygen levels, higher level of turbidity and total hydrocarbons in the samples is an indication of oil pollution.

Alinnor and Nwachukwu (2013). The mean TPH concentrations of groundwater in five communities indicated high concentration of TPH and at all the sampling stations, the mean concentration of TPH decreased as depth increased.

Adewuyi and Olowu (2012) conducted a study in which TPH, oil and grease were analyzed gravimetrically while the levels of heavy metals were determined by atomic absorption spectrophotometry (AAS). Statistically significant difference at $p<0.05$ was found to exist between the concentrations of oil and grease, TPH and the analyzed metals collected from the sites and the control sites.

Laba, et al., (2012) examined the samples for physicochemical parameters, inorganic components and for heavy metals. The undesirable metal (Mn) and the toxic metals (Pb, Cr) (Jonathan et al., 2005) were much higher than acceptable upper limits suggested by the European Union (50 ug/l for Mn, Pb and Cr). The total hydrocarbon contamination was much higher in the wells located near crude oil pipes. It was concluded that high values of TSS are related to crude oil supposedly leaked from pipes.

Ogoko (2014) investigated the concentration of PAHs, TPH and heavy metals (Zn, Cu, As, Pb, Cd and Hg) in the vicinity of an oil storage area. The results revealed that the study site was contaminated with elevated levels of Pb, Hg, Cd and TPH when compared with the control samples.

Olufemi, et al., (2012) collected the groundwater samples in an area of oil spill to determine the O/G, TPH and some related heavy metals in the samples. Measurements of O/G and TPH were done gravimetrically while AAS was used for determination of heavy metals. The results revealed that investigated samples had higher levels of O/G, TPH and heavy metals than regulatory standard limits. This is an indication of pollution of groundwater by petroleum hydrocarbons.

Ohimain et al., (2008) studied the changes in the water chemistry of an area where an oil well access canal was dug. The pH decreased from 7.2 to 4.0, dissolved oxygen (DO) decreased considerably from 6.0mg/l to 0.4 mg/L, while BOD was increased from 1.0 mg/l to 18.0 mg/L. COD, oil and grease, conductivity, TDS and sulphate values similarly increased.

Oyeleke and Okparaocha (2016) worked on the analysis of the relationship between hydrocarbon contamination and heavy metals which include Cu, Cd, Pb, Zn and Cr. Cd was found to be below the detection limits and all the other toxic metals were below the undesirable limits except Pb. The presence of high levels of Pb in the groundwater may be due to improper handling of oil storage containers.

Egborge, (2000); Orubu et al., (2002); and Otukunefor and Biukwu (2005); indicated high degree of hydrocarbons contamination because of indiscriminate disposal of wastes generated from oil exploitation processes and unsuitable exploration procedures that do not meet regulatory compliances.

Amadi, et al., (2014) tested the physic-chemical characteristics and the levels of heavy metals in the surrounding groundwater resources of a petroleum refinery. The physic-chemical properties were all within the acceptable limits. The toxic metals (Fe, As, Zn, Cu, Pb and Cd) were present in increased quantities than the recommended values because the residues from refining activities were directly disposed into the surroundings. These metals are commonly found in the oil. In addition the natural rocks dissociation may also add to the concentration of toxic metals in soils and groundwaters but it is supported by many researches that oil products and byproducts are the main sources of heavy metals contamination.

The water quality of the U.S. villages was examined for any type of hydrocarbon contamination although no case of oil spill was reported in the sampling areas since four years. The results of the experiment were astonishing as the samples were polluted with petroleum products and the degree of contamination was 360 times higher than the permissible limits of European Union. So it can be concluded that after oil spill occurs in a water body, the composites of oil scatter into the surrounding environment. Few of the oil components vaporize, few undergo chemical transformations and few are degraded by microbial activity and settle on the bottom sediments. As a result the sediments quality is affected. Hence the research was conducted to ascertain the effects of oil exploration in the Potohar Plateau as the exploration activities in area stated since 1945 (Ekpenyong and Udofia, 2015).

Ekpenyong and Udofia, (2015) studied the changes in the quality of water after an oil spill occurred. The levels of turbidity and BOD increased than the recommended WHO limits. The quantity of toxic metals including Pb, Cd, Cr and Ni also exceeded the WHO recommended limits. It was reported that the increased concentration of heavy metals may be due to disposal of unwanted fluids generated from domestic, agricultural and industrial sectors and refuses from waste water treatment plants. The concentration of petrochemicals was within the permissible limits.

Ogbuigwe (1998), studied the impacts of gas flaring on the temperature variation of an area and the results showed that the temperature at the place of gas flaring was much high and was 1,600o C. About 43 m far from the site of the fire incident even the mean temperature was 400 C. Alakpodia, (1989, 1995) has also stated that burning of the gas released during exploration and exploitation foe crude oil occurs so intensively that it produces devastation effects on the a much great scale that the plants, animals and other components of the ecosystem suffer to a great extent. Besides, the climate of the area is adversely affected and the acid rain may occur and deteriorate the quality of surface and ground water.

Olobaniyi and Efe (2007), revealed that in an oil impacted area the lead concentration was found to be 0.56 mg/l which is too high and also the pH was found to be low due to occurrence of acid rain. Akpoborie, et al, (2000) stated that pH of well waters that were of less depth, in an area where gas flaring incident occurred was much low due to acid rain. The other impacts of acid rain include damaged ceiling coverings, statues and buildings that commemorate the historical events and other infrastructures. Further the flora is adversely affected and; the surface water resources used by the villagers for drinking and cooking purposes are contaminated. In a United Nations' Human Development Report in 2006, it was forcefully mentioned that the harmful impacts from the oil exploration and refining activities ultimately lead a region towards an ecological disaster. A study conducted by Powell and White (1985) further supported this notion, the analysis of the effects of unintentional releases of petroleum into the environment revealed that the populations of phytoplankons , fish, birds and crustaceans were being lost at an accelerated rate

MATERIALS AND METHODS

3. Materials and Methods

3.1. Study Area

3.1.1. Location

Potohar Region lies at the latitude of 32°22′ N. and 34° N.; and longitude is 71°30′ E. and 73°30′ E; it is bordered with the exterior Himalayan Ranges, River Jhelum flows in the east while River Indus flows in the west of the plateau. The Attock and Rawalpindi Districts, few areas of the Murree, 75% of Chakwal District, 20% of Mianwali District and 15% of Jhelum District are all included in the Potohar Plateau (Khan, 2011). The altitude levels of the plateau lie between 200m in River Indus and 900m in the elevated land in north of Islamabad, so 457m is the mean value of altitude of Potohar Plateau (Warwick and Wardlaw, 1991).

3.1.2. Geography and Climate

The vital sources of water are precipitation, rivers and groundwater. To meet the ever increasing demands for water by agricultural sector and domestic sector, mini dams are constructed. In the south-west arid climatic conditions are experienced whereas in the north-east of the plateau the climate is humid. In the east of the plateau, the Kansi River flows and moves from north to south and ultimately join Jhelum River. On the other hand Haro and Soan are the rivers that flow only in the rainy season from east to west direction and then traversing the areas in the north and then in middle of the plateau finally flow in Indus River. The average yearly precipitation varies spatially from250-1500 mm, in addition the rainfall pattern during Rabi is from 125-650 mm and during Kharif season 60% of the annual precipitation is experienced; this variation is on the basis of the time period (Majeed, et al., 2010).

3.2. Field Sampling

The most important task of water quality analysis is sampling (Rahman, 2013).In the present investigation groundwater samples (both dug wells and tube wells upto a depth ranging from 170ft. to 500ft.) were collected from the areas near oil and gas exploration in Attock district as shown in Figure 3.2. Four groundwater samples were collected from nearby Pari Wali Oilfield; three samples were collected from nearby Sadqal Oilfield and Dhullian

Oilfield whereas two samples were taken each from nearby Dhurnal Oilfield, Meyal Oilfield and Balkassar Oilfield (Table-3.2). Physicochemical parameters i.e. pH, electrical conductivity (EC), turbidity, total dissolved solids (TDS) and dissolved oxygen (DO) were analyzed in-situ during sampling.

Table 3.2 Inventory of Sampling Points

Sr.No.	Code	Latitude	Longitude	Description
1	**Sq-1**	33°35'40.9"	72°39'39.7"	Near Sadqal Oilfield, OGDCL Field (Near Board of Well # 2
2	**Sq-2**	33°35'34.1"	72°39'17.8"	Near Sadqal Oilfield, OGDCL Field (Near Board of Well # 2
3	**Sq-3**	33°34'29.5"	72°37'58.7"	Sadqal Oilfield
4	**D-1**	33°20'22.1"	72°34'54.2"	Dhurnal Oilfield, Near Ocean Oilfield
5	**D-2**	33°19'51.0"	72°35'16.3"	Dhurnal Oilfield, Dhok Bharra
6	**Pw-1**	33°19'07.0"	72°29'24.3"	1 km before Pari Wali Oilfield
7	**Pw-2**	33°19'05.3"	72°28'34.9"	Near Pari Wali Oilfield, Near Khaur
8	**Pw-3**	33°16'01.6"	72°26'16.9"	Near Pari Wali Well-1, Feroz Wali Oilfield, After Khaur on Talaghang Road
9	**Pw-4**	33°15'54.9"	72°26'39.3"	Pari Wali Oilfield, Link Road, Pari Wali Well
10	**Dh-1**	33°11'52.8"	72°15'4.0"	Dhullian Oilfield, Near Pakistan Oilfield, SNGPL Office
11	**Dh-2**	33°10'34.3"	72°18'55.6"	Dhullian Oilfield, Gharib Wal Morr, 70 km after Oilfield
12	**Dh-3**	33°11'33.5"	72°18'25.0"	Dhullian Oilfield, Gharib Wal Morr, from residence on main road
13	**My-1**	33°17'18.2"	72°09'49.6"	Meyal Oilfield, Neyal Village
14	**My-2**	33°17'07.1"	72°12'06.8"	36 km before Meyal Oilfield
15	**Bk-1**	32°56'36.7"	72°39'16.8"	H-20 sample
16	**Bk-2**	32°56'45.5"	72°39'16.9"	Well

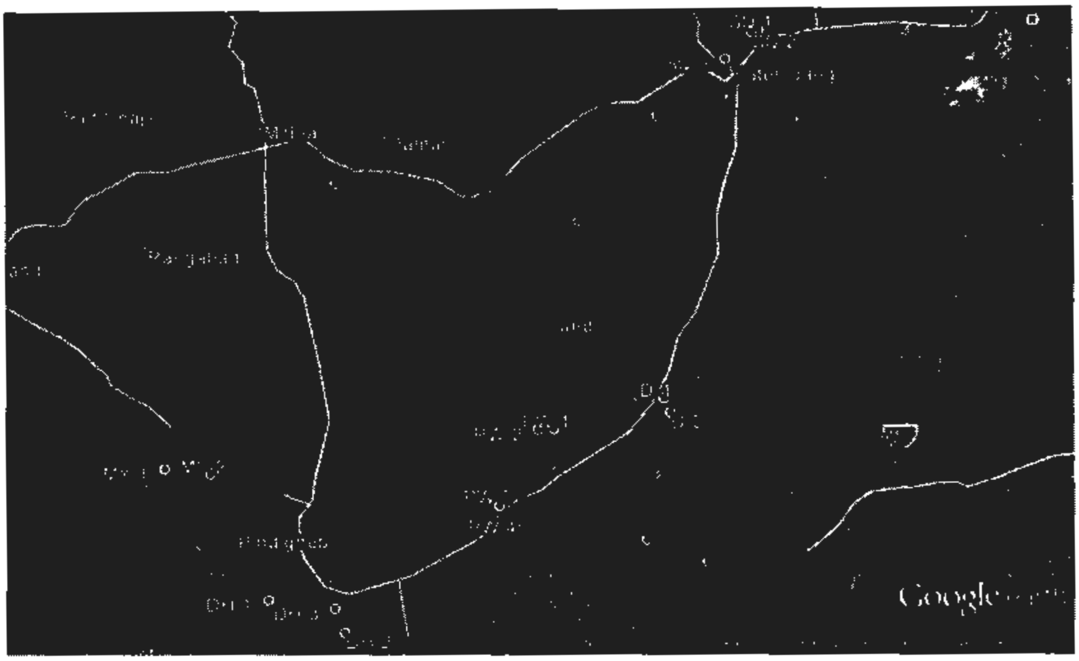

Figure 3.2 Study Area Map

About 5 liters water samples were collected from each sampling point for organic analysis; 11 ml for chemical and 250 ml for stable carbon analysis in clean polythene bottles. Samples for metal analysis were acidified with few drops of 0.5% HNO_3 for analysis of trace metals (Zn, Pb, Cd and Cu). These water samples were properly coded and transferred to the Isotope Application Division (IAD) Laboratory of Pakistan Institute of Nuclear Sciences and Technology (PINSTECH), Islamabad, Pakistan for further processing and analysis.

