Impact of Industrial Effluents on Groundwater Quality in Selected Cities of Punjab

By

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DEDICATION

To my **Mother**,

my beloved nephews Afraz Muhammad Cheema, Salar Muhammad Cheema and family, and to all my teachers, friends and colleagues, Whose moral support and blissful prayers enabled me to complete this uphill task

DECLARATION

I hereby declare that the work present in the following thesis is my own effort, except, where otherwise acknowledged and that the thesis is my own composition. No part of the thesis hasbeen previously presented for any other degree.

Date:-------------------

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Rabia Naz

LIST OF ABBREVIATIONS

SGW	Sheikhupura Groundwater
LGW	Lahore Groundwater
RGW	Raiwind Groundwater
MGW	Mangamandi
KGW	Kasur
GGW	Gujranwala
FGW	Faisalabad
DDE	Dichlorodiphenyldichloroethylene
TCP	Tricholorophenol
DDT	Dichlorodiphenyltrichloroethane
DCP	Dichlorophenol
μg	Micro Gram
EC	Electrical Conductivity
TDS	Total Dissolved Solids
EU	Europeon Union
UV	UltraViolet
NO_3	Nitrates
Cl	Chlorides
HPLC	High Performance Liquid Chromatography
GC-MS	Gas Chromatography mass spectrometery
SPE	Solid Phase Extraction
Ml	milli Liter
OC	Organochlorides
OCPs	Organochlorine pesticides
OP	Organophosphate
-OH	Hydroxyl
OP	Organic Pollutants
MAF	Million Acre Feet
PAHS	Polycyclic Aromatic Hydrocarbons

PCBS	Polychlorinated Biphenyls
PCDD	Polychlorinated Dibenzodioxins
PCDF	Polychlorinated Dibenzofurans
PCRWR	Pakistan Council of Research in Water Resources
PM	Particulate Matter
Zn	Zinc
Cd	Cadmium
Pb	Lead
Cr	Chromium
Cu	Copper
Ni	Nickel
Fe	Iron
Mn	Maganese
Mg	Mili gram
L	Litre
Ppm	Parts Per Million
Ppb	Parts Per Billion
MCL	Maximum Contaminant Level
WHO	World Health Organization
EPA	Environment Protection Agency
Ms	Mili siemens
μS	Micro Siemens
H_3PO_4	Hydrophosphoric acid
Nacl	Sodium Chloride
$Ag\ NO_3$	Silver Nitrate
^{13}C	Stable Isotope Carbon
Ft	Feet
GW	Ground Water
CO_2	Carbon Dioxide
Nm	Nanometer

N	North
E	East
C-18	Carbon 18
ml/min	Mili litre Per Second
A	Absorbance
PSQCA	Pakistan Standards and Quality Control Authority

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Abstract

Punjab is the biggest province of Pakistan in terms of population. It has variety of industries in its major cities like Sheikhupura, Lahore, Raiwind, Mangamandi, Kasur, Gujranawala, and Faisalabad. In these cities, industries are discharging their effluents directly into nearby waste water drains. In urban and sub-urban areas, drain water is being used for irrigation purpose, and large area is exposed to groundwater contamination. And there is high possibility that drain water may infiltrate down into groundwater and can affect its quality. Therefore, in order to assess the groundwater quality, groundwater samples were collected from different areas where waste water was being used for irrigation purpose near waste water drain, industrial, agricultural and residential areas. Preferably ground water samples were collected from shallow water aquifers. Analysis showed that concentration of few organic and inorganic contaminants were above the permissible limits set by WHO and U.S. EPA. DDT, DCP, TCP were observed above the maximum contaminant level pose severe danger to human health. Inorganic/organic analysis has shown the presence of trace metals in drinking water. In sheikhupura, concentration of Endrin and DCP are alarmingly high. In Lahore, Endrin and DDT were found in residential area. TCP and DCP concentrations were also high in Lahore samples. Raiwind samples have shown the highest concentrations of Endrin in agricultural area and DCP in industrial area. DDE and TCP highest concentrations were found in agricultural area. In Mangamandi, Endrin and Cypermethrin concentrations were found high. In Kasur, high concentrations of Endrin, TCP, DCP, DDT were found. In Gujranawala, concentrations of Endrin, Dieldrin, DDE were notably high,while TCP, DCP, and DDT was found only in one sample. Likewise, Faisalabad showed same pattern of organic contamination, Endrin, DCP and DDT. Similarly, Trace Metals in studied areas were observed within the maximum contaminant levels. But its continuous addition into groundwater is still potential threat to human health. Consumption of contaminated drinking water has severe health impacts on human. Contaminated drinking water can cause dysentery, diarrhea, hepatitis and chronic diseases; cancer, respiratory problems, nervous system dysfunction, mental impairment, kidney problems, skin problems etc. Therefore proper treatment of contaminated water is pertinent and to prevent contamination of water resources.

Chapter 1

Introduction

1. Introduction:

Water is an essential for human life and other system on earth. The distribution of water on the Earth's surface is not even. 97% water on earth comprises of oceanic water, and remaining 3% is available as fresh water. 69% freshwater constitutes glaciers, 30% groundwater, and less than 1% is located in lakes, rivers and swamps. Only 1% of the freshwater on the Earth's surface is usable by humans, and 99% of the usable quantity is situated underground. Therefore, groundwater is larger source of drinking water (Bralower T. and Bice, D. 2014). Groundwater constitutes any subsurface water that occurs under the water table in soil and other geologic forms (Rail, 2000).Groundwater is found in soils and sands can retain the water much like a sponge holds water (NGWA, 2010).Water is needed nearly for everything humans and animals need(Chilton, J.,1996). Availability of water ensures the continuation of life on earth. Water had has been used for various things i.e., from medicinal use for human health to industrial processes. Unfortunately, untreated used water is left open into environment and it may pose threat to groundwater resources. Use of toxic chemicals, organic compounds, and bacterial activity has contaminated the water we drink. Geographical variation also affects the groundwater quality. Besides, local geologic set-up human activities are deteriorating the groundwater and rendering water unusable by humans. Nevertheless, analysis of groundwater quality involves the determination of chemical composition of water and their permissible limit in water (Annapoorna and Janardhana, 2015).

1.1. Groundwater:

Groundwater is an essential source of water. It is estimated that groundwater makes up to 95% of all freshwater available for drinking purpose. If the polar ice caps and glaciers are excluded, groundwater remains only consumable freshwater. Groundwater is significant source of water for many municipal water systems. In urban areas people mainly rely upon municipal water systems (Rail, 2000). However, in rural areas, withdrawing water from tube wells is common practice. The growing needs and continuous decrease of water resources has amplified the need to protect the water, which is fundamental to human life and economic activity. Groundwater has been misused for domestic use, agricultural and industrial activities since long time. In addition, withdrawing of the groundwater to the surface and exploitation of water has grown persistently (Chilton, J., 1996). Owing to reckless withdrawal and mismanagement of water resources has caused depletion and contamination of groundwater and adversely affected the human health, therefore, it has threatened human survival in severe environments (Oren, et al., 2004).

Over a large area South Asian countries have a fresh-water aquifer. In many south Asian countries, subsurface water is pumped out through shallow wells or deep tube wells/ turbines, mainly for agricultural and domestic purpose. Canals irrigation is predominantly in public sector whereas, wells/tube wells are largely seen in private sector (M. Hanif). South Asia countries mostly facing water-related environmental problems depleting water resources, water pollution, groundwater degradation and trans-boundary issues that exert pressure on the availability of water (WB., 2013). In Pakistan, about 80% of the population is dependent on groundwater for household use. (WWF, Pakistan, 2007: PCRWR, 2002;Afzal 1999; Bhutta 1999).Ample management in terms of quantity and quality is dire to ensure access to safe drinking water. Access to drinking water is reduced either by a shortage in the quantity of water or by the deterioration/ contamination of the water quality of aquifers (WB., 2013).

1.2. Groundwater Situation in Punjab-Pakistan:

Punjab is the biggest province of Pakistan by population. The one third of total population of Pakistan lives in Punjab. Indus River and its tributaries drain the province (PPSGWP, 1998). The groundwater recharge is dependent on rainfall (Amin, M., 2004).In groundwater areas, unnecessary pumping by tube wells and recharge by drain water and agricultural activities are causing groundwater contamination (NESPAK 1991; Zuberi., 1992; WRRI., et al 1999; Ahmed 1993). Groundwater pollution needed to be eliminated in order to improve its quality by every possible method (Ahmed, S., et al., 2002). In Punjab, different water table depths have been reported, 2.47, 5.78 and 5.08 meter inSheikhupura at various places (Jehangir, W. A., et al., 2003).Many areas mostly comprises of shallow water aquifers, which are usually more prone to contamination by means of seepage of contaminated water through the soil. Selected cities of Punjab have huge industrial infrastructure, wide variety of industries. Following table is showing a brief account of type of industries in respected cities of Punjab-Pakistan.

Table 1.1: Profile of major industrial cities of Punjab-Pakistan

S. No.	Name of City	Total Industrial Area	Major Industries
1	Lahore	875 Acres	Pharmaceuticals, soft drinks, Consumer Goods,Engineering, Electrical Fittings, Chemicals, Consumer Goods, Steel Products
2	Mangamandi	-----	Mechanical, Textiles, Engineering Industries
3	Raiwind	112 Acres	Textiles, Sugar, Power Generation, Garments, Chemicals, Engineering, Food
4	Sheikhupura	20 sq Km	Road, Gas,Electricity
5	Gujranwala	209.65 Acres	Engineering, Chemicals, Textiles, Ceramics, Leather, Ceramics, Electrical Machines, Domestic Machines, Fabrication, Consumers Goods
6	Faisalabad	258.03 acres	Textiles, Engineering works, Food Processing, Hosiery, Rug, Lace
7	Kasur	-------	Tannery, Textiles, Steel, Food, Paper Mill

Source :([11, 12]).

1.3. Groundwater Contamination:

Groundwater is greatly affected by source of recharge. Where the recharge sources are wastewater drain, industrial effluents and/ or agricultural runoff. The recharge water brings certain contaminants which pass through the soil and leach down into groundwater. Soil acts as a natural sorbent and contaminants adsorb onto the surface of soil particles. At certain level, soil reaches to its saturation level and prevents further adsorption of contaminants. At that stage, chances of groundwater contamination rises drastically. Furthermore, porous soil facilitates contamination of shallow aquifers(Tariq et al., 2004).Each source of water has a unique set of contaminants; normally groundwater stores pesticide, chemicals and nitrate while surface water contains most bacteria and other microorganisms. Because of the intermixing of groundwater and surface water, these contaminants might be shared between the two sources. Neither water source can ever be entirely free from water contaminants. Due to the cycle of water (hydrology), these two sources of drinking water nourish each other, sharing contaminants (Chester, R., 2000).Trace metals are important for proper functioning of biological systems but their deficiency or excess could lead to a number of disorders (Ward,1995). Tannery and textile effluents contain a higher amount of metals particularly chromium, copper and cadmium. These untreated effluents released on the land, surface water which eventually seeps down to ground water and lead to contamination (Malarkodi et. al. 2007:Deepali and Gangwar.2010).

1.4. Sources of Contamination:

The chemical composition of groundwater determines its suitability as a source of drinking water, irrigation, and for industrial purposes. Chemistry (quality) of groundwater reflects inputs from the atmosphere, from soil and water-rock reactions (weathering), as well as from pollutant sources such as agriculture, acid precipitation, domestic and industrial wastewater drains (Edmunds, W.M., 2004).The chemical alteration of the ground water depends on numerous factors, such as interaction with solid phases, residence time of ground water, seepage of polluted river water, mixing of groundwater with pockets of saline water and anthropogenic impacts (Stallard and Edmond, 1983; Faure, 1998 and Umar et al., 2003 & 2006). The loss of water quality is causing health hazards, death of livestock and aquatic lives, crop failure and loss of aesthetics (Usali and Ismail, 2010).Groundwater resources of Pakistan are being contaminated in many ways. Major sources of contamination are industrial effluents, sewerage wastewater, agricultural runoff, and natural physical activity. Industries are directly pouring contaminated water into waste water drains and there is no check on them. However, recently in Kasur district responsible authorities has commissioned treatment plants for effluents from the tanneries (Ahmed, S., et al., 2002).

1.4.1. Contamination due to Industrial Effluents:

The chemical composition of groundwater determines its suitability as a source of drinking water, irrigation, and for industrial purposes. Chemistry (quality) of groundwater reflects inputs from the atmosphere, from soil and water-rock reactions (weathering), as well as from pollutant sources such as agriculture, acid precipitation, domestic and industrial wastewater drains (Edmunds, W.M., 2004).The chemical alteration of the ground water depends on numerous factors, such as interaction with solid phases, residence time of ground water, seepage of polluted river water, mixing of groundwater with pockets of saline water and anthropogenic impacts (Stallard and Edmond, 1983; Faure, 1998 and Umar et al., 2003 & 2006). Waterborne diseases are increasing and affecting the ecosystem (Usali., 2010). Major sources of contamination are industrial effluents, sewerage wastewater, agricultural runoff, and natural physical activity. Industries are directly pouring contaminated water into waste water drains. However, recently in Kasur district responsible authorities has installed treatment plants for industrial waste (Ahmed, S., et al., 2002).

Table 1.2: Annual ton of waste water discharged by industries

City	**Urban Population (1998 Census)**	**Total Wastewater Produced (Million m^3/Year)**	**% of Total**	**% Treated**	**Receiving Water Body**
Lahore, Raiwind	5,143,495	287	12.5	0.01	River Ravi, Irrigation Canals, vegetable farms
Faisalabad	2,008,861	129	5.6	25.6	River Ravi, River Chenab, vegetable farms
Sheikhupura	870,110	15	0.7	--	SCARP drains
Kasur	245,321	17	0.8	2	Irrigation canals and agricultural fields
Gujranwala	1,132,509	71	3.1	--	SCARP drains and vegetable farms
Others	19,475,588	967	41.8	0.7	--
Total	**28,875,884**	**1,486**	**64.5**	**28.31**	--

Source: Master Plan for *Urban Wastewater (Municipal and Industrial) Treatment Facilities inPakistan*. Final Report, Lahore: Engineering, Planning and Management Consultants. 2002: Noreen. S., 2013.

1.4.2. Contamination due to Sewerage Wastewater:

Coverage for sanitation in Pakistan is of utmost poor. In many cities of Pakistan, the wastewaters from the urban and sub-urban areas are disposed without treatment in to nearby open drains. In cities, sewage is collected through pipes. The collected sewerage is disposed of in nearby water bodies. In areas, where sewage collection system does not exist, sewage reaches into groundwater through seepage. In rural areas, collection and disposal of sewerage is almost rare. The discharge of sewerage wastes carried by drains and canals to rivers worsens and broadens the spectrum of water contamination (Haq, M. U., et al., 2005: Tariq, M., et al., 2006). Currently, the treatment of effluent waste is not practiced on the municipal front (Ahmed, S., et al., 2002).Despite the contamination in water resources, another possible source of contamination is water transportation. During transportation its quality further declines. In cities, water comes from municipal supply through water pipes, pipes carrying drinking water mostly go side by side with sewage system, and pipes leakage and improper cleaning of the water tanks are the major source of the drinking water contamination (Eisen and Anderson., 1979). While in villages' hand pumps, wells, open tanks filled canal and river water are also exposed to all sorts of contamination (Okoh, A. I., et al., 2004).

1.4.3. Contamination due to Agricultural Runoff:

Pakistan is an agricultural country. Agriculture contributes big share in the economy of country, more than half of its population is directly or indirectly linked with the agriculture. Punjab is the biggest province of country in terms of population. It has fertile land and surplus of water. Punjab is a land of five rivers. It provides enormous of water to the agricultural sector in the province. Agricultural land-use practices also exert a major influence on groundwater recharge quality (Foster et al, 2000; Foster &Candela, 2008). Water percolates through soil and trickles down to groundwater. Furthermore, industrialized countries tend to increase yield of grain, oil-seed, vegetable, fruit and milk production per unit area through the replacement of traditional crop fertilizers with synthetic fertilizers and pesticides sprays. These pesticides sprays are potentially grave problem in recharge areas, where aquifers are showing high susceptibility to pollution from the land-surface pesticides application (Shah, T. 2014). Seepage of water from farmland has been adding dissolved fertilizers, pesticides and insecticides to groundwater. It increased groundwater pollution and deteriorated its quality. In suburbs of major cities, waste water is also being used for irrigation purposes. Industrial effluents contain variety of organic and inorganic contaminants, which trickles down into soil and infiltrates to groundwater. It poses great peril to groundwater quality (Ahmed, S., et al., 2002).

1.4.4. Contamination due to natural physical activity:

Groundwater is normally stored in aqueducts, underground layers of porous rocks that are saturated with water. These aqueducts receive water from recharge areas. These recharge areas are one of the major contributors of contamination to groundwater. It is very important to know the nature of recharge area. If recharge area is contaminated then there is high risk of contamination in groundwater, as water percolates down into soil contaminants may adsorb onto the soil surface and retain on it. After a period of time, when soil reached to its saturation and adsorbing capacity reduces then contaminants may pass to groundwater and cause groundwater contamination. As the aqueducts exceed their capacity for water storage, they will bleed water back into streams or rivers. The aqueducts maintain a natural balance of water, alternately receiving or giving water as their saturation levels oscillate. By this process, water regularly moves between surface and groundwater sources, sharing contaminants (Chester, R., 2000).

1.5. Nature of Contamination:

It is pertinent to know the nature of contaminants, which have been found in Punjab-Pakistan in order to assess their significant impacts on human health. Contaminants could be organic/ inorganic in nature.

1.5.1. Organic Contaminants:

Groundwater has fewer microbes to digest organic pollutants, less oxygen no sunlight and surface from which organic pollutant can evaporate. Especially in slow moving groundwater, pollutants can persist. Organic contaminants include organophosphates Endrin, Dieldrin, Organochlorides, Phenolic compounds; Dichlorophenol and Trichlorophenol, DDT, DDE etc. Threat of pesticides in drinking water varies, depending upon where one lives and what source of drinking water one uses. Comparatively, deep groundwater wells are at less risk than shallow wells (Gustafson, D. Et al., 1993).Contamination by organic compounds is likely to be very persistent and there are evidences of toxicity at even very low concentrations (Lyne and McLachlan, 1949).

1.5.2. Inorganic Contaminants/ Trace Metals:

Disposal of industrial waste is continuously adding heavy metals and trace elements into groundwater aquifers and surface water bodies. Solid municipal waste sites in many cities are the permanent source of organic and biological pollution. Domestic waste is becoming the source of all sorts of epidemics. In Punjab-Pakistan, about 3% water resources having heavy metals contamination (Ahmed, T., et al., 2004: Saqib, A.N. S., ET AL., 2013).The Pakistan Council for Research and Water Resources (PCRWR) and UNICEF has conducted the assessment of drinking water quality since 1999 following the heavy metals crisis in Pakistan (PCRWR, 2002). Therefore, the presence of heavy metal contaminated ground waters 10–200 μg/L has been recognized in many areas of Punjab (PCRWR,2002: Nickson, R.T.,2005). Heavy metals are typically present in trace amounts in natural water but they are toxic even at minute concentration however, many of the metals are vital components of the biological system. Metals such as Pb, Cd, Ni, Cr, Cu and Zn are highly toxic even in minor quantity. Increasing quantity of heavy metals in ground water is result of disposal of industrial effluents (Canter, 1987).

1.6. Groundwater Quality:

Ground water serves many purposes, about 60% of groundwater withdrawn globally used for agriculture, domestic and industrial sectors (NGWA, 2015). Groundwater chemistry varies according to the aquifer geology and flow rate of water. Sometimes water quality problem may not have an anthropogenic source i.e. elevated concentrations of metals could find in the vicinity of an ore body. Agricultural quality problems can be both from point and diffuse sources and so are more extensive than most of the industrial contaminants (EPA, report Ireland). In this regard, it is imperative to set some quality standards to determine water quality. Water quality can be judged with respect to different parameters. It can be checked in terms of clarity, odorless, pH, Turbidity, total dissolved solids, electrical conductivity, nitrates, chlorides, heavy metals and organic contamination.

1.6.1. Water Quality control Organizations:

There are different organizations which are working to improve the water quality and to mitigate the quality related issues. One of the worldly recognized organizations is World Health Organization (WHO) and European Union (EU) and further sub-organizations. Many countries also have their own water quality control organization such as Pakistan has Environmental Protection Agency (EPA), PSQCA and PCRWR. They are aimed to determine quality of water. Identify the toxic and hazardous water resources. There are many agencies and organizations, which have established the water quality standards. World health organization is major organization and has worldwide recognition (EPA, report Ireland).Groundwater quality is judged on the basis of health and safety regulations. No adverse human health effects are known to exist at the recommended MCL's. MCL's have been issued and recommend ended for: inorganic chemicals such; Trace metals and Chlorides for optimal levels; associated with industrial activities; synthetic organic chemicals, agricultural and urban pesticide use (Allan F., 2006). Following table is showing the maximum level contaminants (MCL's) limits of certain elements or compounds in groundwater.

Table 1.3: Groundwater Contaminants and their Maximum Level Contamination

S. No.	Contaminants	U.S.EPA, mg/L	WHO mg/L	EU' MCL µg/L	PSQCA mg/L
Organic Contaminants					
1	Endrin	0.002	0.0006	----	-----
2	Dieldrin	----	0.00003	0.030	0.002
3	Phenolic compounds	< 0.002	-----	--------	-------
4	DDTand metabolites	-----	0.001	------	------
Heavy Metals					
5	Cadmium	0.005	0.003	5.0	0.003
6	Chromium	0.1	0.05	50	0.05
7	Zinc	5	3	-----	3
8	Lead	0.15	0.01	10	0.01
9	Copper	1.3	2.0	2.0	1.0
10	Nickel	-----	0.07	20	0.02

11	Iron	0.3	0.3	200	0.3
12	Manganese	0.05	0.4	50	0.05
Inorganic Parameters					
13	Chloride	250	250	250	250
14	Nitrate	10	50	50	10
15	pH	6.5 - 8.5	-------	-------	6.5 –8.5
16	EC	-----	250 µS /cm	2500 µS/cm	-----
17	Total dissolved solids (TDS)	500	-----	--------	500

Source: (1,2,3,4,5,6,7,8,9,10).

1.7. Literature Review:

Following table presents the summary of literature review:

Table 1.4: Literature Review

Jabbar. A., 1991	Effect of Pesticides and Fertilizers on Shallow Groundwater Quality
Ilyas. M.T., et al.,2004	Pesticides in shallow groundwater of Bahawalnagar, Muzafargarh, D.G. Khan and Rajan Pur districts of Punjab, Pakistan
Aamir. M.K., et al., 2012	Evaluation of ground water quality for irrigation and Drinking purposes of the areas adjacent to hudiara Industrial drain, Lahore, Pakistan
Iqbal. F.., et al., 2013	Assessment of ground water contamination by various pollutants from sewage water in Chakera village, Faisalabad
Asi. M.R., et al., 2008	Solid phase extraction of pesticide residues in water samples: DDT and its metabolites
Mona. A. H., 2013	Water quality assessment and hydrochemical characteristics of groundwater in Punjab, Pakistan
Akhtar.M. and Tang. Z., 2014	Municipal Solid Waste and its Relation with Groundwater Contamination in Lahore, Pakistan
Abida. F., et al., 2007	Toxic fluoride and arsenic contaminated groundwater in the Lahore and Kasur districts, Punjab, Pakistan and possible contaminant sources
Rubina. S. G., et al., 2013	A Study of Drinking Water of Industrial Area of Sheikhupura with Special Concern to Arsenic, Manganese and Chromium
Abbas. M and Cheema. K.J., 2015	Arsenic levels in drinking water and associated health risk in District sheikhupura, Pakistan

Farid. M., et al., 2013	Comparative study of fresh and ground water Quality of different areas of Faisalabad
Akhar. N., et al., 2005	Impact of Water Pollution on Human Health in Faisalabad City (Pakistan)
Saleem. M. Saif., et al., 2005	Heavy Metals Contamination Through Industrial Effluent to Irrigation Water and Soil in Korangi Area of Karachi (Pakistan)
Akram. M.Q., et al., 2014	Spatial distribution of heavy metals in ground Water of sheikhupura district Punjab, Pakistan

1.8. Significance of study:

The sustainability of groundwater resources is a serious issue; gradual decline of water quality and growing demand for industrial, agricultural, and domestic uses is mounting threat to human survival (United Nations, 2012). Groundwater is not adequately managed to ensure its long-term sustainability. In fact, groundwater contaminations are very common throughout the world and have led to indigenous socio-economic impacts. The continuous expansion of the irrigation system, absence of proper drainage system, seepage from unlined canals, infiltration from irrigation fields, and poor exploitation of groundwater resources are major factors leading to groundwater contamination (Ajay., 2014).Globally, nearly 2 billion people are dependent on groundwater as their major source of water supply for both domestic, agricultural and industrial activities. Therefore, Water being vital to human survival should be managed properly and all water related issues must be addressed instantly. If it is not timely coped up, it can jeopardize the survival of next generation. Therefore, this research work is designed to highlight the contaminated areas and to identify the pollutants and their potential impacts on humans (Xifeng., et al.,2014).

1.9. Aims and Objectives:

The Main objective of this study is to determine the magnitude of organic/inorganic pollution in groundwater as affected by agricultural runoff and industrial effluent's open discharge into environment. Specific objectives of the study include:

- Identification of organic/inorganic contaminants in groundwater near Industrial states of selected cities
- Analysis of groundwater by using stable carbon isotope technique

- To delineate regions where groundwater is suitable or unsuitable for drinking purpose
- Possible adverse health impacts on local population caused by contaminated groundwater

Chapter 2

Materials and Methods

2.1. Study Area:

The study area includes big industrial cities of Punjab. Groundwater samples were collected from Sheikhupura,Lahore, Raiwind, Mangamandi, Gujranwala, Faisalabad, and Kasur. Samples were preferably collected from shallow aquifer, nearby waste water drain, residential areas and agriculture land being irrigated by wastewater. The sampling points were chosen on basis of hot spot declared in previous studies on organic profile of drains and depending upon their past or present land use(sumera., 2013).In addition, studyareas are being irrigated by the drainwastewater containing composite waste and it mayincreasethepossibility of groundwater contamination through seepage.

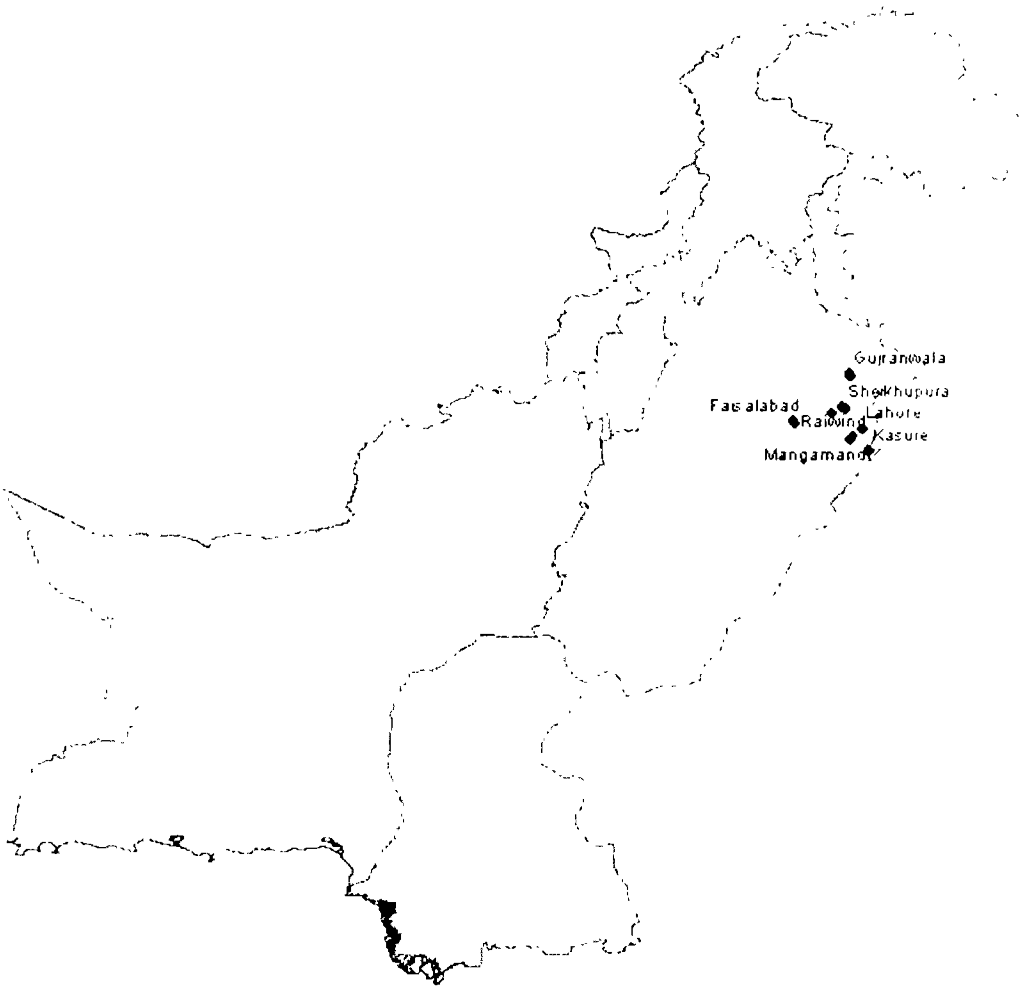


Figure 2.1: Map of Pakistan

Figure2.1.1: Map of Punjab

2.2. Sampling:

Ground water samples were collected from hand pumps, tube wells and bore holes located in residential and commercial areas alongside the waste waterdrain.Groundwater is being used for drinking purpose. Water samples for organic and inorganic analysis were collected in pre-cleaned one liter plastic cane and stored at low temperature. For Stable carbon isotope analysis water samples were collected in 250 ml plastic bottles. Few drops of mercuric chloride solution were added to stop bacterial activities.

Table 2.1: No. of samples from selected cities

S.No.	Name of City	No. of Samples
1	Sheikhupura	20
2	Lahore	09
3	Raiwind	08
4	Mangamandi	08
5	Kasur	10
6	Gujranwala	12
7	Faisalabad	07

2.2.1. Sheikhupura:

Sheikhupura is situated near Lahore, the provincial headquarters. Sheikhupura has variety of industries like; Fertilizers, chemicals, pulp and paper, textile, steel, leather, spinning and oil industries are releasing approximately 313.45 cusec untreated waste water into nearby waste water drain that seeps down into the soil and eventually reaches to groundwater and cause contamination.

Table 2.2:Sampling details and their Coordinates:

S. No.	Sampling Points	Latitude	Longitude
1	SGW-1	31°41`32.2”N	74°02`44.8”E
2	SGW-2	31°41’36.3”N	74°02`49.5”E
3	SGW-3	31°41’44.1”N	74°02`26.6”E
4	SGW-4	31°41’36.3”N	74°02’52.5”E
5	SGW-5	31°41’19.4”N	74°03’41.6”E
6	SGW-6	31°41’19.6”N	74°03’41.9”E
7	SGW-7	31°40’53.8”N	74°04`57.0”E
8	SGW-8	31°41’02.8”N	74°05’1.4”E
9	SGW-9	31°40’52.5”N	74°4’57.2”E

10	SGW-10	31°40’25.0”N	74°06’16.4”E
11	SGW11	31°39’56.3”N	74°06’17.4”E
12	SGW-12	31°40’9.2”N	74°06’33.2”E
13	SGW-13	31°40’9.33”N	74°06’29.52”E
14	SGW-14	31°40’7.76”N	74°06’29.33”E
15	SGW-15	31°40’6.40”N	74°06’30.50”E
16	SGW-16	31°41’00.8”N	74°06’18.0”E
17	SGW-17	31°41’6.09”N	74°06’16.35”E
18	SGW-18	31°41’5.21”N	74°06’16.53”E
19	SGW-19	31°41’4.29”N	74°06’16.73”E
20	SGW-20	31°41’3.98”N	74°06’19.44”E

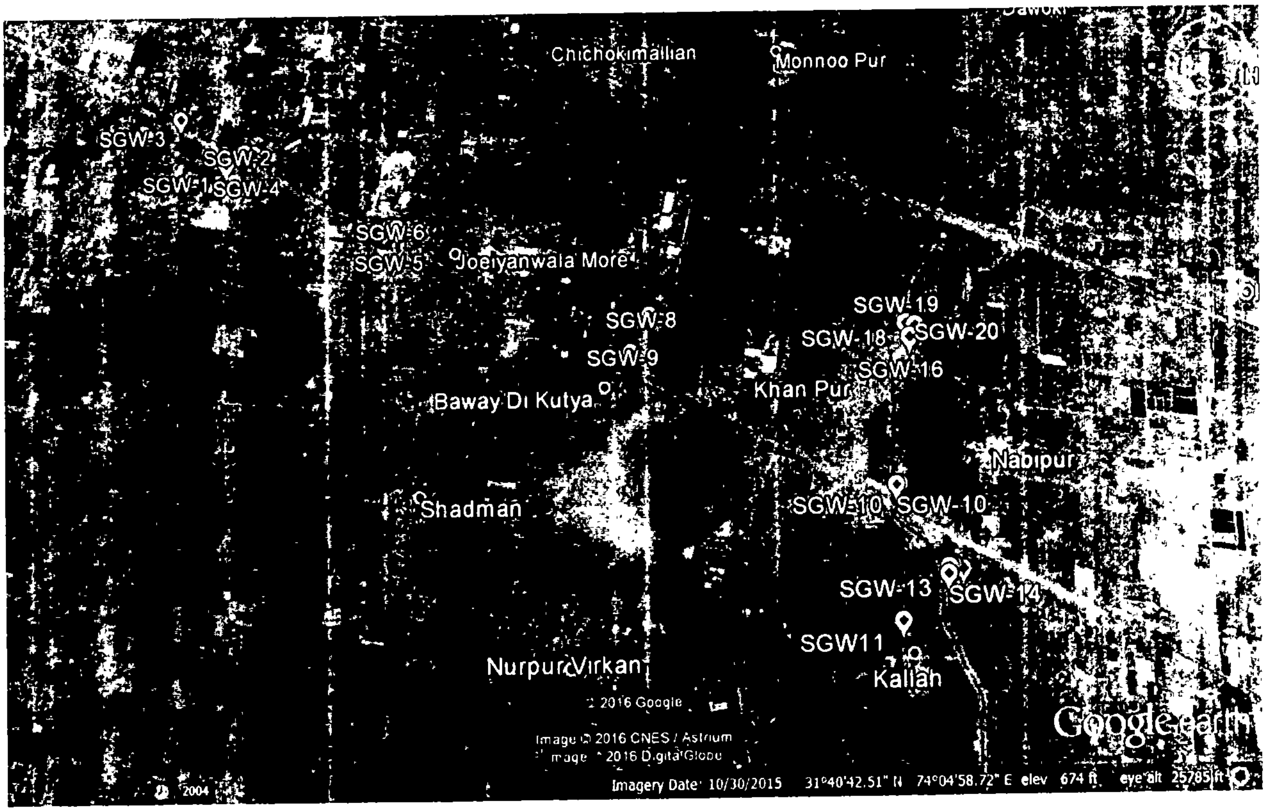


Figure2.2.1: Maps showing the sampling points of Sheikhupura Groundwater

2.2.2. Lahore:

The Lahore is the capital of Punjab and it has large industrial estates consisting of chemicals, paper, steels, pharmaceutical industries etc.Lahore drainage system consists of 14 drains through which sewerage and industrial wastewater of the city and its surrounding townsiscollected.Thesedrainsare interconnected and dispose of the collected sewerage andindustrial wastewater into the River Ravi. River water is used for irrigation and large area is exposed to wastewater contamination. Nine groundwater samples were collected from different points. Following are the details of longitude and latitude of sampling points.

Table 2.3: Sampling details and their Coordinates:

S. No.	Sampling Points	Latitude	Longitude
1	LGW-1	31°23'46.3"N	74°21'47.1"E
2	LGW-2	31°23'46.5"N	74°21'53.5"E
3	LGW-3	31°23'47.9"N	74°22'7.3"E
4	LGW-4	31°23’86.4”N	74°22’19.8”E
5	LGW-5	31°23’44.3”N	74°21’38.7”E
6	LGW-6	31°23’33.7”N	74°21’25.3”E
7	LGW-7	31°23’30.7”N	74°21’20.6”E
8	LGW-8	31°23’20.3”N	74°21’6.0”E
9	LGW-9	31°23’32.9”N	74°21’29.1”E

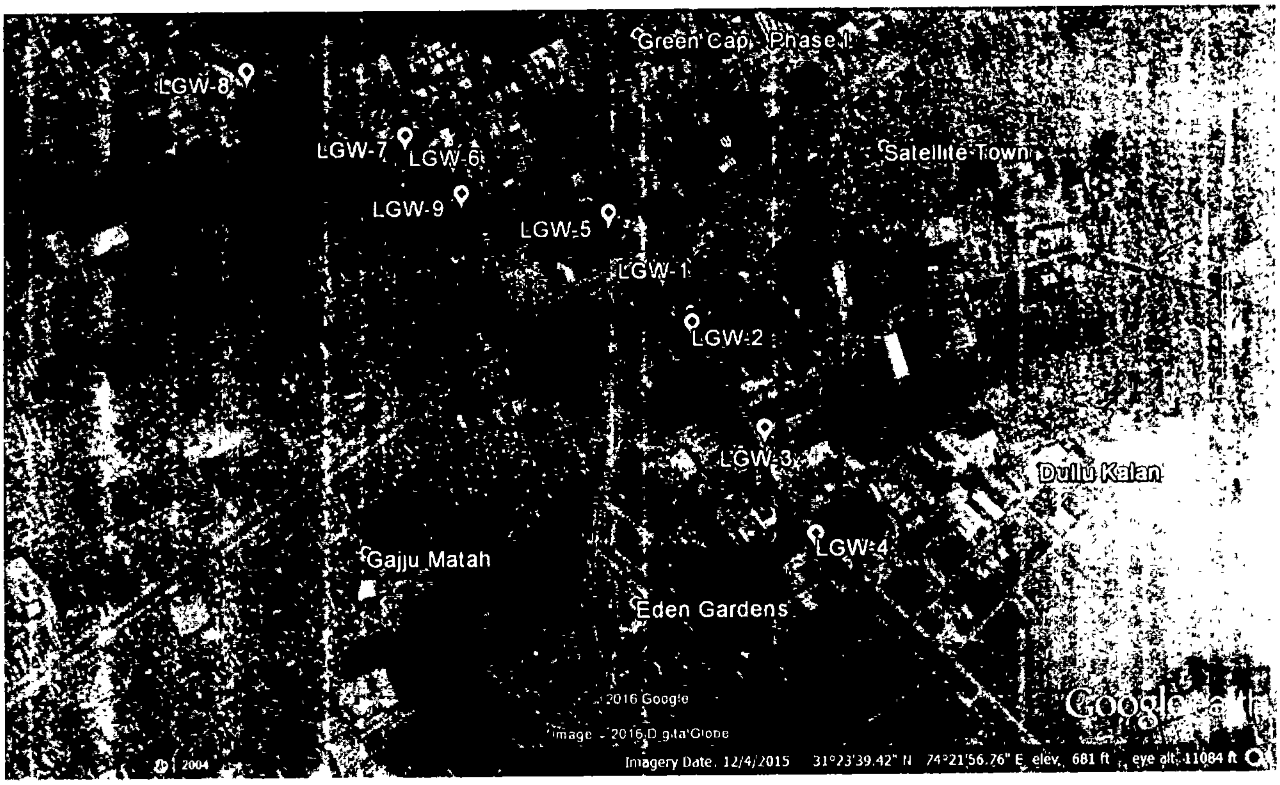


Figure 2.2.2: Map showing the Groundwater sampling points of Lahore

2.2.3. Mangamandi:

Mangamandi is the small town situated at few kilometers away from Changamanga forest near Lahore.There are textiles, Mechanical, Engineering Industries etc. Eight samples were collected from different points alongside the wastewater drain.

