GEOSPATIAL ANALYSIS OF GEOGENIC CONTAMINATION OF ARSENIC AND FLUORIDE IN THE DRINKING WATER RESOURCES OF PAKISTAN AND ITS IMPLICATIONS FOR HUMAN HEALTH

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FINAL APPROVAL

This is to certify that the research work presented in this thesis, entitled **"Geospatial Analysis of Geogenic Contamination of Arsenic and Fluoride in the Drinking Water Resources of Pakistan and its Implications for Human Health"** was conducted by **Ms. Bushra Ghaffar Reg # 05/FBAS/PhDES/F13** under the supervision of Dr. Syeda Maria Ali. This thesis is submitted to the Department of Environmental Science after receiving "Pass" comments by two foreign evaluators and acceptance of the Doctoral Advisory Committee, in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Environmental Science. No part of this thesis has been submitted anywhere else for any other degree.

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بِسْمِ اللَّهِ الرَّحْمَٰنِ الرَّحِيمِ

IN THE NAME OF ALLAH,

THE MOST GRACIOUS AND

THE MERCIFUL

DEDICATION

I dedicate this effort to my husband, parents, father-in-law, elder brother Ch. Akbar, siblings, friends, and respectable teachers, who sometimes believe in me more than I do.

DECLARATION

I, *Bushra Ghaffar*, a Ph.D. candidate in the Department of Environmental Science enrolled under registration No. 05-FBAS/PHDES/F13, at this moment declare that the knowledge contributed by analyses of data collected and results derived to draw the conclusion presented in this thesis titled "*Geospatial Analysis of Geogenic Contamination of Arsenic and Fluoride in the Drinking Water Resources of Pakistan and its Implications for Human Health*" is own original work and has not been submitted as research work or thesis in any form in any other university or institute in Pakistan or abroad for the award of any degree. However, three research articles from this research thesis have already been submitted, and a couple more are in the submission process.

Bushra.

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LIST OF ABBREVIATIONS

UN	United Nations
UNEP	United Nations Environment Program
UNDESA	United Nations Department of Economic and Social Affairs
IFPRI	International Food Policy Research Institute
ICPC	Independent Corrupt Practices & Other Related Offences Commission
As	Arsenic
F	Fluoride
WHO	World Health Organization
UNICEF	United Nations Children's Fund
IUCN	International Union for Conservation of Nature
PCRWR	Pakistan Council of Research in Water Resources
GIS	Geographic information systems
TDS	Total Dissolved Solids
Pak-EPA	Pakistan Environmental Protection Agency
EBK	Empirical Bayesian Kriging
OK	Ordinary Kriging
RBF	Radial Basis Function
WQI	Water Quality Index
ANOVA	Analysis of variance
WoS	Web of Science
VOS	Visualization Of Similarities
KP	Khyber Pakhtunkhwa
mg/L	Milligram per liter
µg/l	Microgram per liter
ppm	Parts per million
ppb	Parts per billion
EC	Electrical Conductivity
NEERI	National Environmental Engineering Research Institute
NF	Nano Filtration
RO	Reverse Osmosis
dc	direct current
BTEX	benzene, toluene, ethylbenzene and xylene
WAPDA	Water & Power Development Authority
EUAD	Environment and Urban Affairs Division
APHA	American Public Health Association
EDTA	Ethylene diamine tetra acetic acid
PCA	Principal Component Analysis
OWQI	Oregon Water Quality Index
DEQ	Department of Environmental Quality
NSF	National Sanitation Foundation
CWQI	Canadian Water Quality Index
IDW	Inverse distance weighting

Al	Aluminum
Ca	Calcium
Cl	Chloride
Mg	Magnesium
NO_3	Nitrate
SO_4	Sulfate
ISO	International Standards Organization
S.D	Standard Deviation
Min.	Minimum
Max.	Maximum
mEq/L	Milliequivalents per liter
MLR	Multiple Linear Regressions
ICP-MS	Inductively Coupled Plasma Mass Spectroscopy
QC	quality control
SSoP	Soil Survey of Pakistan
GSP	Geological survey of Pakistan
FAO	Food and Agriculture Organization
PSQCA	Pakistan Standards & Quality Control Authority
ROS	reactive oxygen species
HAP	hazardous air pollutants
USGS	United States Geological Survey
SRTM DEM	Shuttle Radar Topography Mission Digital Elevation Model
PMD	Pakistan Meteorological Department
LULC	Land use Land cover data
AHP	Analytical Hierarchy Procedure
MCDA	Multi-Criteria Decision Analysis
RS	remote sensing
WOA	weighted overlay analysis
CR	consistency ratio
RI	random index
PFC	Perspective Fluoride Contamination
GW	Groundwater
SDGs	Sustainable Development Goals
VOCs	Volatile organic compounds
CDI	Chronic Daily Intake
HQ	hazard quotient
HI	hazard index
CR	carcinogenic risk
USDOA	United States Department of Agriculture
USNRC	United States National Research Council
RfDs	reference doses
SFs	Slope factors
RI	Risk index
IM	Integrated management
UV	Ultraviolet
HFO	hydrous ferric oxide