3.3. Physicochemical Analysis

Physicochemical analyses of the samples were carried out in-situ in the field according to standard methods with portable meters. Physicochemical parameters included pH, electrical conductivity, total dissolved solids, turbidity, dissolved oxygen, sulphate analysis and phosphate analysis. Each meter was calibrated in accordance with standard procedure before use.

3.3.1. pH

pH was determined using the Adwa AD1030 pH/mn and temperature meter. Meter was first calibrated for pH with the help of buffer solution of pH 4.01, pH 7 and pH 9.21 respectively. The water sample was then taken in a beaker and electrode was dipped into it and the system was allowed to stabilize before making the final reading.

3.3.2. Electrical Conductivity

Electrical conductivity of water samples was measured by LF95 (wtw) Conductivity meter. Prior to analysis the meter was calibrated for EC using the standard solutions having EC 1413 μs/cm, EC 147 μs/cm and EC 12.88 μs/cm at 25°C correspondingly. The EC of water samples was measured in accordance with standard method (Franson, 1995).

3.3.3. Total Dissolved Solids

TDS was also determined by using LF95 (wtw) Conductivity meter along with EC. The value of TDS was recorded in milligram per liter (mg/l).

3.3.1 Dissolved Oxygen

Ion meter HACH Sension 6 was used for measurement of DO values in samples. Prior to analysis, the instrument was calibrated according to standard procedure with the help of NaOH solution and water.

3.4. Anion Analysis

3.4.1. Determination of Phosphate

Phosphate concentration was measured by using UV Spectrometer. The combined reagent for phosphate analysis was prepared by mixing the reagents in specific proportions. 50 ml 5N H_2SO_4, 5 ml potassium antimony tartarate, 15ml ammonium molybdate solution and 30ml ascorbic acid solution were mixed for preparation of 100ml of combined reagent. Standard phosphate solutions were prepared.

50ml of sample was taken into 125ml Erlenmeyer flask. 0.05ml of phenolphthalein indicator was added. The red color developed. 5N H_2SO_4 solution was added drop wise to just discharge the color. Then 8ml of combined reagent was added and mixed thoroughly. No change in color indicated that phosphate was found to be below detectable limit (Standard Method for examination of water and waste water, 2005).

3.4.2. Determination of Sulphate

Sulphate concentration was measured by using UV Spectrometer. 10ml of sample was or standard was taken in an Erlenmeyer flask. Then 0.5ml of concentration reagent and ¼ spoonfuls of $BaCl_2$ crystals were added and were stirred for half minute with magnetic stirrers. Samples were analyzed at 420nm wavelength distilled water was taken for background correction (Standard Method for examination of water and waste water, 2005).

3.5. Determination of Trace Metals

The analysis of Pb, Zn, Cu and Cd was carried out by polarograph 797 Computrace by VA-83 using Hanging Mercury Dropping Electrode (HMDE).

3.5.1. Polarograph

Polarography is a voltammetric measurement whose response is determined by combined diffusion or convection mass transport. Polarograph falls into general category of linear-sweep voltammetry and its specific type of measurement where the electrode potential is altered in a linear fashion from the initial potential to the final potential. Polarographic experiment has a typical sigmoid shape as linear sweep method controlled by convection or diffusion mass transport, the current vs. potential response. Polarography makes use of the dropping mercury electrode (DME) or the static mercury dropping electrode and makes polarography different from other linear sweep voltammetry measurements. A plot of the current vs. potential in a polarography experiment describes the current oscillations corresponding to the drops of mercury falling from the capillary. A sigmoid shape would result if one connected the maximum current of each drop. By Computrace VA797 analysis of Zn, Pb, Cu and Cd was done using Hanging Mercury Dropping Electrode (HMDE).

3.5.2. Measurement Procedure for Zn, Pb, Cu and Cd

All the measurements were performed at room temperature. The working electrode was cleaned properly using distilled water before the analysis of each sample. 10ml of sample with 25 ml of sodium acetate buffer was taken in an electrolytic cell and run in voltammeter. Three additions of standard solutions were made. After the whole process of purging, equilibrating and repositioning, the polarograpgh was obtained showing the concentration of Zn, Pb, Cu and Cd. The results were computed in MS Excel 2007 and expressed in µg/l.

3.6. Stable carbon Isotope Analysis

3.6.1. Stable Isotope

Stable isotopes of many elements are used in hydrological investigations (Aggarwal, Froehlich and Kulkarni, 2004). The stable isotopes are usually measured, using an isotope ratio mass spectrometer, in terms of the isotope ratios of the less abundant to more abundant isotope. The common feature of these ratios is that they can be determined using a few light gases. Hence they share a common technology of Isotope Ratio Mass Spectrometry (Aggarwal, Froehlich and Kulkarni, 2004; Werner and Brand, 2001).

3.6.2. Relative Mass Differences:

Variations in the stable isotope ratios of natural compounds are governed by chemical reactions and phase changes due to the energy difference between chemical bonds in different isotopes of an element. Such energy differences are caused by the relative mass difference between isotopes. The stable isotopes of light elements show greater variations because they have larger relative mass differences.

3.6.3. Relative Deviation:

The interest of an isotope hydrologist lies in the relative deviation of the ratio of less abundant heavy isotope to more abundant lighter isotope (exceptions: helium, lithium and boron isotope ratios) with respect to a reference rather than the "absolute" isotope ratio of a given sample. Therefore, a material is selected as a primary standard, and its stable isotope ratio defines the zero point of a relative conventional scale. For convenience the measurements are not reported as isotope ratios, but given as relative deviation from the isotope ratio of a standard expressed as δ (delta) in permil (‰) and is defined as,

$$\boldsymbol{\delta}\ (\%) = \frac{\boldsymbol{R\ sample - R\ standard}}{\boldsymbol{R\ standard}}.\mathbf{1000}$$

where, δ (e.g., δ2H, δ13C, δ15N, δ18O, δ34S) is the normalised difference of the isotope concentration ratios R (2H/1H, 13C/12C, 15N/14N, 18O/16O, 34S/32S) of a sample and a standard. Carbon has two environmental stable isotopes: 12C (98.89 %) and 13C (1.11 %). 13C/12C measurements are made on CO2 gas using isotope ratio mass spectrometer (IRMS) (Aggarwal, Froehlich and Kulkarni, 2004).

3.6.4. Carbon Dioxide Extraction for Isotope (δ13C) Analysis

For the extraction of CO_2 gas from Total Dissolved Inorganic Carbon of water, 50 ml of water sample was poured into the Pyrex reaction flask. A small burette containing phosphoric acid (H_3PO_4) maintained at -80°C was then attached to the reaction flask (McCrea, 1950). This assembly of the reaction flask was then joined to the vacuum line. The Dewar flask was affixed in the vacuum system. The dewar flask contained liquid N_2-acetone mixture.

To the pre-evacuated reaction flask, 5 ml of H_3PO_4 acid was added. The reaction between phosphoric acid and inorganic carbon fraction of the sample resulted in the formation of CO_2 gas as shown in following equation:

$$H_3PO_4 + \text{Carbonate mineral} \rightarrow CO_2 + H_2O$$

Further, at the temperature of -80°C provided in the burette, the sample was converted into the moisture which mainly consisted of oxides e.g. SO_2, NO_2, CO_2 and H_2O. To trap this moisture in the vacuum system, the cryogenic trap was provided by the dewar flask which was maintained at temperature of -80°C. The CO_2 gas was passed through vacuum line and purified by freezing in U-trap dipped in liquid nitrogen flask. The liquid N_2 flask from CO_2 trap was removed to expand CO_2 in vacuum line which was finally collected in an ampoule dipped in liquid nitrogen flask at the other end of line. The ampoule was labelled and removed from the line for isotope ratio measurements onto the Isotope Ratio Mass spectrometer (IRMS).

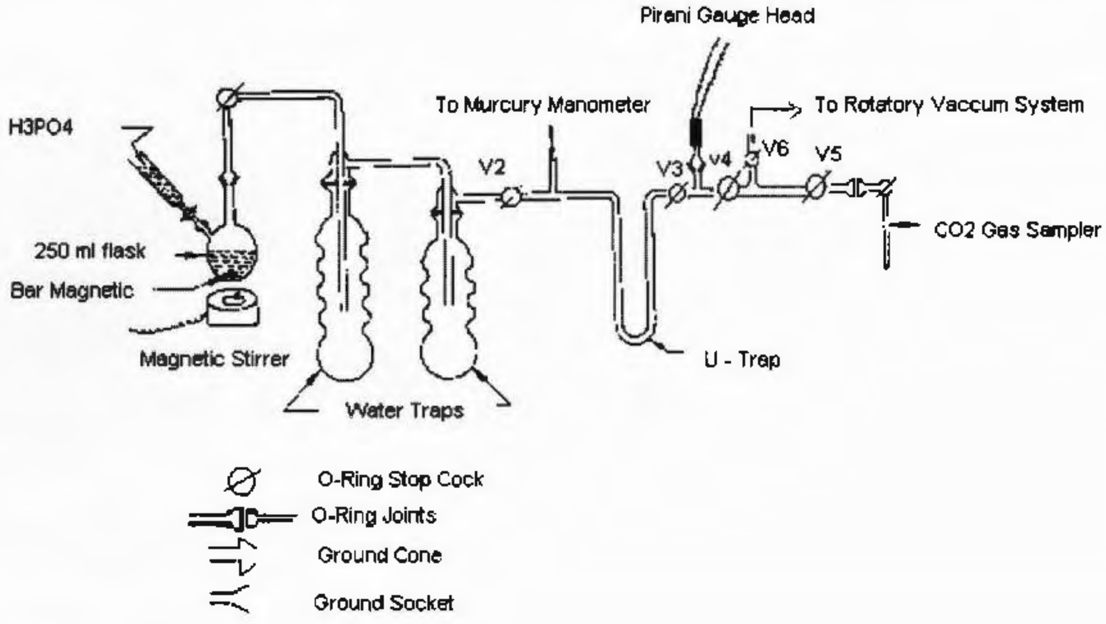

Figure 3.6.5 Vacuum system for the extraction of CO_2 gas from water

3.7. Oil and Grease Determination

Oil and grease is a group of related materials rather than a specific chemical compound extractable by certain solvents (USEPA, 1999; Travis, et.al., 2008). They are non polar so are hydrophobic in nature (Travis, et.al, 2008). The largest source of wastewater is produced during oil extraction processes in most oil mills (Ahmad, et.al, 2005). Oil and Grease was determined by Partition-Gravimetric Method (The American Public Health Association (APHA)'s Method: 5520B Modified: Partition-Gravimetric Method). Dissolved or emulsified oil and grease is extracted from water by intimate contact with an extracting solvent. The extracting solvent is evaporated and residue is weighed for oil and grease content. Liquid-liquid extraction procedure was used in this study (Rasmussen, D.V., 1976; Aremu, D. et al., 2002 and Parageau, M.P., 2004). 500ml of sample was extracted in a two liter (2 L) glass separatory funnel fitted with a glass stopper using 40 ml xylene as extractant. The separatory funnel was shaken vigorously for at least 3 minutes and the organic layer was allowed to separate clearly from the aqueous phase for a minimum of 15 minutes, after which, the organic layer was collected into a separate glass beaker. The extraction was repeated thrice for each sample. Water residues were expelled from the organic layer by passing extracts through funnels containing anhydrous sodium sulphate. When the filtration was complete, extracts were concentrated using rotary hot plate set at approx. 85°C±5° C. Concentrated extracts was transferred to a pre-weighed sample bottle and evaporated to dryness. The difference in weight is equivalent to oil and grease in the sample. Then the beaker was allowed to cool at the room temperature and was weighed (Adewuyi, G.O. and Olowu, R.A., 2012).