Table 2.4: Sampling details and their Coordinates:

S.No.	Sample	Latitude	Longitude
1	MGW-1	31°15’8.1”N	74°10’7.7”E
2	MGW-2	31°15’2.6”N	74°10’4.2”E
3	MGW-3	31°14'44.8"N	74°9'46.0"E
4	MGW-4	31°14'41.5"N	74°09'23.1"E
5	MGW-5	31°14'52.8"N	74°09'5.3"E
6	MGW-6	31°15'36.0"N	74°10'22.0"E
7	MGW-7	31°15'23"N	74°10'11.5"E
8	MGW-8	31°15'24.2"N	74°10'7.4"E

Figure2.2.3: Map showing the sampling points of Mangamandi Groundwater

2.2.4. Raiwind:

Raiwind is situated in Punjab Province about 40 kilometers away from Lahore. In the earlier 1990 an industrial estate was established in the west of town and another industrial zone was set-up in first decade of 21st century from few kilometers away from the Raiwind town known as "Sunder Industrial Estate". Eight samples were collected from different points.

Table 2.5: Sampling details and their Coordinates:

S.No.	Sample	Latitude	Longitude
1	RGW-1	31°15'20.6"N	74°10'56.1"E
2	RGW-2	31°15'23.3"N	74°10'57.0"E
3	RGW-3	31°15'50.1"N	74°11'52"E
4	RGW-4	31°16'29.6"N	74°11'20.2"E
5	RGW-5	31°16'46.4"N	74°11'43.1"E
6	RGW-6	31°16'45.8"N	74°11'42.2"E
7	RGW-7	31°17'18.6"N	74°12'43.2"E

8	RGW-8	31°17'58.5"N	74°13'27.5"E

Figure2.2.4: Map showing the Groundwater sampling points

2.2.5. Kasur:

Main industrial area of Kasur consists of power looms and leather manufacturing industries. In Kasur district about 22 industrial units have been reported disposing of 17.96 cusec untreated industrial wastewater released directly into the surface water bodies, which poses great risk to ground water contamination (Atlas, 2008). Ten samples were collected from different points.

Table 2.6: Sampling details and their Coordinates:

S. No.	Sample	Latitude	Longitude
1	KGW-1	31°06'7.3"N	74°27'33.6"E
2	KGW-2	31°06'7.0"N	74°27'33.4"E
3	KGW-3	31°06'18.4"N	74°27'22.5"E

4	KGW-4	31°06'20.6"N	74°27'23.9"E
5	KGW-5	31°06'22.8"N	74°27'24.8"E
6	KGW-6	31°06'35.2"N	74°27'28.3"E
7	KGW-7	31°06'18.6"N	74°27'20.3"E
8	KGW-8	31°06'1.7"N	74°27'38.3"E
9	KGW-9	31°05'53.3"N	74°27'27.2"E
10	KGW-10	31°05'51.2"N	74°27'21.1"E

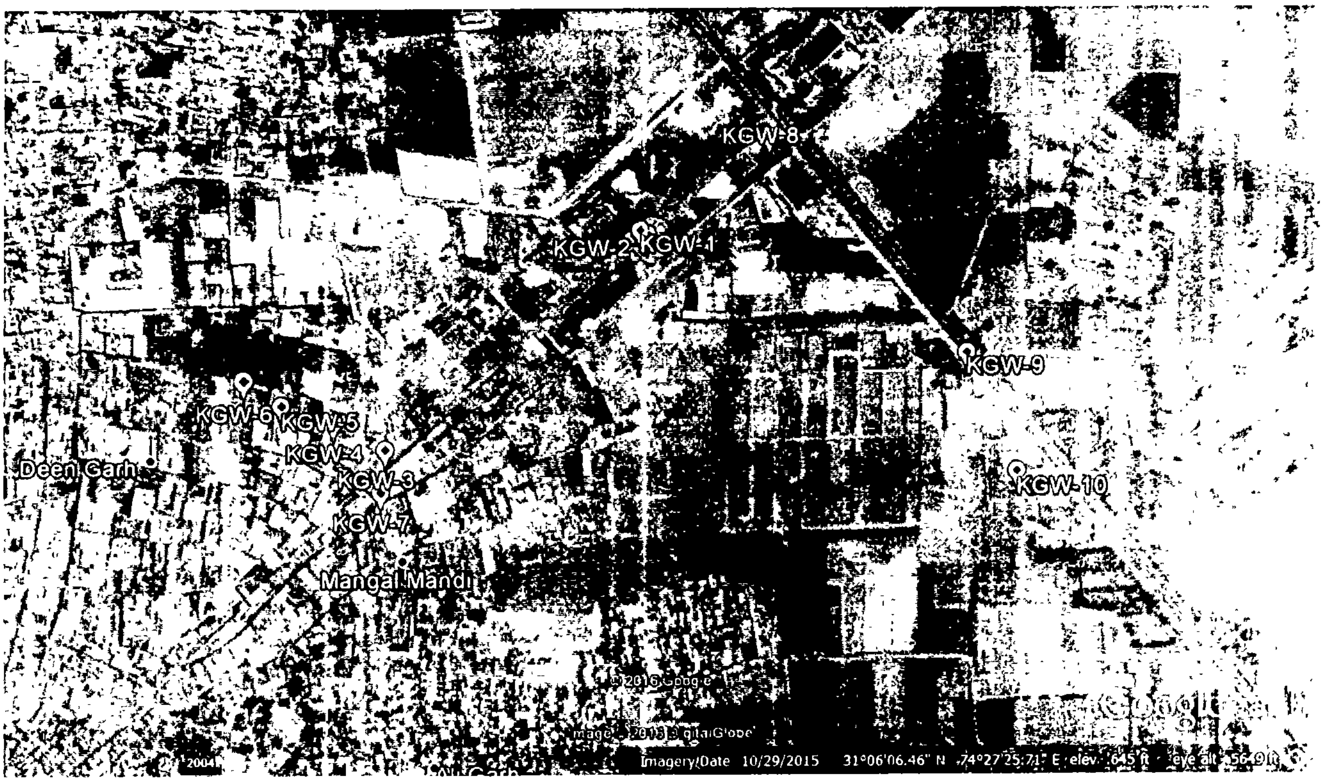


Figure2.2.5: Map showing the sampling points of Kasur Groundwater

2.2.6. Gujranwala:

Gujranwala is an ancient city, Itranks as the third largest industrial center in the country,after Karachi and Faisalabad, The nature of industry here is varied and vast,with a major concentrationof light engineering industry,besides textiles, leather, ceramics, cutlery, electrical engineering, iron, metal, textiles, tannery, sanitary, steel industriesandother industries that release approximately 105.7 cusecs untreated industrial effluent directly into urban drainage system([18])Sugarcane,rice, melons and grains are major export crops of Gujranwala which are irrigated with industrial waste due to being cheaper and easily accessible. Total eleven samples were collected from different points. Preferably samples were collected from shallow groundwater and few from deep aquifer wherever shallow aquifer sample was not possible. . Following are the further details of sampling points:

Table 2.7: Sampling details and their Coordinates:

S. No.	Sample	Latitude	Longitude
1	GGW-1 (ref.)	32°09' 17.7"N	32° 09'17.7"N
2	GGW-1	32° 09'17.7"N	74° 08'51.1"E
3	GGW-2	32° 09'19.7"N	74° 08'53.6"E
4	GGW-3	32° 09'13.0"N	74° 08'45.8"E
5	GGW-4	32° 09'9.2"N	74° 08'40.0"E
6	GGW-5	32°09'13.4"N	74°08'45.5"E
7	GGW-6	32°09'15.4"N	74°08'48.7"E
8	GGW-7	32°07'7.3"N	74°09'56.1"E
9	GGW-8	32°7'7.4"N	74°9'57.3"E
10	GGW-9	32°06'33"N	74°10'45.4"E
11	GGW-10	32°06'32.9"N	74°10'47.2"E
12	GGW-11	32°06'32.9"N	74°10'47.4"E

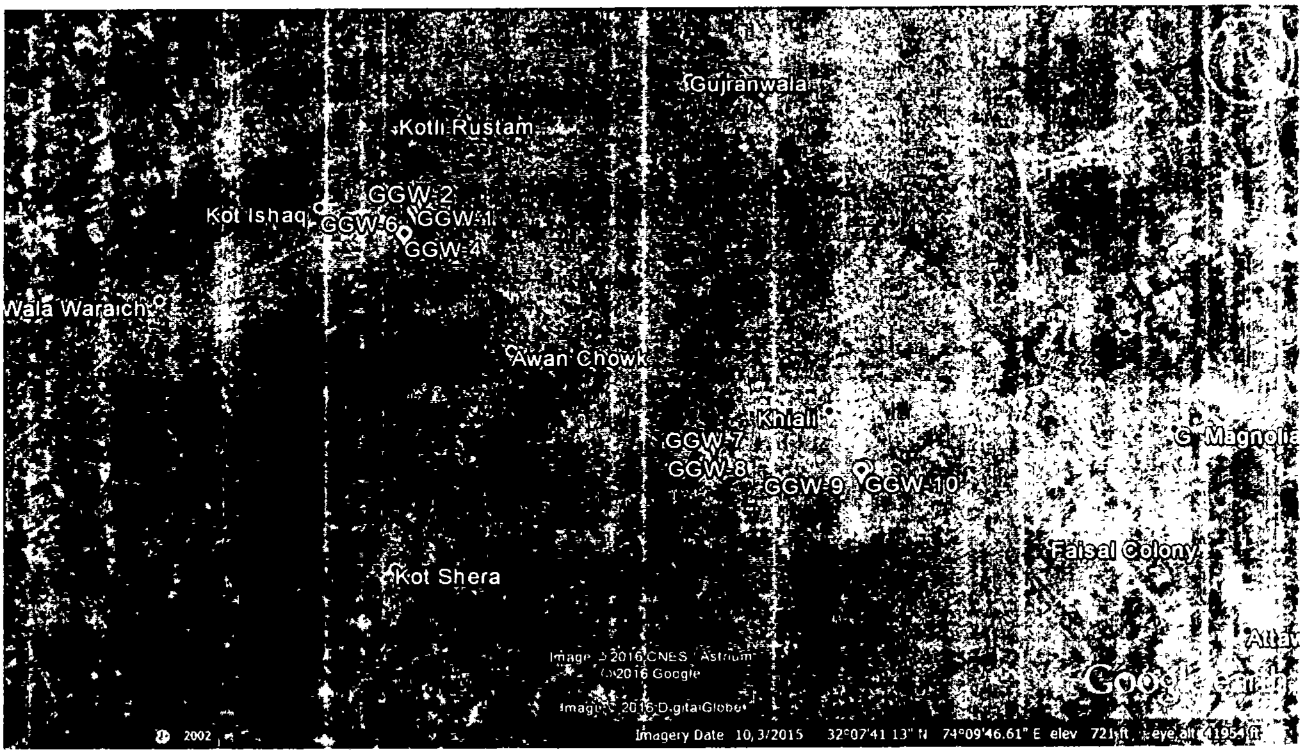


Figure2.2.6: Map showing the sampling points of Gujranawala Groundwater

2.2.7. Faisalabad:

Faisalabad is situated in the center of the Punjab Province.Sewage waste of city is discharged drain(Tebbutt, T. H. Y., 1983). It tremendously affects the ground water resources of that residential area. The wastewater is highly viscous with high-suspended solids and total dissolved solids. (S.Munir, and M. Mukhtar, 2005). In Faisalabad, there are 512 large Industrial units, out of which are 328 textiles, while 92 units are engaged in engineering works and other 92 units with food processing activities. Other industries include: hosiery, carpet, rug, lace, printing, publishing and pharmaceutical industries etc (M. Akram., et al., 2006). Eight samples were collected from different points alongside the wastewater drain and adjacent areas where drain water was being used for irrigation purpose. Following are the details of samples:

Table 2.8: Sampling details and their Coordinates:

S. No.	Sample	Latitude	Longitude
1	FGW-1	31°36'47.0"N	73°53'35.9"E

2	FGW-2	31°36'47.8"N	73°53'35.4"E
3	FGW-3	31°29'45.3"N	73°16' 24.0"E
4	FGW-4	31°29' 41.0"N	73°16'23.2"E
5	FGW-5	31°29' 22.1"N	73°16'27.2"E
6	FGW-6	31° 29' 42.4"N	73°16'29.4"E
7	FGW-7	31°29' 40.3"N	73°16'26.4"E
8	FGW-8	31°27'54.8"N	73° 18' 34.6"E

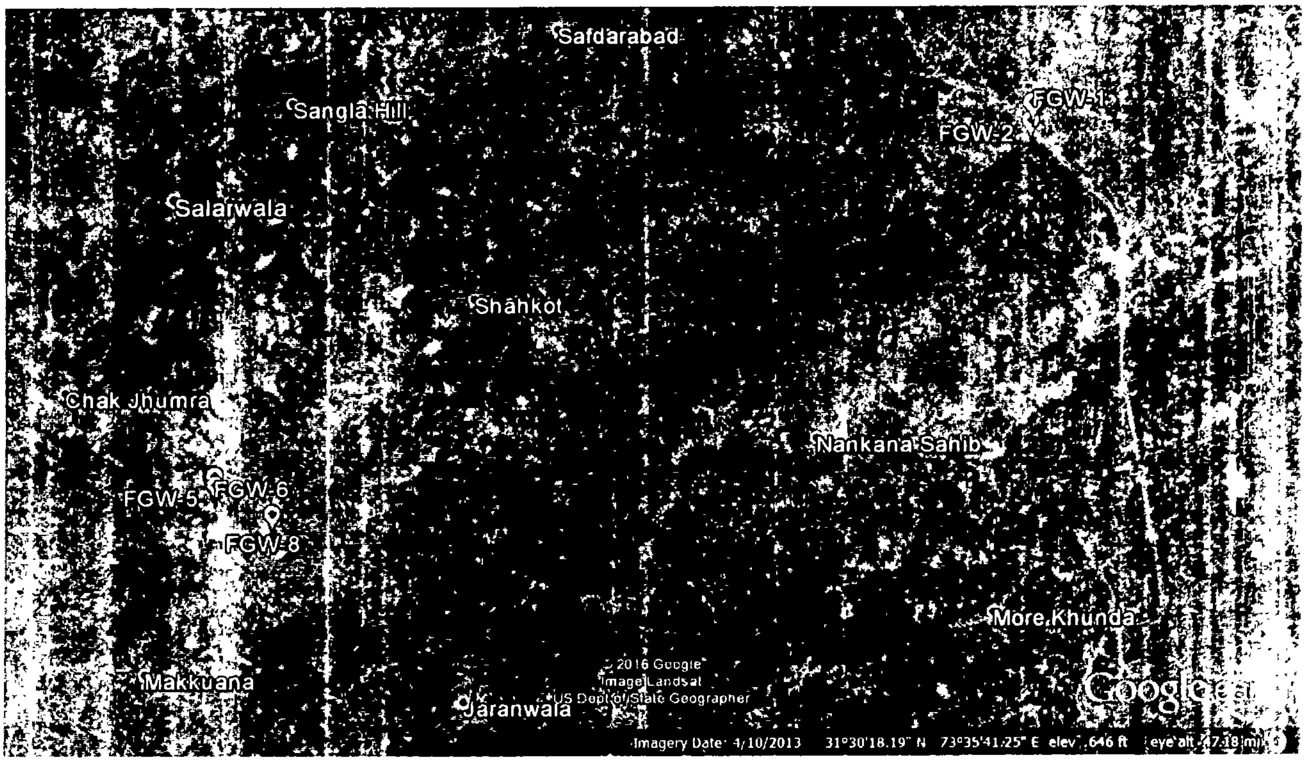


Figure2.2.7: Map showing the sampling points of Faisalabad Groundwater

2.3. Materials and Reagents:

The organic solvents like n-Hexane (extra pure) of Riedal-de Haen, Acetone of scharlau (Merck HPLC grade), Ethyl acetate (analytical reagent grad) of BDH chemical Ltd. Methanol of Analar (BDH) (99.9% pure) and Acetonitrile (Merck HPLC grade) were used in analytical work. SPE cartridges C-18 were used for extraction of organic pollutants. For Chlorides, Silver Nitrate($AgNO_3$) byBDHchemicalsLtdand Potassium dihydrogenphosphate(PH_2PO_4)byFlukaGarantiewereused. SPE cartridges C-18 were used for extraction of organic pollutants. All the glasswarewas washed with 10% HCL and 90% distilled water, rinsed with distilled water before the experimental work. Beakers, volumetric cylinders, pipettes, flasks and small glass bottles were used during research work. All these bottles were oven driedbefore use.

2.4. Instrumentation:

- **pH Meter**: Oyster PP-201, EZODO (china) model was used for measurement of pH
- **Conductivity Meter**: WTW LF 95 (German) model was used for the measurement of EC and TDS.
- **Chlorides**: chlorides were determined by titration method.
- **Nitrates**: Nitrates were determined bymeter Ion 5/6 Acorn series Oakton Instrument.
- **^{13}C stable Isotope:** The stable isotope analyses have been performed using a modified Varian Mat GD-150 Mass Spectrometer.
- **Mass ratio isotope spectrometer:** The stable isotope analyses were performed using a modified Varian Mat GD-150 Mass Spectrometer was used.
- **UV Spectrophotometer:** UV Specord 205 Analytik Jena (Germany) was used for complete scanning of organic pollutants.

2.5. Apparatus and Equipment:

2.5.1. Stable Carbon Isotope (^{13}C) Technique:

The stable isotope values are different for different water samples. ^{13}C values for pure ground water are much different than the waste water. ^{13}C value of groundwater samples havebeen used to determine the possible mixing of wastewater/or recharge source. The stable isotope analyses have been performed using a modified Varian Mat GD-150 Mass Spectrometer. Stable isotope data is reported as for ^{13}C analysis of Total Dissolve Inorganic Carbon. The overall analytical error is± 0.01 ‰ for $\delta^{13}C$ measurement. To ensure precision, standard deviation of the mass spectrometer has also been computed and standard deviation of each sample has been ensured to be within permissible limit. For isotope analysis on mass spectrometer, water samples have been converted into gas phase. Since sample preparation system is used for analysis of C, this system has been accordingly modified/ redesigned in laboratory.

Extraction of Carbon Dioxide from water samples for^{13}C analysis(inorganic fraction:For the extraction of CO_2 gas from Total Dissolved Inorganic Carbon of water. A 50 ml of water sample waspoured into the Pyrex reaction flask. A small burette containing H_3PO_4 acid was then attached to the reaction flask [McCrea, 1950]. The reaction flask assembly was connected to the vacuum line. Dewar flask containing liquid N_2-acetonmixture (temperature, -80^{0}C) was attached to the moisture traps in the vacuum system. About 5 ml H_3PO_4acid was added to the pre-evacuated reaction flask. The CO_2 gas was evolved as a result of reaction between inorganic carbon component/fraction of sample and the phosphoric acid according to the following equation:

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

The moisture produced during the reaction was removed by cryogenic trap of -80^{0}C. The CO_2 gas was passed through vacuum line and purified by freezing in U-trap dipped in liquid nitrogen flask. Other gases were pumped out from line. The liquid N_2flask from CO2 trap wasremoved 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).

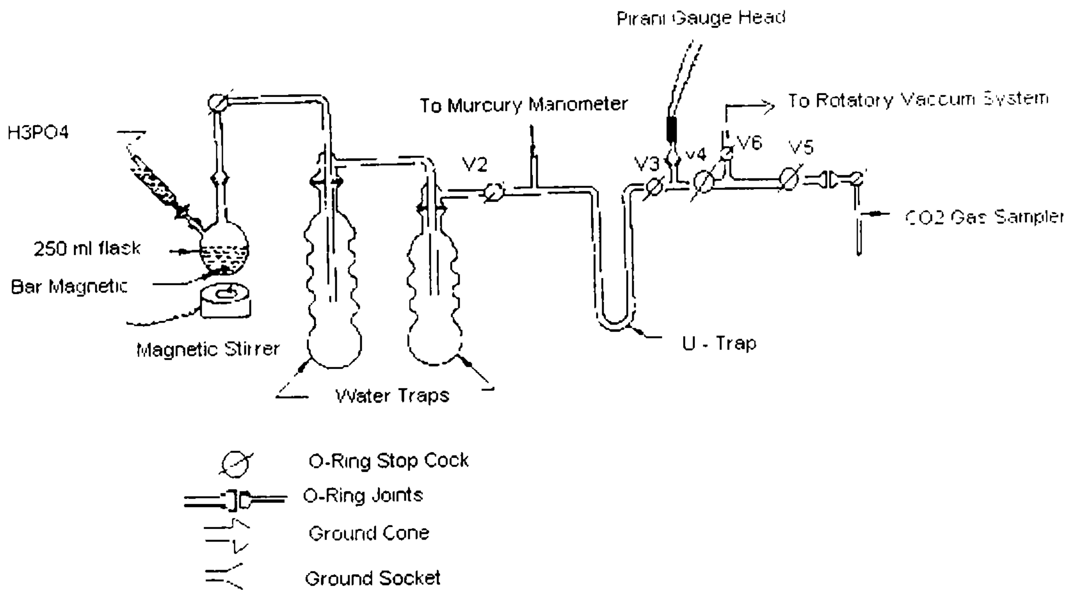


Figure2.5.1: A vacuum system for the extraction of CO_2 gas from water

2.5.2. Isotope Ratio Mass Spectrometer:

The stable isotope analyses were performed using a modified Varian Mat GD-150 Mass Spectrometer Stable isotope data are reported for ^{13}C analysis of Total Dissolve Inorganic Carbon. The overall analytical errors are ± 0.01 ‰ for $\delta^{13}C$ measurements. To ensure precision, standard deviation of the mass spectrometer was also computed and standard deviation of each sample was ensured to be within permissible limit.

Figure2.5.2: Isotope Mass Ratio Spectrometry

For organic pollutants, quantitative analysis has been carried out. Before conducting the analysis, First samples were extracted by using; Extraction and pre-concentration technique which includes:

2.5.3. Pre-treatment:

Filtration was done through Whattman filter paper and 0.45 μm filter paper by using vacuum assisted filtrationsystem.For most of qualitative analysis, UV-visible spectrometry (UV Specord 205 Analytik Jena) was used. Samples were scanned with following instrumental conditions: wavelength 190-500 nm Integration time 0.5, Delta λ 1nmand Scan speed 2 nm/sec.Samples are usually placed in quartz cells; depending on the region of interest, they may also be constructed of glass or plastic. Ultraviolet visible spectroscopy or ultraviolet-visible spectrophotometry (UV-Vis or UV/Vis) refers to absorption spectroscopy or reflectance spectroscopy in the ultraviolet-visible spectralregion.Samples were analyzed by UV spectrometer.Areferencesolutionofdistilled water was used.

2.5.4. Solid Phase Extraction (SPE):

The groundwater samples were beyond detection limit of instrument, for convenience, samples were pre-concentrated by applying solid phase extraction.Then samples were analyzed on High Performance Liquid Chromatography (HPLC)(Tanabe, A. et al., 2000).Solid phase extraction (SPE) is an extraction methodthat requires a solid phase and a liquid phase to extract one, or more of analyte from a solution.The stationary phase is key article which provides space to compound to adsorb onto its surface, it is composed of different nature of compound and it is packed into a glass or plastic column. The column has a frit on top of the stationary phase and might also have a stopper to control the flow of solvent through the column. Different columns are used for the extraction of compounds depending upon the nature of element of interest.In this technique, the organic contaminants present in water samples were passed through solid phase () our desired compounds retained onto stationary phase and then extracted by using following four different organic solvents.

Elution of sample from C18 Cartridge: The flow rate of 1ml /minute was used to elute the adsorbed organic pollutants on the surface of the C-18 tube by using four ml of following solvents.

- Acetone (Merck HPLC grade)
- Hexane (extra- pure) Riedal-de Haen
- Methanol
- Ethyl acetate

In this manner, organic contaminants were pre-concentrated from one liter to 16 ml. C-18 Catridges were used for extraction and purification by SPE. Solid phase extraction techniqueswere used not only to extract traces of organic compounds from environmental samples but also to remove the interfering components of the complex matrices in order to obtain a cleaner extract containing the analytes of interest.This technique was used to increase the detection limits of organic pollutants on instrument. The SPE technique is extensively applied for isolation of analytes from a liquid matrix and purified extracts.Solid Phase Extraction Assembly by SUPELCO Visiprep was used with CNWBOND HC-C18 SPE TUBES for scanning and pre-concentration.Thespecification of C-18 Cartridges isfollowing:

Table 2.9: Cartridge details; bare silica physical properties:

Properties	**Specification**
Particle size(μm)	40-63
Surface area(m2/g)	450-530
Average pore size(Å)	53-67
Cleanliness test	Proprietary
Bonded silica physical properties	
Properties	Specification
Carbon content(C %)	≥15.3
Loading(mmoL/g)	≥0.71
Surface coverage(μmoL/m2)	≥1.77
Volatile content(%,110 °c)	≤4
Cartridge characteristic	
Properties	Specification
Tube purity	Proprietary
Frit purity	"
Luer tip integrity	"
Flow characteristic	"

One litter volume of each sample was passed through C-18 cartridges for DDT,DDE,Endrin, Dieldrin, Cypermetharin, DCP and TCP. The organic pollutants were adsorbed on the surface and the inorganic liquor was collected in a plastic bottle. Flow rate was adjusted as 80 drops / 1ml per minute controlled through vacuum (20 Hg pressure) for maximum adsorption of organic pollutants on C-18.

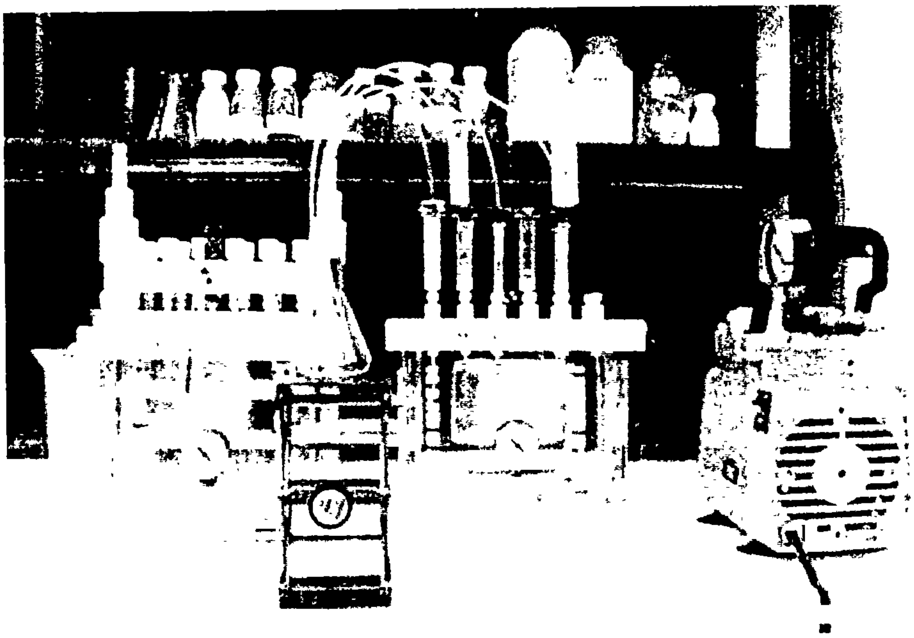


Figure 2.5.4: Assembly of Solid Phase Extraction

2.5.5. After Treatment (UV/Vis Spectrometer):

To evaluate the efficiency of extraction and purification method the samples before treatment and after treatment were scanned on UV/Vis spectrometer in range of 190-500 nm. UV-visible spectrometry (UV Specord 205 Analytik Jena) was used to scan the samples. Samples were scanned with following instrumental conditions: wavelength 190-500 nm Integration time 0.5, Delta λ 1nm and Scan speed 2 nm/sec.A reference solutions consisting of eluting solvents like ethyl acetate, hexane,methanolandacetone, in equal proportion was used. Samples were placedin quartzcells.In Scanning data of samples before treatment and after treatment was compared.

2.6. Chemical Analysis:

2.6.1. Pre-concentration of heavy metals:

Normally groundwater samples have low concentrations of heavy metals. At times, it becomes difficult to analyse their concentration as they appear below detection limit of instrumental techniques. In that connection, groundwater samples were concentrated by simmering/heating it below boiling point by 10 % of their original volume. In this way, sample was concentrated 10 times and then analysed.

Techniques for Metals:There are many analytical methods for metals determination such as Atomic Absorption Spectroscopy, Inductive Coupled Plasma, and etc. In this study, metal concentrations were measured by Inductive Coupled Plasma (ICP-MS) and Voltametrypolarograph 797 Computrace.

2.6.2. Inductively coupled plasma optical emission spectrometry (ICP-OES):

Measuring the concentration levels of trace and ultra-trace elements in different samples is an important analytical task in environmental, biological, clinical, as well as industrial studies. The two most commonly used tools to deal with such analyses are plasma-spectrometry techniques, namely inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS). The suitability of these two techniques relies on their multi elemental capabilities, high selectivity, wide dynamic range, high sample through put, absence of chemical interferences, and easy coupling with different separation techniques (Mermet, 2005).

Working principle: ICP-OES works on the principle that the atoms of elements take up energy from inductively coupled plasma, are thereby excited, and fall back into their ground state again emitting a characteristic radiation. The identification of spectrum of this emitted radiation by a spectrometer gives the qualitative analysis of a sample. A quantitative determination takes place on the basis of the proportionality of radiation intensity and element concentration in calibration and analysis samples (Michael and Nicholas, 1989).

2.6.3. Polarograph:

Polarography is avoltammetric measurement whose response is determined by combined diffusion/convection mass transport. Polarography is a specific type of measurement that falls into the general category of linear-sweep voltammetry where the electrode potential is altered in a linear fashion from the initial potential to the final potential. As a linear sweep method controlled by convection/diffusion mass transport, the current vs. potential response of a polarographic experiment has the typical sigmoidal shape. What makes polarography different from other linear sweep voltammetry measurements is that polarography makes use of the dropping mercury electrode (DME) or the static mercury dropping electrode. Computrace VA 797 was used for the analysis of zinc, cadmium, lead and copper Hanging Mercury Dropping Electrode (HMDE).

2.6.4. Determination of chloride concentration by Titration:

Chloride analysis was carried out by titration method. For it, we required 0.05N solution ofNaCl, 0.05 N solution of $AgNO_3$ and potassium chromate 5%.we took 0.731gm NaCl (extra pure) in 250 ml in distilled water. Then 2.123gm $AgNO_3$ in 250 ml of distilled water and transfer it to amber bottle in dark place(orcovered with aluminum foil). Dissolve 5gm extra pure K_2CrO_4in 100 ml of distilled water. 10 ml sample and transfer it to the 100 ml beaker. Added 2-3 drops of $K_2CrO_4$and mixed about 30 sec. Titrate until pink orange precipitates are formed. Chloride ions were detected using Argentometricmethod, Eq. II (Clarke 1950).

For HCO_3 determination:

$$\text{Concentrat ion in ppm} = \text{molarity} \times \text{molecular weight} \times 1000 \text{ -------------------Eq. I}$$

For Cl^- Determination:

$$\text{Cl(ppm)} = \frac{\text{mlof AgNO3} \times \text{Molarityof AgNO3} \times 1000 \times \text{atomicmassof Cholride}}{\text{Volumeof sampletaken}} \text{ -------------Eq. II}$$

2.6.5..Determination of Nitrates:

Nitrates were determined by Ion meter (Ion 5/6 Acorn series Oakton Instrument). The ion meter5/6 was capable of up to three point calibration with standard solutions to ensure accuracy across the entire range of meter. The nitrate probe was connected to the meter being used for the analysis. Nitrate ions detection was carried out through ion selective electrode method using ion meter (Ion5/6, Acron series: Akton Instrument) (Nitrate 2007).

Nitrate probe/electrode: The electrode used consisted of an inert fluorocarbon body with a detectable PVC membrane unit was used. The sensitive membrane consisted of liquid ion exchange material immobilized in a poly (vinyl- chloride) matrix. The connection to a milli voltmeter is via a BNC plug, though an alternative plug may be satisfied.

Procedure:Nitrate electrode was connected with the meter being used for analysis. The meter was calibrated using three standards of Nitrate solutions i.e., 1, 10 and 100ppm. The standard solutions were prepared from 1000ppm Nitrate stock solution (prepared from Potassium Nitrate). The electrode was rinsed with the distilled water after calibration and blot dry withy lint free cloth. Standard calibration curve was obtained from standard Nitrate solution using mV values on the linear axis and concentration on the horizontal axis. The water samples were dispensed in an analytically clean beaker and electrode was dipped into it until millivolt (mV) reading appears stable on the meter. For the determination of Nitrates concentration in samples calibration curve was plotted in MS-EXCEL 2010 (Basil et al., 2007).

2.6.6. High Performance Liquid Chromatography (HPLC):

High Performance Liquid Chromatography (HPLC) is equipped with the UV detector (Waters, 1525) which was used to identify, quantify and analyze the organic compounds in the samples. It has helped to identify the compounds and their concentration in the sample.

Apparatus:High Performance Liquid Chromatograph (Water Breeze System-1525) was used. It comprises waters 2487 dual λ absorbance detector and Stationary phase consisted of C-18 and C-8 analytical column (Waters, 5μm particle size150mm.2mm i.d. column)was used. And, samples were injected manually through injector.

2.6.6.1. Analysis of DDE:

To determine DDE in groundwater samples, an advanced andmoreaccurate method was developed with reverse phase HPLC and UV detector. The analytical conditions were improved at various wave lengths and flow rate to get extremely calibration curves. The outstanding results were achieved by using mobile phase constituted to 10% double distilled water (H_2O) and 90% acetonitrile passed through C-18column at flow rate of 1ml/min using wavelength 240 nm and retention time was 12 minutes. Standards were injected manually and injection volume was 20µL Determination of DDEingroundwater was done with the standard solution of 10 ppb, 50 ppb, 100 ppb, and 200 ppb. Following calibration curve was achieved.

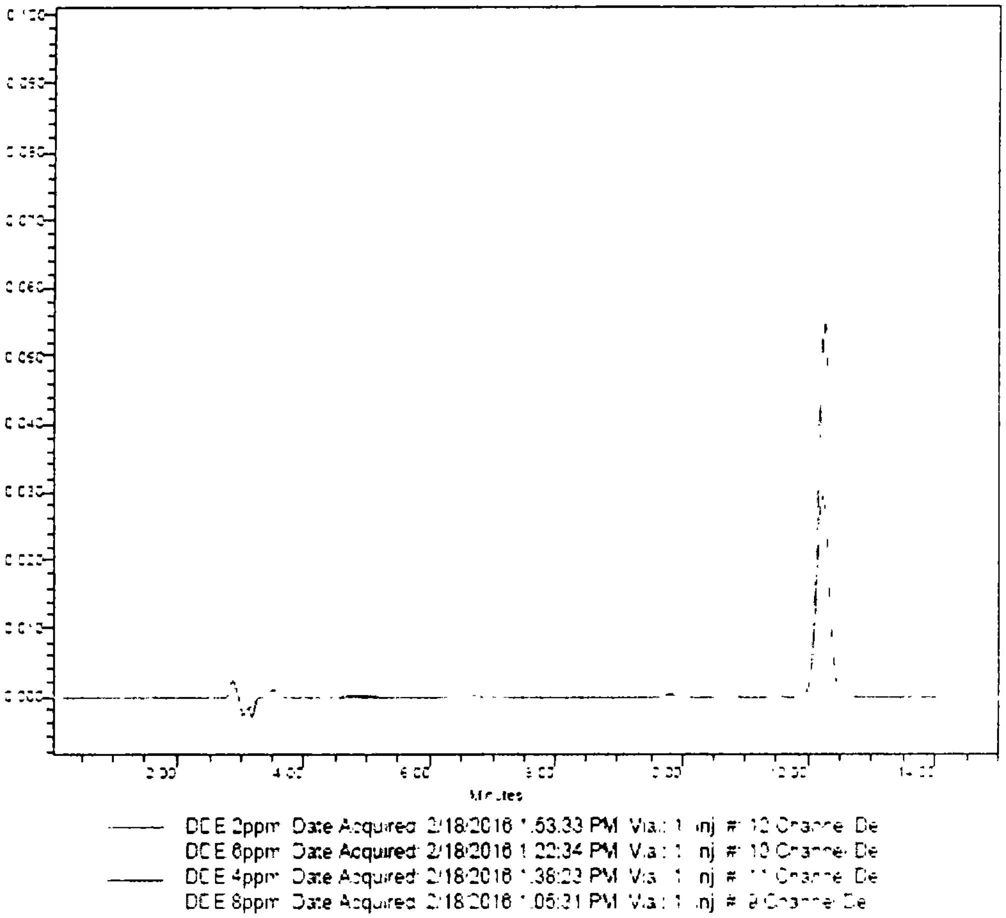


Figure 2.6.6.1: Standards calibration curve of DDE

2.6.6.2 Analysis of Cypermethrin:

The determination ofCypermethrin was done by using mobile phase constituted to 30% double distilled water (H_2O) and 70% acetonitrile and C-18column was used as stationary phase .The flow rate of mobile phase was 1ml/min at 230 nm and retention time of 5 minutes. The quantitative determination of Cypermethrin was achieved by following calibration curve with four different concentrations (10ppb, 20ppb, 30ppb and 40pp) of Cypermethrin.