TOC	total organic carbon
TICB	TiO_2-impregnated chitosan bead
NOM	natural organic material
ARD	Arsenate respiring bacteria
PR	pipe reactor
PR-MF	pipe reactor microfiltration
MRL	method reporting limit
ZVI	Zero-valent iron
AA	activated alumina
RO	reverse osmosis
MCL	Maximum Contaminant Level
ICOH	Intercountry Centre for Oral Health
IISc	Indian Institute of Science
GAC	granular activated carbon
SDPs	Sustainable Development Programs
NGOs	Non-Governmental Organizations
FA	Factor analysis
DSS	Decision Support Systems

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Bushra.

Bushra Ghaffar

ABSTRACT

Evaluation of groundwater resources is essential for sustainable utilization of water for drinking, agriculture, and industrial purpose. The present study highlighted the high-risk areas containing arsenic (As) and fluoride (F) throughout Pakistan through predictive models and validated through groundwater data samples. Hotspot areas were identified regarding As and F distribution in Pakistan. In total, 1573 representative groundwater samples were collected. Spatial distribution models were produced using Inverse Distance Weighting (IDW) interpolation and a knowledge-driven Analytical Hierarchical Process (AHP) based Multi-Criteria Decision Analysis (MCDA) in ArcGIS. Multivariate statistical analysis i.e., Factor Analysis (FA), Correlation Analysis (CA), and Principal Component Analysis (PCA) were performed for source identification. Gibbs plots and piper charts were plotted to show rock water interaction and water types respectively.

The results of the present study highlighted that water chemistry is primarily impacted by geogenic sources, but the role of anthropogenic activities also contributed to the pollution of groundwater resources. As and F spatial models indicated that groundwater in upper and lower Indus Plain is extremely polluted due to geologic conditions. Gibbs plots highlighted that groundwater samples fall in the rock dominance region while the piper trilinear chart revealed that groundwater belongs to $CaHCO_3$ water types.

The geological and geochemical processes are the primary sources of As and F in groundwater also anthropogenic pollution sources such as industrial wastes significantly contribute to the problem. The geological, hydro-chemical, and climatic conditions contribute to the enrichment of the pollution-causing elements in an aquifer. Many biogeochemical processes, particularly those of soluble minerals in As-rich soils, have been identified as the cause of As in groundwater contamination, while weathering of granitic rocks causes F to seep into the environment. Additionally, evaporation, dissolution, precipitation, adsorption, co-precipitation, ion exchange, oxidation-reduction, and the aquifer's nature have been identified as contributing to the contaminants' availability in groundwater.

The concentrations of water and As vary due to a variety of factors, including redox potential (Eh), adsorption/desorption, precipitation/dissolution, As speciation, pH, competing ions, and biological transformation. The adsorption and desorption reactions, As species, Eh, pH, and solid-phase dissolutions and precipitations all vary according to the aquifer characteristics. Fluoride dissolution and solubility in groundwater are dependent on a variety of factors, including the level of calcium and sodium hydroxide in groundwater, geographic location, groundwater retention time, pH, depth, and temperature. At a pH of 5, F ions can form complexes with metal ions. At high pH values, the F ion predominates in water.

The study revealed that like other Southeast Asian countries including India, Bangladesh, China, and Vietnam, Pakistan also has a serious threat from As and F

contamination in drinking water sources which most of the people are getting from groundwater sources. Long-term exposure to these deadly poisons may cause cancer risks along with other diseases like skin lesions, neurological, reproductive and, cardiovascular diseases results from As contamination. In contrast, the excess of F causes dental and skeletal fluorosis, Alzheimer's disease, and forms of dementia.

The WQI results show that the groundwater quality in Sindh province is not drinkable in Thar parker and Nagarparker, very poor in Umer Kot, Jacobabad, Shiakrpur, Larkana, and Badin, and poor in Sanghar. Whereas in Punjab province very poor in Khushab, Jhang, and Faisalabad and poor in Mandi Bahauddin, Sargodha, and Hafizabad. While in Balochistan the water quality index showed that the water quality is poor in Barkhan, Dera Bugti, Jafarabad, Nasirabad, Jhal Magsi, Kalat, Mastung and Killa Saifullah, Khuzdar, Lasbela, Awaran, Punjgur, Kharan, Chaghai and very poor in Bolan, Sibi and Loralai. Among these, 37.98% of samples demonstrated excellent water quality, 41.22% percent demonstrated good water quality, 16.79% percent demonstrated poor water quality, and 2.29% and 1.72% percent demonstrated very poor water quality and water unfit for drinking purposes, respectively.