Oil and Grease mg/l = Gain in weight of beaker (mg)/Volume of sample (ml) × 1000

3.8. Determination of Total Petroleum Hydrocarbons

Silica gel for column chromatography was activated at 200°C for 4 hrs. The silica gel was then deactivated by adding 5% of its weight of distilled water to it in a bottle. The bottle was tightly capped and the content was mixed and allowed to equilibrate overnight to prevent the formation of artifacts. 4 g of the silica gel was weighed into a bottle and capped tightly. The oil and grease obtained was re-dissolved in dichloromethane (DCM) and the solution of extract was transferred to the bottle in which 10 ml of xylene had been added.

The mixture was stirred for 5 minutes with a magnetic stirrer with the bottle properly and tightly capped. The solution was filtered into a pre-weighed flask through a filter paper moistened with hexane. The silica gel and filter paper was washed down with 10 ml hexane. The solvent was then concentrated and evaporated to dryness in a rotary evaporator and water bath preset at 85°C. The flask was reweighed to constant weight. Oil and grease derived from the blank determination was subject to the same procedure to obtain the blank for total petroleum hydrocarbons(Adewuyi, G.O. and Olowu, R.A., 2012). The formula was applied:

$$\text{TPH (mg/)} = \frac{a-b*1000}{\text{Sample volume (ml)}} L$$

3.9. Organic Analysis

The groundwater was filtered through Whatmann (41) filter paper in order to remove suspended particles and turbidity. After the removal of suspended particles the sample was passed through Millipore of 0.45 μm filter paper for the removal of small and fine particles. HPLC filtration assembly was used for filtration with the help of vacuum filtration system.

Many extraction methods are used for extraction and pre-concentration of organic compounds but Solid Phase Extraction (SPE) method is a progressively beneficial which was used for extraction and pre-concentration of organic pollutants from the groundwater.

3.9.1. Extraction of Organic Compounds

The 800ml volume of each sample was passed through C18 cartridges for polycyclic aromatic hydrocarbons (PAHs) for DCP and TCP. For maximum contract of sample with C18 adsorbent, the flow rate was adjusted to 40 drops /1ml per minute controlled through vacuum (20 Hg pressure). The PAHs were adsorbed on the surface and the inorganic liquor was collected in a plastic bottle.

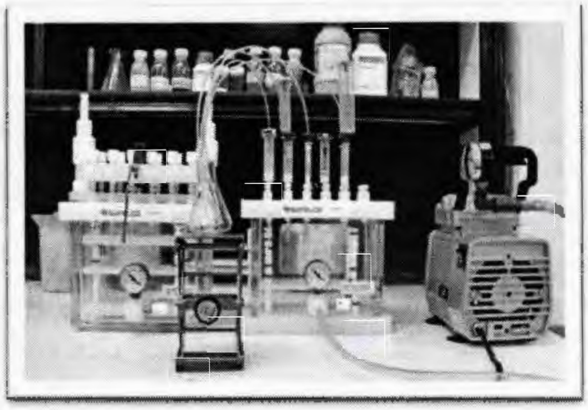

Figure 3.9.1 Solid Phase Extraction Assembly

3.9.2. Pre-Concentration of Organic Compounds

Then by the flow rate of 18 drops or 0.5 ml/ minute was used to elute the adsorbed organic pollutants on the surface of the C18 tube by using 10 ml of the following solvents.

1 Acetonitrile

2. Dichloromethane

After the extraction and pre-concentration, the 800ml volume of each sample was converted into 20 ml and then organic extract was collected in a glass bottle from each sample and was stored at low temperature.

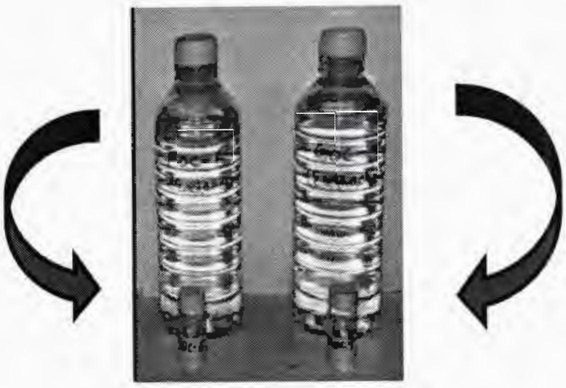

Figure 3.9.2 Pre-concentration of groundwater

3.9.3. UV-visible spectrometry

For most of qualitative analysis, UV-visible spectrometry (UV Specord 205 Analytik Jena) was used. Samples were scanned with following instrumental conditions: wavelength 90-900 nm, Integration time 0.5, Delta λ and Scan speed 2nm/sec. A reference solution consisting of eluting solvents of acetonitrile and dichloromethane was used.

RESULTS AND DISCUSSION

4. Results and Discussion

4.1. Physicochemical Analysis

The results of the physicochemical analysis are depicted in the table4.1 below.

Table4.1 Physicochemical analysis of groundwater

Sr. No.	Sample Code	pH	EC (µs/cm)	TDS (mg/l)	Turbidity (NTU)	DO (mg/l)	SO4 (mg/l)
1	Sq-1	7.25	1365	819	5.14	3.82	7.79
2	Sq-2	7.23	1419	852	5.27	3.5	25.12
3	Sq-3	7.11	2090	1261	9.1	4.49	31.06
4	D-1	7.91	2140	1455	6.71	5.03	45.69
5	D-2	8.09	1047	630	3.7	4.94	11.92
6	PW-1	7.41	1421	856	4.33	3.42	20.91
7	PW-2	8.15	1833	1102	15.9	2.72	29.25
8	PW-3	7.21	6680	ND	5.1	4.77	50.96
9	PW-4	7.42	2140	1287	7.26	4.83	28.99
10	Dh-1	7.95	944	564	41.9	5.2	13.30
11	Dh-2	7.67	3300	ND	6.82	2.81	65.25
12	Dh-3	8.25	5300	ND	6.67	5.58	34.52
13	My-1	7.57	3900	ND	42.6	4.07	41.74
14	My-2	7.66	2200	1320	17.5	2.59	8.99
15	Bk-1	7.23	2570	1023	7.85	4.78	11.77
16	Bk-2	8.01	3410	1225	110	4.97	36.03
	Average	**7.63**	**2609.94**	**1032.84**	**12.39**	**4.22**	**28.95**
	Min	**7.11**	**944**	**564**	**3.7**	**2.59**	**7.79**
	Max	**8.25**	**6680**	**1455**	**110**	**5.58**	**65.25**

4.1.1. Hydrogen ion concentration (pH)

The physicochemical characteristics of groundwater are significantly affected by the ionized ion of hydrogen that exists in H^+ form in water as it gets involved in rearrangement of molecular or ionic structures occurring in the aqueous media. The amount of different types of chemical species in a solution is determined by the acidity or alkalinity of the solution and hence the physical properties like color and smell of the solution are affected. If the alkalinity is raised from 5.0 to 9.0 then the intensity of chemical reactions accelerates from 0.075 to 0.450 mg/l. According to WHO, the permissible limit of pH is from 6.5-8.5 (WHO, 1984).

pH values in ground water in the sampling area ranged from 7.11– 8.25 (Figure 4.1.1) and were within the accepted WHO limit of 6.5-8.5. Natural water is expected to have pH value of between 6 and 8 (Ramesh, 1998; Jee, et al., 2005). The lowest pH value of 7.11 was recorded in sample Sq-3 and the highest value at 8.25 in Dh-3. At D-2, PW-2, Dh-3 and Bk-2 the pH values were above 8 indicating that water is alkaline in nature.

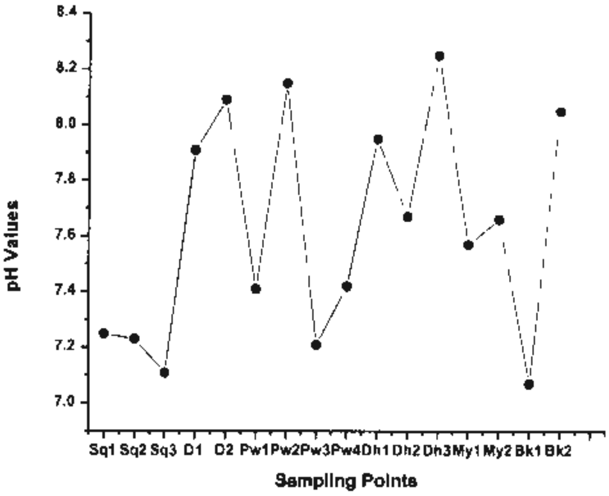

Figure 4.1.1 pH Values of the Groundwater Samples

4.1.2. Electrical conductivity (EC)

Electrical conductivity is the measure of a material's ability to allow the transport of an electric charge. Electrical conductivity of collected water samples are presented in table4.1. The values of EC for groundwater lie in the range of 944 to 6680µS/cm with the mean value of 2609.94µS/cm as shown in Fig. 4.1.2.

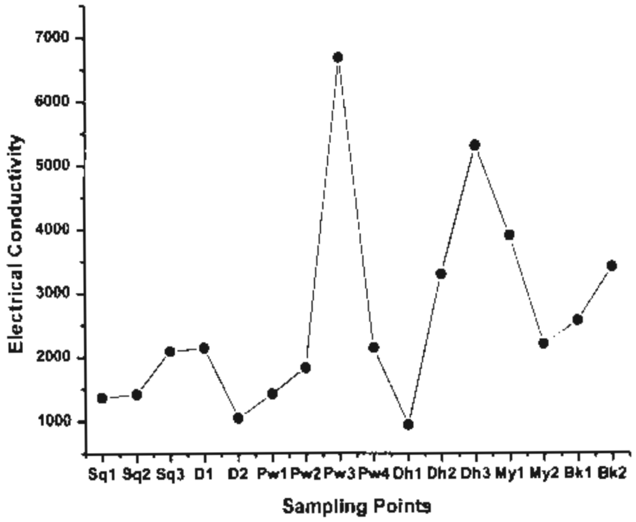

Figure 4.1.2 Electrical Conductivity Values of Groundwater Samples

EC is lowest at Dh-1 and D-2. EC of four samples were slightly above 2000 µS/cm (SQ-3, D-1, PW-4 and MY-2). While three samples bear EC above 2570 µS/cm (BK-1, DH-2 and BK-2) whereas three samples have EC values ranging between 3900-6680 µS/cm (MY-1, DH-3 and PW-3). Highest value of 6680 µS/cm is observed at My-2 sampling point.

4.1.3. Dissolved Oxygen (DO)

The level of dissolved oxygen (DO) in a water body depends on the parameters like degree of hotness or coldness of water, the minerals concentration, the process of aquatic plants photosynthesis and pressure (Zhou, et al., 2000). In an aquatic system, the DO participates in many biological processes and chemical reactions and hence maintains the health of an aquatic system (Chapman & Kimstach, 1992). If the amount of gaseous oxygen becomes lower than 5mg/l in a water body then it poses negative impacts on the biological processes and if the concentration of DO further gets lower than 2mg/l then it may threaten the existence of biological community in an aquatic system (Chapman & Kimstach, 1992; Hertz et al, 1975).

The negative effects on the physicochemical properties of water and the suitability of water to be used for drinking purposes can be accessed through the measurement of DO level. Hence to check the water quality and the efficiency of a waste water treatment plant, first of all the DO level is evaluated. According to WHO, DO levels should not be less than 8mg/l for the palatable water (WHO, 1984). If the quantity of DO is below 8mg/l then it is a symptom of bacterial pollution.

As shown in the Table 3.1, the DO values for the samples ranged from 2.59-5.58 mg/l. The variation in DO range between different samples is depicted in Figure 4.1.3. In the Figure 4, it is clear that the highest DO was recorded at Dh-3 and the lowest was at PW-2.