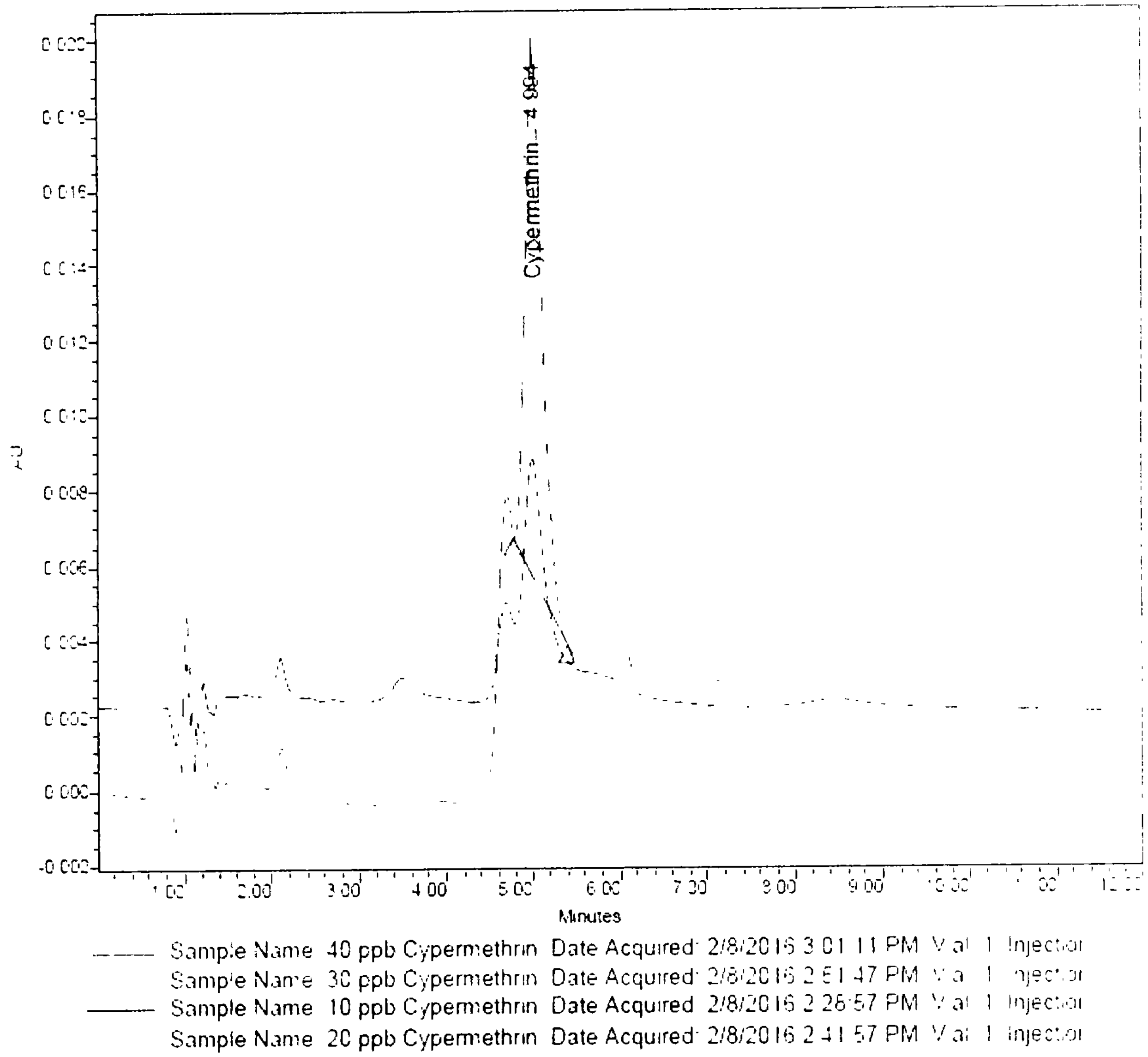


Figure 2.6.6.2: Standards Calibration Curve of Cypermethrin

2.6.6.3. Analysis of Dieldrin:

Dieldrin was determined by developed method. Mobile phase consisting of (60% acetonitrile + 40% water) was used with flow rate of 1 ml/min in isocratic mode.Dieldrin exhibit significant UV absorptive at wavelengths of220nm, retention time was 2minutes.Determination of Dieldrin in groundwater was done with the standard solution of 4 ppb, 6 ppb, 8 ppb, and 10 ppb to achieve calibration curve .Following are calibration curve:

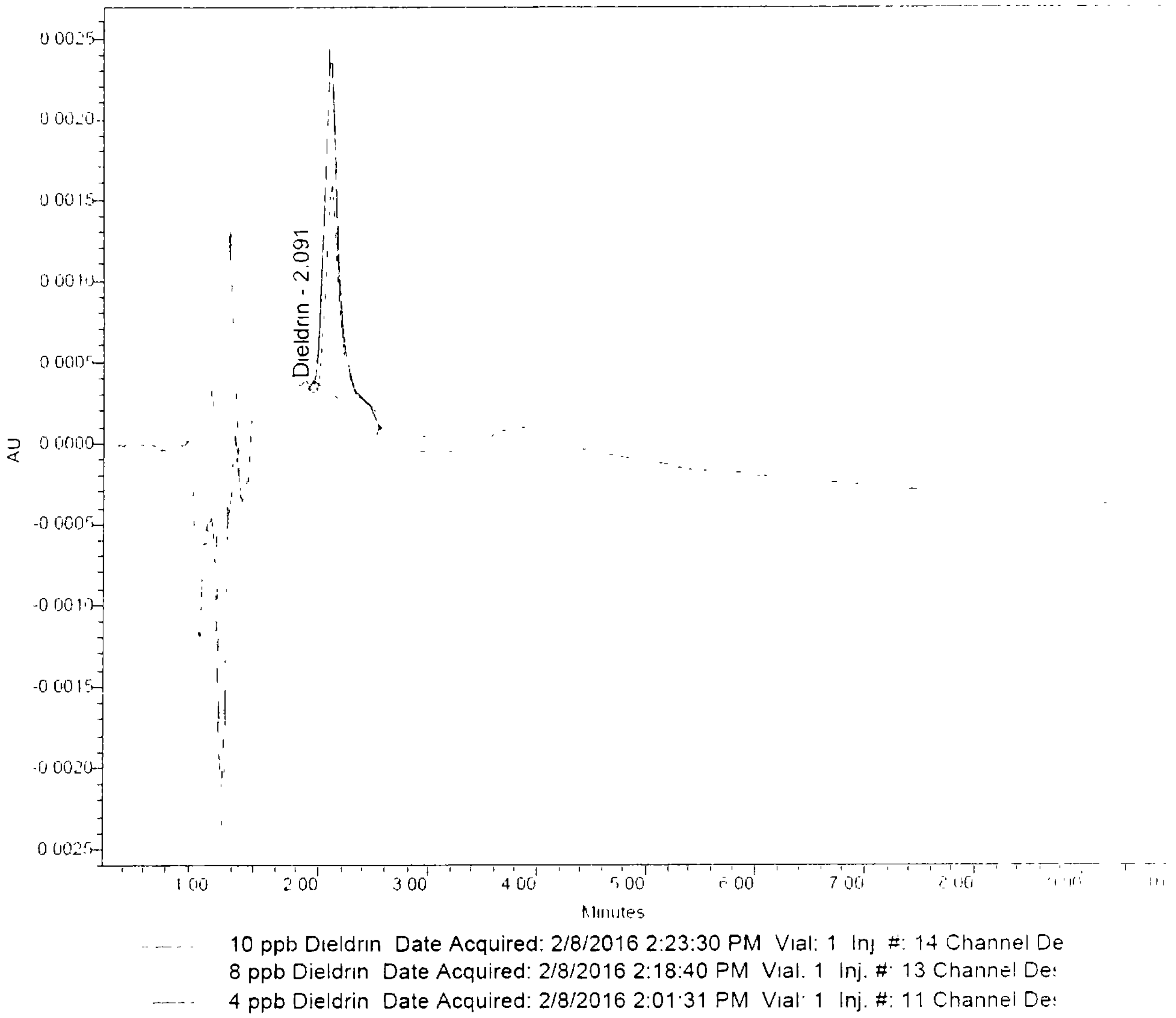


Figure 2.6.6.3: Standards Calibration Curve of Dieldrin

2.6.6.4. Analysis of Endrin:

For the determination of Endrin in groundwater samples by using mobile phase of 40% double distilled water (H_2O) and 60% acetonitrile was passed through C-18column at flow rate of 1ml/min using wavelength 230 nm and retention time was 3 minutes. Determination of Endrin in groundwater was done with the standard solution of 4 ppb, 8 ppb, 16 ppb, and 20 ppb. Following calibration curve was achieved.

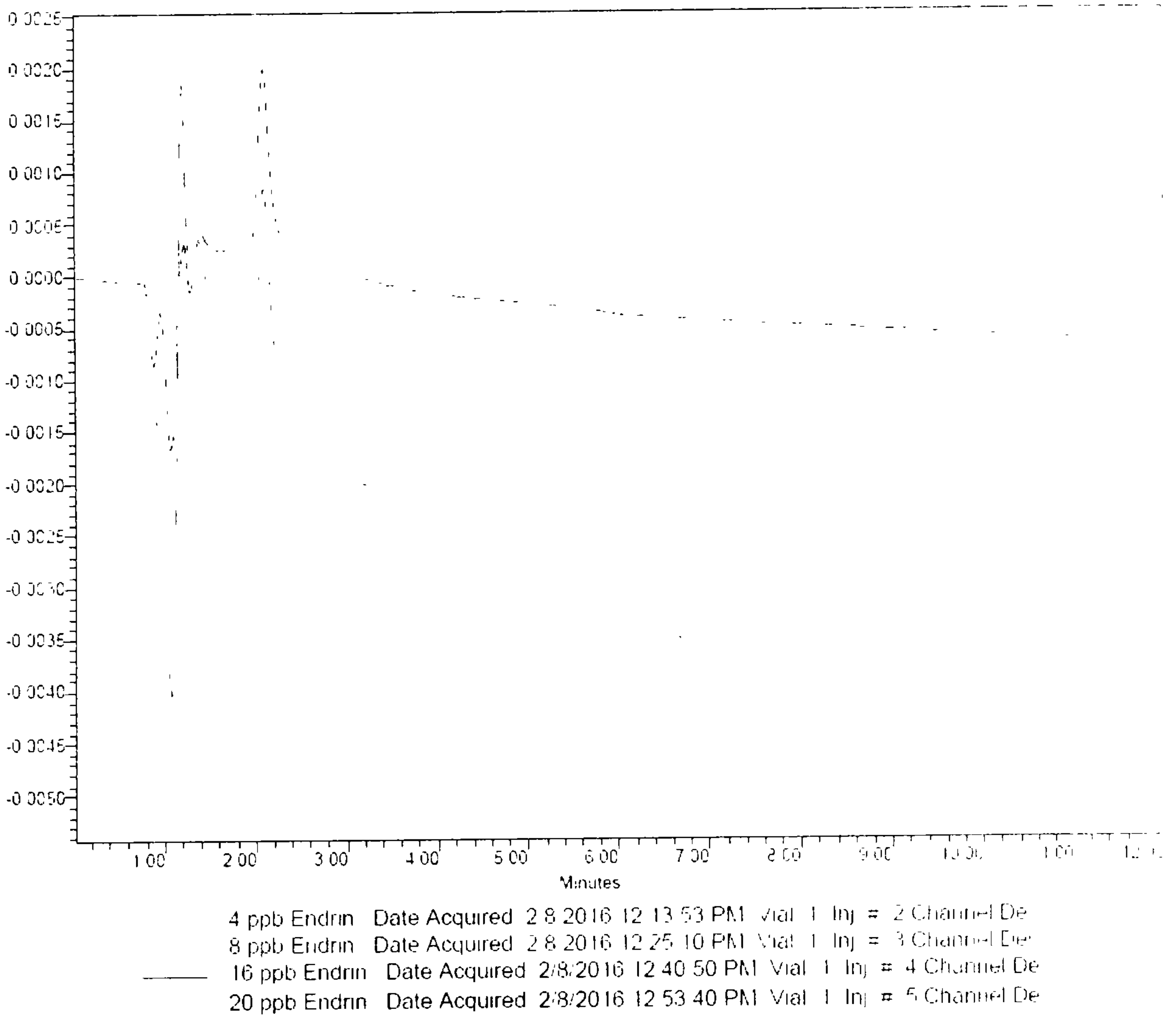


Figure 2.6.6.4: Standards Calibration Curve of Endrin

2.6.6.5. Analysis of DDT:

Determination of DDT in groundwater samples was carried out by using Mobile phase of acetonitrile and water 90% and 10% respectively at the wavelength of 240 nm. The retention time was 3.5 minutes Determination of DDT in groundwater was done with the standard solution of 10 ppb, 50 ppb, 100 ppb, and 200 ppb. Following calibration curve was achieved.

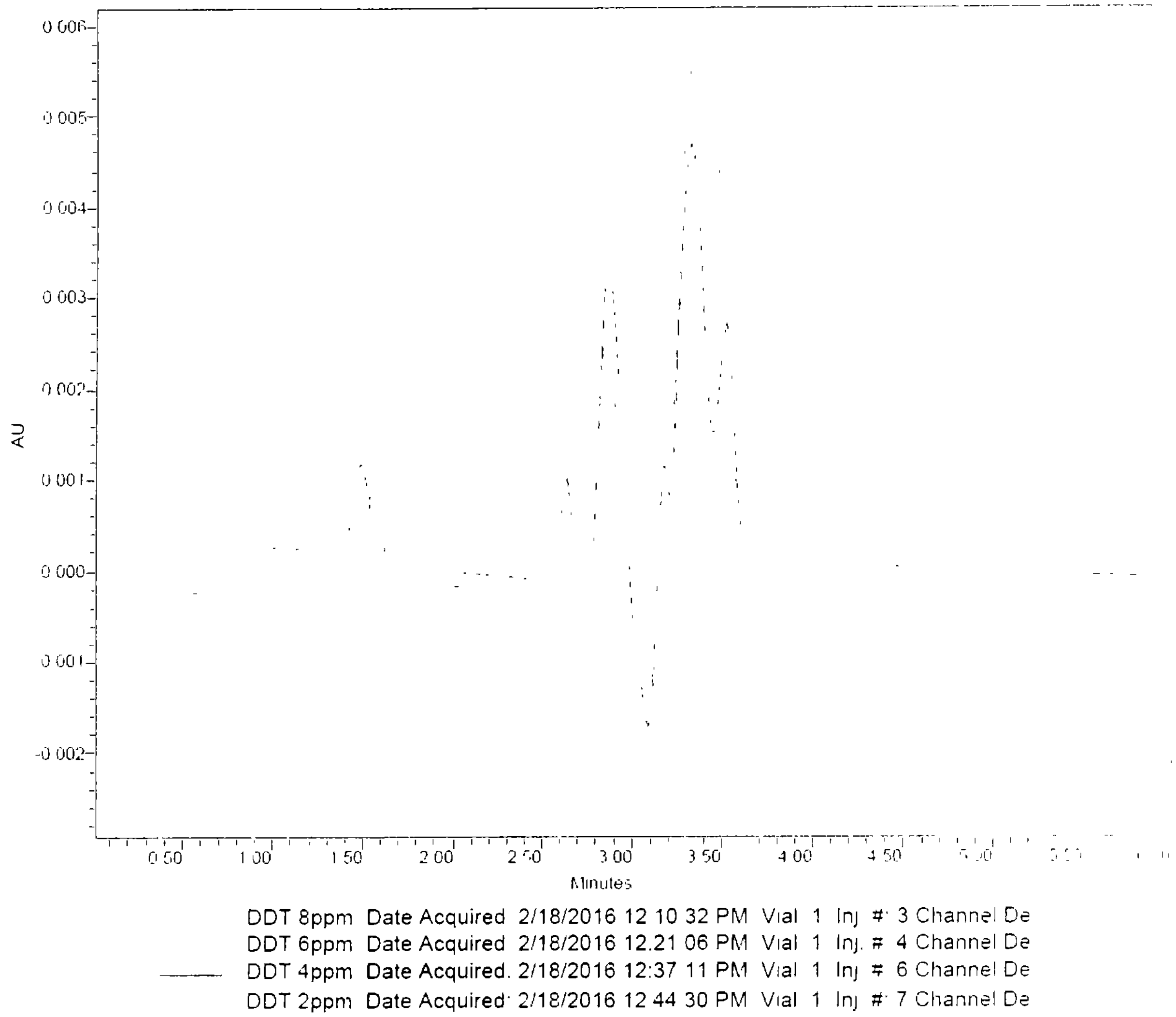


Figure 2.6.6.5: Standards Calibration Curve of DDT

2.6.6.6. Analysis of Dichlorophenol and Trichlorophenol:

Dichlorophenol and Trichlorophenol were determined by using mobile phase of (Methanol and water 50:50 and 0.05MKH_2PO_4 pH 2.7) at the wavelength of 240 nm.C-8 column was used for the analysis of TCP and DCP. The retention time of DCP was 3.1 minutes and of TCP were 4.1. Analysis of groundwater was done with the standard solution of 0.5 ppm, 2 ppm, 4 ppm, and 6 ppm. Following calibration curve was achieved.

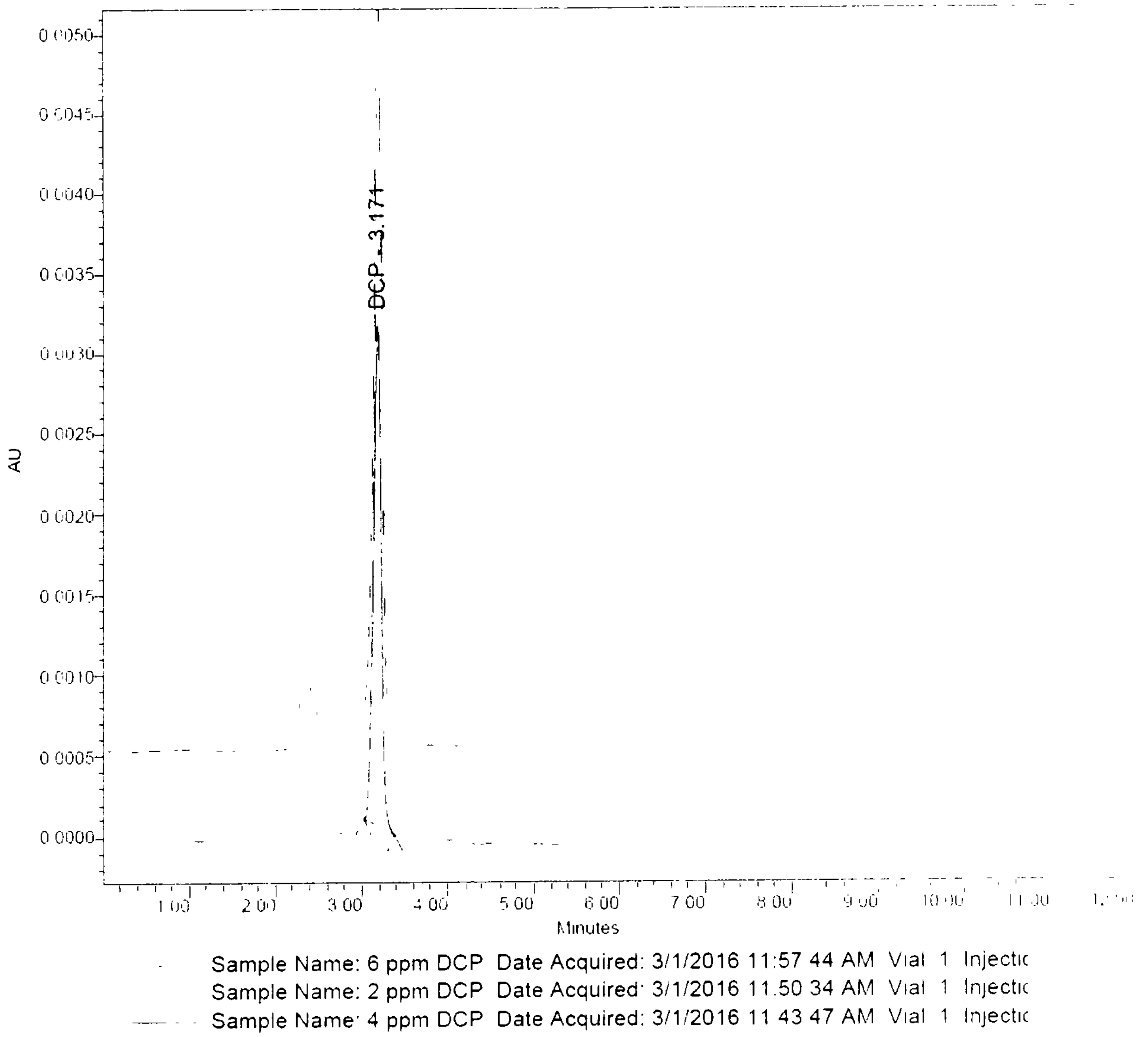


Figure 2.6.6.6: Standards Calibration Curve of DCP

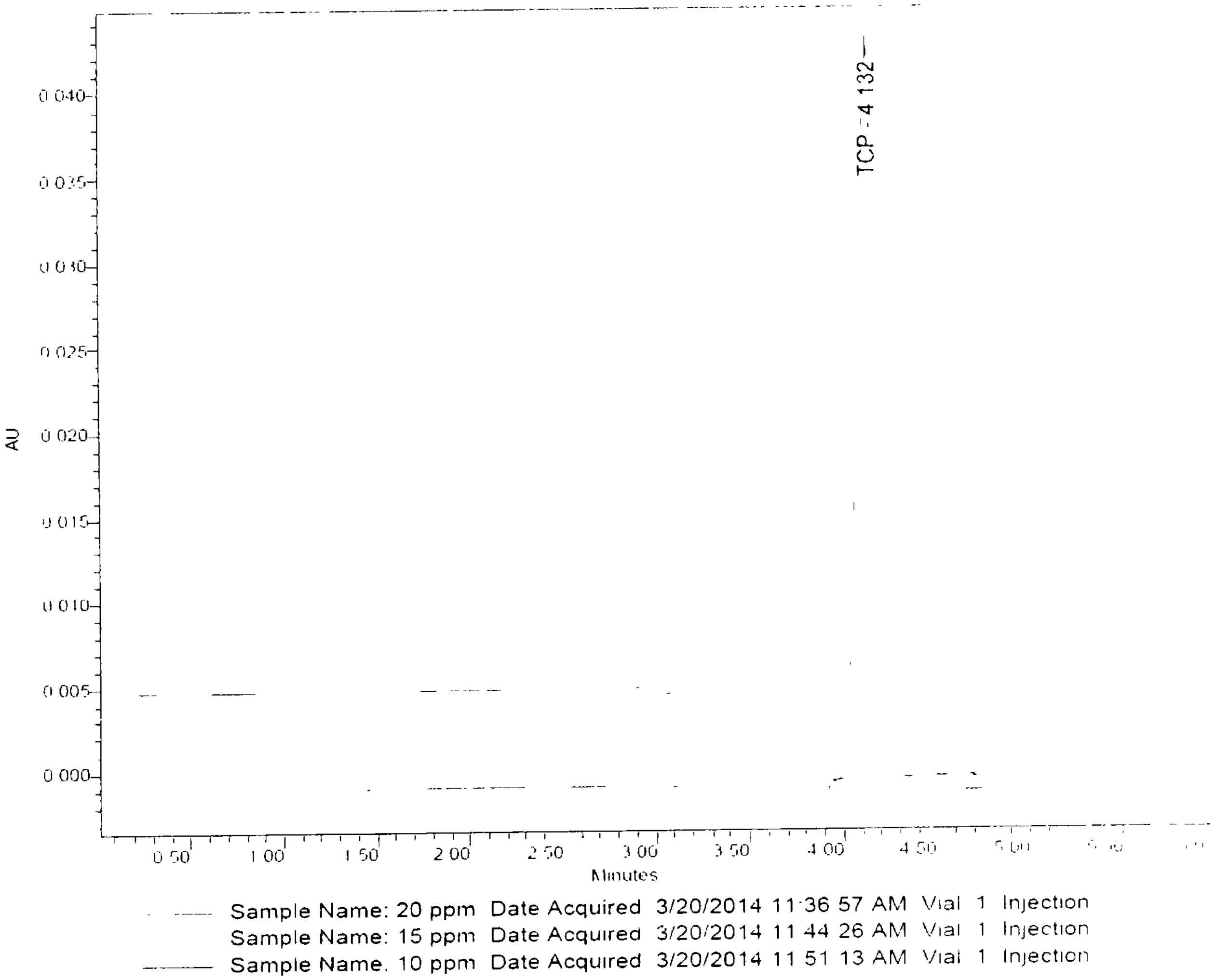


Figure 2.6.6.7: Standards Calibration Curve of TCP

Chapter 3

Results and Discussions

3.1. Physico-chemical Parameters:

3.1.1. Sheikupura:

Total dissolved solids varied between 578 to 1329mg/l.All samples were out of permissible limit of PSQCA and WHO quality standards. The level of TDS in groundwater increased due to high concentration of salts (Din et al., 1997).Electrical conductivity ranged from 959 to 2021μS/cm lied within the permissible limit by WHO (2500 μS/cm).

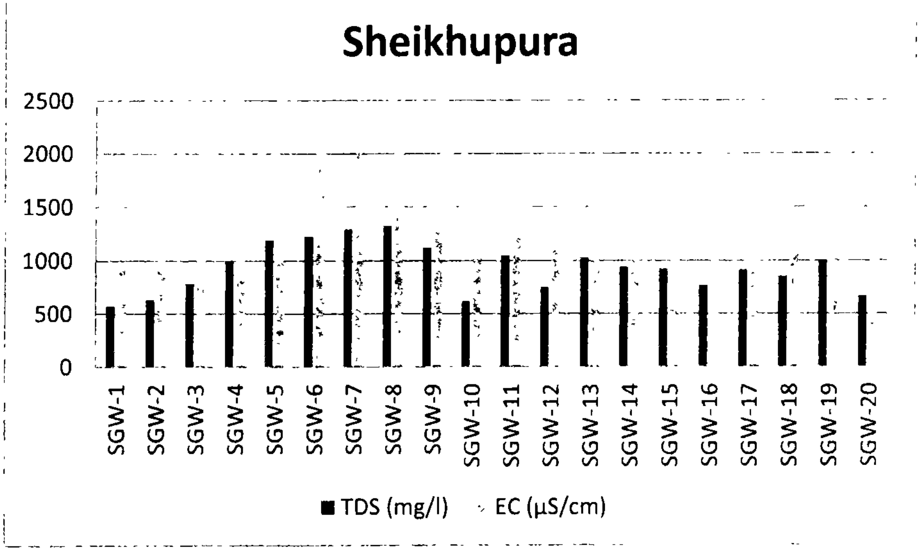


Figure 3.1.1.1: TDS and EC of Sheikhupura Groundwater

While, pH ranges from 7.3 to 7.82 is within the permissible limit. However, nitrates ranged from 169 to 191 mg/l. Nitrates are above the permissible limits, however, chlorides varied from 7.1 to 131.35mg/l and remained within the set limits.

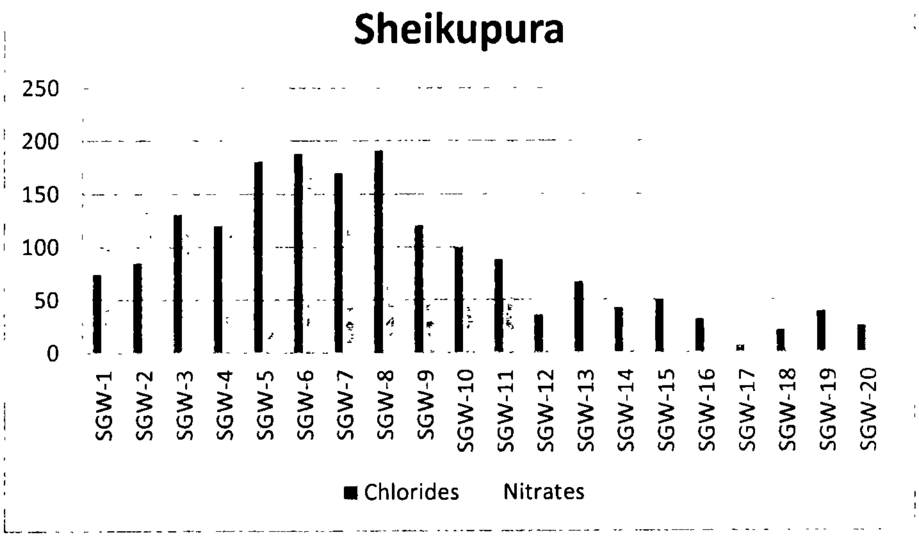


Figure 3.1.1.2: Chlorides and Nitrates of Sheikhupura Groundwater

3.1.2. Lahore:

In Lahore samples TDS was found between 939 to 1530mg/l and EC was also above the 1500mg/l only in one sample EC was 1439mg/l.These concentrations are above the permissible limits.

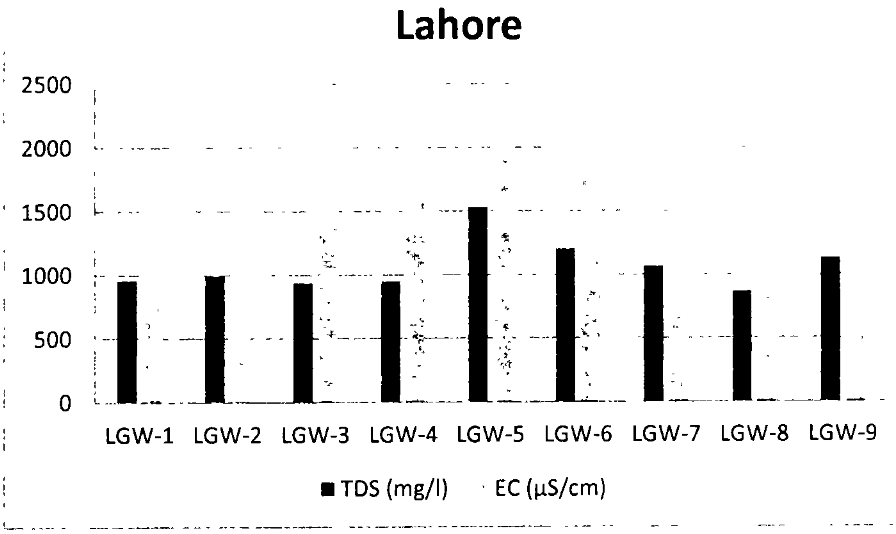


Figure 3.1.2.1: TDS and EC of Lahore

However, pH ranged from 7.2 to 8.04 and Chlorides are 7.1 to 191.7 mg/l remained within the limits. Nitrates are observed above the palatable limits set by WHO.

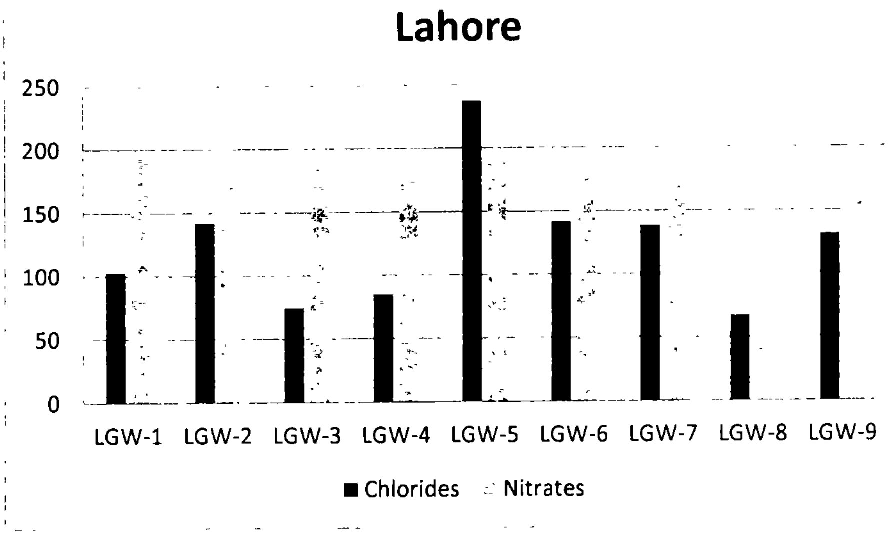


Figure 3.1.2.2: Chlorides and Nitrates of Lahore Groundwater

3.1.3. Raiwind:

In Raiwind samples TDS was found 649mg/l to 1700mg/l. While EC ranged from 1079mg/l to 3056mg/l. These concentrations are above the maximum contaminant level.

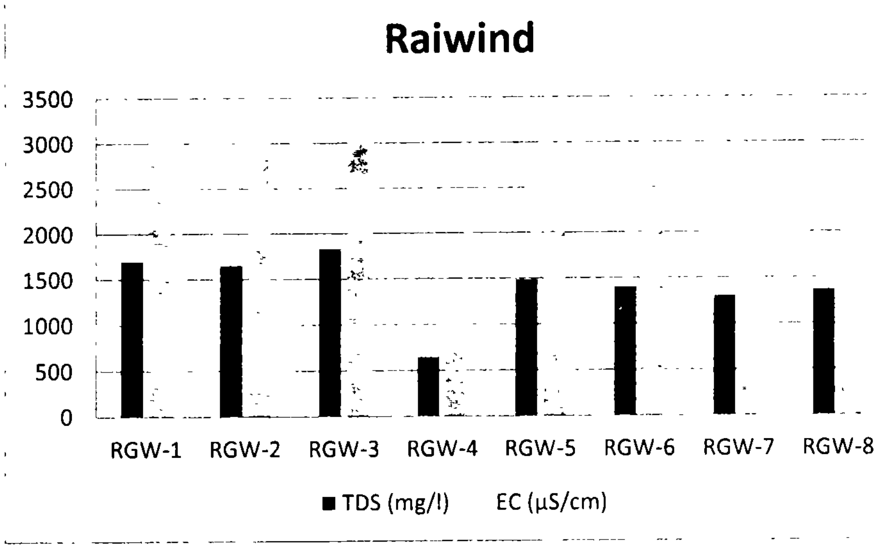


Figure 3.1.3.1: TDS and EC of Raiwind Groundwater

Although, pH ranged from 7.2 to 8.4, and minimum concentration of Chlorides was found 79 mg/l while maximum concentration was observed 518mg/l. chlorides were found above the limits only in two samples. Maximum concentration of Nitrate was found 200 mg/l.While, nitrates were also observed above the permissible limits.

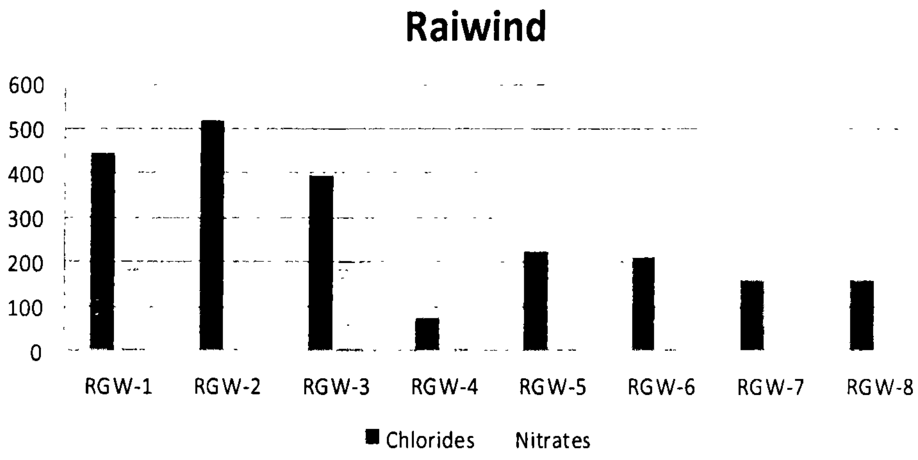


Figure: 3.1.3.2:Chlorides and Nitrates of Raiwind Groundwater

3.1.4. Mangamandi:

In samples of Mangamandi TDS were found in the range from 1001mg/l and 1573mg/l. EC ranged from 1662mg/l to 5052mg/l. these concentrations were above the maximum contaminant level. Whereas pH ranged from 7.12 to 8.12.And it is within the set limit by WHO quality standards.

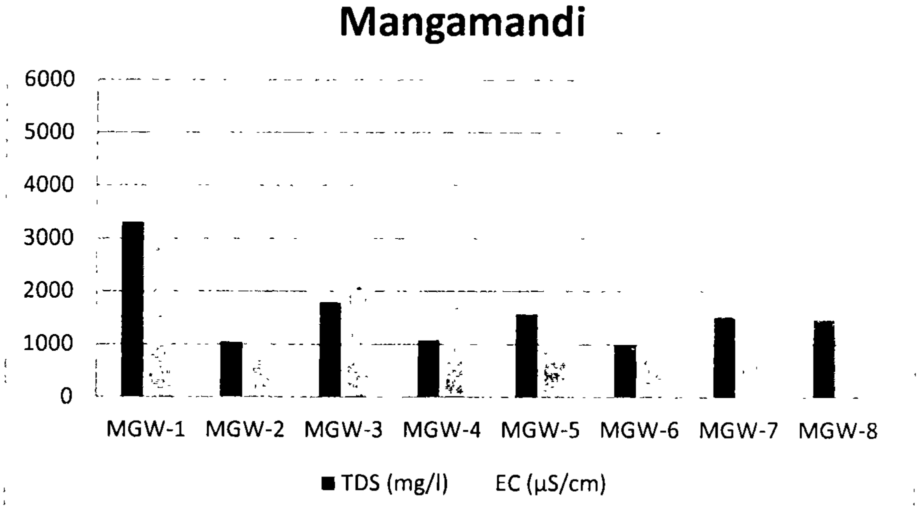


Figure 3.1.4.1: TDS and EC of Mangamandi Groundwater

Chlorides were found from 205.9mg/l to 770.35mg/l. nitrates 183mg/l to 190mg/l. Nitrates and chlorides are above the palatable limits set by WHO and U.S. EPA.

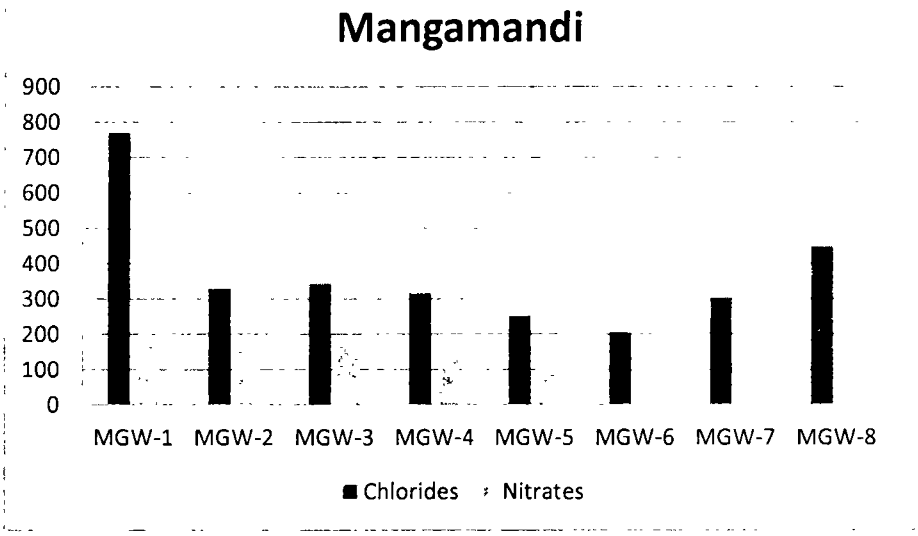


Figure 3.1.4.2: Chlorides and Nitrates of Mangamandi Groundwater

3.1.5. Kasur:

TDS were detected from 331mg/lto3424mg/l. while, EC was ranged from 543mg/l to 10045mg/l and it is too high from acceptable limit set by quality standards organization. However, pH ranged within the limits.

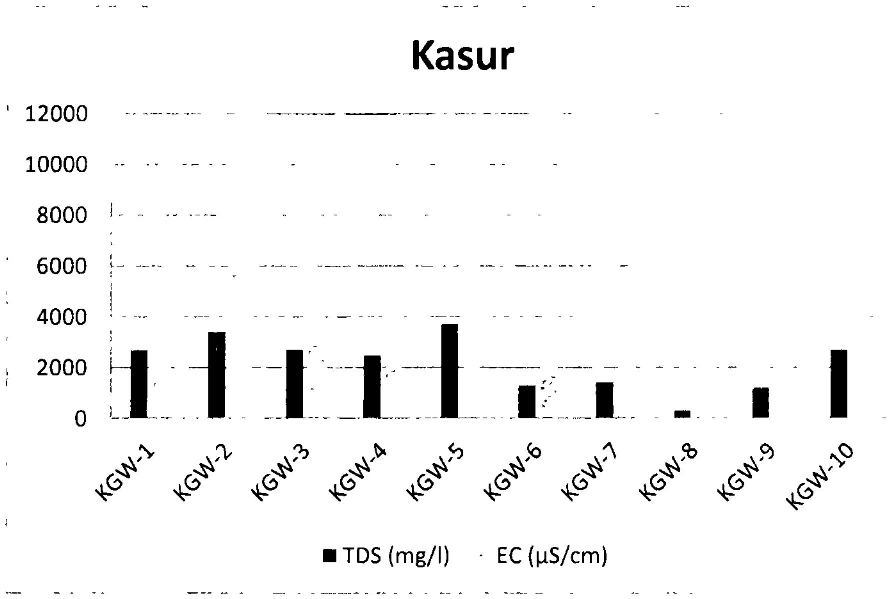


Figure 3.1.5.1:TDS and EC of Kasur Groundwater

Minimum concentration of chlorides was found 42.6mg/l and highest concentration was 1366.75mg/l. chlorides are above the limits. Nitrates were calculated from 1.09 mg/l to 16.63mg/l, nitrates remained within the set limits.