The present study observed the highest concentrations of As (150 μg/l) in Jhang, Okara and Faisalabad followed by Patoki (130 μg/l) and Pindi bhattiyan (Hafizabad) (120 μg/l) in Punjab province. Whereas in Sindh province the highest concentration was reported in Jam Nawaz Ali (Sanghar) and NARA Khair Pur i.e. 500 μg/l followed by Sinhjoro (475 μg/l), Kot Digi (450 μg/l), Shikarpur and Khipro (Sanghar) (400 μg/l), Rato Dera (Larkana) (375 μg/l), Khanpur (Shikarpur) and Shahdadpur (Sanghar) (350 μg/l) and Mirpur Mathelo (Ghotki) (300 μg/l).

Most of the areas in KP and the Indus river plain (Punjab & Sindh) is showing the medium F tendency which can become high in future whereas some part of KP in north and the Balochistan province is showing the both medium F tendency in some areas as well as low. In the PFC expanse, the category 'medium' accounts for 36.39% (or 346762.38 Km^2) followed by 'low' 63.42% (or 604324.78 Km^2) and 'very low' 0.195% (or 1856.68).

Decision support tools provide a way for water management authorities to analyze and resolve difficult problems that include geological, financial, legal, and environmental factors. While open-source water management models are becoming more prevalent, the use of Decision Support Systems (DSS) or collaborative processes is a rarity. The benchmark environmental data can be utilized by decision makers, policy makers and stakeholders for urban groundwater management in Pakistan and other regions facing similar issues. Additional information is required on As and F pollution in Pakistan's subsurface aquifers. While conventional data are abundant, country-specific data are scarce. Countrywide sampling produces scant concrete evidence. Additionally, the project sought to develop simple and low-cost methods for lowering As and F levels in groundwater, thereby reducing disease burden. Water treatment technology is currently prohibitively expensive, complex, and incapable of supporting a large population. Pakistan must develop a framework of action in order to grow. Pakistan's drinking water currently contains 50 g/l As. Current policies should benefit future generations, whom emerging technologies will benefit. The policy mix includes dams that replenish depleted underground water supplies. Intergovernmental committees will examine and update water policies and future course of action. Eliminating conflicts of interest facilitates policy stagnation. It is critical to streamline funding for research and development aimed at reducing As and F levels in drinking water. Additionally, this would aid in the development of critical data for pollution mitigation policy development.

CHAPTER-1

INTRODUCTION

1.1 General Introduction

Water is vital to life, and every human should have access to clean water. Universal access to water and water quality is an important goal of the UN-Water 2050 Agenda to the Water for all by 2030 Initiative. At least a million people per year die of water-related diseases (Ritchie *et al.*, 2018) because of inadequate sanitation and innovation, particularly due to a dearth of planning. Water, the leading risk factor in health care for two billion people, can be hard to come by for over 2 billion people around the world (Ritchie *et al.*, 2018).

The desire for water is expected to rise until the year 2050, with a compound population growth. The demand for water is predicted to rise by an additional 1% per year globally due to population growth and increased use of water, among other contributing factors. Industrial and domestic demand for water would surpass agricultural demand, despite being the highest globally. Much of the growing water use would be in the industrialized and developing nations viz Pakistan, India, China, Bangladesh etc. Since the early 1990s, water contamination has spread effectively in rivers worldwide (UNEP, 2016a). Water quality is likely to deteriorate even further in the future, increasing the unavoidable industrialization health hazard, the climate, and to include the poor health of natural resources and production.

Worldwide water use has expanded by a factor of six to some extent recently with a 1% yearly increment (Wada *et al.*, 2016; AQUASTAT, n.d.). The global growth, economic development, and rising patterns of consumption are significant factors regarding growing water demand. In 2017, there is a projected global population growth of 7.7 billion, with two thirds of urban population expected to rise from 9.4 billion to 10.2 billion by 2050. Africa (1.3 billion) is anticipated to have more than a half of its estimated rise with Asia expected to make the second major possible contributor (+0.75 billion) to increasing population (UNDESA, 2017).

Burek *et al.,* 2016 in his findings concluded that the current worldwide water demand is projected at about $4.6e^{+12}$ m3 per year and is expected to grow by 20%-30% to between $5.5e^{+12}$ and $6e^{+12}$ m3 per annum by 2050. Water quality is deteriorating in almost all rivers in Asia, Africa, and Latin America since 1990 (UNEP, 2016a). The threats to human health, the environment, and sustainable development will intensify over the next few decades as water quality deteriorates (Veolia/IFPRI, 2015).