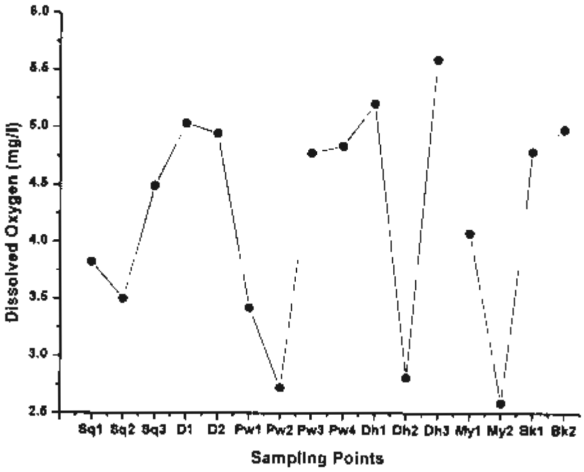

Figure 4.1.3 Dissolved Oxygen Values of the Groundwater Samples

4.1.4. Total Dissolved Solids

The term TDS means all the organic and inorganic species present in water from different sources which may include natural clays, industrial streams and waste water from sewers (Ojo, et. al., 2012). The concentration of TDS in water represents the quantity of minerals present (Freeze and Cherry, 1979). According to WHO (1993), the TDS in the water being used for drinking purpose should not exceed more than 250mg/l. But in the case of fisheries and household uses, WHO (1993) suggest that TDS should not exceed the limit of 1000mg/l (Dami, et al., 2013). The values of TDS in the samples ranged from 564-1455mg/l as shown in Figure 4.1.4.

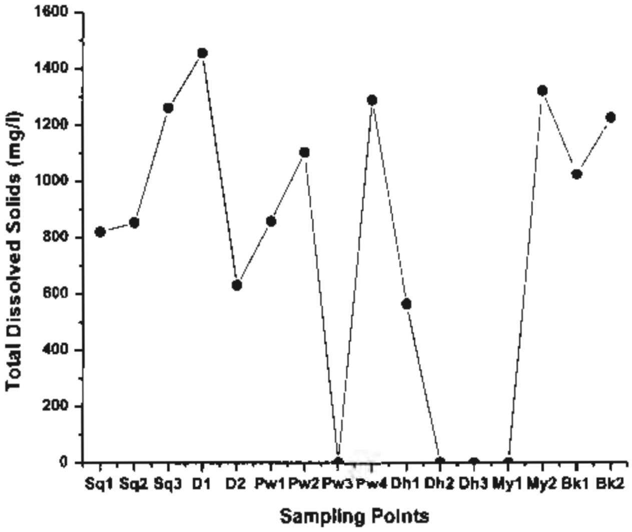

Figure 4.1.4 Values of TDS at Different Sampling Sites

The observed values of TDS in all the groundwater samples were exceeding when compared with WHO 250mg/l prescribed limit except for five samples i.e. PW-3, Dh-2, Dh-3 and My-1 as shown in Table 4.1. In the sampling areas of Sq-3, D-1, PW-3 and PW-4 TDS values were much higher than the standard drinking water values prescribed by WHO.

If TDS are present in a drinking water above the prescribed level then they may lead to health issues like diseases of stomach and intestine and in the long term may cause kidney stones and heart diseases (Sarala and Babu, 2012). When the concentration of TDS in water is below 600 mg/L then it does not develops a bad taste but when the level of TDS rises to 1200mg/l in drinking water then the water has an undesireable taste (Ahmad, 2014). When the waste water from the houses and market areas are not properly discharged then the nearby groundwater resources get polluted.

4.1.5. Turbidity

The deterioration in the clarity of water because of suspended particles or biological or non-biological components present in water is termed as turbidity (Rputheti et al., 2008). Actually different types of dissolved and suspended materials in water which may include phytoplankton, microbes, particles of silt and clay add to the reflective and refractive characteristics of water which is then referred to as turbidity of water (WHO, 1984). The turbidity is measured in Nephelometric Turbidity Unit (NTU) (Ahmad, 2014).The permissible limits of turbidity for water to be used for household purposes stated by WHO is 5NTU (WHO, 1984).

Turbidity poses negative impacts on both the physical and chemical characteristics of a water body. The turbid substances in water affect its color, the activity of bacterial population is enhanced thus deteriorating water quality and the processes of chemical transformation between the toxic metals and suspended particle further deteriorates the water quality (WHO, 1984).

The turbidity for all the sampled water ranged from 3.7-110NTU (Table 4.1) as shown in Figure 4.1.5. Majority of samples had turbidity values above the WHO accepted standard (5 NTU) except for the two samples D-2 and PW-1 having turbidity of 3.7 and 4.33 respectively (Figure 3.2). In the Figure 3.2 it is clearly observable that five samples had much high turbidity values at 110NTU, 15.9 NTU, 41.9 NTU, 42.6 NTU, 17.5 NTU and 11.0 NTU of Bk-2, PW-2, Dh-1, My-1, My-2 and Bk-2. It may be attributed to some impact of exploration in the area(Dami,et al., 2013).

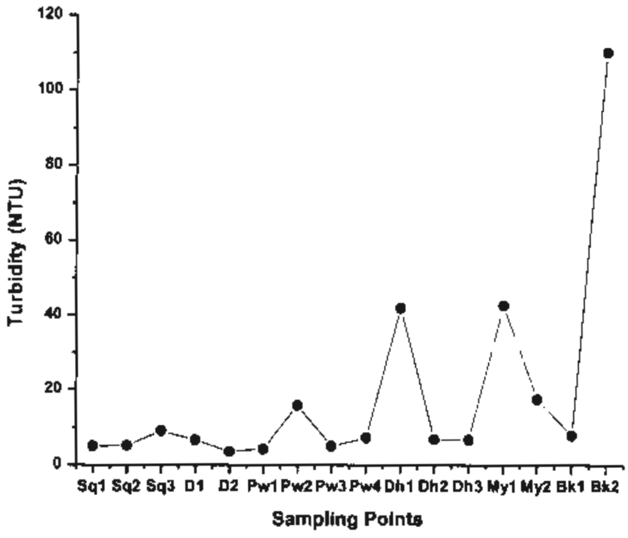

Figure 4.1.5 Turbidity Values of the Groundwater Samples

Highest value of turbidity was recorded at 42.6 NTU for My-1. The high range of turbidity may be a consequent of oil related activities like gas flaring and oil spillage could have serious health implications for the residents within the study area (Dami,et al., 2013).

4.2. Anion Analysis

4.2.1. Sulphate Analysis

It was reported that some non-hydrocarbon constituents exist in the crude oil for example nitrogen, sulphur or oxygen and these constituents are referred to as hetero-atoms (Zemo and Foote, 2003).The sulphate ion concentration in the samples ranged between 7.79-65.25mg/l as depicted in Figure 4.2.1. In the groundwater samples the lowest sulphate ions were found in Sq-1 i.e. 7.79mg/l and the highest sulphate ions were found in sample Dh-2 i.e. 65.25 mg/l. Average value was found to be 28.96 mg/l. All the values of sulphate ions were not exceeding the limits i.e. 250mg/l recommended by WHO. It means that ground water had no significant geological difference (WHO, 2004).

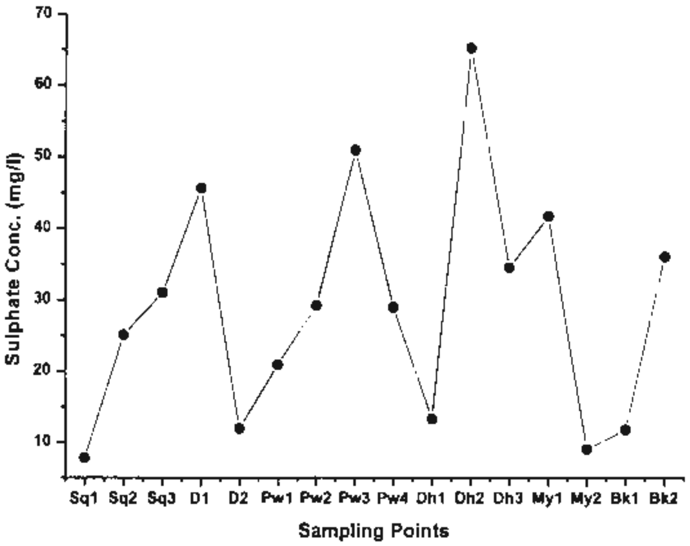

Figure 4.2.1 Values of Sulphate Ion Concentration of the Groundwater Samples

4.3. Heavy Metals Analysis

Heavy metals are considered as one of the hazardous pollutants in natural environment due to their toxicity, persistence, risk (direct/indirect) to human beings and aquatic life (Tam and Wong, 2000; Ackerfors, 1971 ; Bryan, 1971 and 1976) and long-term damage to the environment (Fatoki and Mathabatha, 2001;Tam and Wong, 2000). Metal elements are added to water bodies of our environment either through natural processes and/or anthropogenic activities.

If the amount of transition metals in an environmental media exceeds the permissible limits then it poses negative impacts on the ecological system and the term heavy metal pollution is assigned to this process. In the present era, the industrial activities involving extraction and purification processes, fabrication of variety of industrial chemicals and waste from residential sector are increasing the metal contamination in the environment. Although, few metallic elements are significant for synthesizing the specific enzymes and proteins in living organisms but if they exceed a certain limit then their bioamplification starts in the food chain and through biochemical transformation processes they enter into the water supplies (Adelekan and Abegunde, 2011).

Chronic problems associated with long-term heavy metal exposures are mental lapse (lead); toxicological effects on kidney, liver and gastrointestinal tract (cadmium); skin poisoning and harmful effects on kidneys and the central nervous system (arsenic). There is a link between long term exposure to copper and decline of intelligence in young adolescents (Adelekan and Abegunde, 2011)

The results of the heavy metal analysis are shown in the table 4.3. The permissible limits of heavy metals are stated by many organizations including World Health Organization (WHO), European Union Standard (EU). According to WHO (1996) the maximum permissible limits of heavy metals in drinking water are Cadmium (0.003 mg/l), Copper (2.0 mg/l), Lead (0.05 mg/l) (WHO, 2011), Zinc (3mg/l).

Table 4.3 Concentrations of Heavy Metals at Different Sampling Sites

Sr. No.	Sample Code	Zn (µg/l)	Pb (µg/l)	Cd (µg/l)	Cu (µg/l)
1	Sq-1	9.89	4.96	0.37	BDL*
2	Sq-2	22	3.23	0.59	BDL
3	Sq-3	358	6.13	0.45	BDL
4	D-1	294	4.83	1.11	BDL
5	D-2	33.7	5.79	0.58	3.27
6	PW-1	27.1	5.41	BDL	BDL
7	PW-2	24.5	2.49	0.36	18.795

8	PW-3	164	4.71	0.18	BDL
9	PW-4	8.43	2.66	0.55	BDL
10	Dh-1	344	5.53	0.2	2.92
11	Dh-2	295	4.37	0.31	BDL
12	Dh-3	5510	2.92	0.13	BDL
13	My-1	3436	4.6	1.17	BDL
14	My-2	166	2.6	0.85	BDL
15	Bk-1	49.9	2.35	0.57	3.32
16	Bk-2	5600	2.91	0.16	1.98
	Average	**1021**	**4.0931**	**0.534**	**6.057**
	Min	**8.43**	**2.35**	**0.13**	**1.98**
	Max	**5600**	**6.13**	**1.17**	**18.795**

*BDL: Below Detection Limit

Zinc is a natural trace element. If zinc is present in water then it develops an unpleasant stringent taste. In natural surface and groundwater the zinc is present not more than0.01mg/litre and0.05mg/litre, respectively. In the household water the level of zinc may slightly rise because of dissolving a minute amount amount from the pipelines. A human body requires 15-20mg/day of Zinc. In Pakistan, 5mg/l is suitable although 3mg/l is recommended by WHO (Akhter, 2013).