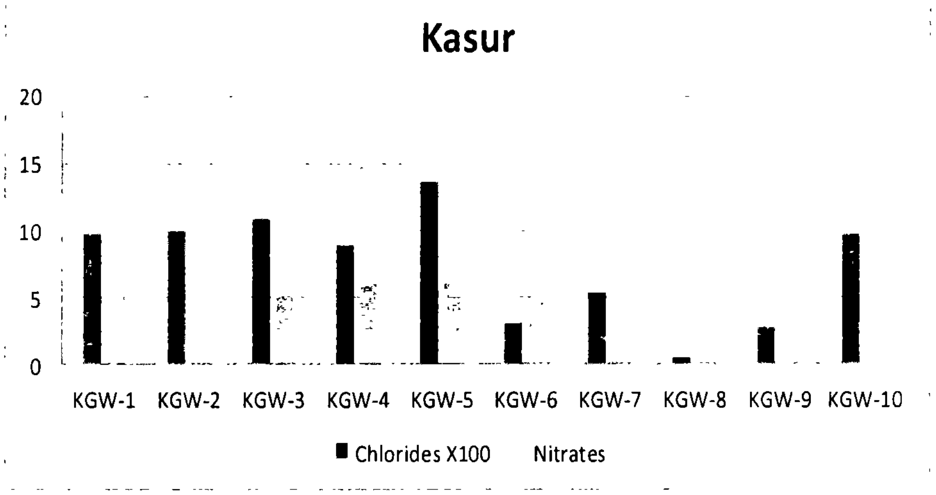


Figure 3.1.5.2: Chlorides and Nitrates of Kasur Groundwater

3.1.6. Gujranawala:

TDS was calculated from 276mg/l to 1337mg/l. EC was ranged from 454mg/l to 2019mg/l.TDS and EC were observed above the permissible limits. While, pH was observed within the limits.

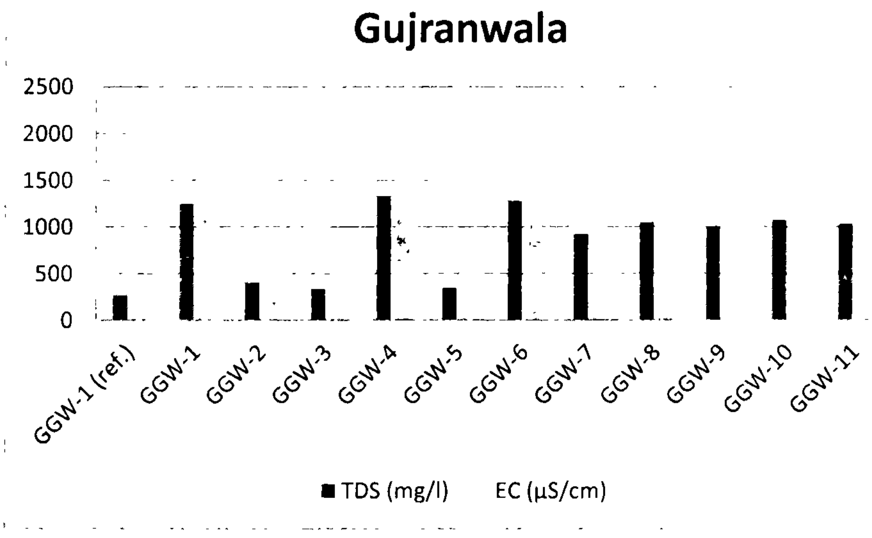


Figure 3.1.6.1: TDS and EC of Gujranwala Groundwater

Chlorides were detected from 14.2mg/l to 227.2mg/l. Nitrates was found from 9.68mg/l to 17.75mg/l.However in Gujranwala samples Nitrates and Chlorides were found within the permissible limits.

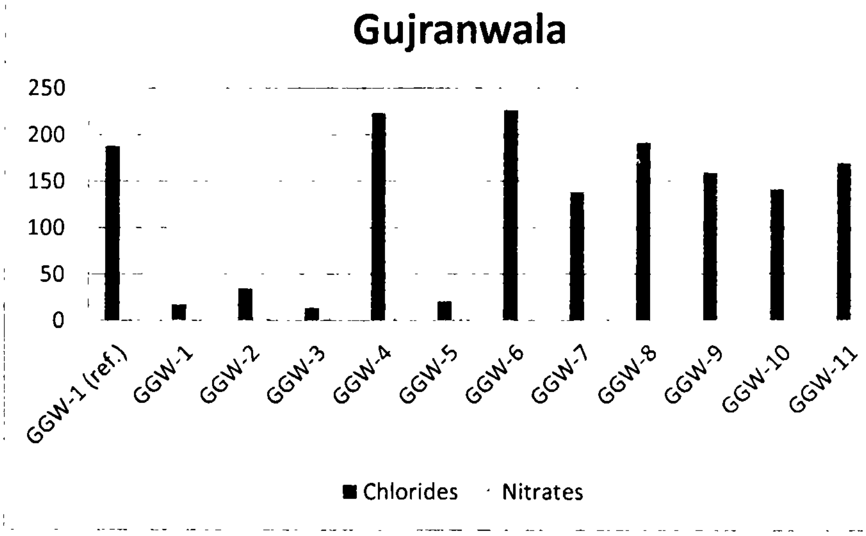


Figure 3.1.6.2: Chlorides and Nitrates of Gujranwala Groundwater

3.1.7. Faisalabad:

TDS was detected from 273mg/l 2706mg/l. EC was ranged from 238mg/l 4032mg/l. these two are found above the permissible limits. And, pH ranged from 7.1 to 7.8 and it is within the set limits.

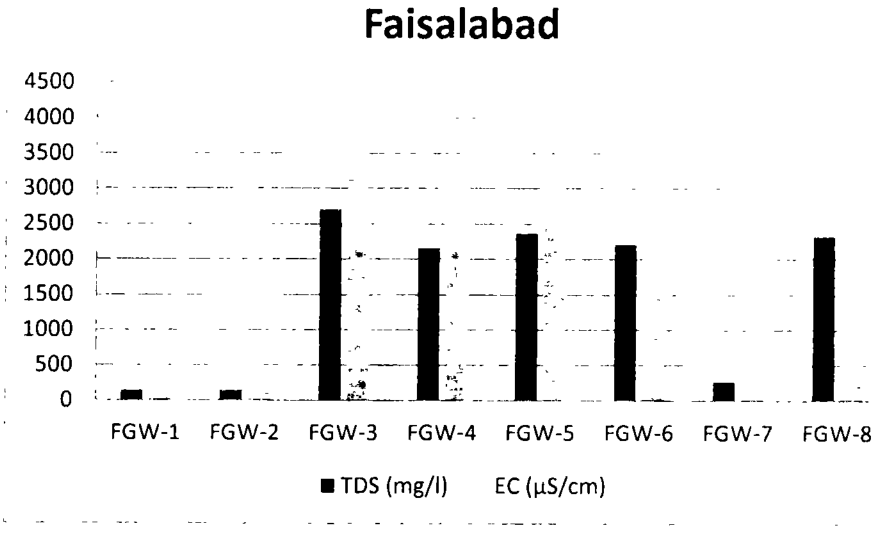


Figure 3.1.7.1: TDS and EC of Faisalabad Groundwater

Chlorides ranged from 7.61mg/l to 763.25mg/l. Nitrates were detected from 2mg/l to 34.5mg/l. Chlorides and Nitrates were above the set limits and few samples were within the permissible limits.

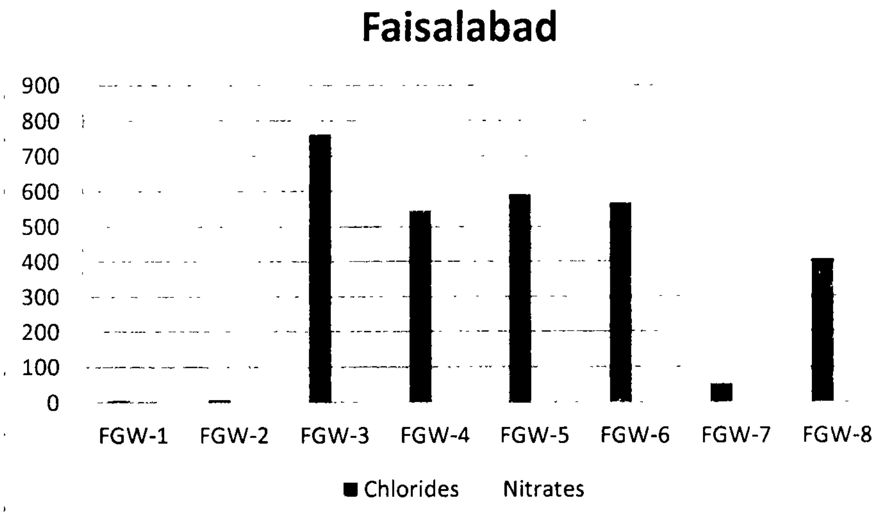


Figure 3.1.7.2: Chlorides and Nitrates of Faisalabad Groundwater

3.2. Stable Carbon Isotope ($\delta^{13}C$):

Carbon has two stable, naturally-occurring isotopes; $\delta^{12}C$ (98.89%) an $\delta^{13}C$ (1.11%). Ratios of these isotopes are reported in ‰ relative to the standard VPDB (Vienna Pee Dee Belemnite). The $\delta^{13}C$ of the atmosphere is -7‰.During photosynthesis, the carbon that becomes fixed in plant tissue is significantly depleted in ^{13}C relative to the atmosphere. There is a bimodal distribution in the $\delta^{13}C$ values of terrestrial plants resulting from differences in the photosynthetic reaction utilized by the plant. The $\delta^{13}C$ values of dissolved inorganic carbon (DIC) in subsurface waters are generally in the range of -5 to -25 ‰. The primary reactions that produce DIC are:

- Weathering of carbonate minerals by acidic rain or other strong acids;
- Weathering of silicate minerals by carbonic acid produced by the dissolution of biogenic soil CO_2 by infiltrating rain water; and
- Weathering of carbonate minerals by carbonic acid. The first and second reactions produce DIC identical in $\delta^{13}C$ to the composition of either the reacting carbonate or

carbonic acid, respectively, and the third reaction produces DIC with a $\delta^{13}C$ value exactly intermediate between the compositions of the carbonate and the carbonic acid. Consequently, without further information, DIC produced solely by the third reaction is identical to DIC produced in equal amounts from the first and second reactions. The $\delta^{13}C$ values of organic materials can provide extremely useful information about sources of contaminants. Carbon stable isotope analysis has been extensively used in estuaries as a tracer of the major sources of organic carbon (Haines and Mon- tague, 1979; Hughes and Sherr, 1983; Gearing et al.. 1984: Sinienstad and Wissniar. 1985;Saliot et al. 1988: Lucotte. 1989). Stable carbon isotopes have also been used to quantify the mixing processes between continental and marine particulate organic carbon (POC) in estuaries where river and ocean end-members were the only sources (Fontugne and Jouanneau. 1987).

3.2.1. Sheikhupura:

In Sheikhupura samples have $\delta^{13}C$ values ranging from -0.42 to -21.91 ‰ PDB. SGW-4 collected from industrial area near the waste water drain , SGW-5 collected from industrial area at a distance from wastewater drain with the depth of 80 feet. SGW-6 was also collected from a point near to previous point with the depth of 40 feet, SGW-8 was collected from industrial area near the wastewater drain with the depth of 60 feet, SGW-13 was 40 feet deep , SGW-14 was 40 feet deep, SGW-19 was collected from residential area and SGW-20 was 200 feet deep and collected from residential area near the wastewater drain. Higher depleted values of abovementioned samples convincingly suggested that samples were contaminated with wastewater recharge. Results of these sampling points show the depleted values of $\delta^{13}C$, which indicates the mixing of waste water into groundwater.

3.2.2. Lahore:

Lahore shallow groundwater samples have $\delta^{13}C$ values ranging from -0.25 to -6.41 ‰ PDB.In Lahore samples, only in LGW-5 $\delta^{13}C$ value was found -6.41 ‰ PDB. This sample was collected from a point located at the edge of wastewater drain it. Other sample did not have depleted $\delta^{13}C$‰ values. The data have some contrast with the metal data. Samples showing metal contamination but did not have depleted $\delta^{13}C$ values. It suggested that samples collected from very shallow aquifer where water has sufficient aeration by plant roots respiration of contact by air.

3.2.3. Raiwind:

$\delta^{13}C$ in Raiwind ground water samples varies from -1.59 to -15.36 ‰ PDB.Only RGW-4was collected from industrial area located near the waste water drain with the depth of 100 feet. Its $\delta^{13}C$ value was -15.36 ‰ PDB. Higher depleted values of sample suggested that there is significant adverse impact of wastewater on groundwater quality in this area.$\delta^{13}C$ values of other samples were within the normal range. It depicts that samples do not have depleted $\delta^{13}C$ values it might be due to the high dissolved oxygen contents, as these samples were collected from shallow aquifers.

3.2.4. Mangamandi:

$\delta^{13}C$ (TDIC) of Mangamandi ground water is around -4.02 to -15.77 ‰ PDB.^{13}C values of MGW-4 is -15.77‰ PDB which is located near the industrial area. Higher depleted values of C-13 suggested wastewater mixing with groundwater at this point. Whereas, $\delta^{13}C$ value of MGW-5 is -6.56 ‰ showing minor depletion but suggesting small adverse impact of wastewater on the groundwater table. This point was collected from industrial area very near to drain.$\delta^{13}C$ of MGW-7 has -6.78‰value and this point is also located in industrial area near the drain.

3.2.5. Kasur:

In Kasur samples $\delta^{13}C$ values ranging from -0.27 to -6.3 ‰ PDB. KGW-2 was collected from industrial area with the depth of 100 feet. Its values show the mixing of waste water into ground water.

3.2.6. Gujranawala:

Gujranawala shallow groundwater samples have $\delta^{13}C$ values ranging from -2.2 to -8.41 ‰ PDB.GGW-1 was collected with the depth of 60 feet from industrial area near the drain.GGW-4 with the depth of 30 feet collected from agricultural land near the wastewater drain.GGW-7, was collected from industrial area near the drain.GGW-8 was collected near the previous point with the depth of 40 feet, GGW-10 was collected from industrial area with the depth 10 feet, GGW-11 was collected from previous point with the depth of 50 feet. In general, in minor quantities groundwater is affected by waste water.

3.2.7. Faisalabad:

In Faisalabad, only two samples showed the depleted $\delta^{13}C$. FGW-5 was collected from depth of 55 feet from industrial area near the wastewater drain. While, FGW-7 with the depth of60 feet collected from residential area near the drain. Faisalabad groundwater samples have $\delta^{13}C$ values ranging from -2.78 to -7.76 ‰ PDB. Overall Faisalabad samples showed less wastewater mixing into groundwater is certainly affected by industrial effluents.

3.3. Trace Metals:

Inductively coupled plasma optical emission spectrometry (ICP-OES) was used for measuring the concentration levels of trace and ultra-trace elements in different samples. The suitability of technique relies on its multi-elemental capabilities, high selectivity, wide dynamic range, high sample through put, absence of chemical interferences, and easy coupling with different separation techniques (Mermet, 2005). Fe, Ni, Zn, Cr, Cu, Pb, Cd, Mn were analyzed in groundwater.

3.3.1. Sheikupura:

Concentrations of trace metals in Sheikupura were not so high. Only four metals were detected in Sheikhupura. Groundwater sample SGW-10 has significant concentration of cadmium along with high contents of nitrates and chlorides. Sample SGW-10 was collected from hand pump located in agricultural land, where, drain waste water irrigation is being practiced. Whereas,SGW-11 and SGW-13 showed relatively high Zn concentrations as compared to other trace metals but they still lied within the permissible limits.SGW-4showed trace quantities of metals and it was also collected from hand pump located in residential areas alongside the main waste water drain. SGW-7, SGW-8, SGW-14 and SGW-15 also exhibited minute quantities of trace metals but these concentrations were within the palatable limits. High concentration of metals, chlorides, nitrates depicted that groundwater is being contaminated by wastewater through seepage or infiltration process. It is worth mentioning that TDS and EC values were also much higher, advocating the recharge from wastewater source. However, SGW-1, SGW-3 SGW-5 and SGW-6 do not have high concentration of metals, although these samples were also collected from industrial zone but the depth of these groundwater samples were 400 and 300 feet respectively. It suggests that, deep aquifers in this area, in contrast to shallow aquifer, are still not affected by waste water drain. It shows that soil in this area has buffering capacity to adsorb the metal contents. Zn concentrations were found prominent as compared to other trace metals but theystillfound within the permissible limits set by WHO and U.S EPA. These samples were collected from shallow water.

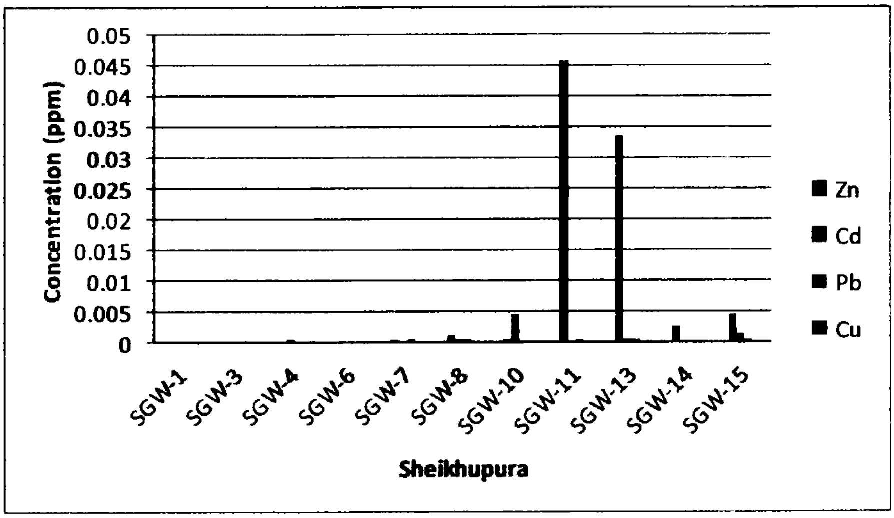


Figure 3.3.1: Trace metals in Sheikhupura Groundwater

3.3.2 Lahore:

Trace metals concentration in Lahore groundwater samples were not significant as compared to other cities of the Punjab. LGW-4, LGW-5, LGW-6 showed no trace metals concentrations. Concentrations of Cd and Pb were observed in LGW-7 however, theseconcentrations were within the permissible limits. LGW-7 point was located in residential area alongside the drain with shallow aquifers. LGW-8 also showed relatively higher concentrations as compared to other samples but these concentrations were within the permissible limits.LGW-8 was located in agricultural area with shallow aquifer and is being irrigated by waste water. Metal contamination in groundwater samples with high concentration of chlorides and nitrates suggests that, waste water irrigation has affected the groundwater quality through seepage process. LGW-9 with shallow aquifer showed relatively higher metal concentrations and high contents of chlorides and nitrates. The quality of groundwater was so poor in this area that soon after pumping out water from hand pump it turned yellow. This highly contaminated groundwater was being used for drinking purpose by local community Zinc was found in two, Cadmium and Lead were found in three samples while, Copper was found only in one sample. Concentrations of these samples were within the permissible limits set by WHO and U.S EPA. LGW-7 was collected relatively from depth while LGW-8 and LGW-9 were collected from shallow water.

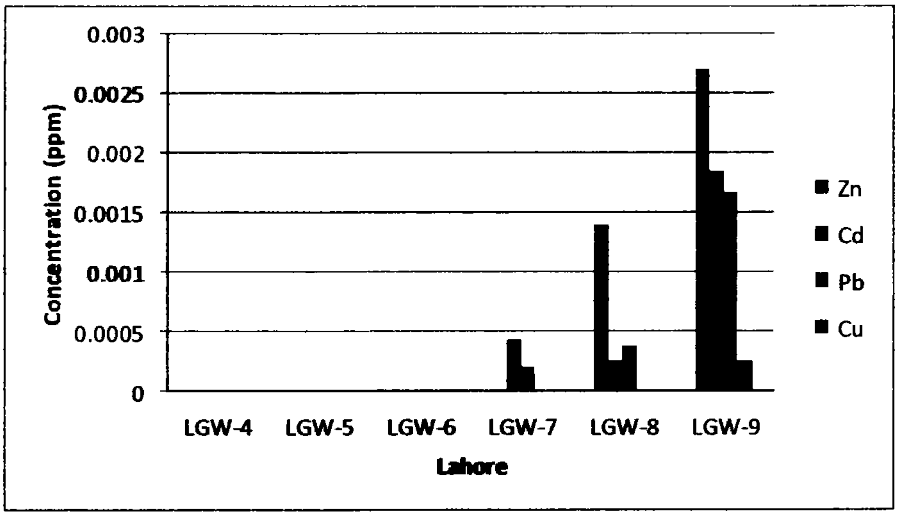


Figure 3.3.2: Trace metals in Lahore Groundwater

3.3.3. Raiwind:

In Raiwind, highest concentration of Zn 0.0013mg/l was found in RGW-5 and remained within the permissible limits. Highest concentration of Cadmium was found in RGW-6 and it also didn't exceed palatable limits. Lead's highest concentration was found in RGW-8 and Copper's highestconcentrationwas found in RGW-7. All the samples were collected from shallow aquifers.Trace concentration of metal in shallow aquifers and no metals in deep aquifers suggest that ground water in this areas is recharged by nearby wastewater drain that affects up to limited depth to shallow aquifer and rarely have any significant impact on deep aquifer due to buffering phenomenon of soil that naturally have potential to adsorb the metals and other contaminants. Shallow water aquifer samples also have comparatively high concentration of nitrates and chlorides. That is also due to the impact of nearby wastewater drain. It is observed that, groundwater quality of the waste water irrigated areas was much poor than residential areas with almost same depth. Overall sampleswerewithin the permissible limits set by WHO and U.S EPA.

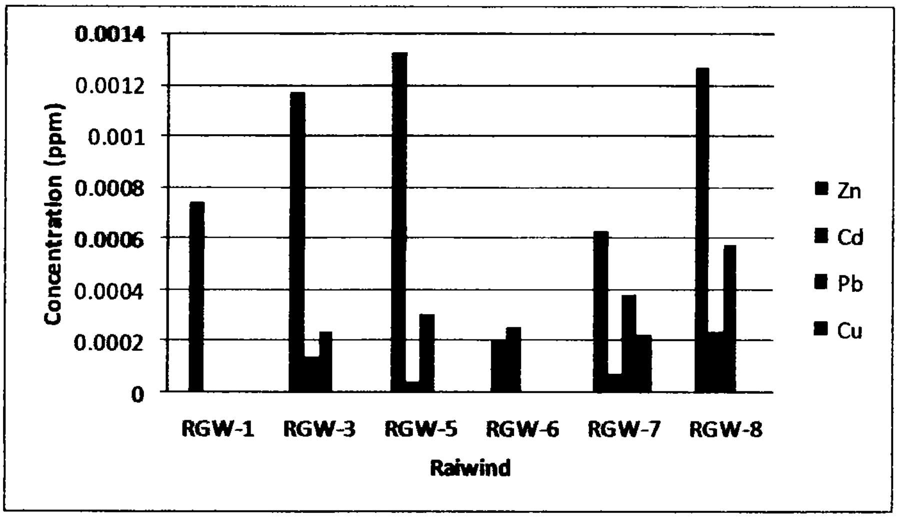


Figure 3.3.3: Trace metals in Raiwind Groundwater

3.3.4. Mangamandi:

Metals analysis of Mangamandi showed two samples contained trace quantities of metals MGW-2, MGW-5. These points were located in industrial area and have a shallow aquifer. Nonetheless, other samples collected from Mangamandi suburbs and have not shown metals concentration. No trace metals were found in sampling point MGW-6 adjacent to MGW-5 which has relatively high trace metals concentration. It shows that drain has least effect on sampling point MGW-6 however, adversely affected MGW-5. This might be due to the difference in the depth of the groundwater table and buffering capacity of soil. There is high possibility one sampling point soil has reaching to its saturation point. Chlorides and nitrates concentrations in Mangamandi were significantly high. High concentrations of chlorides and nitrates might be attributed to geology of the soil. This statement is further strengthened by the presence of high EC and TDS values. Zinc concentrations were found in two samples. These concentrations were found within the palatable limits set by WHO and U.S EPA. These samples were collected relatively from deep water.

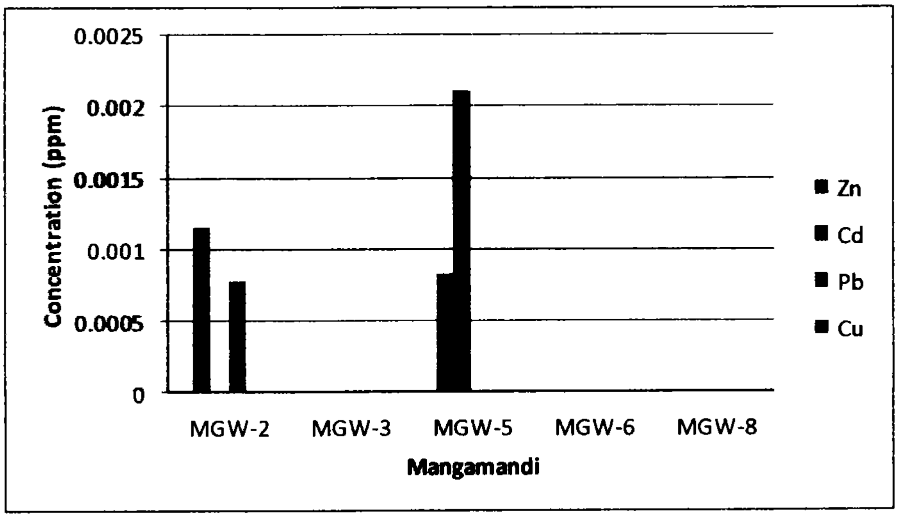


Figure 3.3.4:Trace metals in Mangamandi Groundwater

3.3.5. Kasur:

Trace metals concentrations were observed in KGW-1, KGW-6, KGW-8 and KGW-10 samples. Cd and Zn concentrations were observed in KGW-1, KGW-6 and KGW-8samples. KGW-1, KGW-6 and KGW-8 were collected from industrial area whereas; KGW-10 sampling point was located in the vicinity of industrial area. KGW-10 contains concentration of Zn, Pb and Cd. This point is a little far away from industries and sample was collected from 100 ft. depth. Presence of trace metals in groundwater suggested that aquifer of this area has been contaminated by industrial discharges. No significant concentration of nitrates in groundwater samples was found. This suggests that water table in this area is not being contaminated by fresh industrial discharges. Presence of metals might be due the previous mixing of industrial effluents which is now being reduced by the dilution factors. This might be due to the better planning for industrial effluents treatment by installing and running of treatment plants in recent past few years. These samples were collected relatively from deep water and containing the concentrations above the palatable limits set by WHO and U.S EPA.

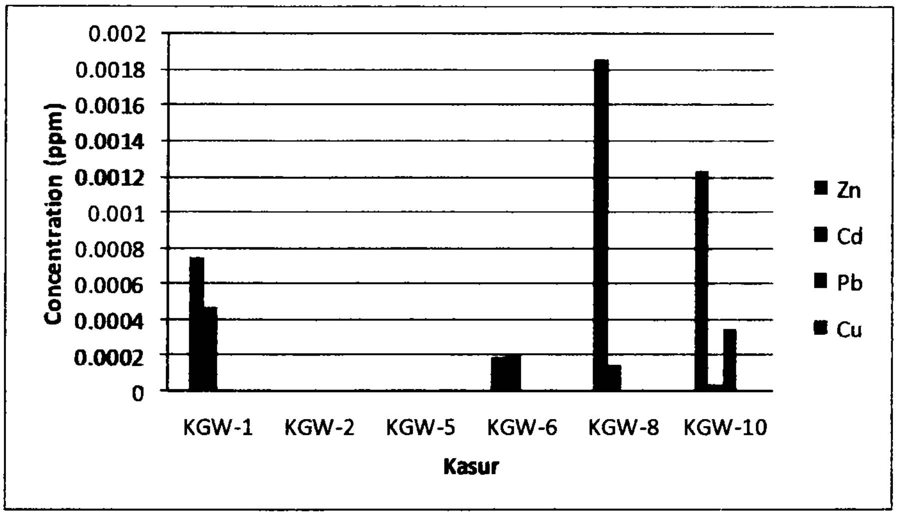


Figure 3.3.5: Trace Metals in Kasur Groundwater

3.3.6. Gujranwala:

Trace metals concentration in groundwater of Gujranwala varies from sample to sample. Samples were collected from industrial area despite being industrial area trace metals were not found high in it. However, samples collected from agriculture areas showed relatively higherconcentration of trace metals. Samples GGW-2, GGW-3, GGW-5, GGW-10 and GGW-11 have concentration of trace metals and these samples were taken from hand pumps located in agricultural areas, where the waste water irrigation is normal practice. This data show that waste water irrigation has prominent adverse impact on the groundwater in this area. Soil is porous containing higher clay content makes it more vulnerable to wastewater seepage and contaminating the groundwater consequently.Soil acts as filter, buffer and degradation capacity with respect to adsorption of pollutant with the help of soil organic carbon (Burauel and Bassmann, 2005). Chlorides and nitrates in this area are reasonably high. Zinc was found within the permissible limits, Lead was found in three samples GGW-3, GGW-5, GGW-10and these samples were collected from shallow water. All the trace metals were found within the palatable limits set by WHO and U.S EPA.

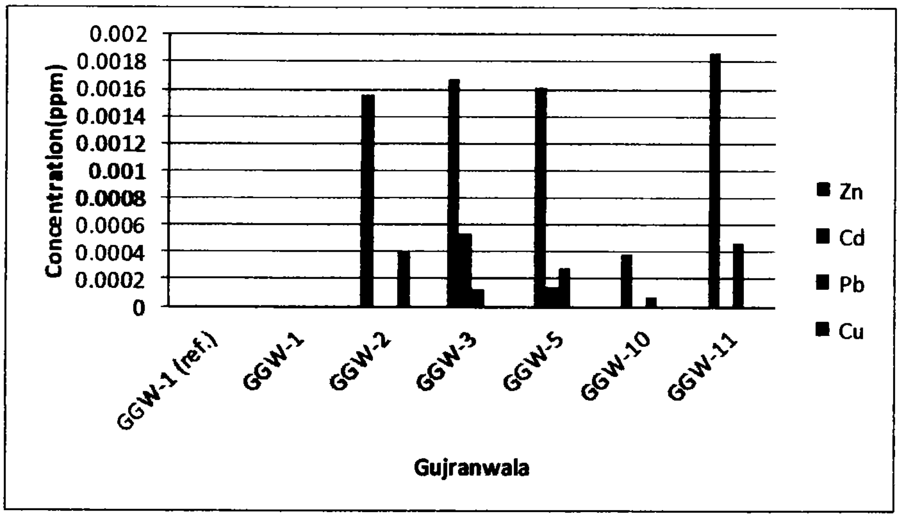


Figure 3.3.6: Trace Metals in Gujranwala Groundwater

3.3.7. Faisalabad:

Concentrations of trace metals were found in Faisalabad but varied from point to point. Higher metal concentrations were found in FGW-2Cu,Pb and Zn,FGW-5 andFGW-7showedCu,Pb, Cd and Zn, and FGW- 8 Zn and Cd. The sampling point FGW-5, FGW-7 andFGW-8 were located in residential areas near the waste water drain with shallow aquifer. Presence of zinc lead cadmium and copper was clearly indicating the mixing of waste water with groundwater. FGW-2 sample was collected from the depth of 250 feet but still showing the high concentration of metals. This point was located at the junction of waste water drain and freshwater canal. At this point, industrial waste water drain was falling in canal. It suggests that, waste water is seeping down into ground water and soil has reached to its saturation point and its buffering capacity might be reduced. Eventually, it has contaminated the deep water. Chlorides and nitrates concentration were also higher in this area. Zinc, Cd, Pb and Copper concentrations were found within the permissible limits set by WHO and U.S EPA. These samples were located in shallow water except FGW-2 was collected from deep water.

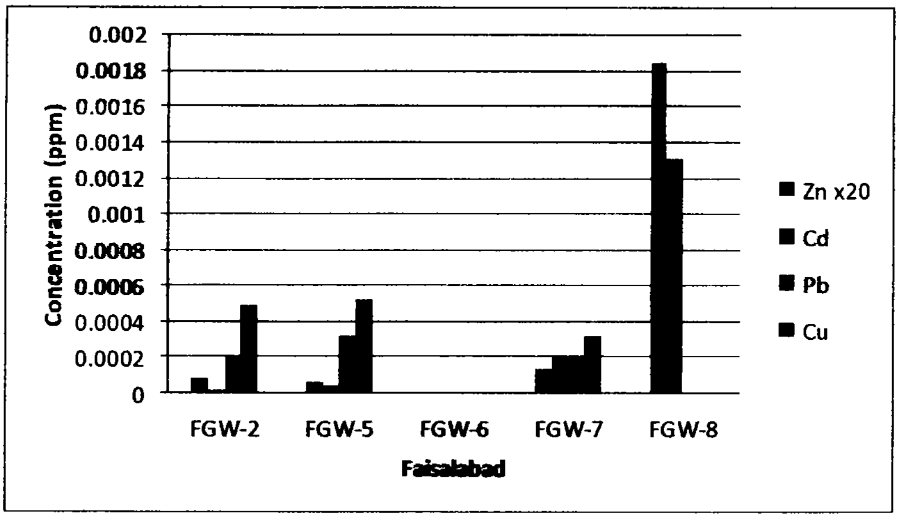


Figure 3.3.7: Trace Metals in Faisalabad Groundwater

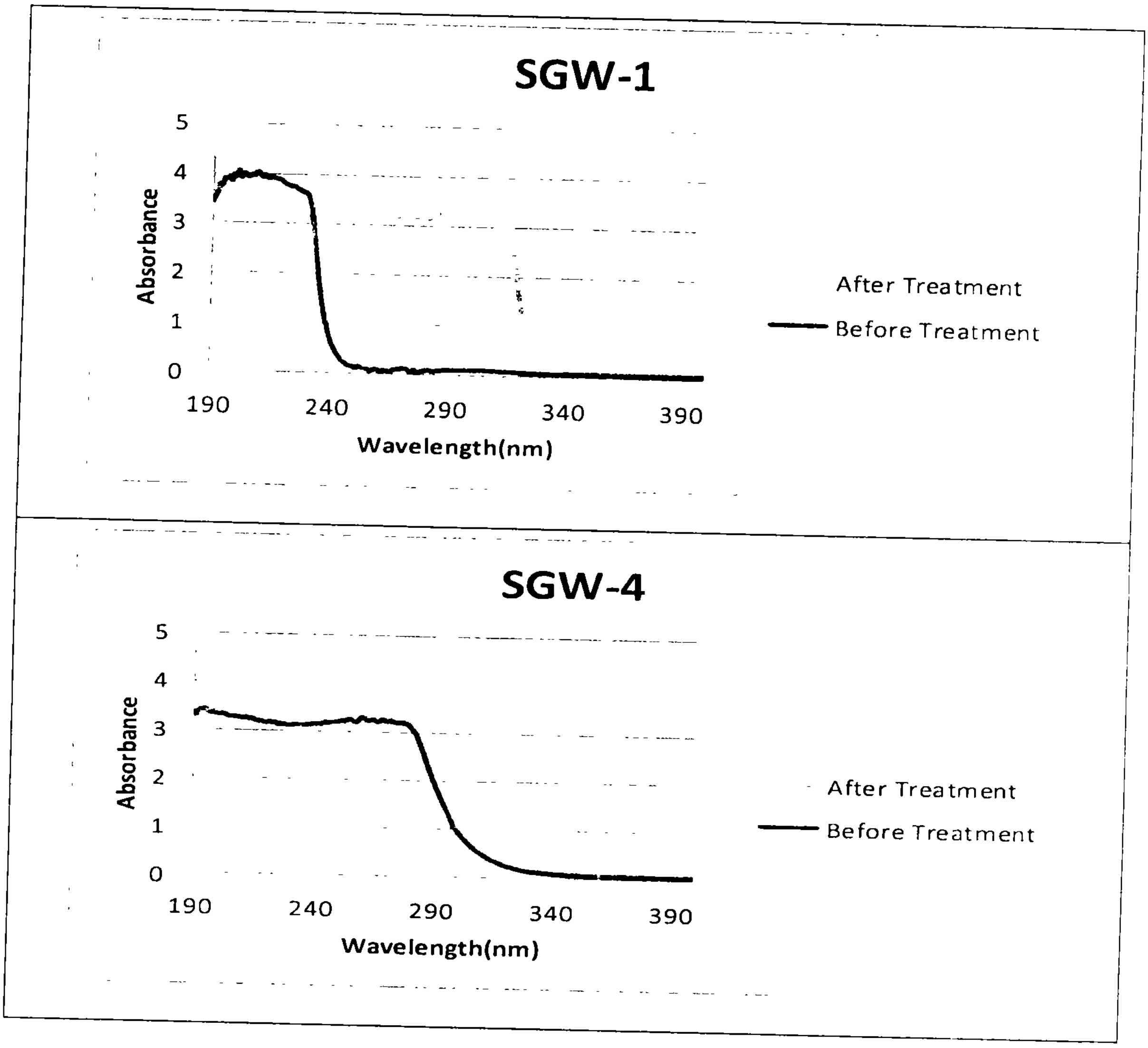
3.4. Comparison Before and After Treatment:

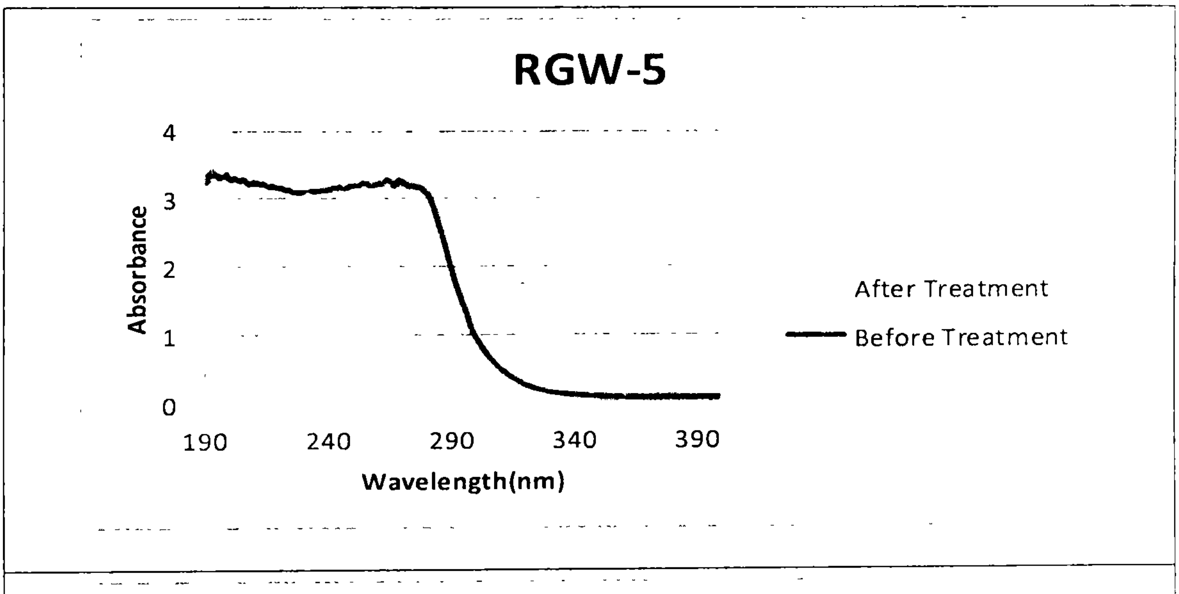
UV/Visible scanning of samples was carried out to check the efficiency of solid phase extraction. Following graphs are showing the comparison between before and after treatment of samples. Comparison shows that sample has concentrated and prominent peaks show the presence of compounds in sample.

3.4.1. Sheikupura:

Sheikhupura samples were UV scanned to monitor the peak trend of contaminants present in the ground water samples. Absorbance and wavelength showed the presence of contaminants. Contaminants fall in the region of UV spectrum.After the treatment of samples, they were again scanned on UV to check the efficiency of Sold Phase Extraction. After treatment scanning peaks were more visible and showed different trend as compared to before treatment. Concentration of contaminants has increased many times and showed more absorbance. Thus Solid Phase Extraction technique has increased the concentration of pollutants many times and can detect in any instrument to calculate their accurate concentration.

Table3.4.1: Comparison of before and after treatment of Sheikhupura Groundwater




RGW-5
Absorbance
4
3
2
1
0
190
240
290
340
390
Wavelength(nm)
After Treatment
Before Treatment

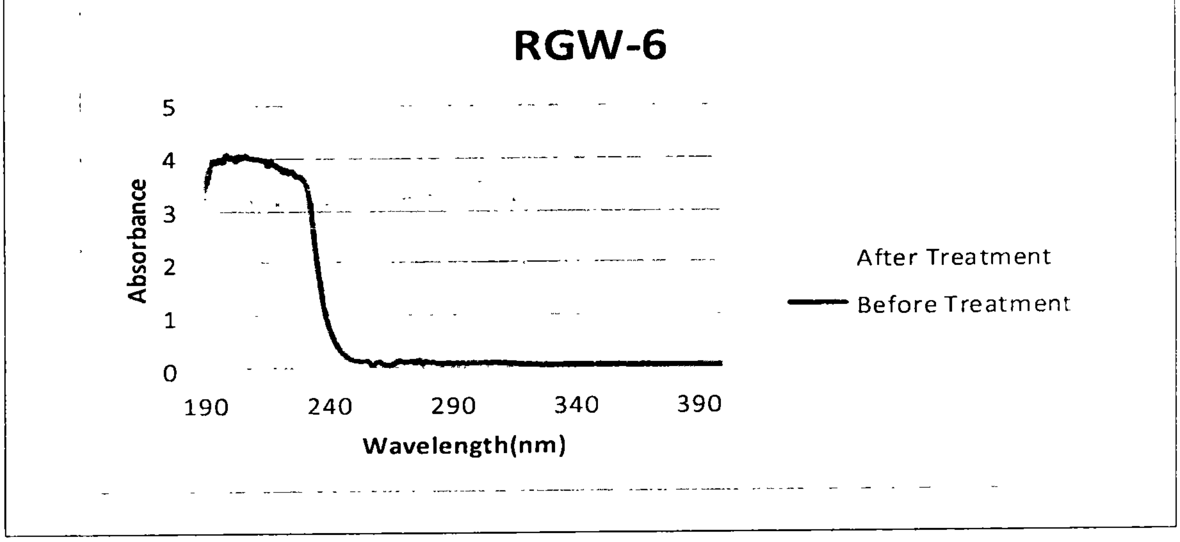
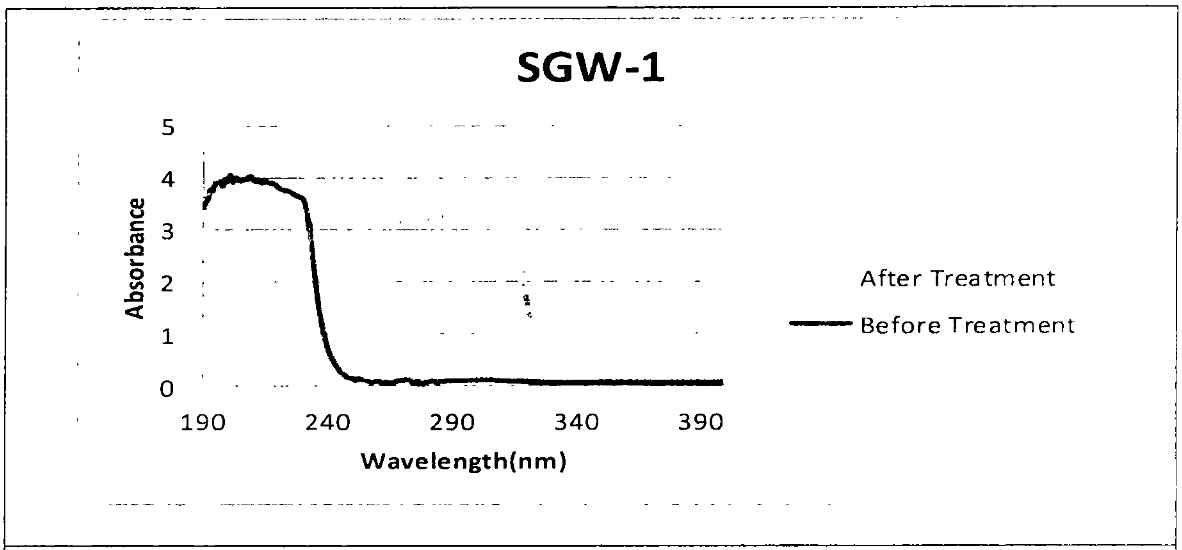
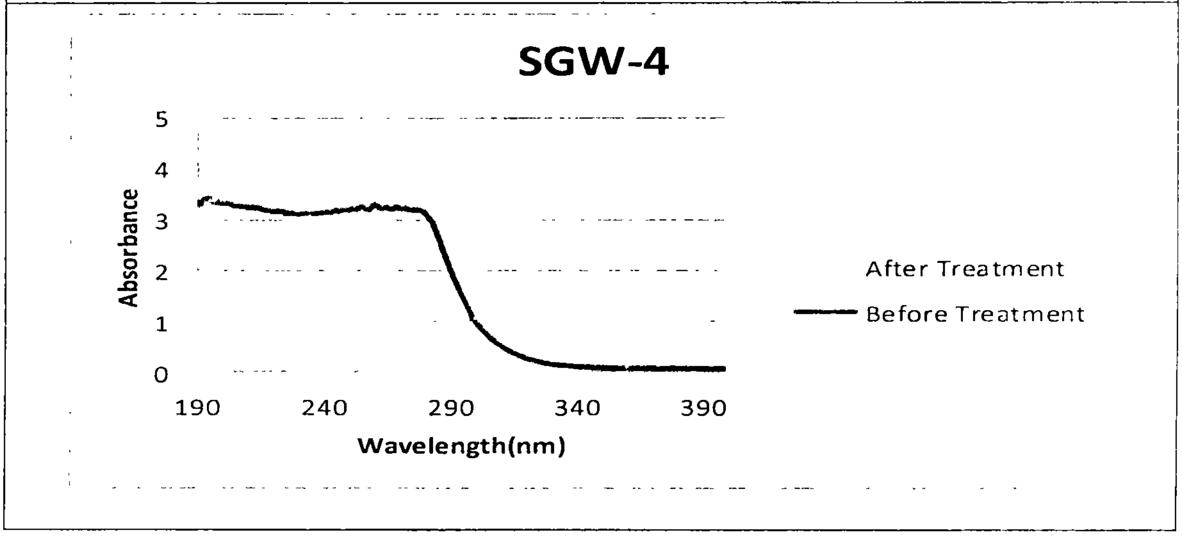
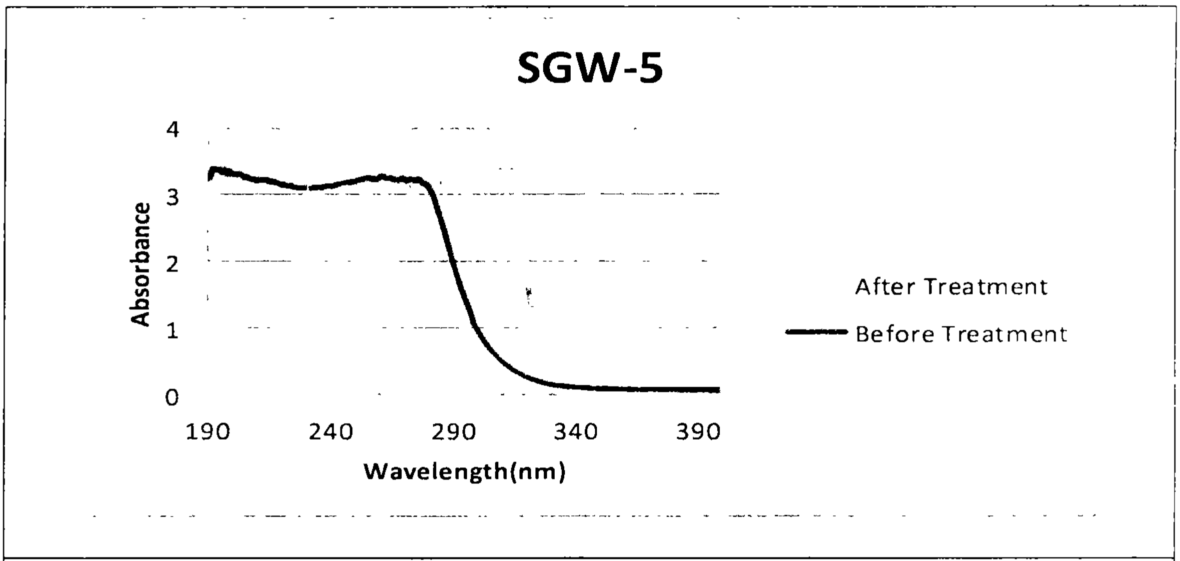
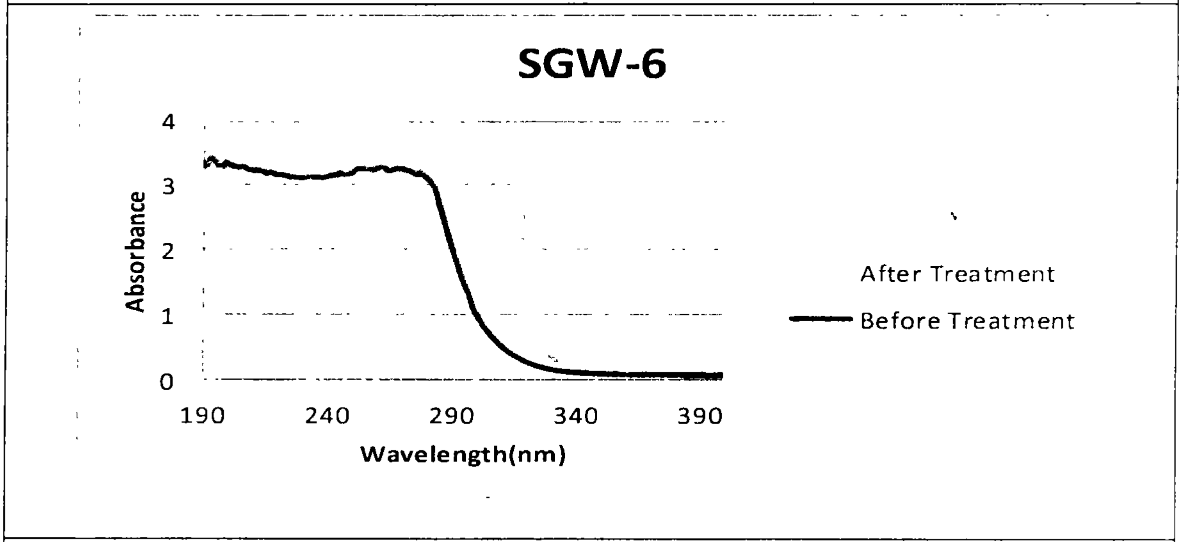

RGW-6
Absorbance
5
4
3
2
1
0
190
240
290
340
390
Wavelength(nm)
After Treatment
Before Treatment

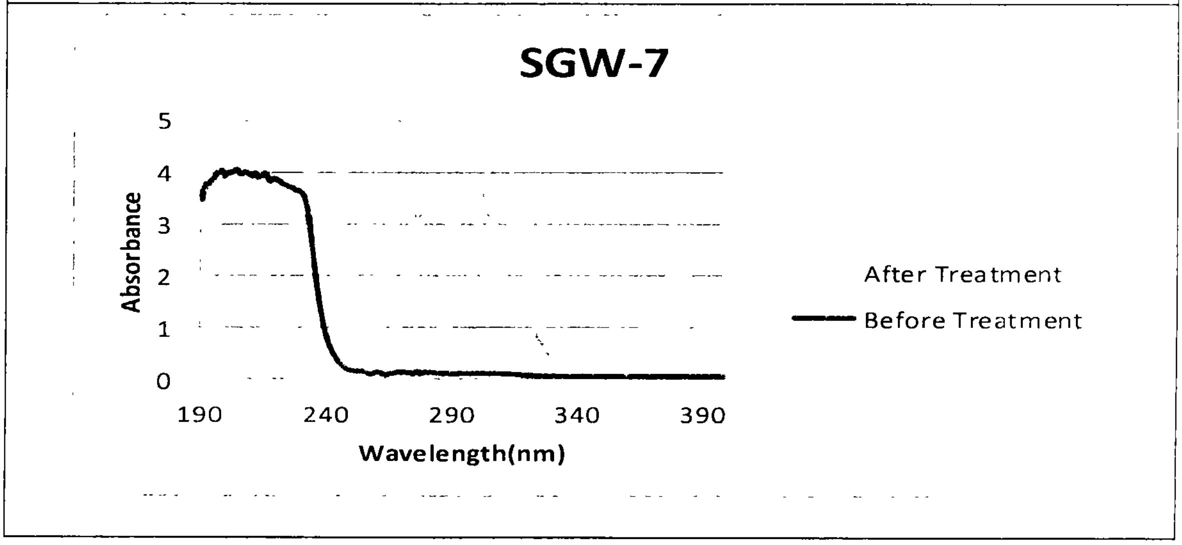
Table3.4.1: Comparison of before and after treatment of Sheikhupura Groundwater

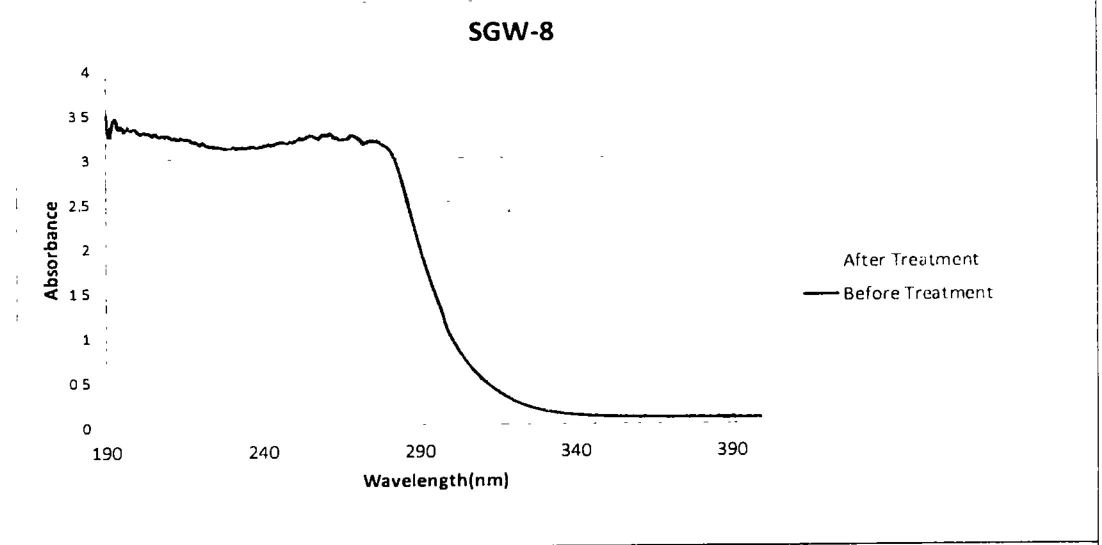


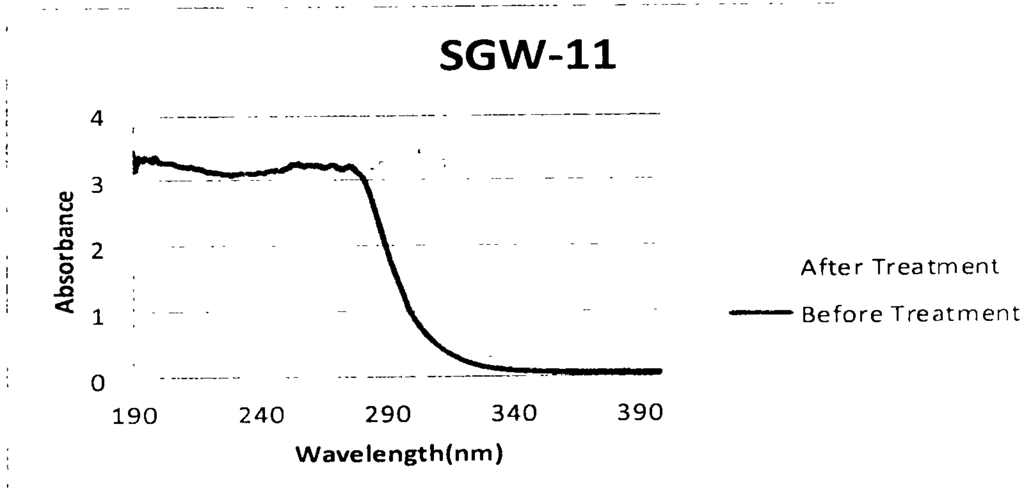


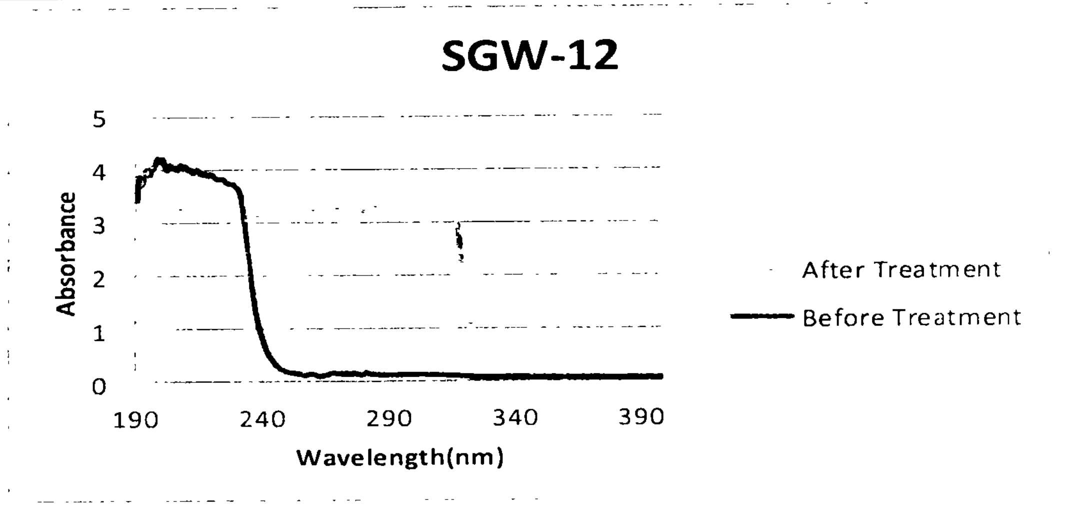

SGW-5
4
3
2
1
0
Absorbance
190
240
290
340
390
Wavelength(nm)
After Treatment
Before Treatment

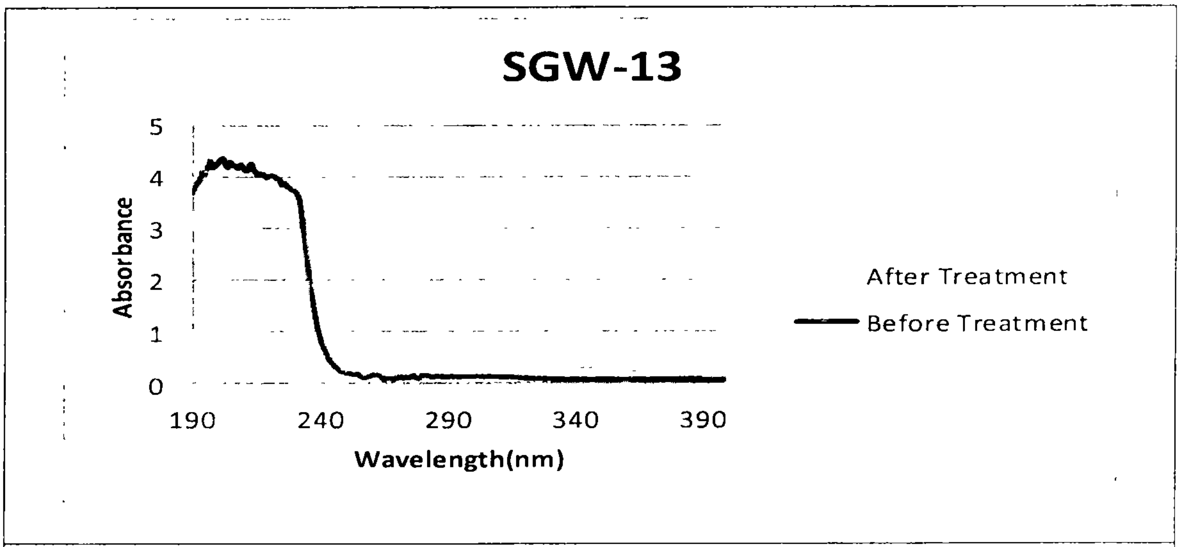

SGW-6
4
3
2
1
0
Absorbance
190
240
290
340
390
Wavelength(nm)
After Treatment
Before Treatment

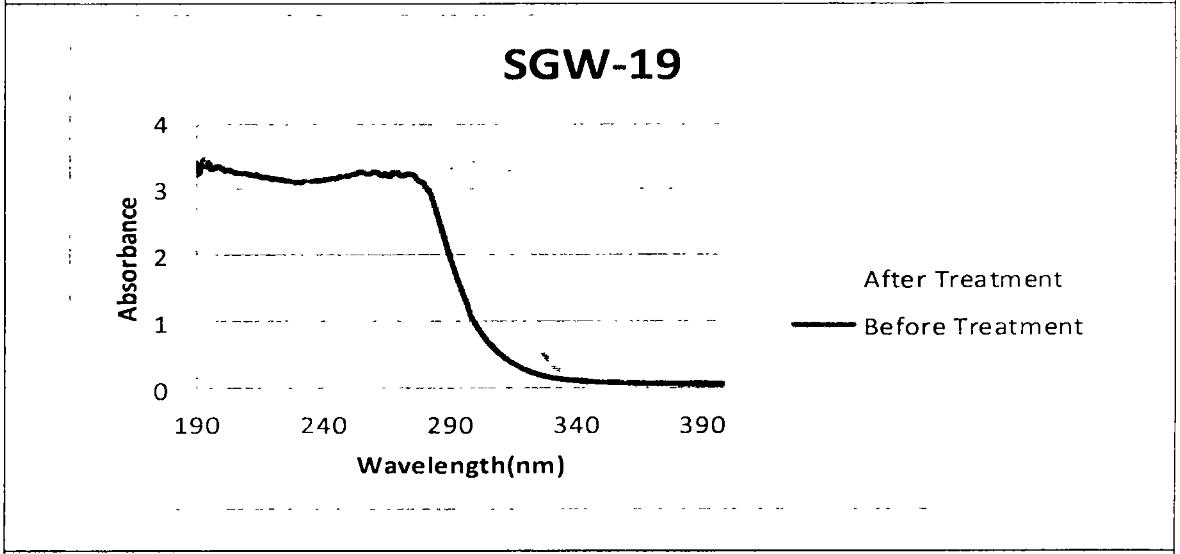

SGW-7
5
4
3
2
1
0
Absorbance
190
240
290
340
390
Wavelength(nm)
After Treatment
Before Treatment

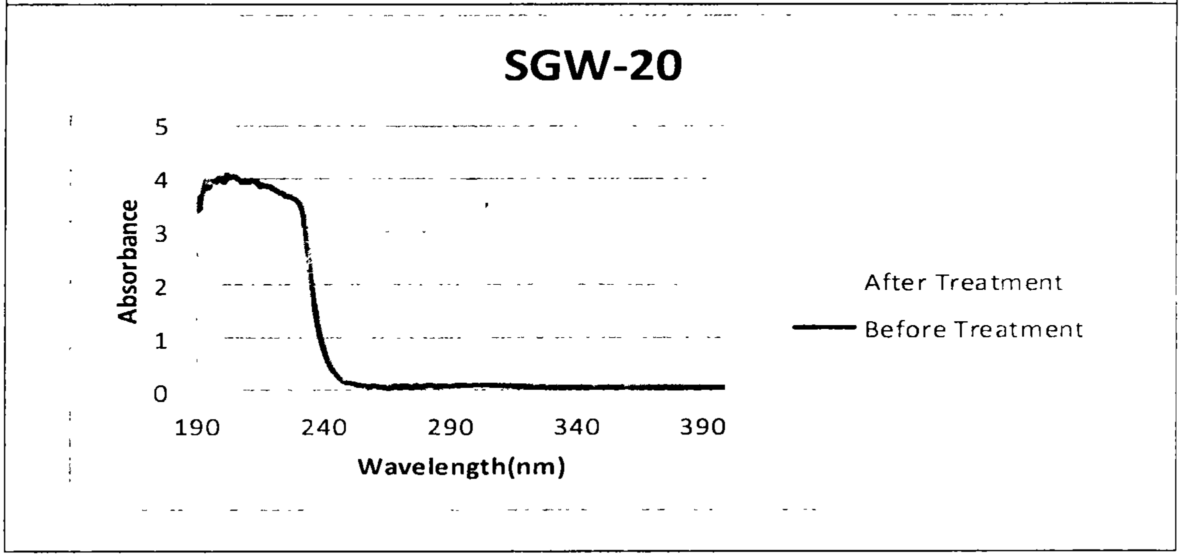

SGW-8
Absorbance
4
3.5
3
2.5
2
1.5
1
0.5
0
190
240
290
340
390
Wavelength(nm)
After Treatment
Before Treatment


SGW-11
Absorbance
4
3
2
1
0
190
240
290
340
390
Wavelength(nm)
After Treatment
Before Treatment


SGW-12
Absorbance
5
4
3
2
1
0
190
240
290
340
390
Wavelength(nm)
After Treatment
Before Treatment


SGW-13
Absorbance
5
4
3
2
1
0
190
240
290
340
390
Wavelength(nm)
After Treatment
Before Treatment

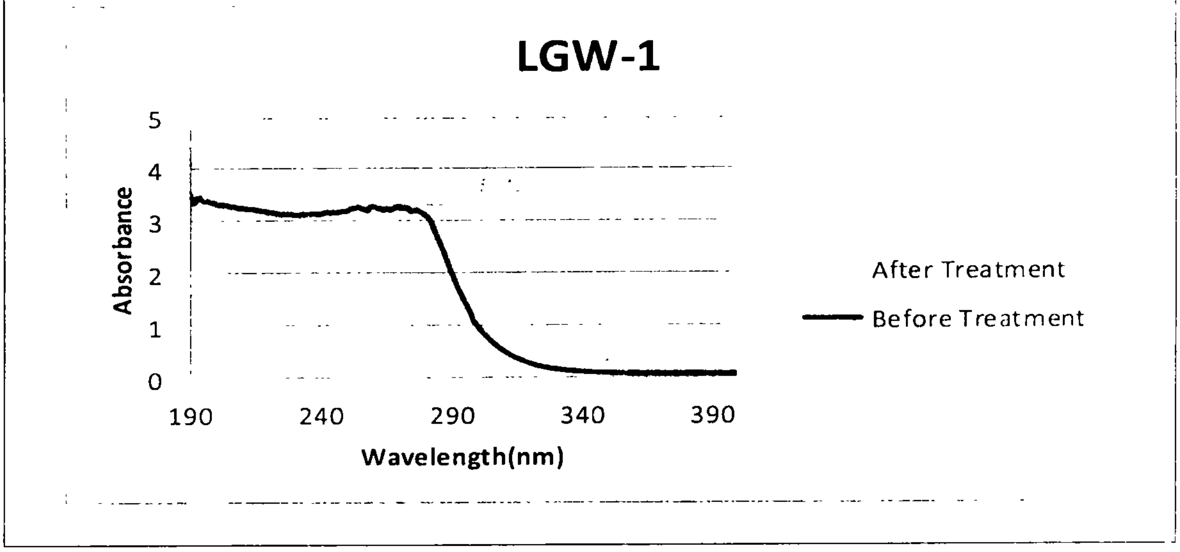

SGW-19
Absorbance
4
3
2
1
0
190
240
290
340
390
Wavelength(nm)
After Treatment
Before Treatment

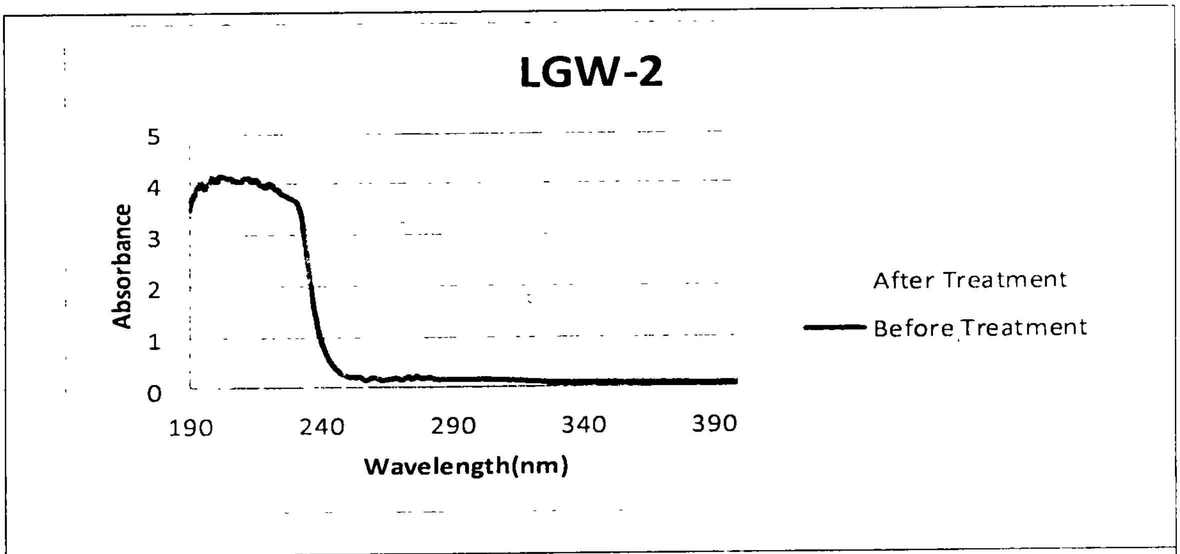

SGW-20
Absorbance
5
4
3
2
1
0
190
240
290
340
390
Wavelength(nm)
After Treatment
Before Treatment

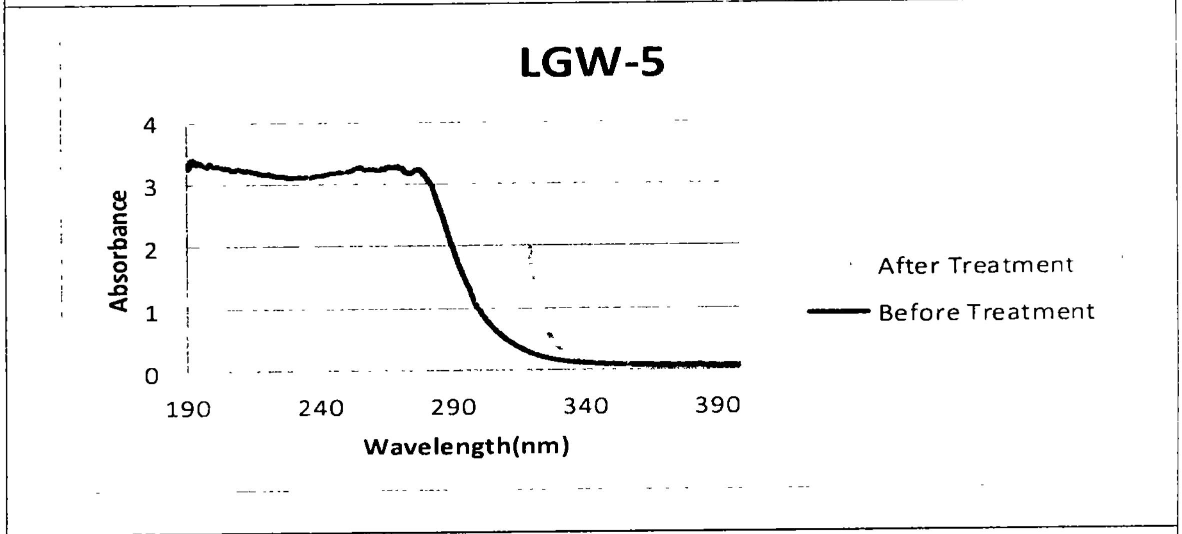
3.4.2. Lahore:

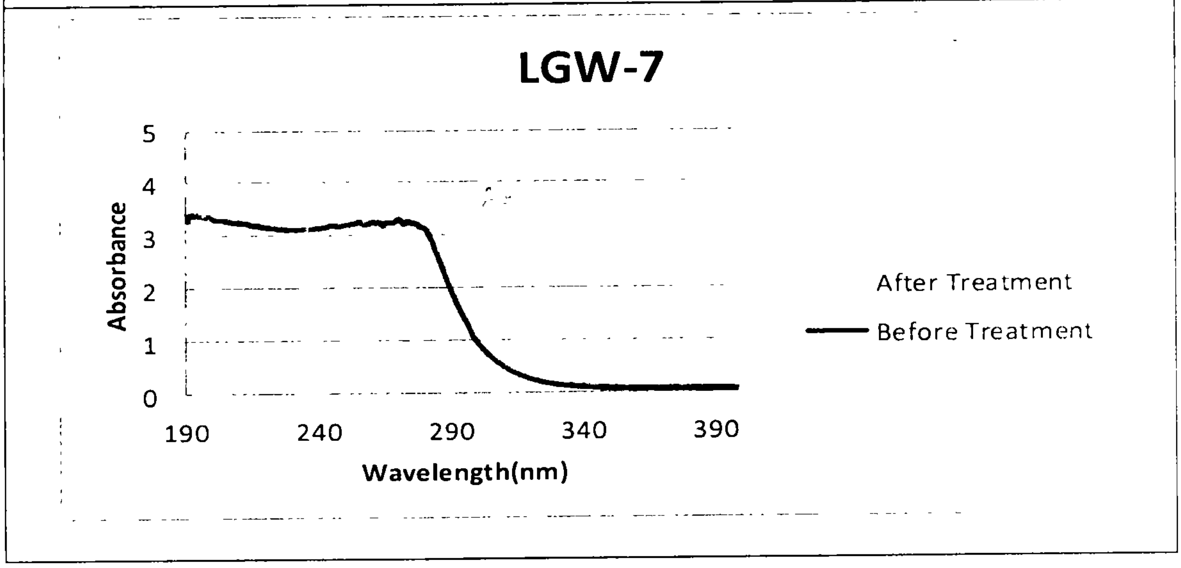
Lahore samples were scanned on UV spectrometer to check the efficiency of solid phase extraction. It is inferred that applied method for extraction and pre-concentration of organic pollutant is helpful for the concentration of organic compounds in the groundwater samples. The peaks in the graphs showed that a large portion of organic pollutants has been extracted in a concentrated form that were previously present in trace quantities whereas, the portion where the peaks are not as high as the before treatment chromatographs peaks represent that quite a lot of inorganic compounds such as nitrates, sulphates, iodides, halogens and some heavy metals released from the industrial waste water are now removed.