Zinc concentration in the sampling points ranged from 8.43 to 5600 ppb (Table 4.3). All samples lied within the permissible limits of WHO except three having above 3 mg/l of zinc. These three samples as depicted in figure 4.3.1 were MY-1, DH-3 and BK-2 with zinc values as 3.44, 5509.82 and 5600 mg/l respectively. The lowest concentration of zinc was observed at Sq-1 (0.00989 µg/l) and highest value was observed for BK-2 (5600 µg/l). Whereas samples SQ-3 and DH-1 had zinc levels comparatively higher than other samples i.e. 0.36 and 0.34 mg/l respectively. Increased concentration of zinc in groundwater of My-1, DH-3 and BK-2 may be due to the anthropogenic sources like from old houses, wood preservatives, shampoos and soaps (Lew, 2008). Besides, the zinc contamination is found to occur in areas where oil extraction and refining processes are conducted. Zinc is used frequently in drilling fluids in the form of zinc carbonate and decreases the risk of corrosion in well control technique. Well control technique is applied in drilling operation to maintain the fluid column hydrostatic pressure and formation pressure to maintain influx of formation fluids into the wellbore (Asia et al., 2007).

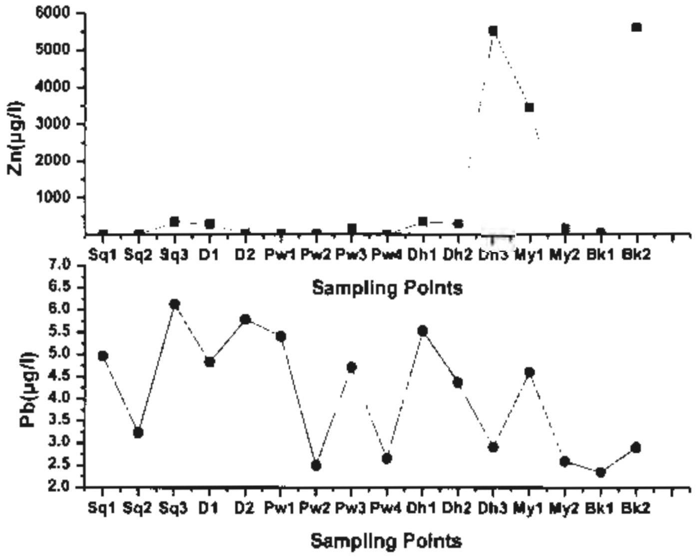

Figure 4.3.1 Concentrations of Zinc and Pb at Different Sampling Sites

Lead is one of the hazardous and potentially harmful polluting agents. It has impact on humans and animals. Lead poisoning symptoms usually develop slowly. It inhibits the formation of hemoglobin by reacting with SH group and interfering with many enzyme functions (Anwar and Vanita, 2014).The main source of lead in groundwater is from the rocks containing lead sulfide and oxides. The household plumbing fixture made up of lead may contribute lead in the drinking water. The other contributors are the leaded gasoline and lead in paint (Khan, 2011).

Considering drastic effects of lead, for Pakistan the value has been set at less than or equal to 0.01mg/l (Pak-EPA, 2008). The allowable limit in human whole blood is 10-25µg/l. Excess quantities of lead may impact human health, especially affecting small children. Therefore a very conservative limit has been set at 0.05mg/l of lead in drinking water (WHO, 2011; McCubbin, 2001).

The concentration of lead (Figure 4.3.1) in groundwater of sampling area varied from 2.35 to 6.13µg/l (Table 4.3) with the average of 4.093µg/l. All the samples were within permissible limits defined by WHO, EU and Pak-EPA.

In groundwater samples, Cd concentrations ranged from 0 to 1.17µg/l as shown in table 4.3. The highest value was observed at My-1 and lowest value was found at DH-3. In drinking water maximum acceptable concentration of cadmium is 0.005mg/l (EU) and 0.003 mg/l (WHO, 2011). All the values of Cd were found to be below permissible limits (Figure 4.3.2).

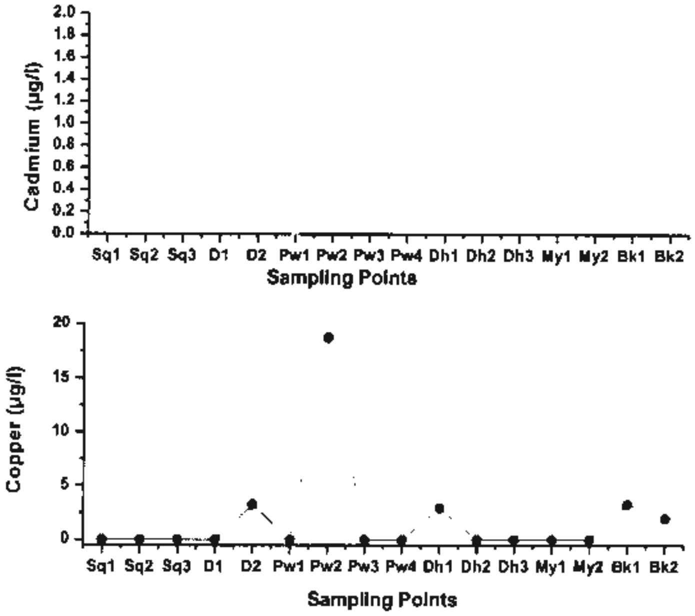

Figure 4.3.2 Concentrations of Cd and Cu at Different Sampling Sites

The permissible limit of Cu according to EU, WHO and Pakistan Standard Values is 2mg/l. The Cu concentration in the groundwater varied from 0 to 18.795µg/l as shown in Table 4.3. Copper in all the samples was found below the limits recommended by WHO, Pak-EPA and EU (Figure 4.3.2).

The groundwater samples met the WHO (1993, 1996, 2004) guideline values set for Pb, Cd and Cu but exceeded the limit for Zn. For samples DH-3 and BK-2, the concentration of zinc was measured as 5509.82 and 5600µg/l respectively, which is above the limit value of 500µg/l recommended by WHO.

Besides hydrocarbons, some heavy metals can give information about the origin of contamination, since crude oils and heavy distillates contain a wide range of trace metals. Zn is present in the oils as metallo-porphyrin complexes as well as non-porphyrin complexes and their concentration increases with increasing hydrocarbon heavy fraction contents (Adewuyi and Olowu, 2012).

4.4. Oil and Grease Analysis

The oil and grease content in samples ranged from 0.14-3.58µg/l as shown in Table 4.4 below. The highest value of oil and grease was 3.58, 1.25, 0.56, 0.47, 0.44, 0.41, 0.38 and 0.33 recorded at MY-1, Dh-3, Sq-3, Bk-2, My-1, PW-3, Sq-1, Dh-1 and Dh-2 (Figure 4.4). All the values of oil and grease were below the 1mg/l as reported in a study for uncontaminated sites (Adewuyi and Olowu, 2012).

The results of the zinc concentration in groundwater samples show that the higher concentration of zinc was 5510µg/l, 5600µg/l and 3435µg/l recorded at Dh-3, Bk-2 and My-1 respectively. It was observed that the oil and grease concentration at Dh-3, Bk-2 and My-1 were also high as 1.25µg/l, 0.47µg/l and 3.58µg/l. Heavy metals pollution of water contaminated by crude oil exudates has been reported previously (Olufemi, et al., 2012)

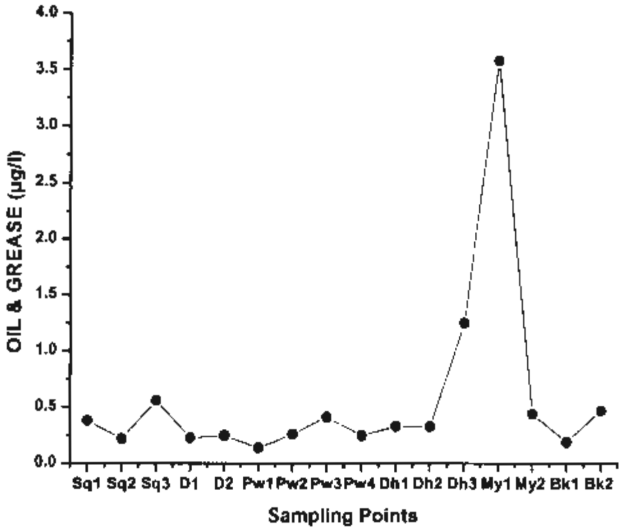

Figure 4.4 Concentrations of Oil and Grease at Different Sampling Sites

Table 4.4 Values of Oil and Grease and TPH at Different Sampling Sites

Sr. No.	Sample Code	Oil & Grease (µg/l)	TPH (µg/l)
1	Sq-1	0.38	71.00
2	Sq-2	0.22	42.00
3	Sq-3	0.56	673.33
4	D-1	0.23	888.00
5	D-2	0.25	1241.00
6	PW-1	0.14	1342.00
7	PW-2	0.26	345.50
8	PW-3	0.41	486.00
9	PW-4	0.25	1054.67
10	Dh-1	0.33	82.00
11	Dh-2	0.33	380.80
12	Dh-3	1.25	5414.67
13	My-1	3.58	1582.00
14	My-2	0.44	1148.24
15	Bk-1	0.19	2202.22
16	Bk-2	0.47	54.67

4.5. Total Petroleum Hydrocarbon (TPH)

The computable quantities of the hydrocarbons that naturally occur in the crude oil are referred to as Total Petroleum Hydrocarbons (TPH) (Adewuyi and Olowu, 2012). TPH concentrations in samples ranged from 0.042-5.414µg/l as shown in Figure 3.9. These values were below the European Union limits of 0.2 to 10µg/l (Lang et al., 2013). The highest concentrations of TPH were 5.414, 2.202, 1.582, 1.342, 1.241 and 1.148 µg/l at Dh-3, Bk-1, My-1, PW-1, D-2 and My-2. The comparatively lower ranges were 1.054, 0.888 and 0.673 µg/l at PW-4, D-1 and Sq-3 respectively. It can be stated that the groundwater sources near the oil exploration sites were containing TPH but the levels detected were below the EU suggested limits.

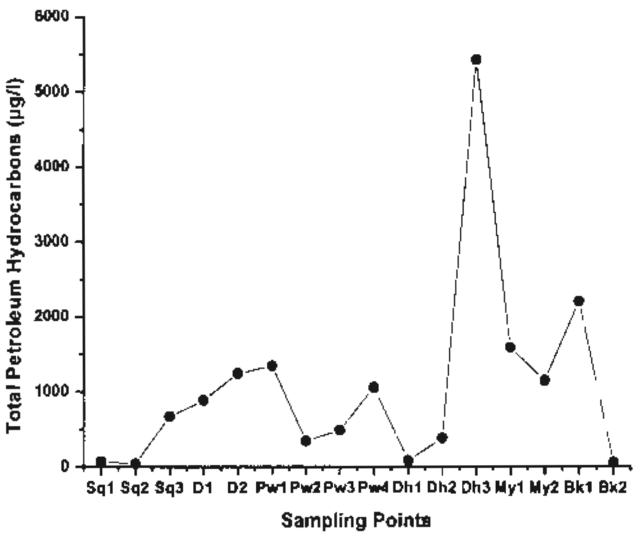

Figure 4.5 TPH concentrations at Different Sampling Sites

From each sampling site 2, 3 or 4 samples were collected from some distance and the variation is observed in the results of the samples of same area. This variation may be due to variation in TPH that are more soluble in water. Besides as oil percolates down through the soil, a portion of oil may be dissolved in the soil depending upon the ability of the soil to dissolve it. Overland flow may also be responsible for varying the concentration of TPH between the sampling points of the same area. The different types of the hydrocarbons have different properties of solubility, percolation, volatilization and biodegradation so this may also be a reason for the variation observed in the results (Alinnor et al., 2014).

4.5.1. Qualitative Analysis by UV Visible Spectrometry

Hydrocarbons, as defined in water quality monitoring, are substances originating from or produced out of crude oil and natural gas. This group comprises a huge amount of different molecules, ranging from aromatic substances (e.g. benzene) to linear alkanes (e.g. hexane). The signal in the UV-absorption spectrum for these substances varies with their chemical structure, but it is known that depending on the application about 30 - 80 percent of the substances that contribute to the parameter Total Hydrocarbons produce a useful optical signal, either by conjugated double bounds, or by chromophore functional groups.

Overlaid UV spectra of some hydrocarbons are shown in Figure 4.5.1 and 4.5.2.

Absorption peak around 190 nm in sample Sq-2, Sq-3, D-2, PW-1, PW-2, PW-3, DH-1, DH-2, MY-1 and BK-1 was due to the delocalization of the electrons taking part in the conjugated double bonds. All are non-aromatic hydrocarbons and elute very close to each other, which means that the spectrum of a conjugated diene. In sample Dh-3 peaks in the region from 282 - 322 indicated presence of TPH.

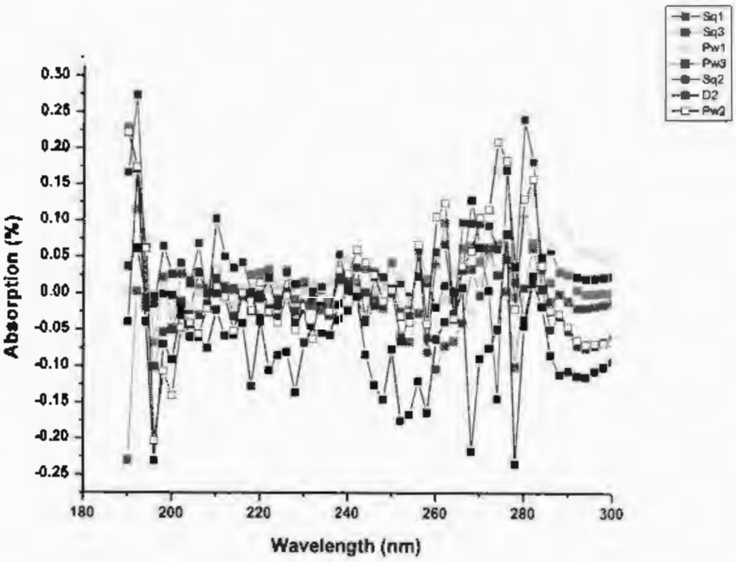

Figure 4.5.1 UV Spectrometric Peaks at Sq., Pw. and D.

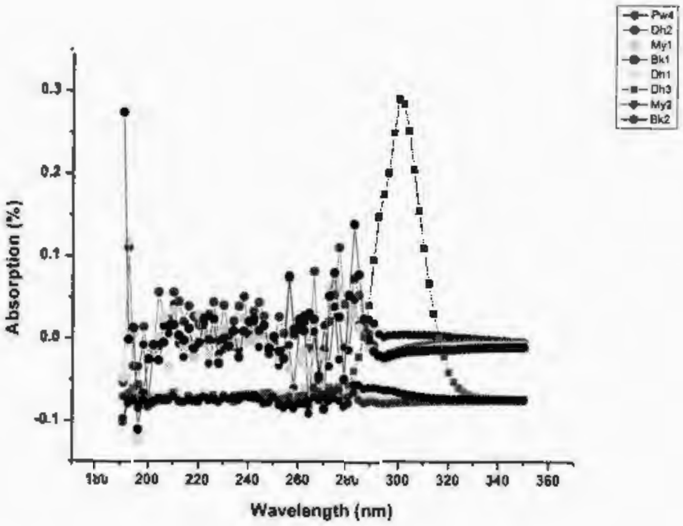

Figure 4.5.2 UV Spectrometric Peaks at Pw., Dh., My. And Bk.

4.6. Stable Carbon Isotopic Analysis

Carbon is present in the environment as two main stable stable isotopes, ^{12}C and ^{13}C, which make up 98.9% and 1.1% of the earth's carbon pool respectively (Brocks & Pearson, 2005; Farquhar, Ehleringer, & Hubick, 1989; O'Leary, 1981). The ratio between ^{13}C and ^{12}C is represented by the $\delta^{13}C_{(TDIC)}$ of a sample. This is measured by comparison to an internationally established standard, Vienna Peedee Belemnite (Boschker & Middelburg, 2002), calculated using the equation:

$$\delta^{13}C = ((^{13}C/^{12}C_{sample} - {}^{13}C/^{12}C_{standard}) \times 1000\%) / {}^{13}C/^{12}C_{standard}$$

Petroleum is generated by the thermal degradation of modern carbon material over thousands of years. Stable isotope tracing can be a highly useful tool in the identification and fingerprinting of petroleum in the environment. Inorganic depleted $\delta^{13}C$ represents mixing of petroleum hydrocarbons (Natter et al., 2012; Jackson, Pardue, & Araujo, 1996). Stable carbon isotope of groundwater is presented in table 4.6.

Table 4.6 Stable Carbon Isotope Values for Groundwater Samples

Sr. No.	Sample Code	$\delta^{13}C\%$
1	Sq-1	-8.95
2	Sq-2	-9.93
3	Sq-3	-9.79
4	D-1	-10.75
5	D-2	-12.58
6	PW-1	-9.84
7	PW-2	-13.21
8	PW-3	-9.07
9	PW-4	-10.24
10	Dh-1	-4.84
11	Dh-2	-11.86

12	Dh-3	-11.07
13	My-1	-11.73
14	My-2	-10.14
15	Bk-1	-7.9
16	Bk-2	-8.93

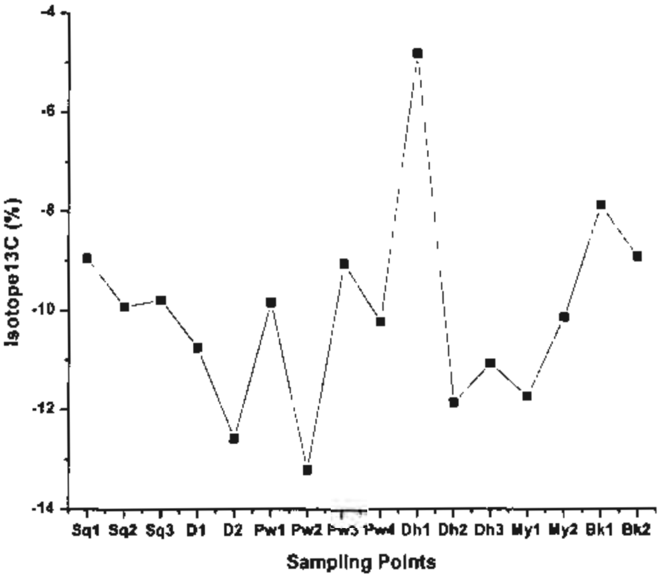

Figure 4.6 $\delta^{13}C$ Values at Different Sampling Sites

Depleted C-13 was observed for the samples D-2, PW-2.PW-4, Db-2, Dh-3 My-1 andMy-2 which indicated possible mixing of petroleum hydrocarbon in these samples. Samples having C-13 values in the range of -4 to -8 indicated no mixing of petroleum hydrocarbon.

4.7. Correlation Analysis

Statistical equation of linear correlation was applied between the physicochemical and organic parameters. If the values of correlation coefficient are less than 0.5 then it means a weak correlation and if value is greater than 0.8 then it shows a strong correlation. If the water is acidic in nature then the concentration of carbonate ions in water would be low and CO_2 degassing would be insignificant. In 12 groundwater samples the pH values ranged from 7.11-7.91 i.e in neutral range so the concentration of stable carbon isotope ratio was normal.

The correlation coefficient evaluated via E Views 8 is -0.297036 which depicts that the pH and C13 values are negatively correlated (Deutsch and Siegel, 1997).

Changes in pH in water bodies can affect the availability and toxicity of constituents such as trace metals, non-metallic ions such as ammonium and essential elements for example, selenium (Okoye, et al., 2014). Alkaline water would promote the transformation of heavy metal cations into suspended forms and their deposition onto bottom sediment because in the presence of free oxygen insoluble metal carbonates and hydroxide becomes stable at pH values higher than 8 (Fostner,1981). The alkaline water may decrease the solubility of metals (Sarala and Babu, 2012). So the concentration of heavy metals would increase in low pH. At low pH levels, the metals of variable valency termed as transition metals for example Pb, Zn, Cr and Cu have the possibility of more than 10mg/l accumulation. As the pH ranged from neutral to slightly alkaline nature so the concentration of heavy metals was very insignificant in the groundwater samples. Statistical equation of linear correlation was applied between pH and values of heavy metals. The values of linear correlation coefficient, 'R' between Ph and Pb, Cd, Cu and Zn were 0.096735, 0.214673, 0.550338 and 0.572571. These values of regression analysis of Ph with Pb and Cd indicated the weak correlation whereas the R values of pH with Cu and Zn showed a slight positive correlation.

The high alkalinity of groundwater in certain locations in the study area may be due to the presence of bicarbonate and some salts (Okoye, et al., 2014). As the pH of the samples ranged from neutral to slightly alkaline ranges so the correlation between pH and sulphate concentration was 0.06421 which indicates a weak correlation.

TDS in water comprise of charged species that allow the flow of electric charges to pass through water and this property of water to conduct electricity increases as the proportion of the TDS increases (Wood, 1976; Lloyd and Heathcote, 1985 & Hem, 1985). The correlation coefficient value for EC and TDS was 0.632447 which means that the variables were positively correlated. The correlation analysis was also performed for the EC and the sulphate concentration because the salts breakdown into positive and negative ions and assist in conductance and the result of correlation analysis showed a positive correlation of 0.623345 between EC and sulphate concentration.

The EC decreases when the concentration of salts increases above a certain threshold value because it results in formation of ionic bonds that reduce the strength of ionic charges.

Hence above this point EC would not increase with increasing quantity of TDS. In other words, the EC is directly related to ionic species which are present in groundwater in dissolved form (Sarala and Babu, 2012).

If the carbonates and sulphates concentration increases in a water body then it may raise the hardness of water and hence raising the level of TDS (Ojo, et. al., 2012). A positive correlation of 0.699214 was computed between TDS and sulphate concentration. The correlation analysis between oil and grease and TPH was 0.319461 which showed that the two variables had a weak positive correlation.

CONCLUSION

5. Conclusion

Alkaline nature of the groundwater samples may be attributed to the spilling of petroleum products in the vicinity of the oil extraction area. The sulphate ion concentration showed that ground water has no significant geological difference. The results of the zinc concentration in groundwater samples show higher concentration of zinc and oil and grease at Dh-3, Bk-2 and My-1. These observations reflect impact of exploration related activities in these areas. TPH concentrations in samples ranged from 42.00-5414.67µg/l. The highest concentrations of TPH indicate presence of hydrocarbons in groundwater which may be attributed to exploration activities in nearby areas. UV-absorption spectrum for groundwater showed absorption peak around 190 nm in tthe samples. In sample Dh-3 peaks in the region from 282 -322 nm indicated presence of TPH. Depleted C-13 values are observed indicated possible mixing of petroleum hydrocarbon in these samples.

Statistical equation of linear correlation was applied between the physicochemical and organic parameters. The correlation coefficient value depicted that the pH and C13 values are negatively correlated. Statistical equation of linear correlation was applied between pH and values of heavy metals. The values of linear correlation coefficient, 'R' between Ph and Pb, Cd, Cu and Zn were 0.096735, 0.214673, 0.550338 and 0.572571. These values of regression analysis of Ph with pB and Cd indicate the weak correlation whereas the R values of pH with Cu and Zn show a slight positive correlation. The correlation between pH and sulphate concentration was 0.06421 which indicates a weak correlation. The correlation coefficient value for EC and TDS showed that the variables are positively correlated. The EC and the sulphate concentration were also positively correlated. A positive correlation was computed between TDS and sulphate concentration. The correlation analysis between oil and grease and TPH showed that the two variables have a weak positive correlation. It is concluded from the present investigation that oil exploration activities in study area contaminate nearby groundwater sources which ultimately cause serious health issues to local population consuming polluted groundwater.