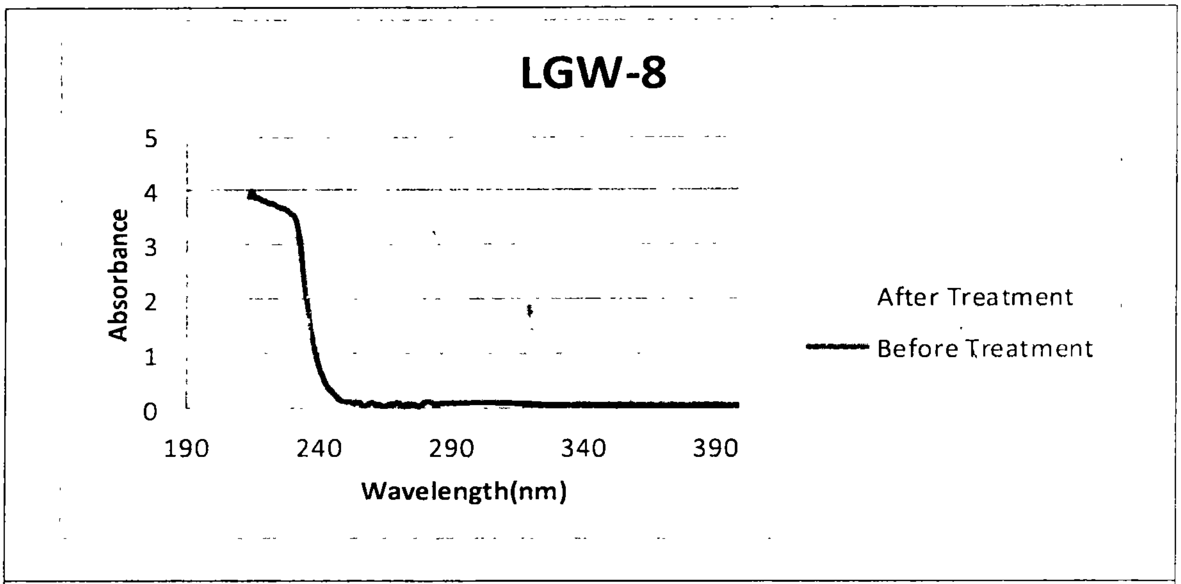
Table3.4.2: Comparison of before and after treatment of Lahore Groundwater

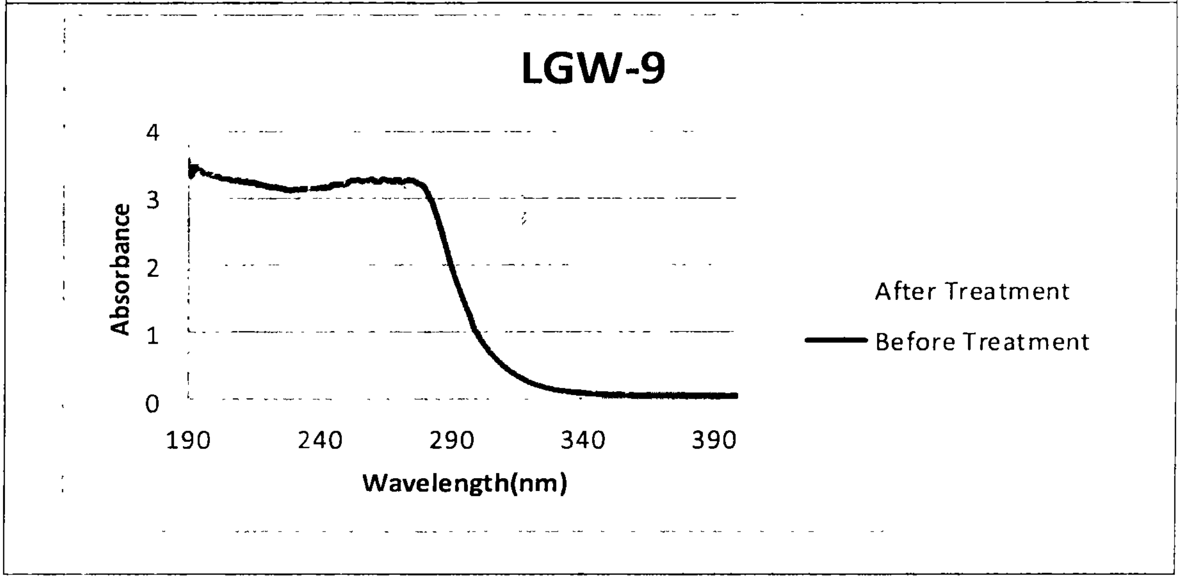



LGW-2
Absorbance
5
4
3
2
1
0
190
240
290
340
390
Wavelength(nm)
After Treatment
Before Treatment


LGW-5
Absorbance
4
3
2
1
0
190
240
290
340
390
Wavelength(nm)
After Treatment
Before Treatment


LGW-7
Absorbance
5
4
3
2
1
0
190
240
290
340
390
Wavelength(nm)
After Treatment
Before Treatment



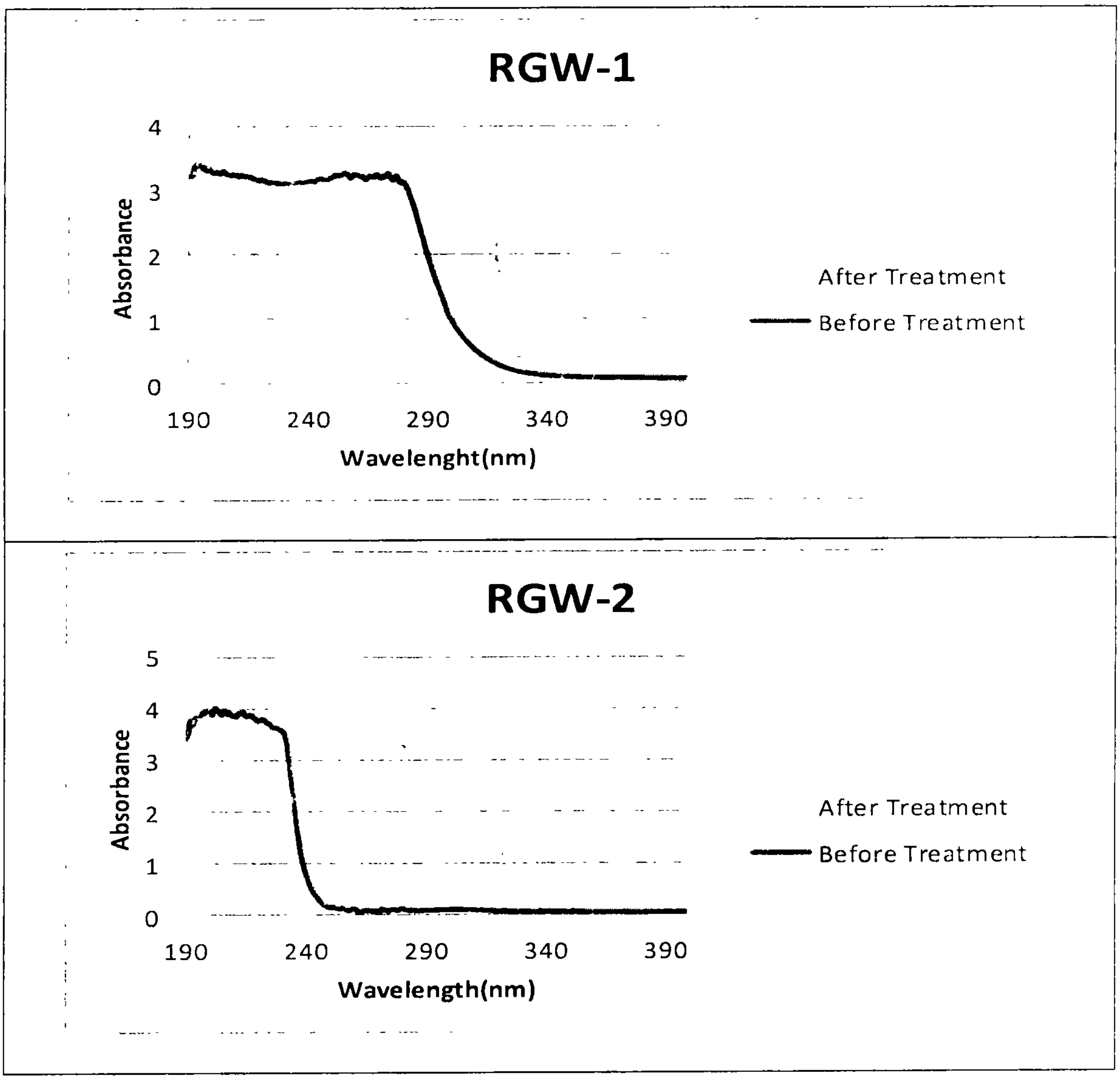


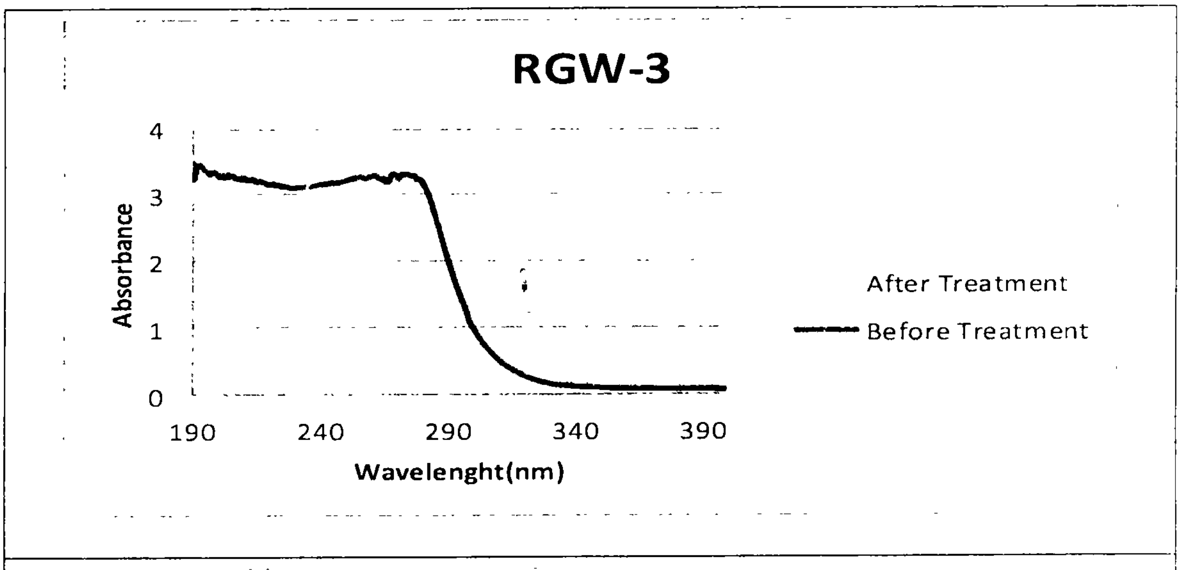
3.4.3. Raiwind:

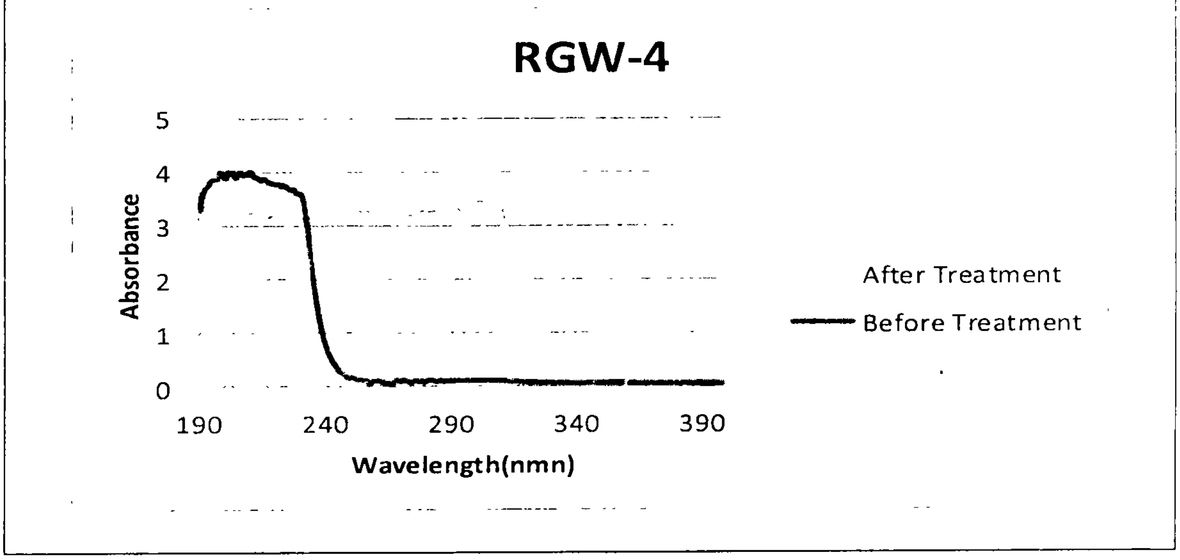
All the Raiwind samples were UV scanned to check the peak trend of contaminants present in the ground water samples. Absorbance and wavelength showed the presence of contaminants. Contaminants fell in the region of UV spectrum.After the treatment of samples, they were again scanned on UV to check the efficacy of Sold Phase Extraction. After treatment scanning peaks were more visible and exhibited dissimilar trend as compared to before treatment. Concentration of contaminants has increased many times and showed more absorbance.

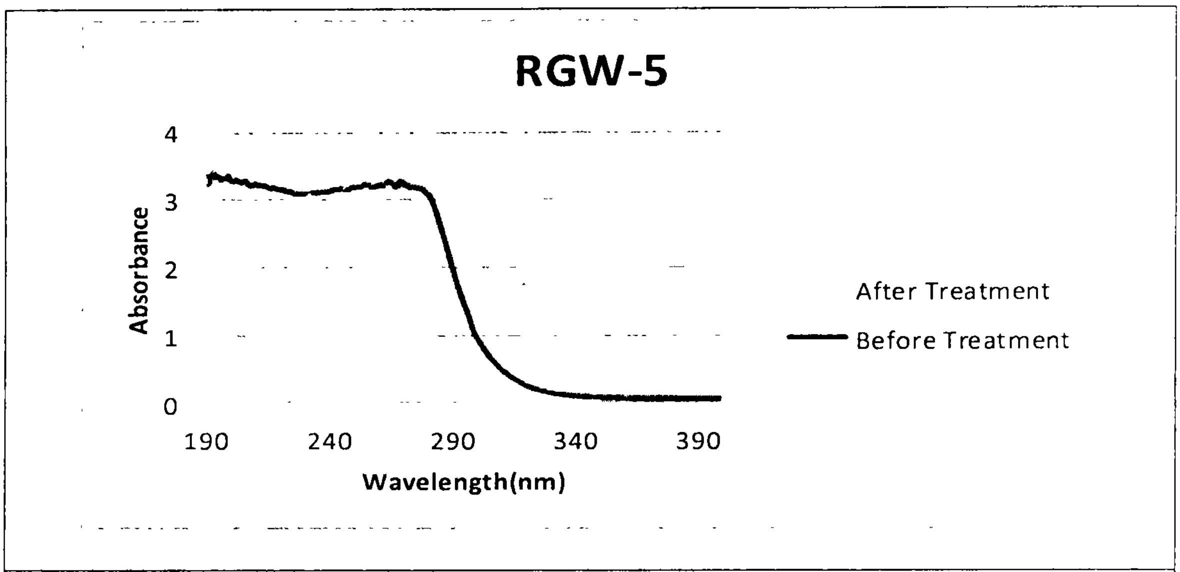
Hence, Solid Phase Extraction technique has increased the concentration of pollutants many times and can detect in any instrument to calculate their precise concentration.

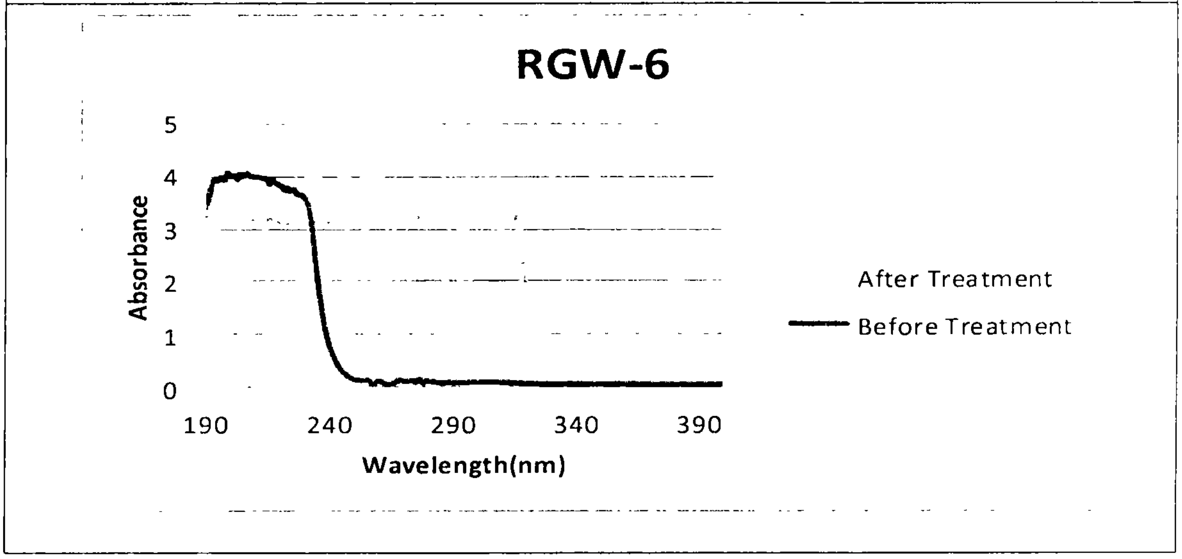
Table3.4.3: Comparison of before and after treatment of Raiwind Groundwater

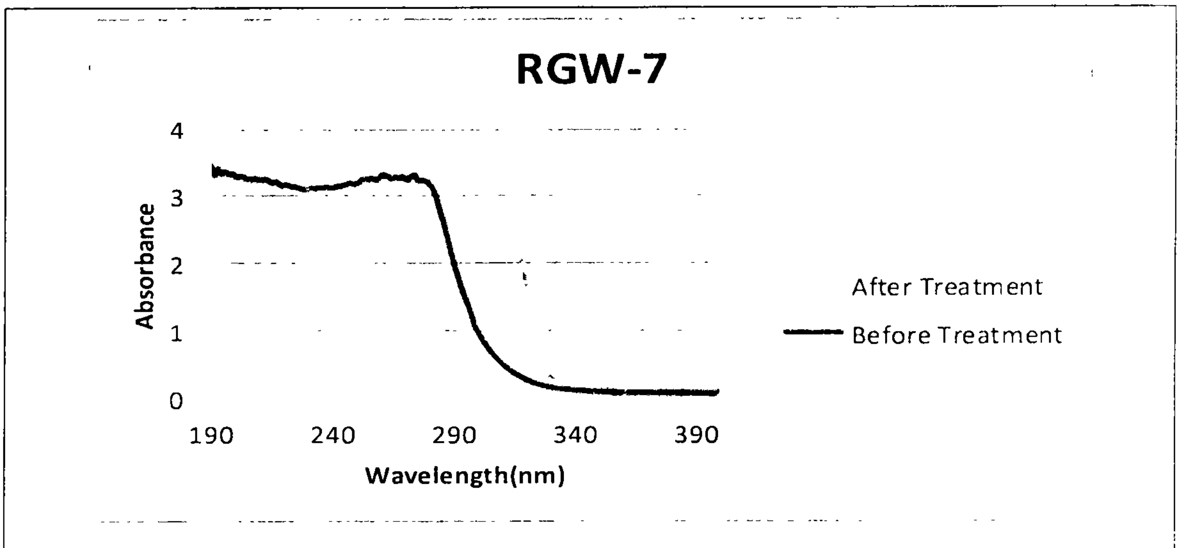


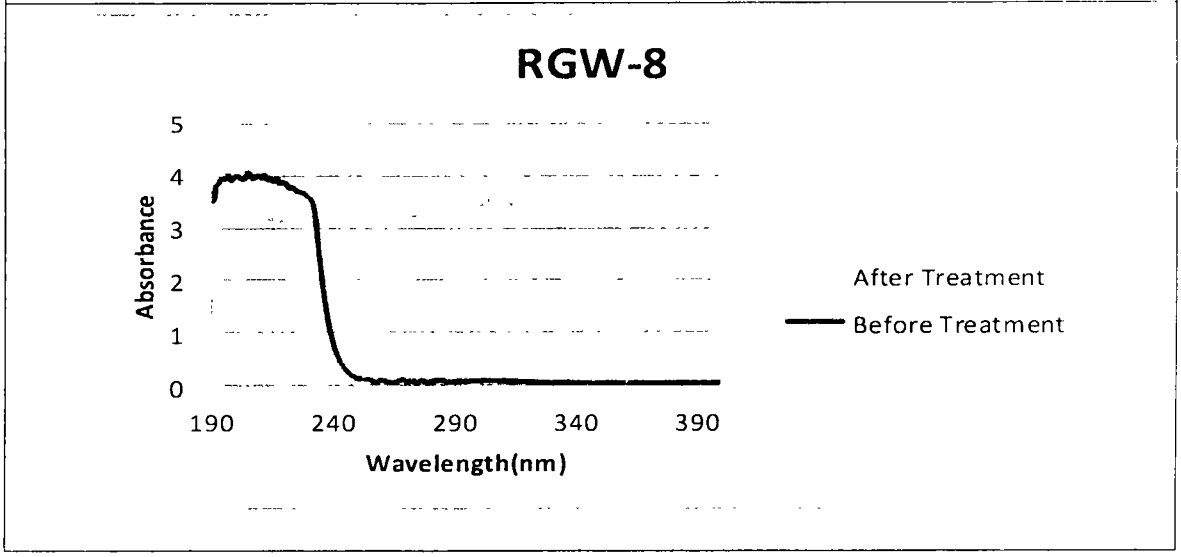

RGW-3
Absorbance
4
3
2
1
0
190
240
290
340
390
Wavelenght(nm)
After Treatment
Before Treatment


RGW-4
Absorbance
5
4
3
2
1
0
190
240
290
340
390
Wavelength(nmn)
After Treatment
Before Treatment


RGW-5
4
3
2
1
0
Absorbance
190
240
290
340
390
Wavelength(nm)
After Treatment
Before Treatment


RGW-6
5
4
3
2
1
0
Absorbance
190
240
290
340
390
Wavelength(nm)
After Treatment
Before Treatment

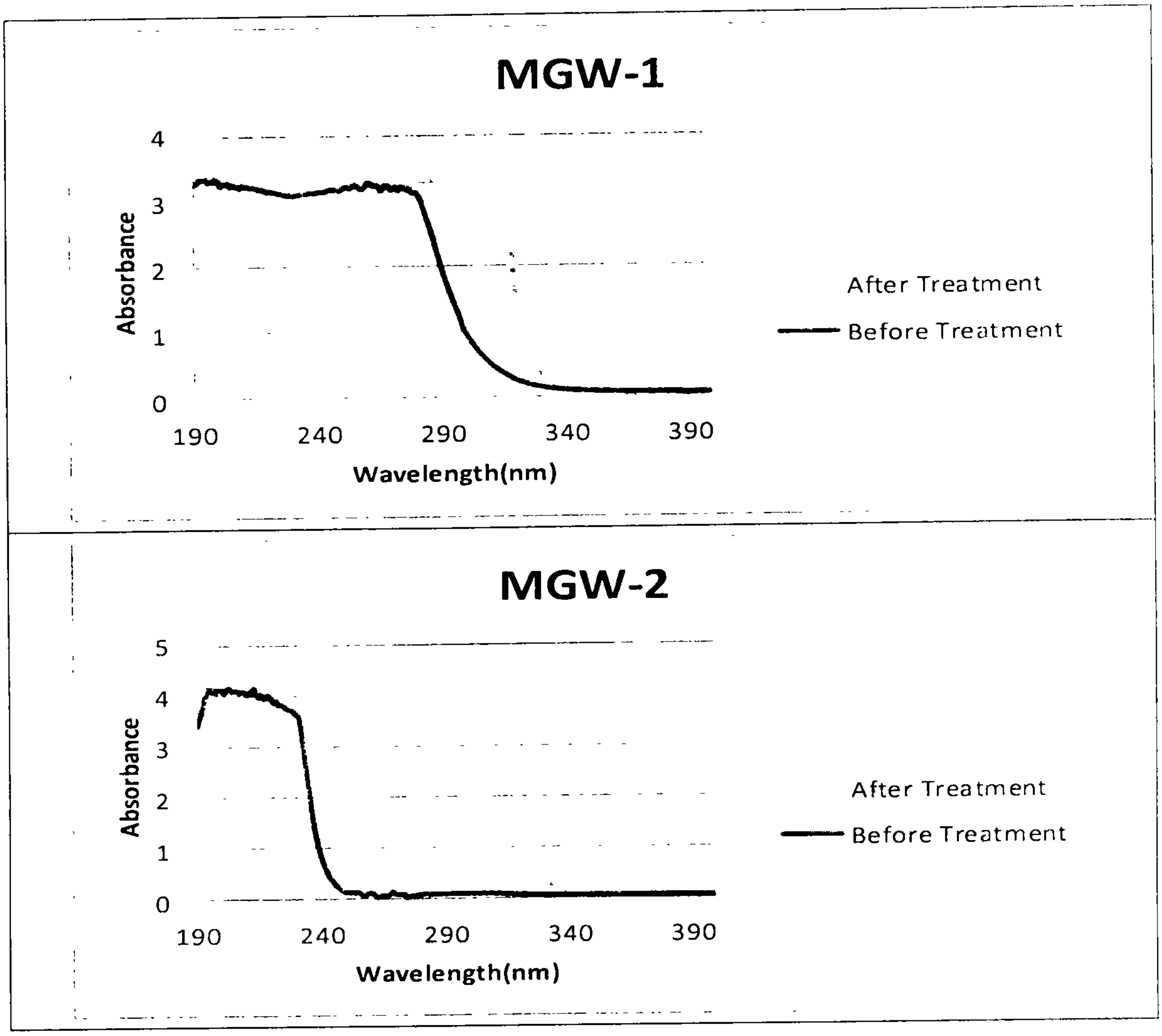


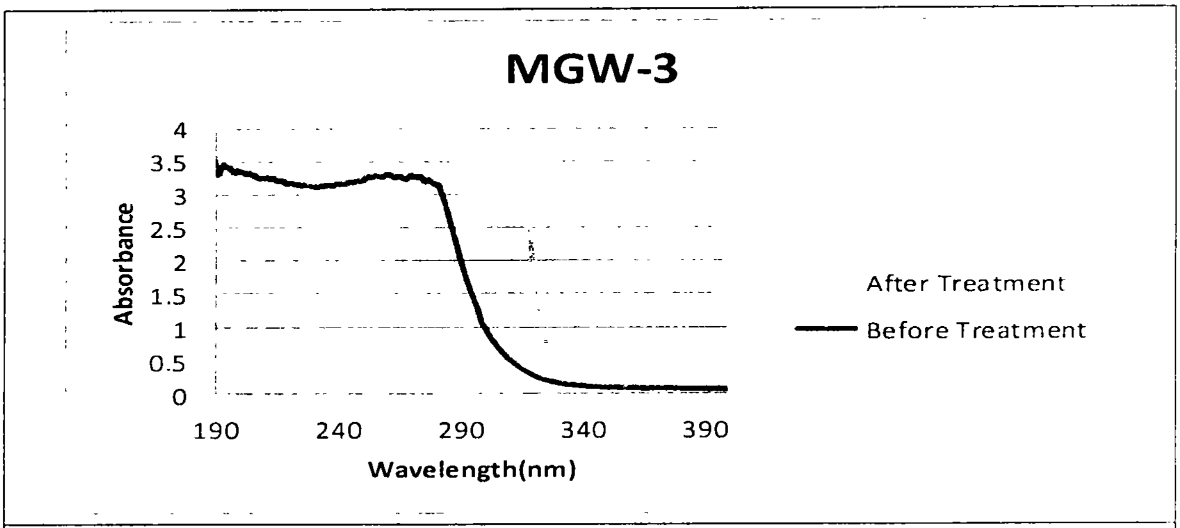


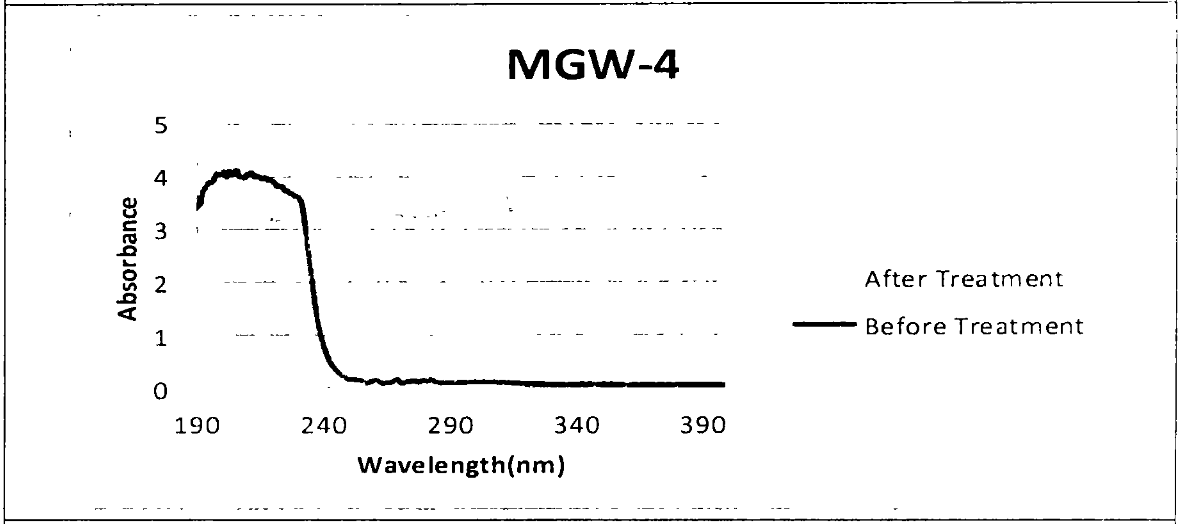
3.4.4. Mangamandi:

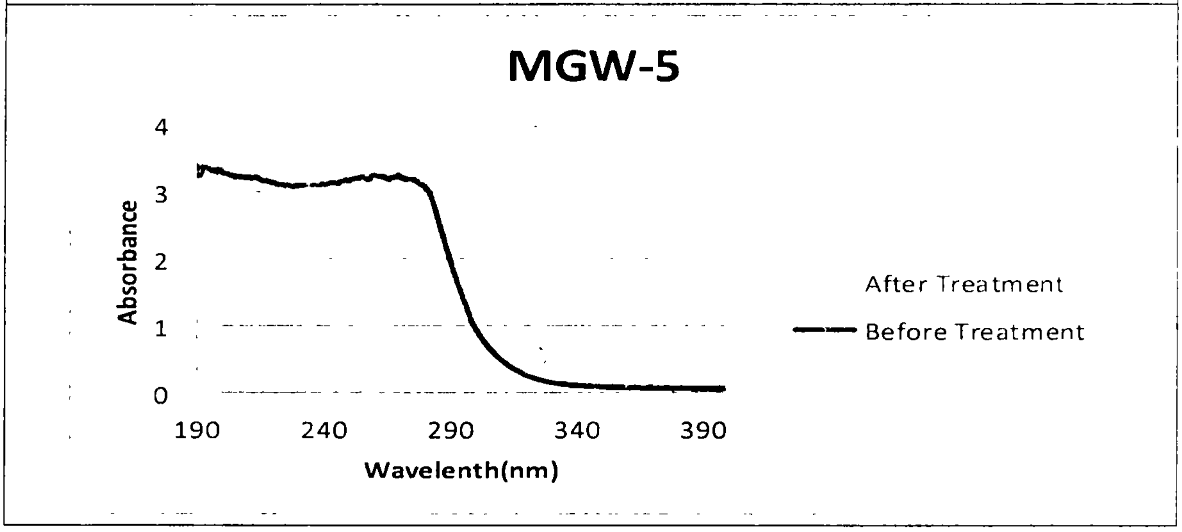
All the samples were scanned on UV spectrometer before and after treatment. Samples were run on Solid Phase Extraction Assembly for extraction and pre-concentration of organic pollutants. The graphs have showed tremendous difference in peaks before and after treatment. The organic extract obtained through elution was then scanned on UV spectrometer.The UV spectrometer graphs visibly suggested that applied method for extraction and pre-concentration of organic pollutant is effective. The concentration of organic pollutant and were increased many times as a result of extraction and pre-concentration method. The peaks are more visible and clear as compared to before treatment.

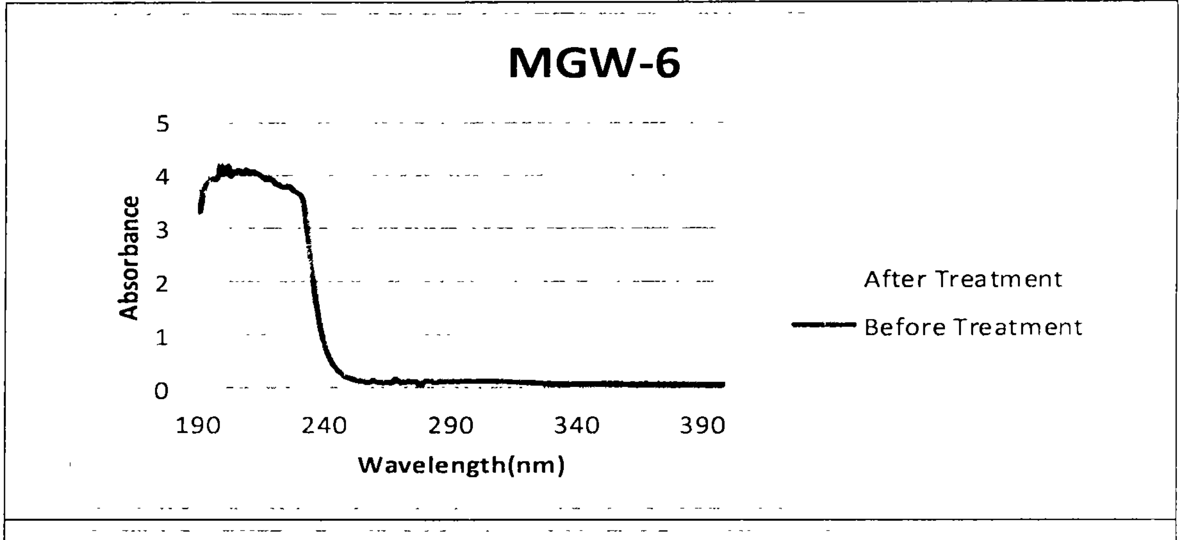
Table3.4.4: Comparison of before and after treatment of Mangamandi Groundwater

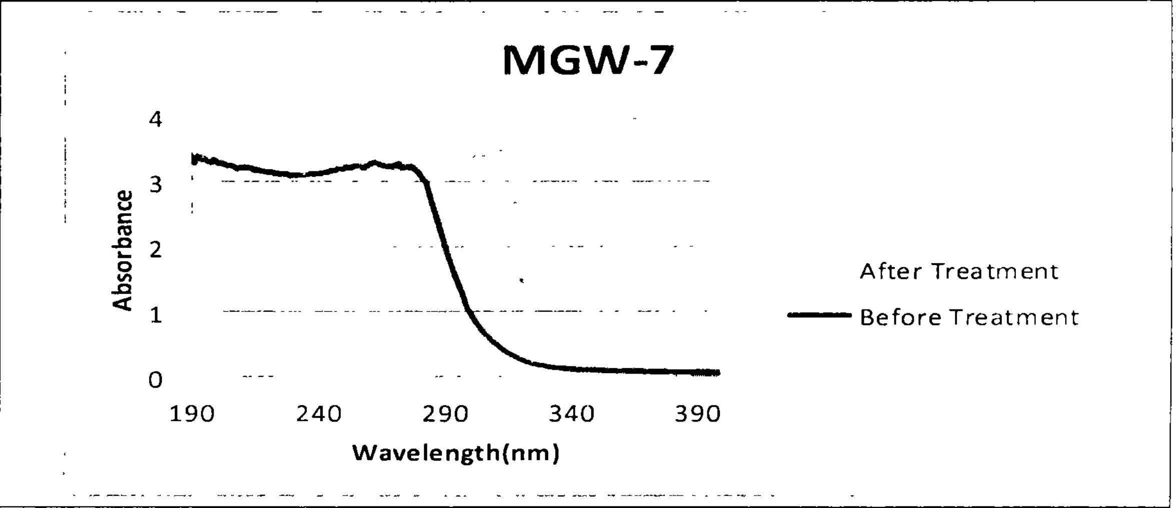


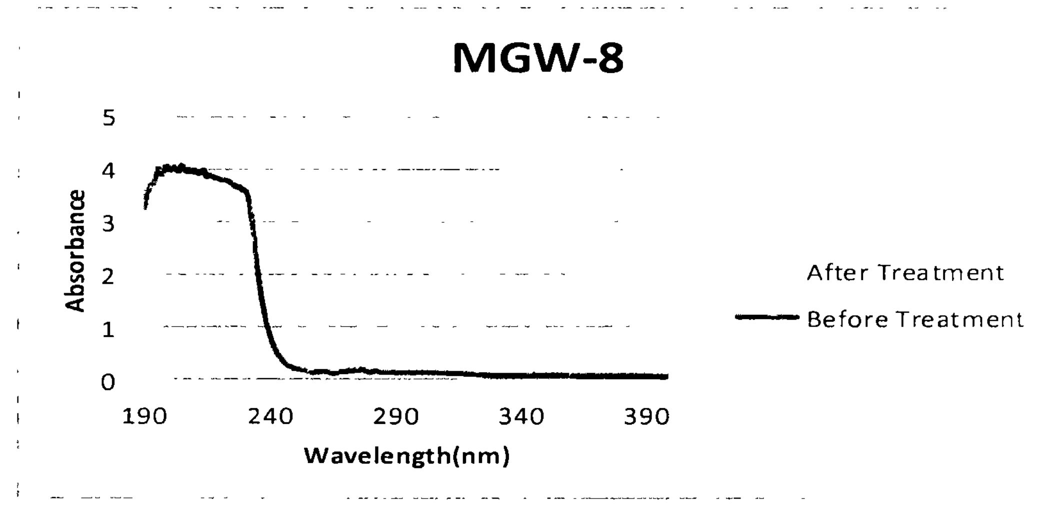

MGW-3
Absorbance
4
3.5
3
2.5
2
1.5
1
0.5
0
190
240
290
340
390
Wavelength(nm)
After Treatment
Before Treatment


MGW-4
Absorbance
5
4
3
2
1
0
190
240
290
340
390
Wavelength(nm)
After Treatment
Before Treatment


MGW-5
Absorbance
4
3
2
1
0
190
240
290
340
390
Wavelenth(nm)
After Treatment
Before Treatment


MGW-6
Absorbance
5
4
3
2
1
0
190
240
290
340
390
Wavelength(nm)
After Treatment
Before Treatment

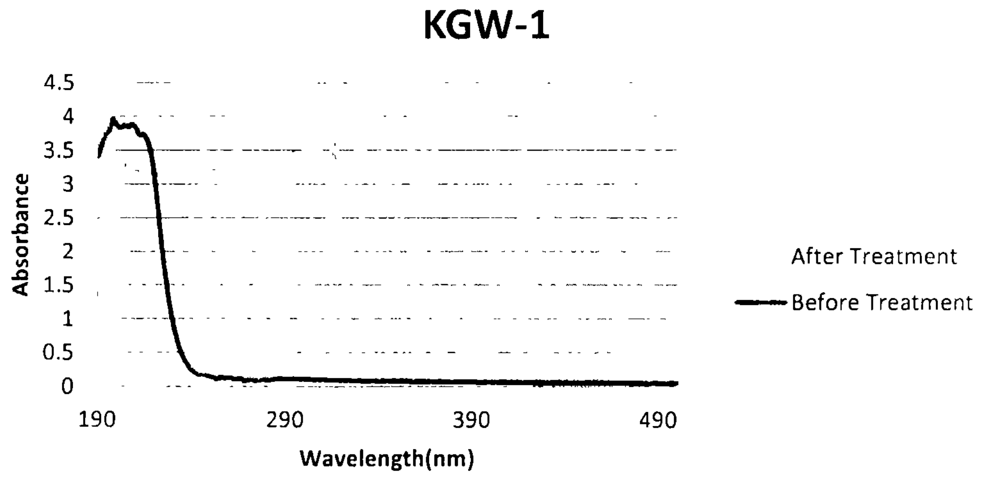

MGW-7
Absorbance
4
3
2
1
0
190
240
290
340
390
Wavelength(nm)
After Treatment
Before Treatment

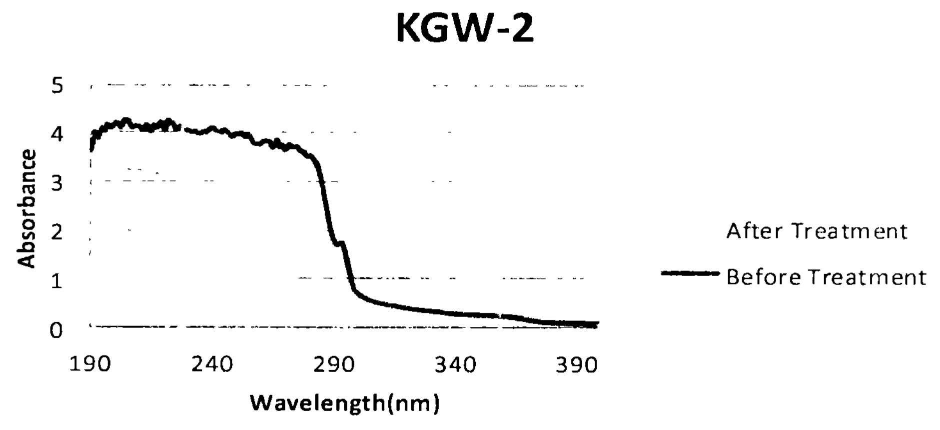

MGW-8
Absorbance
5
4
3
2
1
0
190
240
290
340
390
Wavelength(nm)
After Treatment
Before Treatment

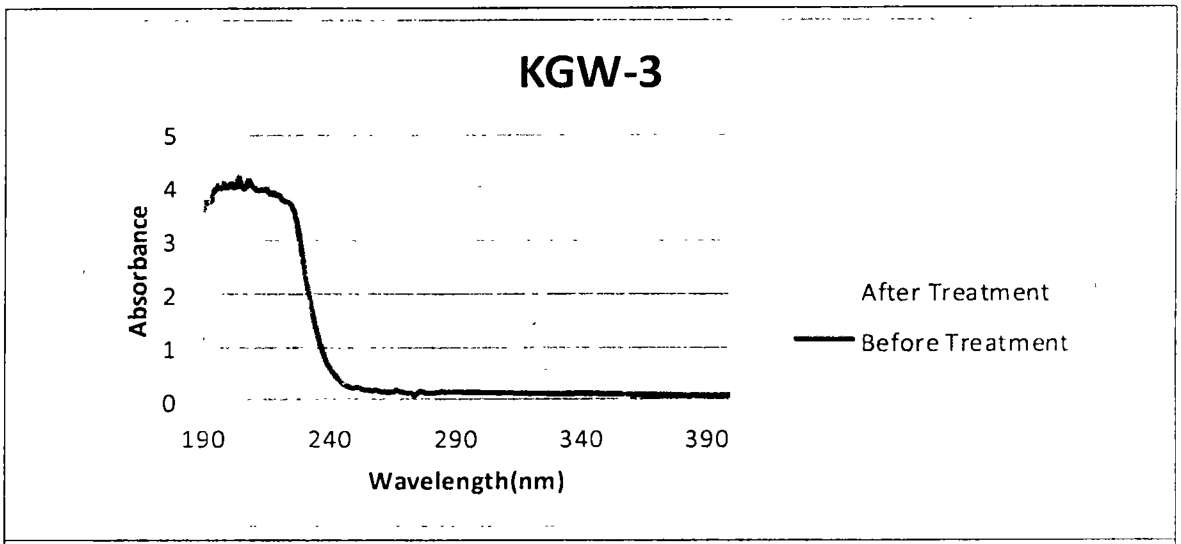
3.4.5. Kasur:

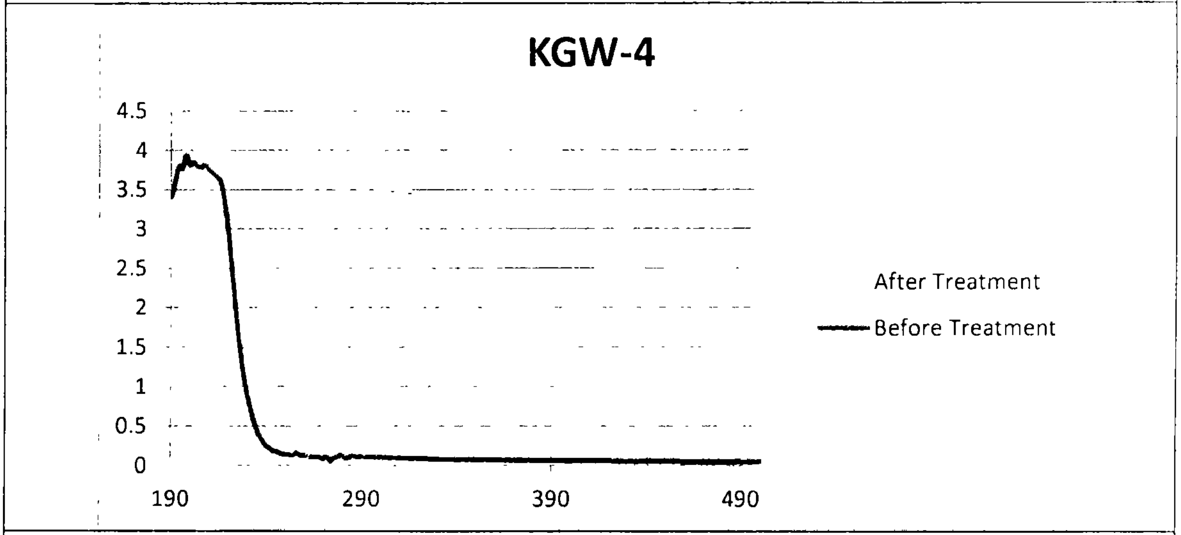
Samples were collected from different locations of Kasur. All the samples were scanned on UV spectrometer. The chromatographs demonstrated substantial peaks showing absorbance and wavelength of different compounds.Then samples were passed through Solid Phase Extraction Assembly for extraction and pre-concentration of organic pollutants. The organic extract obtained from elution was then scanned on UV spectrometer.

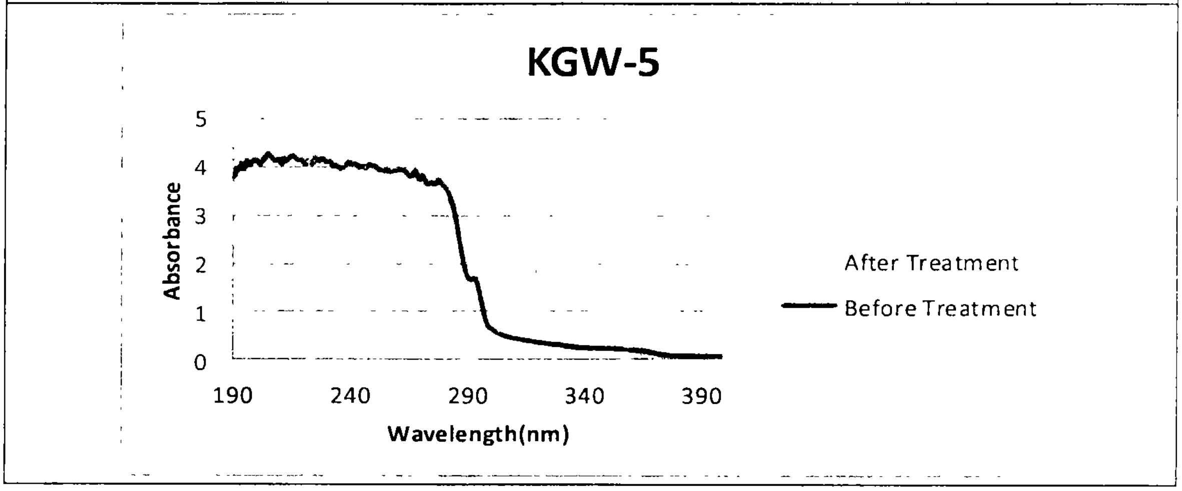
Table3.4.5: Comparison of before and after treatment of Kasur

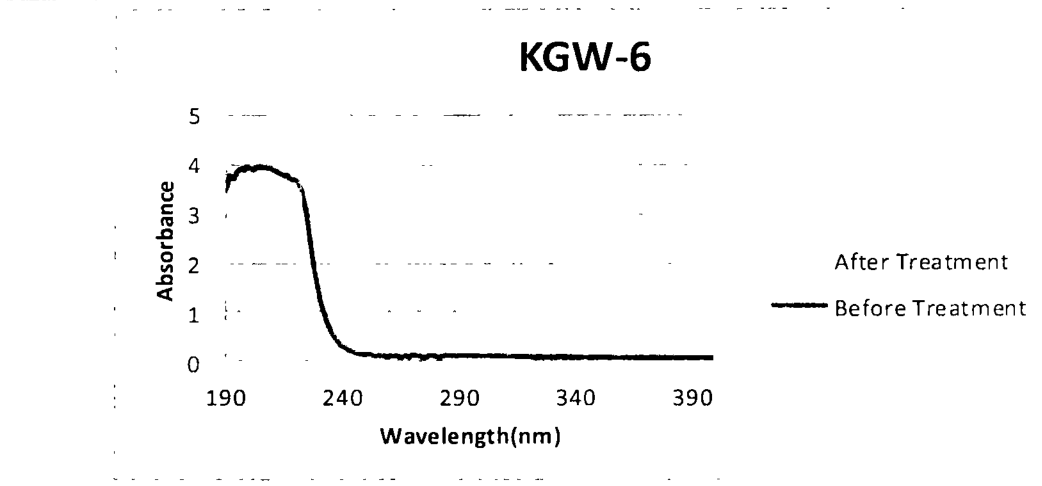


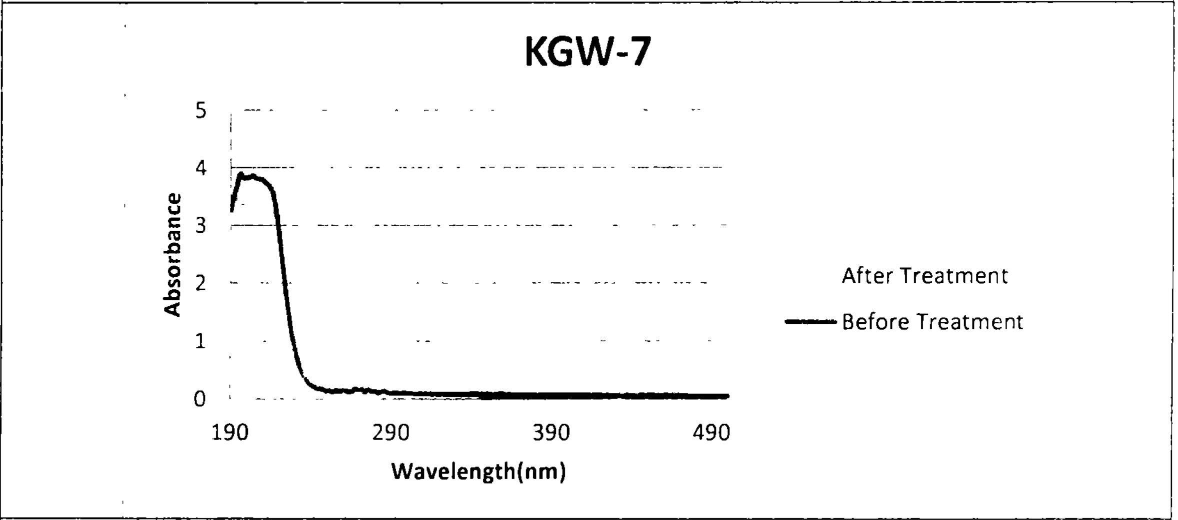


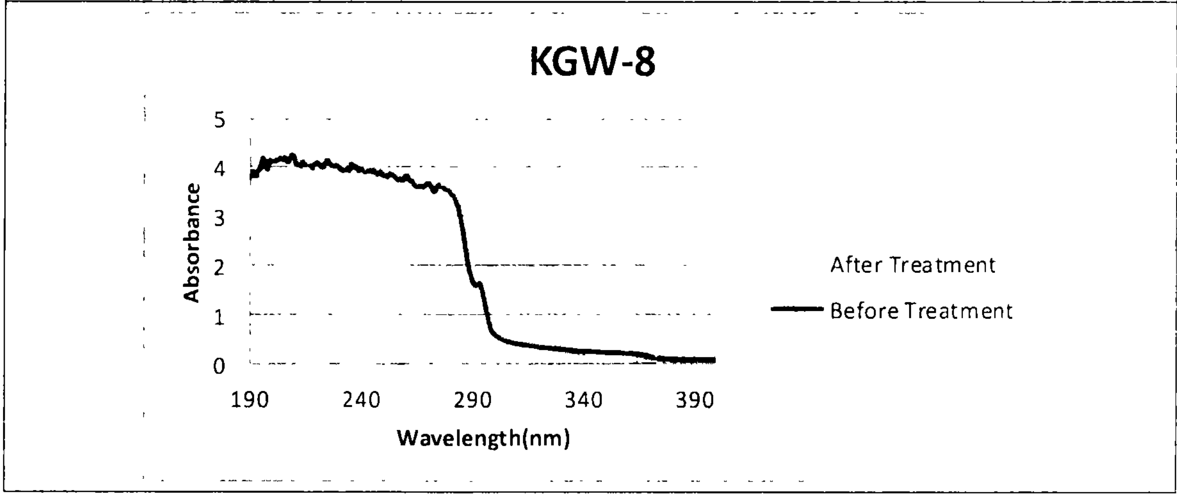

KGW-3
Absorbance
5
4
3
2
1
0
190
240
290
340
390
Wavelength(nm)
After Treatment
Before Treatment

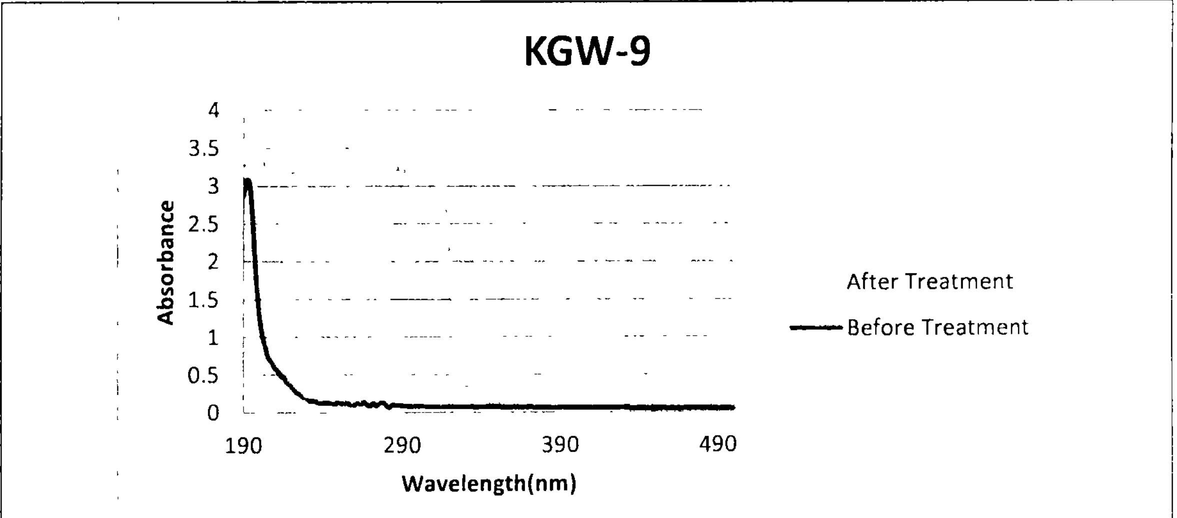

KGW-4
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
190
290
390
490
After Treatment
Before Treatment

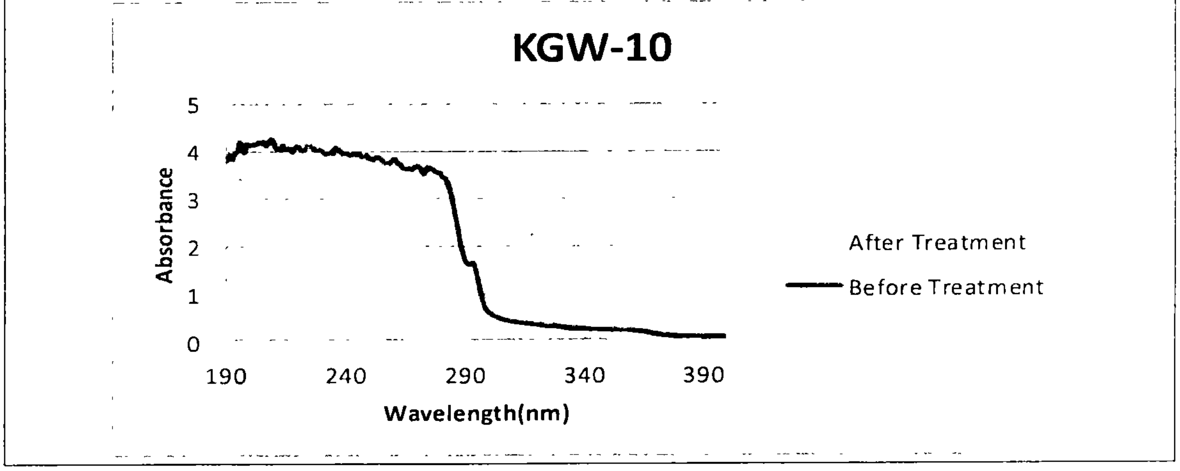

KGW-5
Absorbance
5
4
3
2
1
0
190
240
290
340
390
Wavelength(nm)
After Treatment
Before Treatment


KGW-6
5
4
3
2
1
0
Absorbance
190
240
290
340
390
Wavelength(nm)
After Treatment
Before Treatment


KGW-7
5
4
3
2
1
0
Absorbance
190
290
390
490
Wavelength(nm)
After Treatment
Before Treatment


KGW-8
5
4
3
2
1
0
Absorbance
190
240
290
340
390
Wavelength(nm)
After Treatment
Before Treatment

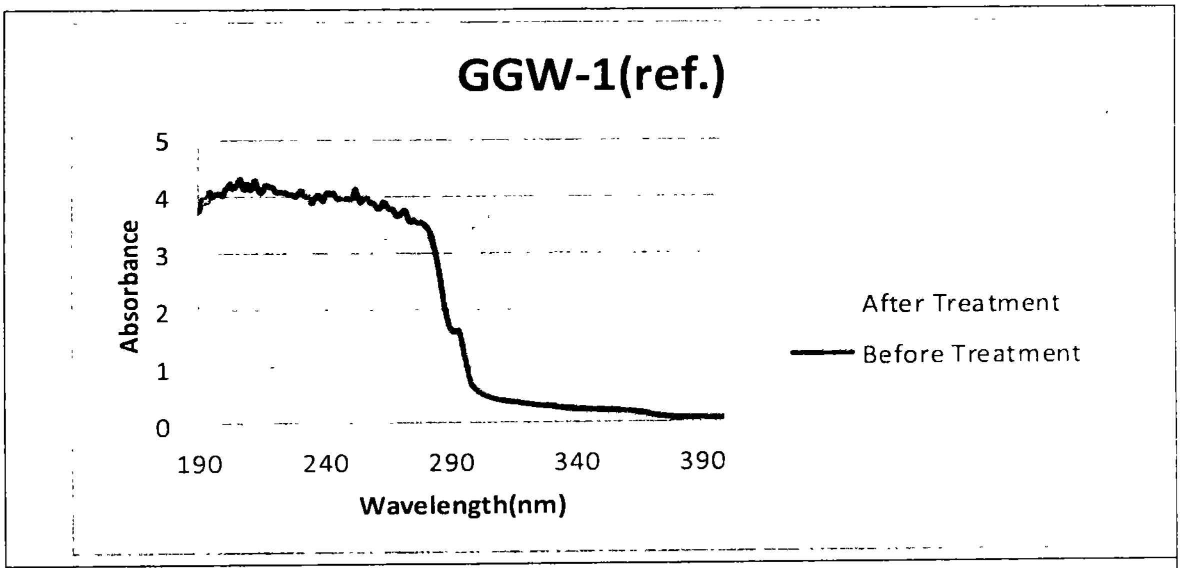


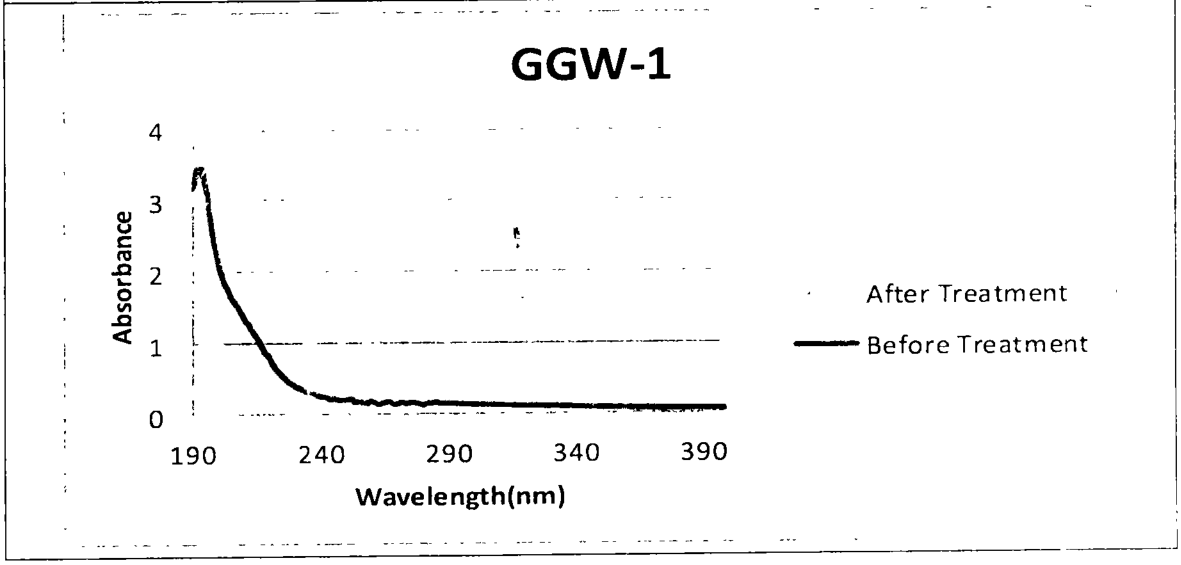


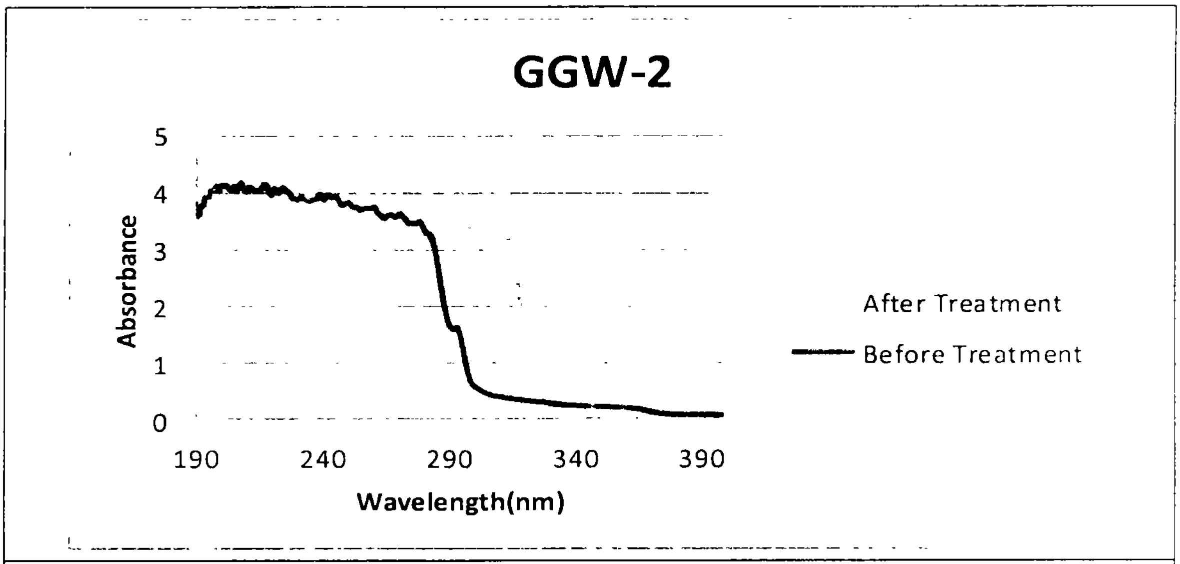
3.4.6. Gujranawala:

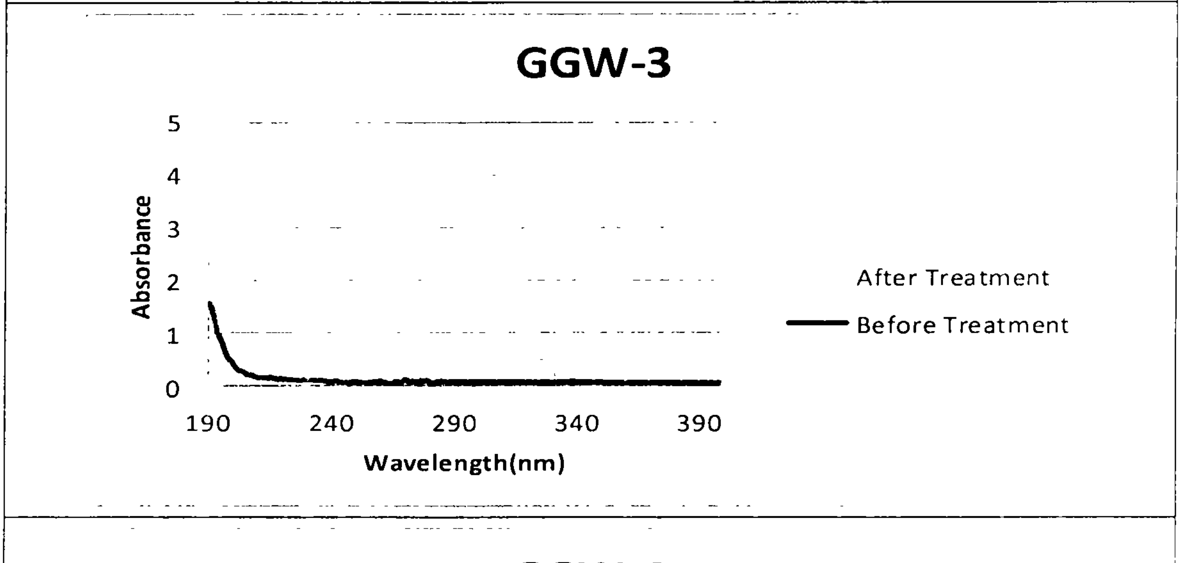
Gujranwala samples were scanned on UV spectrometer to check the efficiency of solid phase extraction. It is inferred that applied method for extraction and pre-concentration of organic pollutant is helpful for the concentration of organic compounds in the groundwater samples. The peaks in the graphs showed that a large portion of organic pollutants has been extracted in a concentrated form that were previously present in trace quantities whereas, the portion where the peaks are not as high as the before treatment chromatographs peaks represent that quite a lot of inorganic compounds such as nitrates, sulphates, iodides, halogens and some heavy metals released from the industrial waste water are now removed.

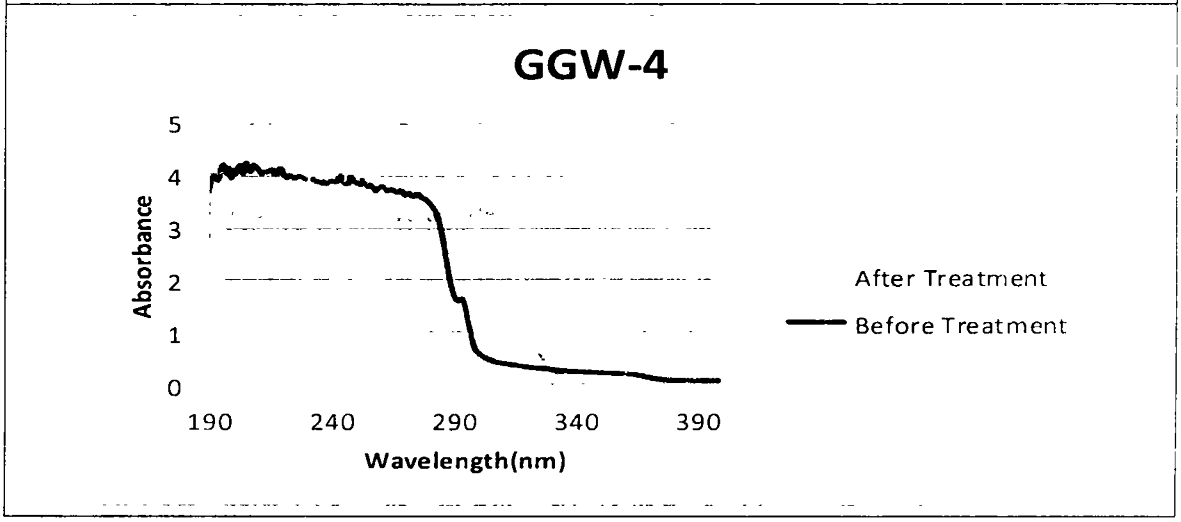
Table3.4.6: Comparison of before and after treatment of Gujranwala Groundwater






GGW-2
Absorbance
5
4
3
2
1
0
190
240
290
340
390
Wavelength(nm)
After Treatment
Before Treatment


GGW-3
Absorbance
5
4
3
2
1
0
190
240
290
340
390
Wavelength(nm)
After Treatment
Before Treatment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Absorbance
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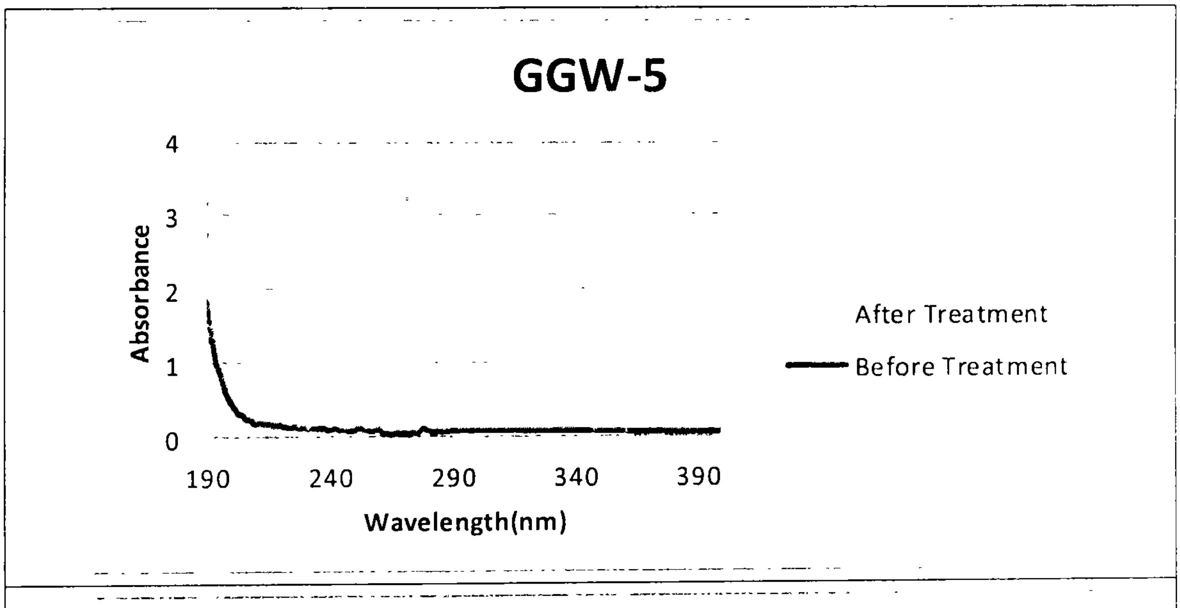
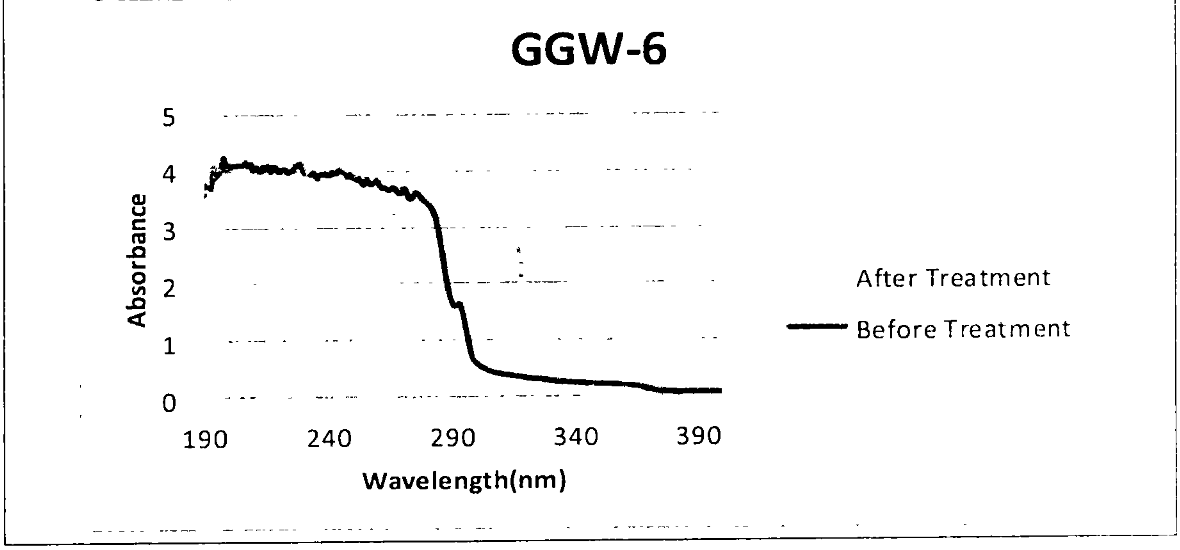
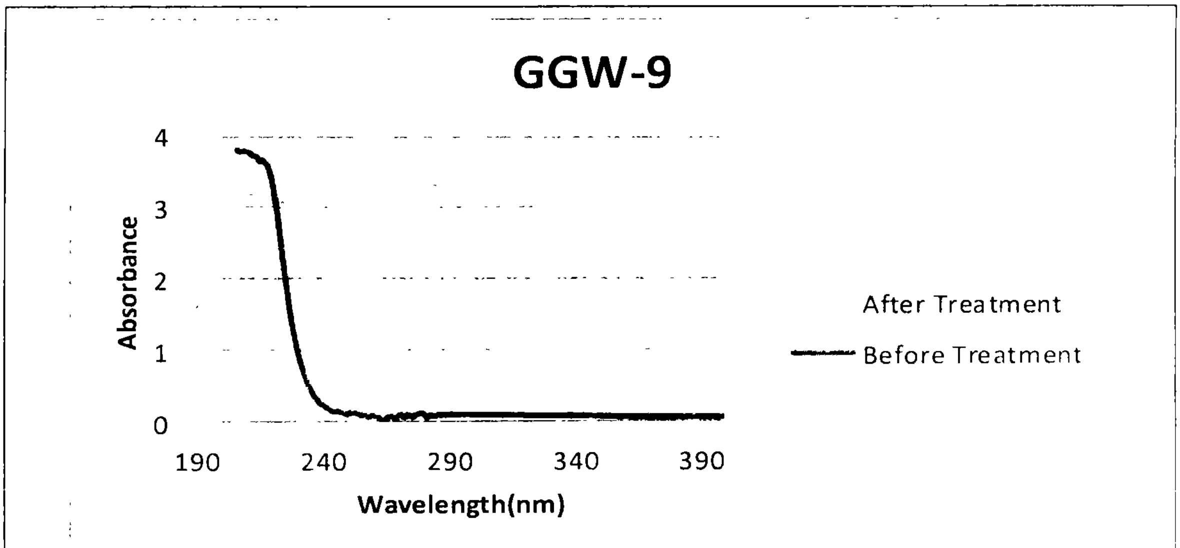
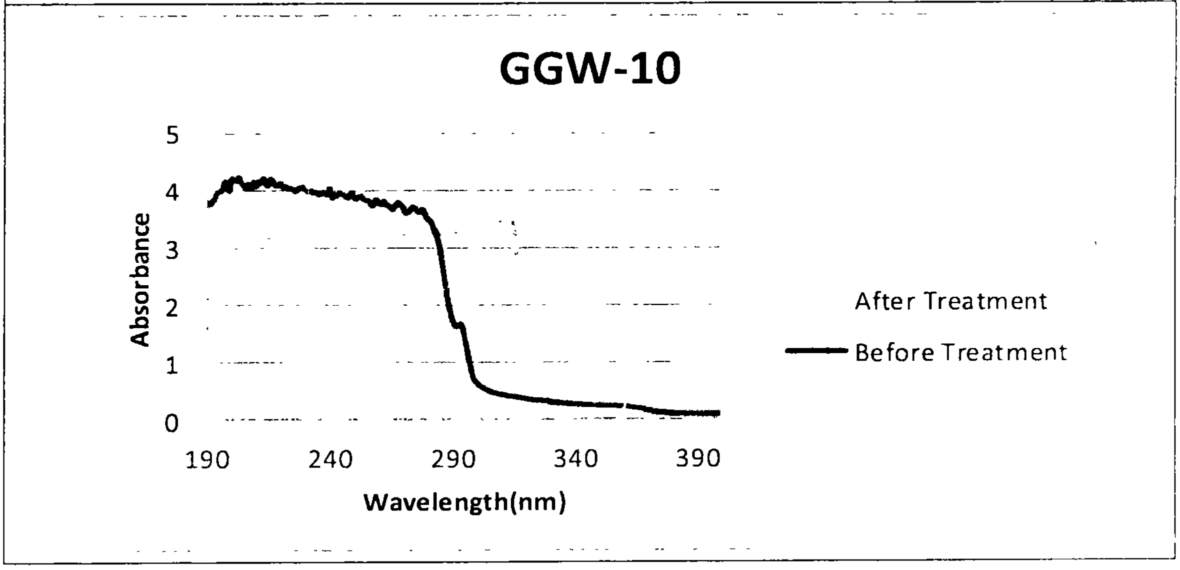
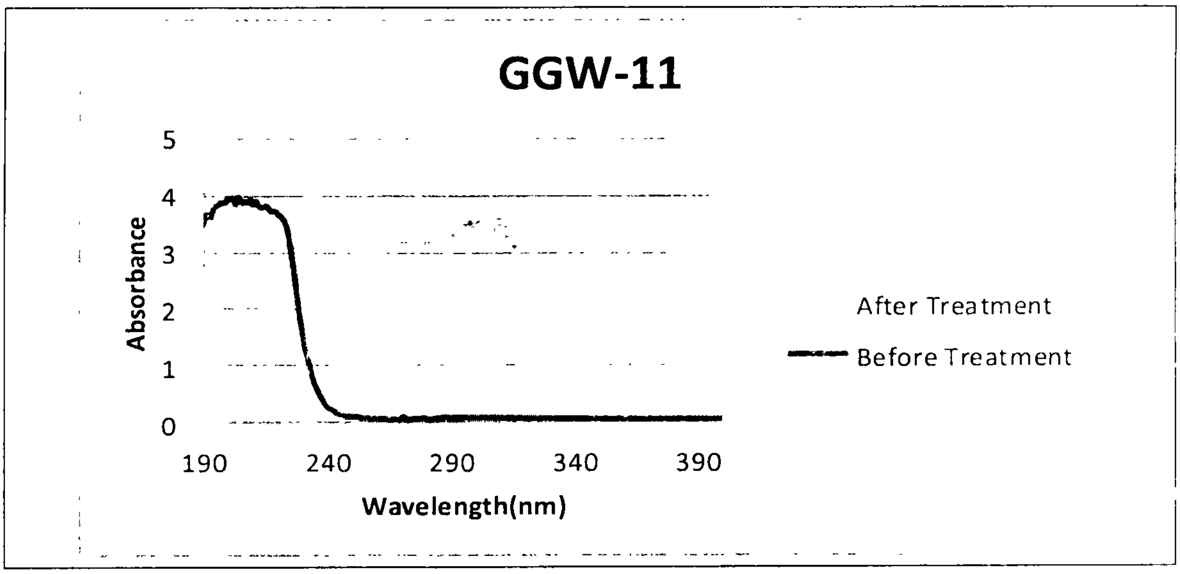
4
3
2
1
0
190
240
290
340
390
Wavelength(nm)
After Treatment
Before Treatment


GGW-5
Absorbance
4
3
2
1
0
190
240
290
340
390
Wavelength(nm)
After Treatment
Before Treatment


GGW-6
Absorbance
5
4
3
2
1
0
190
240
290
340
390
Wavelength(nm)
After Treatment
Before Treatment


GGW-9
Absorbance
4
3
2
1
0
190
240
290
340
390
Wavelength(nm)
After Treatment
Before Treatment

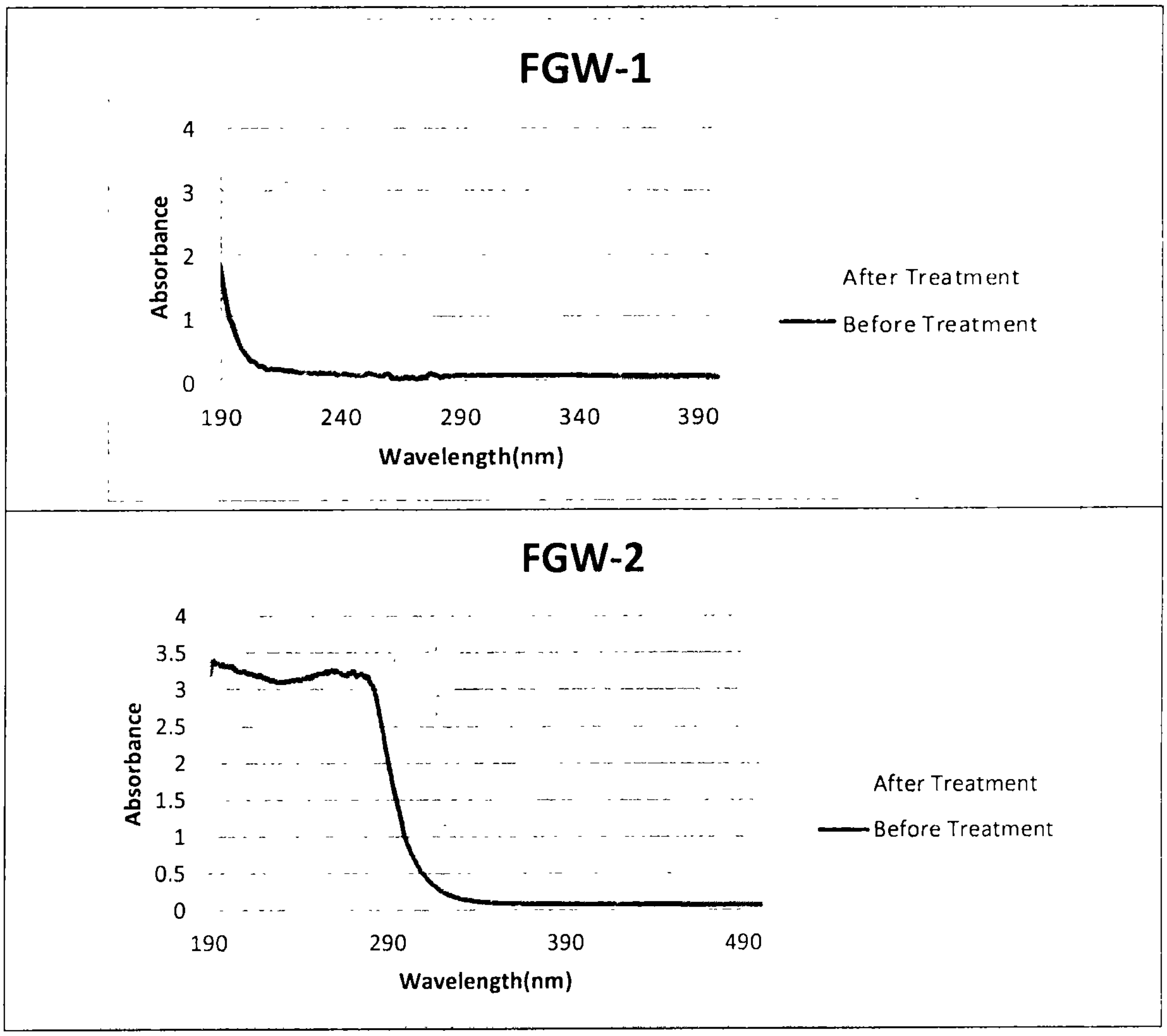

GGW-10
Absorbance
5
4
3
2
1
0
190
240
290
340
390
Wavelength(nm)
After Treatment
Before Treatment

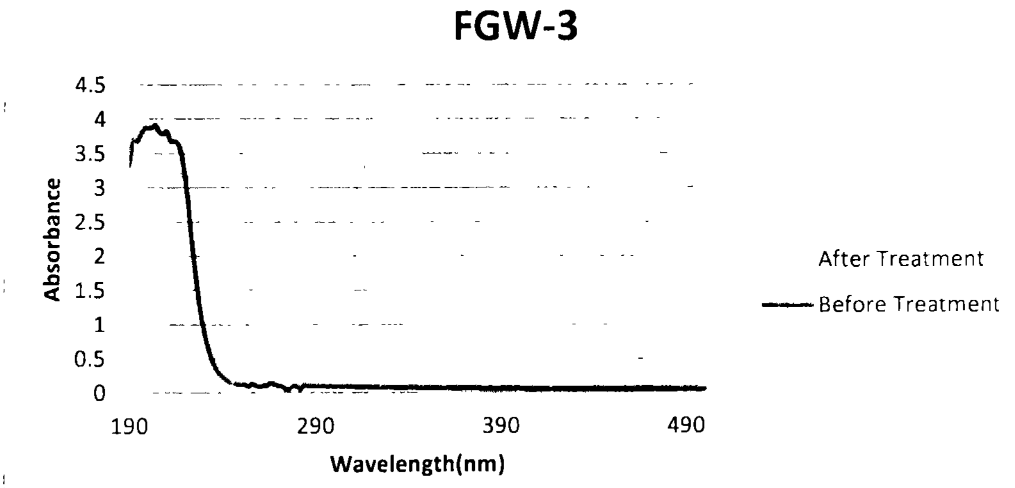


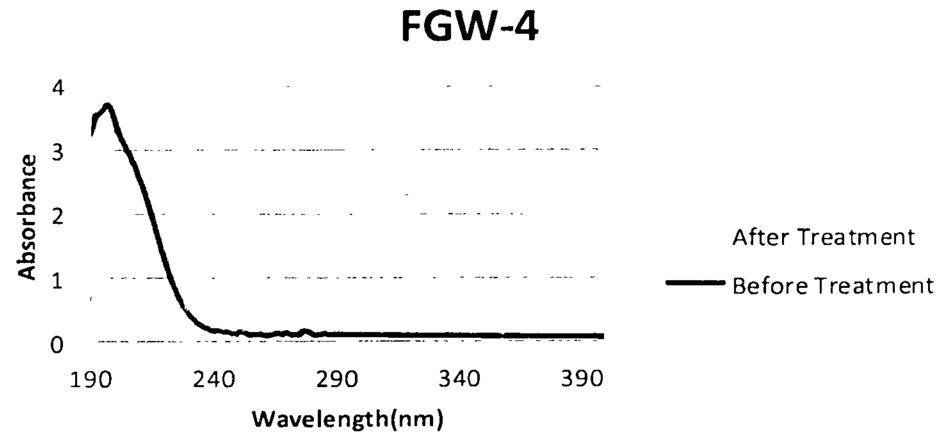
3.4.7. Faisalabad:

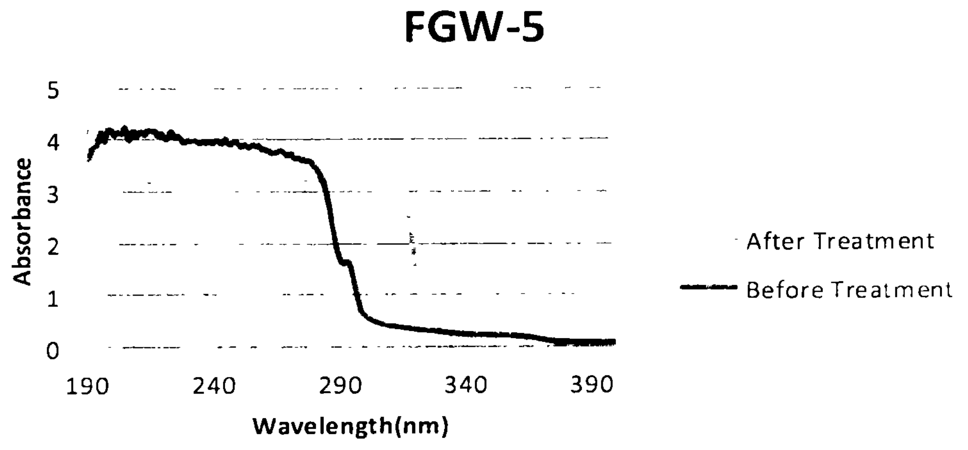
All the samples were scanned on UV spectrophotometer. The chromatographs illustrated significant peaks showing absorbance and wavelength of different compounds.Samples were run through Solid Phase Extraction Assembly for extraction and pre-concentration of organic pollutants. The organic extract obtained through elution was then scanned on UV spectrometer.The UV spectrometer data clearly suggested that applied method for extraction and pre-concentration of organic pollutants in ground water showed the significant results. The concentrations of organic pollutants were increased as a result of extraction and pre-concentration method. The comparative data obtained through UV spectrometer, 'before treatment and after treatment of samples showed enhanced concentrations of organic pollutants and their visible peaks suggested that our desired compounds has been concentrated and extracted that were previously present in very minute quantities whereas, the portion where the peaks are not as high as the before treatment chromatographs peaks represent that quite a lot of inorganic compounds such as nitrates, sulphates, iodides, halogens and some heavy metals released from the industrial waste water are now removed.