REFERENCES

6. References

1) Ackerfors, H. (1971). Mercury pollution in Sweden with special reference to conditions in the water habitat. *The Royal Society*, 177: 365-387

2) Adeniyi, A.A., Yusuf, K.A. and Okedeyi, O.O. (2008). Assessment of the exposure of two fish species to metal pollution in the Ogun river catchments, Ketu, Lagos, Nigeria. *Environ. Monit.Assessment*. 137: 145-458

3) Adelekan, B.A. and Abegunde, K.D. (2011). Heavy metals contamination of soil and groundwater at automobile mechanic villages in Ibadan, Nigeria. *Int. J. Phys. Sci.* 6(5): 1045-1058

4) Adewuy, G.O. and Olowu, R.A. (2012). Assessment of oil and grease, total petroleum hydrocarbons and some heavy metals in surface and groundwater within the vicinity of NNPC Oil Depot in Apata, Ibadan Metropolis, Nigeria. *IJRRAS*. 13 (1):166-174

5) Memon, A.R. (2008). Status of Petroleum Sector in Pakistan - A Review. *NICE-RJCS*. 1-15.

6) Ahmad, S. and Mishra, A. (2014). A Study on Physico-Chemical Properties of Ground Water Quality of Various Locations of Kanpur City. *IJSR*. 3: 177-179

7) Akhter, S.A.F.M., (2013). Performance Assessment of Macrophyte Stabilization Pond- A case Study of Eight Parameters. *IJSRP*. 3(6): 2250-3153.

8) Akpoborie, I.A., Ekakite, A. O. and Adaikpoh, E.O. (2000), The Quality of Groundwater from Dug wells in Parts of the Western Niger Delta, Knowledge Review 2: 72-79.

9) Aremu, D., Olawuyi, F., Metshitsuka, S. and Sridhar, K. (2002). Heavy Metal Analysis of Groundwater from Warri, Nigeria. *Int. J. Environ. Health Res.*12:61-72.

10) Aggarwal, P.K., Froehlich. K. and Kulkarni, K.M. (2004). Environmental Isotopes in Groundwater Studies. *Groundwater*. 2: 1-11

11) Aggarwal, P.K., Gat, J.R., Klaus, F.O. and Froehlich, K.F.O. (2006). Isotopes in the Water Cycle Past, Present and Future of a Developing Science. Dordrecht: Springer.

12) Agency for Toxic Substances and Disease Registry (ATSDR) (1999). Toxicological profile for total Petroleum hydrocarbon. Atlanta, GA: U.S. Department of Health and Human Services, Public Health Service.

13) Alakpodia, I. J. (1989). The Effects of Gas Flaring on the Micro-climate and Adjacent Vegetation in Isoko Area of Bendel State. (Unpublished M.Sc Thesis, University of Ibadan).

14) Alakpodia, I. J. (1995). The Oil Industry and the Economic Environment of the Niger Delta. Paper presented at the 30th Annual Conference. Nigeria Geographical Association, at the University of Benin. Benin City. Nigeria.

15) Alinnor, I.J., Ogukwe, C.E. and Nwagbo, N.C. (2014). Characteristic Level of Total Petroleum Hydrocarbon in Soil and Groundwater of Oil Impacted Area in the Niger Delta Region, Nigeria. Journal of Environment and Earth Science. 4:188-195

16) Amyx, J.D., Bass and Whiting, R.L. (1960). Petroleum Reservoir Engineering, McGraw-Hill Company, New York.

17) Anderson, E.L., Howlett E., Kolluru, V., Reed, N., Spaulding, M. (1993). The Worldwide Oil SpillModel (WOSM): An Overview. Ontario Environment. Chicago University Press.

18) Anwar, K.M. and Vanita, A., 2014. Analysis of groundwater quality using statistical techniques: A case study of Aligarh City (India). International Journal of Technical Research and Applications e-ISSN: 2320-8163, www.ijtra.com Volume 2, Issue 5 (Sep-Oct 2014), PP. 100-106

19) A O MajolagbeA AKasali and O L Ghaniyu Quality assessment of groundwater in the vicinity of dumpsites in Ifo and Lagos, Southwestern Nigeria. Advances in Applied Science Research, Vol. 2 no 1 2011, 289-298

20) Ashurst, P.R. and Dennis, M.J.(1995). Food authentication. London: Blackie Academic and Professional.

    a. Asia, I. O. , Jegede, S. I., Jegede, D. A., Ize-Iyamu, O. K. and Akpasubi, E. B. (2007). The effects of petroleum exploration and production operations on the heavy metals contents of soil and groundwater in the Niger Delta. International Journal of Physical Sciences Vol. 2 (10), pp. 271-275

21) Akoteyon, I.S., Mbata, U.A. and Olalude, G.A. (2011). Investigation of heavy metal contamination in groundwater around landfill site in a typical sub-urban settlement in Alimosho, Lagos-Nigeria. *Journal of Applied Sciences in Environmental Sanitation*. 6(2): 155 – 163.

22) Amadi, A.N., Okoye, N.O., Alabi, A.D., Tukur, A. and Angwa, E.M., 2014. Quality Assessment of Soil and Groundwater near Kaduna Refinery and Petrochemical

Company, Northwest Nigeria. Journal of Scientific Research & Reports 3(6): 884-893

a. Bryan, G. W. (1971). The effects of heavy metal (other than mercury) on marine and estuarine organisms. Proceedings of Royal Society London Series Biological, 177, 389.

b. Bryan, G. W. (1976). Heavy metal contamination in the sea. In: R. Johnston, Eds. Marine pollution. Academic Press, New York and London. 186-302.

23) Brown, R.H., Kasperson, R. E. and Raymond, S. (1990). Trace Pollutants. In the Earth as Transformed by Human Action. U.S.A: Cambridge University Press. Pp. 437 – 454.

24) Bruins, M. R.; Kapil, S.and Oehme, F. W., (2000). Microbial resistance to metals in the environment. *Ecotox. Environ.Safe.* 45: 198-207

a. Bruvold, W.H., Ongerth, H.J. (1969). Taste Quality of Mineralized Water. Journal of The American Water works Association. Vol. 61:170.

25) Bayode, O.J.A., Adewunmi, E.A. and Odunwole, S. (2011). Environmental implications of oil exploration and exploitation in the coastal region of Ondo State, Nigeria: A regional planning appraisal. *JGRP.* 4(3): 110-121

26) Burbank, D.W. (1982). The chronological and stratigraphic development of the Kashmir and Peshawar intermountain basins, northwestern Himalaya, Hanover, New Hampshire, Dartmouth college, p. 291.

27) Burbank, D.W. and Tahirkheli, R.A.K. (1985). The magneto-stratigraphy, fission-track dating and stratigraphic evolution of the Peshawar intermountain basin, Northern Pakistan, Geol. *Soc. America Bull.* 96: 539-552.

28) Chinedu, O. and Lovette, O. (2014). Impact of Oil Spill on Land and Water and its Health Implications in Odugboro Community, Sagamu, Ogun State, Nigeria. World Journal of Environmental Sciences & Engineering. 1(1):1-21

29) Clark, I.D. and Fritz, P. (1997). Environmental Isotopes in Hydrology. Boca Raton: Lewis.

30) Cook, P.G. and Herczeg, A.L (2000). Environmental Tracers in Subsurface Hydrology. Boston: Kluwer Academic Publishers.

31) Chatterjee, S.N., Chandra, G., and Dangler, T.K. (2005). Physio Chemical Properties and Bacteriological Examination of Mondeswari River of Hoogly Distinct West Bengal. *J. Appl.* 16 (2): 242 -244

32) Christensen, J.B., Jensen, D.L., Gron, C., Filip, Z. and Christensen, T.H., (1998). Characterization of the dissolved organic carbon in landfill leachate-polluted groundwater. *Water Res.* 32: 125-135.

33) Costello, J. (1979). Morbidity and Mortality Study of Shale Oil Workers in the United States, Environmental Health Perspectives. 30: 205-208,

34) Riccardi, C., Fillippo, P., Pomata, D., Incoronato, F., Marco, B., Marco, P.P. and Spicaglia, S. (2008). Characterization and distribution of petroleum hydrocarbons and heavy metals of groundwater from three Italian tank farms. *Sci. Total Environ.* 393: 50-63.

35) Dami, A., Ayuba, H.K. and Amukali, O. (2013). Groundwater Pollution in Okpai and Beneku Ndokwaeast local government area, delta state, Nigeria. *J. Environ. Res. Manage.* 4(1):171-179

36) Deutsch, W.J. and Siegel, R. (1997). Groundwater Geochemistry: Fundamentals and Applications to Contamination. Lewis Publishers, Boca Raton London, New York, Washington, D.C. Pg No. 11,12 194

37) District Census Reports (1998). District Census Reports for each District containing General Description of the District and Broad Analysis of Population and Housing Data followed by detailed statistical tables. Population Census Organization, Pakistan.

38) Egborge, A.B.M. (2000), Government, Oil Companies, The Peoples and the Niger-Delta Environment: 4th Convocation Lecture of Delta State University, Abraka. Nigeria. 106.

39) Ekpenyong, N.S. and Udofia, U.S. (2015). Oil Pollution and Its Impact on Water Quality in Ibeno Community. Studies in Sociology of Science. 6(2):8-12.

40) Emken, E.A (2001). Stable isotope approaches, applications, and issues related to polyunsaturated fatty acid metabolism studies. Lipids; 36:965-73.

41) Ekundayo, J.A. (1988). Development in a fragile economy, 1998. Foundation Lecture Series. Federal University of Technology, Akure.

42) Energy Information Administration, (2005-06) Energy InformationAdministration. Pakistan country brief analysis. http://www.eia.doe.gov/cabs/Pakistan/Background.html

a. EPA, U.S. (1999): Drinking water and Health. EPA 816-k001.

43) http://www.doh.wa.gov/epa/water.htm(Assessed: 2011 March 7)

a. Fatoki, O. S. and Mathabatha, S. (2001). An assessment of heavy metal pollution in the East London and Port Elizabeth harbors Water SA, 27(2): 233-240

b. Frost, T.K., Johnsen,S. and Utvik,T.I. (1998). Environmental Effects of Produced Water Discharges to the Marine Environment, OLF, Norway.

44) http://www.olf.no/static/en/rapporter/producedwater/summary.html.)

a. Franson, M.A.H. (1995). American Public Health Association, American Water Health Association Water Environment Federation. Methods. 6:84.

b. Gustafson, J.B. (2007). Using TPH in Risk - Based Corrective action.

c. Hem, J.D (1985). Study and Interpretation of the Chemical Characteristics of Natural Water, 3rd ed. U.S. Geological Survey Water-Supply Paper, vol. 2254. Washington, DC.

d. Hussain, N. (2013), 'Pakistan's Energy Crisis and Iran-Pakistan Gas Pipeline', IPRI

45) Journal Conference, Islamabad.

a. Hogan, C.M. (2010). Encyclopedia of Earth, National Council for Science and the Environment, Washington DC.

b. J.A. Vodela, S.D Renden,.W.H. Lenz, MchelHenney and B.W. Kemppainen, "Drinking water contaminants".*Poult.Sci.*, Vol. 76, 1997.pp 1474-1492.

46) (Vodela, J.A. et.al., 1997)

47) Jackson, R.N., Baird D. and Els S.. (2005). The effect of the heavy metals, lead (Pb2+) and zinc (Zn2+) on the brood and larval development of the burrowing crustacean *Callianasskraussi. Water S.A.*, 31(1): 107-116.

48) Jain, P.K. and Bajpai, V., 2012. Biotechnology of bioremediation- a review. International Journal of Environmental Sciences. Volume 3, No 1, 535-549.

49) Jones PJH, Leatherdale ST. Stable isotopes in clinical research: safety reaffirmed. Clin Sci (Colch) 1991; 80:277 80.

50) Kahlown, M.A., Tahir, M.A. and Sheikh, A.A., 2004. Water Quality Status In Pakistan, Second Report 2001-2003. Ministry of Science & Technology.

51) Koir IJ, Kocjan~i~ M, Ogrinc N, Jurkica Kidri~ J. Use of SNIF-NMR and IRMS in combination with chemometric methods for the determination of chaptalisation and geographical origin of wines (the example of Slovenian wines). Anal Chim Acta 2001; 429:195-206.