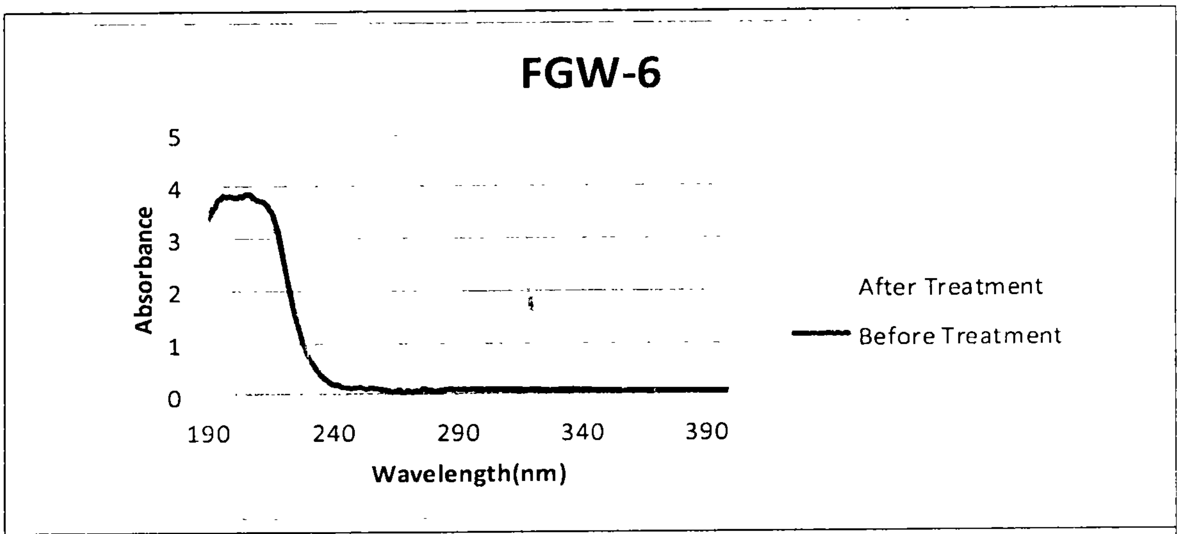
Table3.4.7: Comparison of before and after treatment of Faisalabad Groundwater

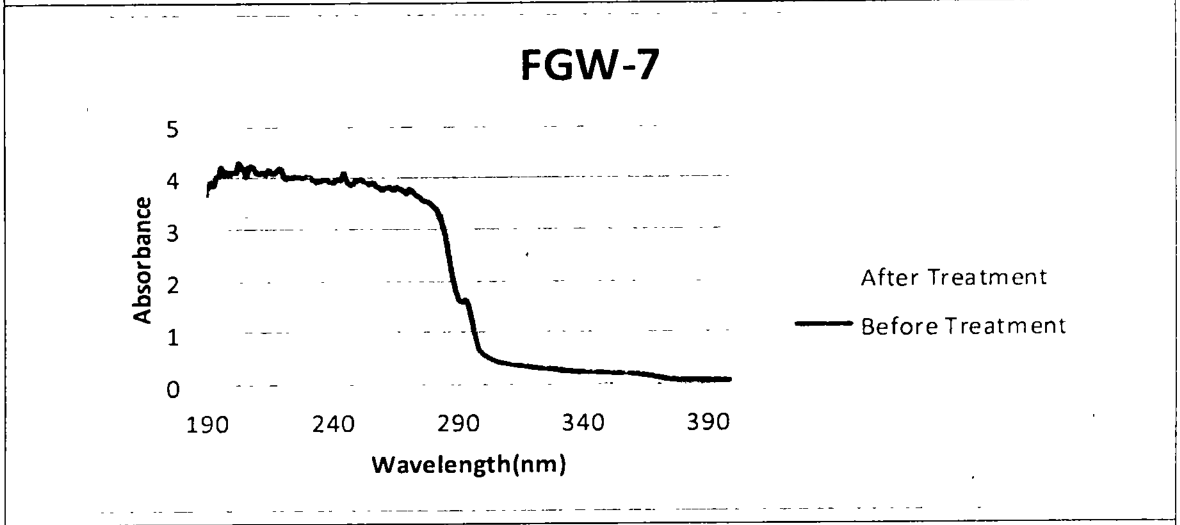


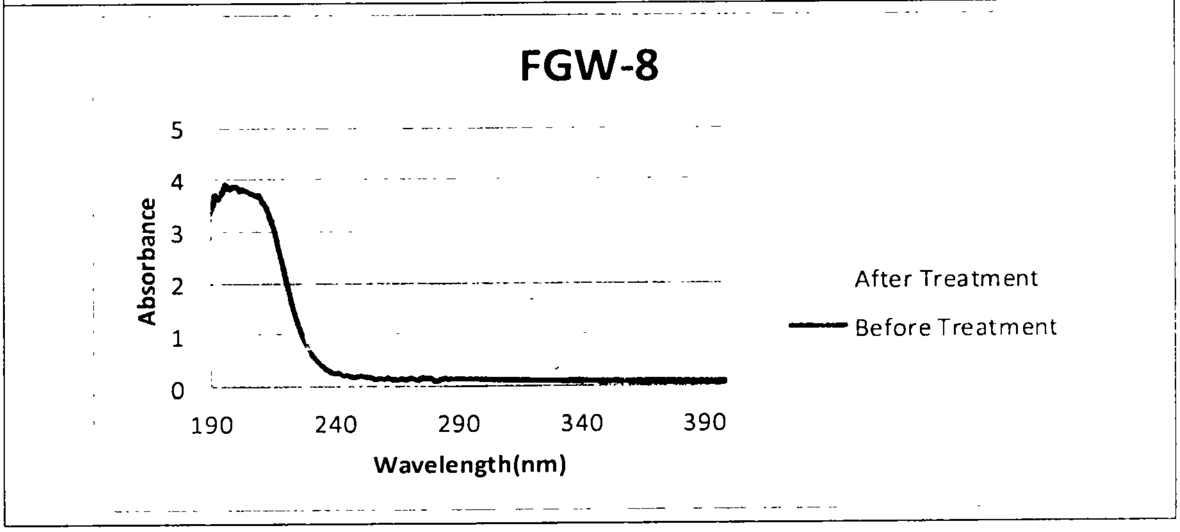

FGW-3
Absorbance
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
190
290
390
490
Wavelength(nm)
After Treatment
Before Treatment


FGW-4
Absorbance
4
3
2
1
0
190
240
290
340
390
Wavelength(nm)
After Treatment
Before Treatment


FGW-5
Absorbance
5
4
3
2
1
0
190
240
290
340
390
Wavelength(nm)
After Treatment
Before Treatment


FGW-6
Absorbance
5
4
3
2
1
0
190
240
290
340
390
Wavelength(nm)
After Treatment
Before Treatment


FGW-7
Absorbance
5
4
3
2
1
0
190
240
290
340
390
Wavelength(nm)
After Treatment
Before Treatment


FGW-8
Absorbance
5
4
3
2
1
0
190
240
290
340
390
Wavelength(nm)
After Treatment
Before Treatment

3.5. Organic Compounds Analysis:

High Performance Liquid Chromatography (HPLC) was used to identify, quantify and analyze the organic compounds in the samples. HPLC equipped with the UV detector (Waters, 1525) have been used for qualitative and quantitative analysis. It has helped us to identify the compounds and their concentration in the sample. Following organic compounds were analysed: Endrin, Dieldrin, Cypermethrin, DDT, DDE, Trichlorophenol, Dichlrophenol (Tariq., et al., 2007).

3.5.1. Sheikhupura:

In Sheikhupura, highest concentration of Endrin and Dieldrin were found in SGW-12 located in agricultural land and sample was collected from shallow water aquifer, whereas highest concentration of DDE was found in SGW-6. High concentrations of DCP were found in SGW-6 and SGW-8. In SGW-8 DCP concentrations were found highest as compare to other samples and zinc and cadmium were also found in it, this sampling point is located in residential areas near the waste water drain and these samples were collected from hand pump its source was also shallow water aquifer their depth was 40 and 60 feet respectively. Cypermethrin was found only in four samples out of 20 samples. These four points were located inindustrial areas. It shows that it has been used in few manufacturing processes. Cypermethrin is commonly not used in industries except in specific industries. However, TCP and DDT were not found in Sheikhupura groundwater samples. TCP is used in mainly paints and dyes manufacturing industries, while DDT has been banned in Pakistan so, that is the reason it is not found in samples because of its prohibition. All samples collected from Sheikhupura were shallow water except SGW-1 was 400 feet deep. Concentration of all compounds lied above the permissible limits set by WHO and US EPA.

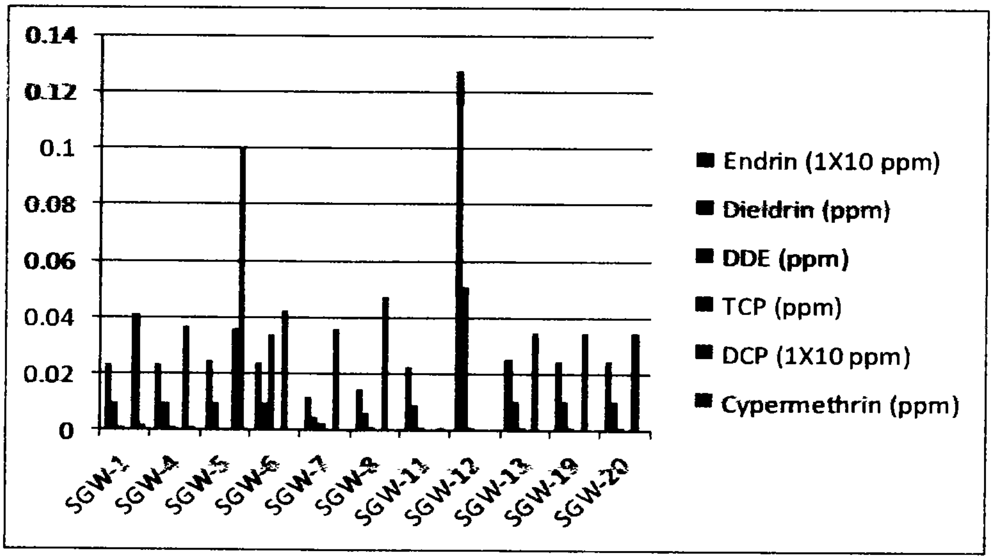


Figure 3.5.1: Analysis of Organic Compounds in Sheikhupura Groundwater

3.5.2. Lahore:

In Lahore, highest concentration of Endrin and Dieldrin were found in LGW-1, LGW-2 collected from residential areas alongside the waste water drain and LGW-9 from agricultural area. Highest concentration of DCP was found in LGW- 2, LGW-7 located in residential area at the edge of waste water drain and LGW- 9 samples were collected from deep bore holes, except LGW-9, it was collected from hand pump. Highest concentrations of TCP were found in LGW-2, LGW-5 and LGW-7. DCP concentrations were high in LGW-1 and LGW-2. They were collected from deep bore holes. DCP and DCP are usually used in dyes, paints industries and sampling point was industrial area. Presence of organic contaminants in deep ground water depicts the contamination of soil has reached to its saturation point and contaminants are seeping down in deep water aquifers. DDE was found only in two samples LGW-7 was collected from the bank of waste water drain from shallow water depth and LGW-8 was also collected from shallow water aquifer and sampling point was located inagriculturalarea. These two samples were also contaminated with heavy metals (Cd, Pb, Zn). DDT was found in four samples and their sampling point was residential area near the waste water drain only LGW-8 was located in agricultural area. Their depth was deep bore holes except LGW-8 was collected from hand pump. DDT has agricultural source. Since it has been banned in Pakistan since 1975, its presence in ground water depicts that it might be the residues of previous uses.Whereas,Cypermethrin was not found in Lahore samples. Lahore samples were collected both from shallow and deep water aquifers. After analysis, it is cleared that both sources are contaminated. Shallow water being near to drain water and waste irrigation has contaminated the groundwater, whereas, deep water was contaminated due to contamination of soil. Furthermore, ground water contamination suggested that buffering and degradation potentials of different soilexhibiteddifferentsoil organic carbon sorption coefficient (Koc) (Tariq et al., 2004). They observed inconsistent Koc values, this deviation is might be due to variable and changing nature of organic matter in soils used, clay contents and pH of soil that lead to great variability in the results (Wauchope et al. 1992).These compounds lied above the permissible limits set by WHO and U.S EPA.

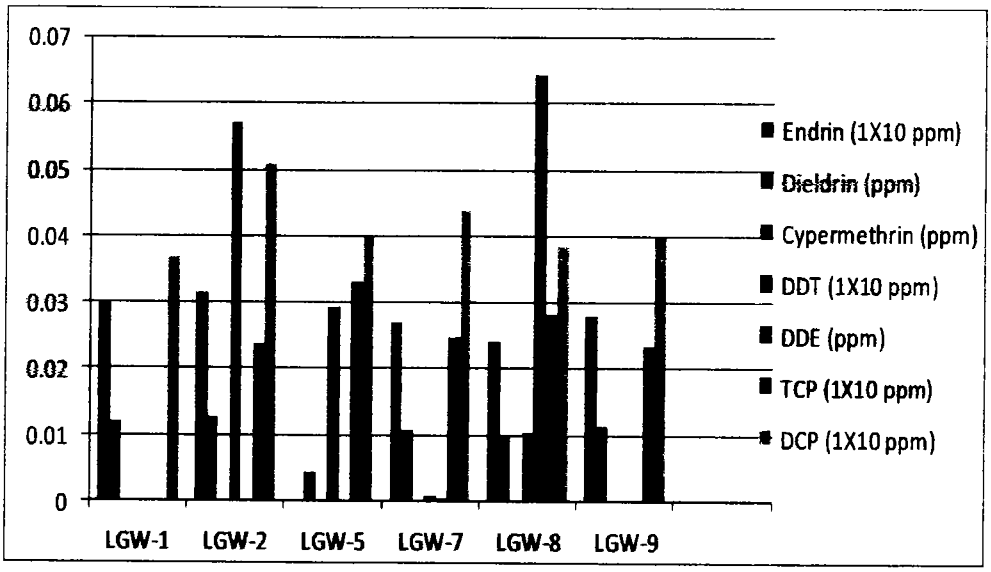


Figure 3.5.2:Analysis of Organic Compounds in Lahore Groundwater

3.5.3. Raiwind:

Highest concentrations of Endrin and Dieldrin were found in RGW-7 located in agricultural area, RGW-3 from industrial area and RGW-2 agricultural area. They were collected from shallow water aquifers except RGW-2 was 150 feet depth. DCP concentration were found only in four samples; RGW-7 and RGW-6 located in agricultural area while, RGW-1 and RGW-5 located in industrial area. While TCP and DDE were found only in two samples RGW-6 located in industrial area and RGW- 8agricultural area. These samples were collected from shallow water DDT and Cypermethrin were not found in Raiwind samples. All Raiwind samples were collected from shallow water aquifer except RGW-1 and RGW-4. Agricultural and industrial activities and drain water has affected the ground water quality. Concentration of all samples lies above the permissible limits set by U.S EPA and WHO.

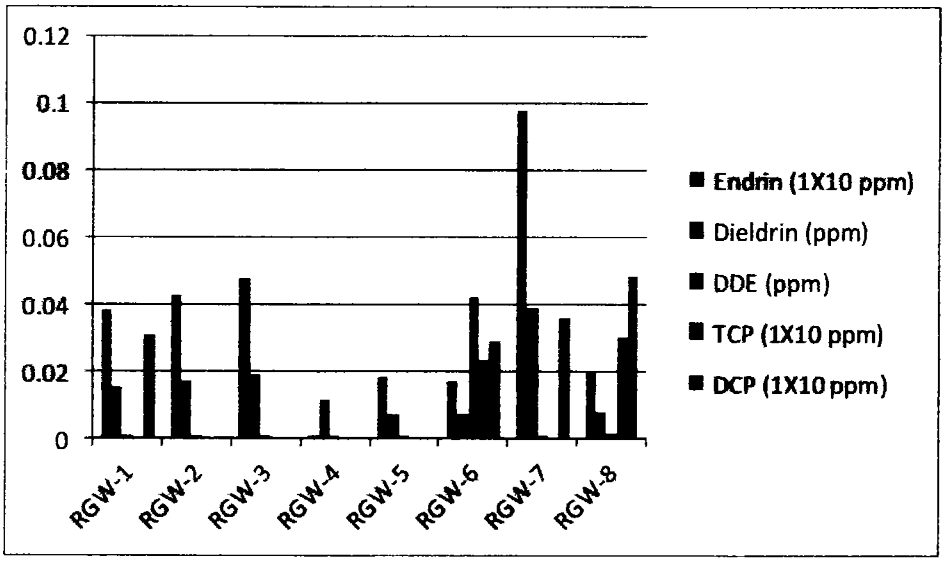


Figure 3.5.3:Analysis of Organic Compounds in Raiwind Groundwater

3.5.4. Mangamandi:

In Mangmandi, Highest concentrations of Endrin were found high in MGW-8, MGW-7, MGW-1industrial area at the bank of waste water drain and MGW-3 from agricultural area, and highest concentrations of Dieldrin were found in MGW-6, MGW-7 and MGW-8. These samples were collected from deep water aquifer except MGW-3, was collected from hand pump. MGW-8, MGW-7 sampling points were located in industrial area.DCP was found high in MGW-1, MGW-3 and MGW-8 these points were located in agricultural area and were collected from bore holes except MGW-3 was hand pump. It might be due to ponding irrigation which is commonly practicedinPakistan, might be resulting in faster water flow infiltration along with pesticides to contaminate the groundwater (Flury et al., 1994). TCP was found only in three samples MGW-2, MGW-6 and MGW-8 were taken from deep bore holes it depicts the seepage of contaminants down into ground water and saturation of soil. These points were situated near waste water drain. And it could also have been leached down from the depth of nearby waste water drain. High concentrations DDE were found in MGW-3 was collected from hand pump and located in agricultural and industrial area near the waste water drain and MGW-1 was collected from bore hole it might have been leeched down into groundwater and sampling point was located near the waste water drain. Cypermethrin was found only in one sample MGW-2 source bore hole and was located in industrial area at brink of waste water drain. DDT was not found in any sample of Mangamandi and it might be due to its ban in Pakistan. Mangamandi samples were collected from deep ground water and two were from shallow water. Contamination of deep ground water shows that soil has reached to its saturation point and contaminants are seeping down into ground water and caused contamination. It is fact that the soil provides a potential pathway of pesticide transport to contaminate water, through runoff and subsurface drainage; interflow and leaching(Abrahams, 2002). These concentrations lied above the permissible limits of WHO and U.S EPA.

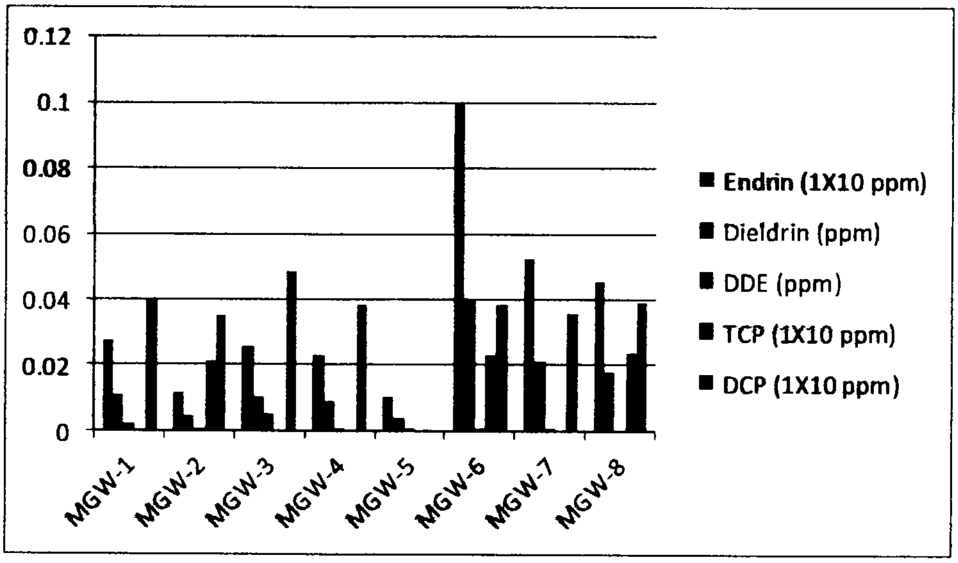


Figure 3.5.4: Analysis of Organic Compounds in Mangamandi Groundwater

3.5.5. Kasur:

In Kasur, high concentrations of Endrin were found in KGW-2, KGW-3, KGW-6 and KGW-8. These samples were collected from industrial areas. Dieldrin was high in KGW-2, KGW-3 and KGW-5. DCP was high in KGW-2, KGW-5 and KGW-8. TCP concentration was found in KGW-3, KGW-6 and KGW-8. DDE was found only in four samples; KGW-2, KGW-3, KGW-7 and KGW-9 sampling point was placed in agricultural area. Samples were taken from shallow water aquifers.DDT was found only in two samples KGW-2 located in industrial area near the agricultural fields and KGW-4 .This shows that, pesticides sprays used for agricultural practices have reached to ground water through infiltration and contaminated the soil consequently, DDT has reached to groundwater and contaminated to it. However, DDT is banned in Pakistan so it might be the residual of past uses. That is the reason it is found only in two samples only where its residues were left. While, Cypermethrin was not found in Kasur samples. In general, KGW-2, KGW-3, KGW-8 were highly contaminated, these samples were collected from 100 feet depth and located in industrial area. In Kasur, maximum samples were collected from industrial areas except few near agricultural areas. Heavy metals (Zn, Cd) were also found in KGW-8. This shows that industrial effluents were discharged into drains and gradual seepage into ground water has contaminated groundwater. In past industrial waste were directly discharged into waste water drains and it has badly affected the groundwater quality. Now days, direct and untreated discharge in not in practice in Kasur, resultantly, it has gradually revived the groundwater quality. Concentrations of organic compound were above the permissible limits set by WHO and U.S EPA.

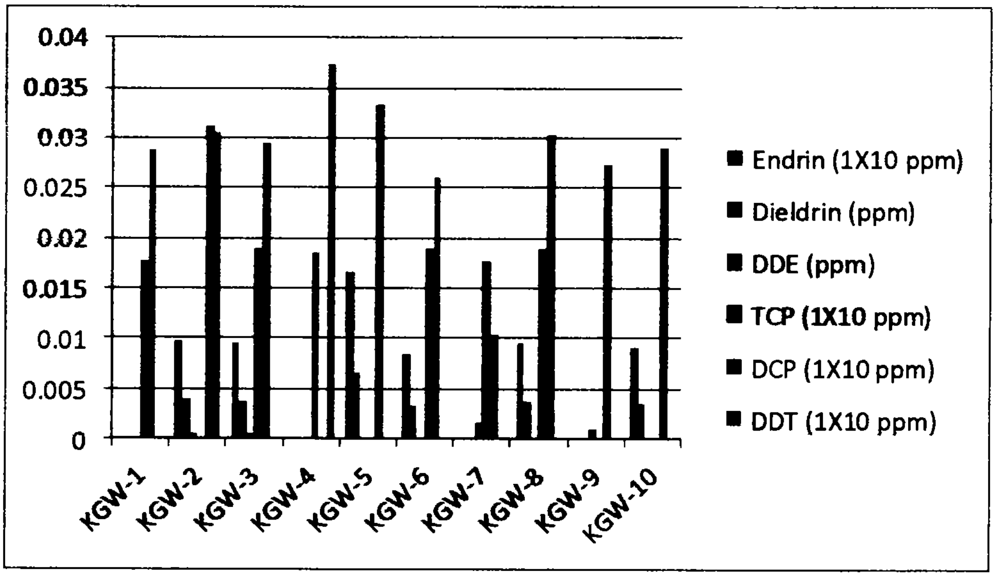


Figure 3.5.5: Analysis of Organic Compounds in Kasur Groundwater

3.5.6. Gujranawala:

Concentration of Endrin and Dieldrin were found high in GW-1, GGW-3 and GGW-8. These samples were collected from shallow water aquifers located in agricultural area near residential area. And high concentrations of DCP were found in GGW-3, GGW-7 and GGW-11 however, TCP high concentrations were found in GGW-1, GGW-3 sited near residentialarea and GGW-11was collected from industrial area and from shallow water aquifers. Presence of TCP and DCP suggests that, it is been used in industrial processes in the manufacturing of dyes, paints and greases etc. its open discharge into waste water drains has contaminated the groundwater through seepage. DDE was found in GGW-3, GGW-7 and GGW-9 were sited near the agricultural land or previously it has been used for agricultural purpose. DDT was found only in one sample GGW-10 situated at the brink of waste water drain which depicts that it is only residual of past use. While, Cypermethrin was not found in Gujranawala samples. It is not commonly used in industries except in few. Generally GGW-3, GGW-4, GGW-10 and GGW-11 were more contaminated as compared to other samples. In GGW-10 and GGW-11 heavy metals were also found. These samples were collected from shallow water. There is high possibility that contaminants were leached down into groundwater and caused contamination. Overall concentrations of all contaminants were found above of the permissible limits set by WHO and U.S EPA.

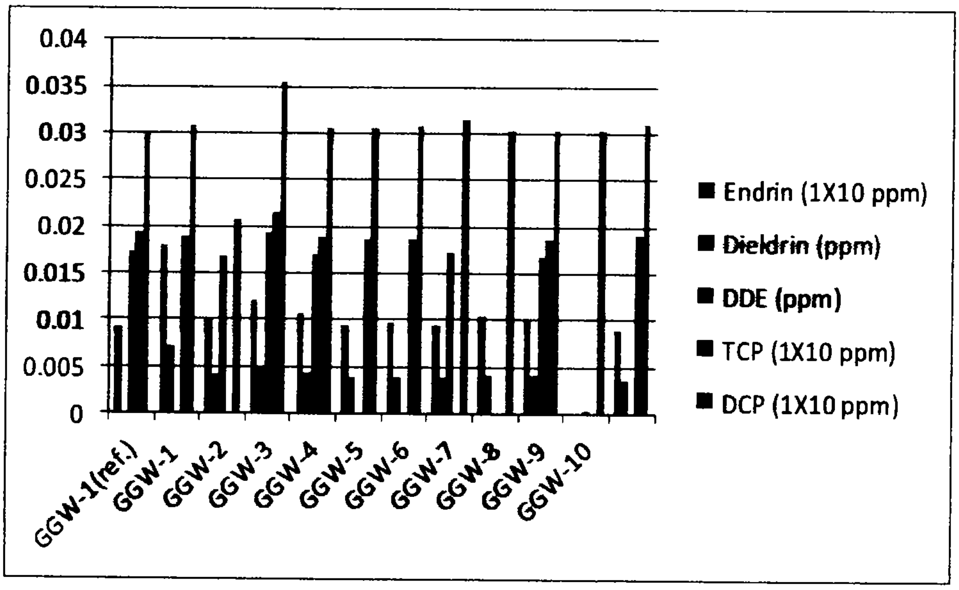


Figure 3.5.6: Analysis of Organic Compounds in Gujranwala Groundwater

3.5.7. Faisalabad:

Endrin and Dieldrin highest concentration were found in FGW-5, highestconcentrations of DCP were found in FGW-4 located in agricultural area at the bank of waste water drain, FGW-5 sited in industrial area near the waste water drain, while TCP was found only in one sample FGW-8 collected from shallow water and situated at the junction of industrial and agricultural area. DCP and TCP are used in industries and their presence in ground water depicts the mixing of industrial effluents in ground water. DDE was found only in three samples; among three samples FGW-4 was comparatively high in concentration. DDT was found only in FGW-3 collected from shallow water located in industrial area at the edge of waste water drain, though it has been banned in Pakistan it might be the residual of past usage. However Cypermethrin was not calculated in any sample.Because, it is not commonly used in industries. All samples from Faisalabad were collected from shallow water except FGW-2 was collected from 250 feet depth. Contamination of shallow water samples shows that use of drain water in agricultural activities and pesticides sprays over a long period and industrial effluents seepage into ground water has caused contamination in shallow water. Concentration of contaminant may not so high but their continuous seepage into ground water can result in accumulation which can be difficult to treatthe other possible reason to reach the pesticides in aquatic environment is through direct runoff, leaching, careless disposal of empty containers, equipment washings, etc (Ahad et al., 2000, 2001; Tariq et al., 2004a, 2006). In brief, FGW-3, FGW-4 and FGW-8 were highly contaminated, presence of more contaminants as compared to rest of samples make them highly contaminated, these sampling points were located in industrial area at the edge of waste water drain. Concentrations of contaminants were above of the permissible limits set by WHO and U.S EPA.

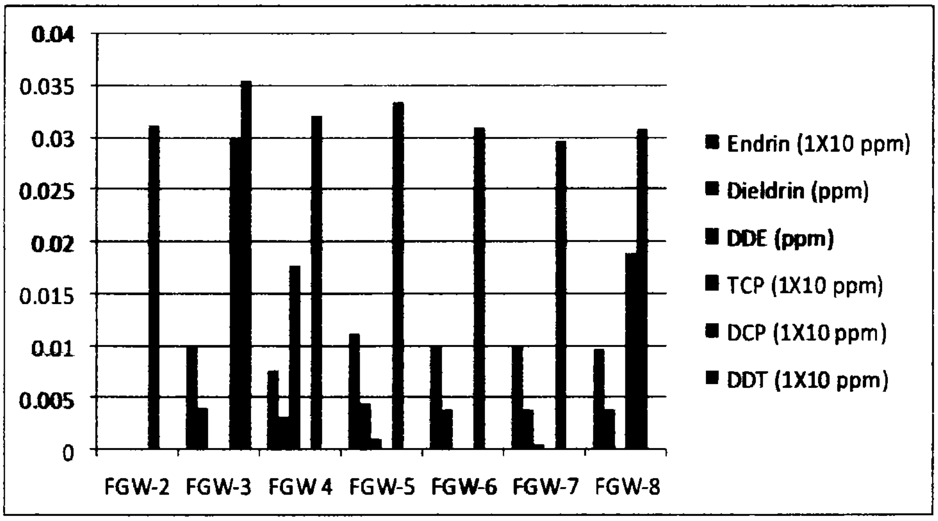


Figure 3.5.7: Analysis of Organic Compounds in Faisalabad Groundwater

3.6. Impacts of Contaminated Groundwater on human health:

Drinking contaminated groundwater can have serious health effects. Diseases such as hepatitis and dysentery may be caused by drinking contaminated water. Over a long time consumption can have chronic effects such as certain types of cancer, neurological effects. diabetes, respiratory diseases, fetal diseases, and genetic disorders may also result.Drinking and bathing in polluted water are the most common routes for the spread of diseases with symptoms like abdominal pain, hair loss, numbness in hands, loss of appetite, eye infections, irritation of skin and fever (Rizwan, U., et al., 2009). In Punjab about 40% of deaths are related to water-borne diseases. According to Pakistan Council of Research in Water Resources (PCRWR) report 2003-04, it is estimated that around 40% of all reported diseases and deaths are due to poor water quality in the country ([17])(Okoh, A. I., et al., 2004). There are thousands of evidences showing that organic/inorganic contaminations have severe impacts on human health (Richter, 2002). Their severity could be different depending on the degree, nature and the type of exposure (Henrik,A., et al 2014).Frequent exposure to certain pesticides significantly increases the risk of cancer (Lynch et al.,2009; Alavanja et al.. 2003; Beane et al., 2005). High-intensity and cumulative pesticide exposure contributes to depression among pesticide applicators (Beseler et al., 2008). Exposure to organochlorine compounds and organophosphate is associated with increased prevalence of diabetes (Cox et al., 2007; Montgomery et al., 2008). Pesticide exposure is causing women specific disorders regarding early menopause and issues in conceiving (Farr et al. (2006). In another study it is stated that exposure of cypermethrin, DDT and DDE can cause liver, kidney dysfunctions and respiratory tract infection (Azmi et al 2006).

Lead is hazardous to health as it accumulates in the body and affects the central nervous system, mental impairment by depositing in brain. Children and pregnant women are at high risk. Manganese can affect the kidneys and developing fetus. Copper can cause irritation in nose, eyes and mouth, vomiting and diarrhea. Chromium can cause cardiovascular diseases. Excess of Iron can cause destruction of hemoglobin and disturb its oxygen absorbing capacity.Drinking water that gets contaminated with nitrates can prove fatal especially to infants that drink formula milk as it restricts the amount of oxygen that reaches the brain causing the 'blue baby' syndrome. It is also linked to digestive tract cancers. Excess of Trace metals can cause damage to the nervous system, kidney, and other metabolic disruptions.

3.7. Conclusion:

Water is an essential for human life and ecosystems on earth. Water is needed nearly for everything humans and animals and plants. In Punjab, many areas mostlycomprises of shallow water aquifers, which are usually at high risk to contamination by means of seepage of contaminated water through the soil. Industrial effluents and agricultural activities are major contributors to water contamination. In studied areas of Punjab; Sheikhupura, Lahore, Raiwind, Mangamandi, Kasur, Gujranwala and Faislabad, samples were collected from different points and from shallow water. This water is being used for drinking purpose. Analysis showed that concentration of few organic and inorganic contaminants were above the permissible limits set by WHO and U.S. EPA while rest compounds were within the palatable limits. DDT, DCP, TCP were observed above the maximum contaminant level pose severe danger to human health but remaining within the limits. Continuous increase of contaminants into groundwater would result in contamination of soil and groundwater and it will make the resource unusable. Therefore keeping in view the scarcity of water in country and contamination of water resources is unbearable. Hence it is obligatory to restore the quality of groundwater unless it becomes difficult to treat. Furthermore consumption of contaminated drinking water has severe health impacts on human, animals and ecosystem. Contaminated drinking water can cause dysentery, diarrhea, hepatitis and chronic diseases: cancer , respiratory problems, nervous system dysfunction, mental impairment, kidney problems, skin problems etc. Therefore apt treatment of contaminated water is pertinent and to manage the water resources sustainably to prevent any hazard to precious resource of water.

3.8. Recommendations:

- Pak EPA and all other environment regulatory authorities need to do proper legislation regarding industrial effluents discharge into water bodies without prior treatment
- Ensure laws implementation at each level whether large or small industry
- Prevent use of toxic and banned compounds in agricultural and industrial activities
- Set heavy fines and strict penalties to violation
- Raise environmental awareness related to banned chemicals/ compounds and excessive use of chemicals and their toxic effects on human health
- Cemented wastewater drains to prevent seepage
- Develop and implement remediation techniques for the removal of toxic compounds from groundwater and ensure the protection of aquifers
- Provide safe and drinking water to local people living near/or adjoining wastewater drains and industrial areas.

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