52) Klein PD, Graham DV. Minimum analysis requirements for the detection of Helicobacter pylori infection by the 13C Urea Breath Test. Am J Gastroentrol 1993;88:1865-9.

    a. Khan, M.A., 2011. Production Possibilities in Catchment Areas under Dharabi Dam in Chakwal. Bibliografische Information der Deutschen National bibliothek: Die Deutsche Bibliothek. 1: Pg.2.

53) Kharaka, Y.K., Thordsen, J.J., and Ambats, G., 1995, Environmental degradation associated with exploration for and production of energy sources in USA, in Kharaka, Y.K., and Chudaev, O.V., eds., Water-Rock Interaction (WRI-8), Rotterdam, A.A. Balkema, p. 25-30.

54) Kharaka, Y.K. and Hanor, J.S., 2003, Deep fluids in the continents: I. Sedimentary basins. In Drever, J.I., ed., Treatise On Geochemistry, v.16, p. 294-336.

55) Kharaka, Y.K. and Dorsey, N.S., 2005. Environmental issues of petroleum exploration and production: Introduction. Environmental Geosciences, v. 12, no. 2 (June 2005), pp. 61–63

56) Kendall C, McDonnell JJ, editors. Isotope Tracers in Catchment Hydrology. Amsterdam: Elsevier Science; 1998.

57) Lajtha K, Michener RH. Stable isotopes in ecology and environmental science. Oxford: Blackwell Sci Publication; 1994.

    a. Lang, R., Rebecca, K., and Jones, B.H., 2013. Evaluation of groundwater pollution by hydrocarbons and heavy metals (Northeast of Algeria). African Journal of Environmental and Waste Management ISSN: 2375-1266 Vol. 3 (2), pp. 165-168

    b. Lew, K. (2008). Understanding the elements of the periodic table: zinc. New York, USA: Rosen Publishing Group. Pp 3-14.

58) Levy, J.M., 2005. Hazmat Chemistry Study Guide. Firebelle Productions. 2nd Edition. Pg. 96

59) Lide, D. CRC, Handbook of Chemistry and Physics, 1992, 73rd Edition. Boca Raton, FL: CRC Press.

    a. Li, S.L., Liu, C.Q., Tao, F.X. Lang, Y.C. and Han, G.L., 2005. Carbon Biogeochemistry of Groundwater, Guiyang, Southwest, China.Ground Water. 43 (4):494-499.

    b. Lloyd, J.W. and Heathcote, J.A. (1985). Natural Inorganic Hydrochemistry in Relation to Groundwater, Clarendon Press, Oxford, England.

Environmental Issues and Management in Nigerian Development, Ibadan: Evans Brothers (Nigeria Publishers) Limited, Ibadan, pp. 208-223.

71) National Standards for Drinking Water Quality (NSDWQ), 2008. Pakistan Environmental Protection Agency. Ministry of Environment, Government of Pakistan.

72) Ojo,O.I., Otieno,F.A.O. and Ochieng, G.M., 2012. Groundwater: Characteristics, qualities, pollutions and treatments: An Overview. IJWREE 4(6): 162-170

73) Oklahoma Department of Environment Quality (ODEQ). (2010).

74) Okoye, C. O. and Lovette,A.O., 2014. Impact of Oilspill on Land and Waterand its Health Implications in Odu-Gboro Community, Sahgamu, Odun State, Nigeria. World Journal of Environmental Sciences & Engineering Vol. 1, No. 1, Pg:1-21.

75) Olobaniyi, S.B.; Efe, S.I. (2007), Comparative assessment of rainwater and groundwater quality in an oil producing area of Nigeria: environmental and health implications, Journal of Environmental Health and Res. (6)2: 111- 118.

76) Olufemi, A.G., Titilayo, E.A. and Tunde, E.O., 2012. Evaluation of Total Petroleum Hydrocarbons (TPH) and some related heavy metals in soil and groundwater of Ubeji Settlement, Warri Metrolpolis, Nigeria. Terrestrial and Aquatic Environmental Toxicology 6(1): 61-65.

77) Otokunefor T.V. and Obiukwu, C. "Impact of Refinery Effluent on physicochemical Properties of a water body in Niger Delta". Applied Ecology & Environ. Research, 3(1) 2005, 61-72

78) Ogbuigwe, A (1998), "Judicial Activism in the Enforcement of Environmental Regulations in the Petroleum Industry: Past, Present and the Future." Proceedings of 1998 International Conference on the Petroleum and the Nigerian Environment 83-123.

79) Ogrinc N, Lojen S, Faganeli J. A mass balance of carbon stable isotopes in organic-rich methane producting lacustrine sediment (Lake Bled, Slovenia). Glob Planet Change 2002:33; 57-72.

80) Orubu, C O (2002), Petroleum-Induced Environmental Diseconomies and Sustainable Development. In: The Petroleum Industry, the Economy and the Niger-Delta Environment. (Eds), Orubu, C.O., Ogisi, D.O. and Okoh, R.N. 17-31.

81) Otukunefor, T V; Biukwu C O (2005): Impact of Refinery Influent on Physico-chemical Properties of a Water body on the Niger Delta. Applied Ecology and Environmental Research. 3(1) 61-72.

82) Oyeleke, P.O. and Okparaocha, F.J., 2016. Assessment of Some Heavy Metals in Groundwater in the Vicinity of an Oil Depot in Nigeria. American Chemical Science Journal 12(3): 1-7

83) Pivnik, D.A., Johnson, G.D. 1995. Depositional response to Pliocene–Pleistocene foreland partitioning in northwest Pakistan. Geol. Soc. America. 107, 895-922.

84) Powell and White, (1985), An Impact Assessment of the 1983 Oshika Oil Spill.

85) Parageau, M. P., A., Mirin, F. Seby, C Guimon, E Krupp, C. Percheyran, J. Poulleau and O.F. Donard, "Partitioning of Metals species during an enriched fuel combustion experiments, speciation in the gaseons and particulate phases", Environ. Sci. Technol, Vol. 38, 2004, :252-263.

86) Ramesh RP (1998). Studies on pollution aspects of aquaculture development in east coast region of Nellore district, Andhra Pradesh, India, PhD thesis submitted to the Andhra University, Visakhapatnam for the award of the degree of Doctor of Philosophy pp. 1-4.

87) Richter BC, Kreitler WC (1993). Geochemical Techniques for Identifying Sources of Groundwater Salinization, Boca Raton, Florida, C.K. Smoley, CRC Press, Inc.CRC Press, New York. US Environmental Protection Agency, USEPA, (1987). Technical support document on risk assessment of chemical mixture, US Environ. Protection Agency, Cincinnati, Ohio.

88) Rputheti RN, Okigbo MS, Advanapu RL (2008). Ground water pollution due to aquaculture in east coast region of nelore district, Andhrapraesh, india. AJEST. 2(3):046-050.

89) Roberts, J.R. (1999) Metal toxicity in children. In Training Manual on Pediatric Environmental Health: Putting It into Practice Jun. Emeryville, CA: Children's Environmental Health Network (http://www.cehn.org/cehn/trainingmanual/pdf/manual-full.pdf).

90) R.A Olowu, O.O.; Ayejuyo, G.O. Adewuyi, A.O Babatunde,. I.A. Adejoro, A.A.B, Denloye, and A.L Ogundajo,. "Heavy metals in fish tissue ,water, sediment from Epe and Badagry lagoons Nigeria". *E-Journal of Chemistry* Vol.7 no 1, 2010, pp 215-221

91) R.A. Olowu, C.T. Onwordi, A.A. Denloye, M.O Osundiya, N.O. Adebayo, M.S. Owolabi, O.O. Tovide, B.A. Moronkola, O.A. Omoyeni ,O.R. Ajuwon "Heavy Metals in *Oreochromisniloticus*(Linnaeus, 1758) (Persiformes: Cichlidae),

Ictaluruspunctanus(Rafinesque, 1818) (Suliriformes: Ictaluridae) and Bottom Sediments from Lagos Lagoon Proximal to Egbin Power Plant, Ijede, Ikorodu, Lagos Nigeria". *Research Journal of Environmental and Earth Sciences Vol.* 4 no 3, 2012, pp 237-243.

92) Richter, B.C. and Kreitler C.W., 1993, Geochemical techniques for identifying sources of ground-water salinization: Boca Raton, C. K. Smoley, CRC Press, 258 p.

93) Rasmussen, D.V., "Characterization of oil spill by capillary column gas chromatography," Analytical. Chemistry, Vol.48 no11, 1976, 1536-1566.
    a. Sarala, C. and Babu, R., 2012. Assessment of Groundwater Quality Parameters in and around Jawaharnagar, Hyderabad. International Journal of Scientific and Research Publications. 2: 1-6.

94) S. A Uzoekwe,.and F.A Oghosanine, "The effect of refinery and petrochemical effluent on water quality of Ubeji creek Warri, Southern Nigeria". *Ethiopian Journal of Environmental Studies and Management* Vol. 4 No.2 2011 pp 107-116

95) Sidle WC. Environmental isotopes for resolution of hydrology problems. Environ Monit Assess 1998; 52:389-410.

96) Slater GF. Stable isotope forensics-when isotopes work. Environ Forensics 2003; 4:13-23.

97) Standard Methods for the Examination of Water and Waste Water, 2005. 21st Edition, APHA, AWWA, WEF.

98) S.E. Kakulu, and Osibanjo, "Trace Heavy Metal Pollutional status in sediments of the Niger Deltas Area of Nigeria" *J. Chem. Soc. Nigeria,* vol. 13, 1988, pp 9-15.

    a. Tam, N. F. Y. and Wong, Y. S. (2000). Spatial variation of heavy metals in surface sediments of Hong Kong mangrove swamps. Environmental Pollution, 110, 195-205.

99) Tibbetts, PJC; Buchanan, IT; Gawel, LJ; Large, R (1992). A Comprehensive Determination of Produced Water Composition, In: Produced Water, J.P. Ray and F.R. Englehart (eds.), Plenum Press, New York

100) T.V. Otokunefor and C. Obiukwu, "Impact of Refinery Effluent on physicochemical Properties of a water body in Niger Delta"*Applied Ecology & Environ. Research,* 3(1) 2005, 61-72

101) Tirmizi F 2011, 'The Myth of Pakistan's infinite gas reserves', The Express Tribune,14th March, http://tribune.com.pk/story/124157/energy-crisis-pakistan-to-seekfree-oil-from-kuwait/

102) USEPA, 1987, Management of wastes from the exploration, development and production of crude oil, natural gas and geothermal energy: EPA/530-SW-88-003.

103) USEPA, EPA. Method 1664 revision A: N-hexane extractable material (HEM; oil and grease) and silica gel treated N-hexane extractable material (SGT-HEM; non-polar material) by extraction and gravimetry. Washington DC: United States Environmental Protection Agency, 1999.

104) Vryzas, Z., G. Vassiliou, C. Alexoudis and M.E. Papadopoulou, 2009. Spatial and temporal distribution of pesticide residues in surface waters in northeastern Greece, J. Water Res., 43(1): 1-10.

105) Vidal, J. (2010). Nigeria's Agony Dwarfs the Gulf Oil Spill, Macmillan Press, London.

106) Vodela, J.K., J.A. Renden, S.D. Lenz, W.H. Mchel Henney and B.W. Kemppainen, 1997. Drinking water contaminants. Poult. Sci., 76: 1474-1492.

107) World Health Organization, 2004.International statistical classification of diseases and related health problems (Vol. 1). World Health Organization.

108) www.pakistan.gov.pk/ministries/environment-ministry/media/mtdf.htm

109) Webb, M. (ed.) 1979a: The geochemistry, Biochemistry and Biology of Cadmium. Elsevier/Noyth Holland Biomedical Press, Amesterdam.

110) Warwick, P.D. and Wardlaw, B.R., 1991. Chapter A of Regional Studies of the Potwar Plateau Area, Northern Pakistan. Overview of the Geography, Geology, and Structure of the Potwar Regional Framework Assessment Project Study Area, Northern Pakistan. Warwick, P.D., U.S. Department of Interior, U.S. Geological Survey. Bulletin 2078-A

111) Werner, R.A. and Brand, W.A., 2001. Review: Referencing Strategies and Techniques in Stable Isotope Ratio Analysis. Rapid Communication in Mass Spectrometry. 15: 501-519.