In order to assure water availability, we must find alternate sources of supply (Witek and Jarosiewicz, 2009). Owing to over-pumping, urbanization, industrial use, and irrigation, fresh water supplies are becoming scarcer and less plentiful worldwide. This is a significant health hazard where ground water and drinking water come from (Kumar, 2004).

Countries around the world including Egypt, Libya, Syria, Iran, Afghanistan, Pakistan, Northern India, China, and Indonesia are struggling with water pollution issues (Brindha and Elango, 2011). Most of these countries rely on groundwater for domestic use and drinking. Globally, half of the population is bound to rely on groundwater for daily sustenance.

Many pathogens may be eliminated from groundwater, but its chemical content may be compromised by natural contaminants in the aquifers. In general, the chemical composition of groundwater is influenced by the pH, oxygen content, salinity, and contaminants in the aquifer rocks and sediments. Contaminants will become ample in the ground water if they are capable of accumulating in the earth's crust, like F, or they will be confined if they are harmful, like As (Ravenscroft *et al.,* 2009). According to an ICPC press release, both As and F pose a significant threat to human health worldwide, including infertility, skin cancer, and neurological diseases.

The strain on the resources of industry, urbanization, and population growth have left Pakistan with huge needs for water. Water is critical in all aspects of life, including growth and development (Postel, Daily and Ehrlich, 1996). Because of technical advances, drinking water can be tested for impurities which can be physical, biological, or chemical. Biological impurities are the most destructive to humans and to their wellbeing (Soomro and Khokhar, 2011).

Industrial or household wastewater is released into streams, lakes, rivers, and reservoirs where bacteria and harmful chemicals find a home. Fecal bacteria can be found in the water from humans and livestock. With the rainy season, bacterial growth and expansion happen at their maximum levels (Arora, 2007). Parallel drinking water and drainage lines result in the loss of water quality. Researchers estimated that 2.5 million people die from waterborne diseases per year because of pathogenic bacteria and protozoan parasites in groundwaters of Pakistan (Byass *et al.*, 2011).

According to Pakistan Agriculture Scientists Association, available water per person in Pakistan fell by 406% between independence until 2010 i.e., from 5,260 to 1,038 cubic meters (Hussain, 2012). If nothing is accomplished, the water supply in Pakistan will be reduced to 660 in 2025, and then to a level of 550 cubic feet by 2050 (Mustafa, 2012).

In Pakistan, the supply of current water is about 79% (Chilton *et al.*, 2000). The public's health is threatened due to inadequate and poor water supply. The water quality is degrading because of hazardous chemicals from urban locations and factories are being released into waterways without treatment, which can harm both people and the environment. Considering rising water requirements, it has had attempted to give greater attention to the supply of water and not the quality of water. Lack of funding, customer knowledge, facilities, infrastructure, and treatment techniques can be the possible reasons. (Aziz, 2000).

Water pollution is a worldwide issue. A vehicle for various pathogens may be found at the water supply, in the distribution network, as well as at the individual level. A large percentage of the population in poor nations is ignorant of basic sanitary procedures due to a lack of knowledge among varying degrees in different societal levels. (Bedada *et al.,* 2018)

The WHO report stated that up to 80% of all illnesses and diseases worldwide are water related, which results this number at conservatively 78 million people globally get water from unimproved sources, with the figure for surface drinking. Approximately 1.3 billion people receiving water from unwholesome and almost 2 billion people using fecal-contaminated water. According to the UNICEF to expand on this, we might claim that in developing and less developed countries, there are a large percentage of facilities lacking modern sanitation and handwashing facilities as well as usable water (WHO and UNICEF, 2017).

Pathogens, bacteria, and minerals, as well as various chemicals from polluted water negatively impact human health. Most people in developing countries suffer from poor water quality and microbiological pollution. There were five million children who died due to polluted drinking water supplies in the Third World, mostly in developing countries (Huang & Xia, 2001). If the population grows, so will the number of severe water pollution problems. (Huang & Xia, 2001; Van Leeuwen, 2000; Gale, 2000).

These two factors lead to widespread water-borne diseases in Pakistan: urban and industrial wastewater disposal, and the lack of water treatment and regulation of water quality. Aziz *et al.,* 2000, found that 40% of the communicable diseases can be traced to poor water quality. Pakistan has all kinds of water-related diseases, including typhoid, giardiasis, parasites, and diarrhea, all of which include cryptosporidium infections, along with others. The highest rate of infant deaths in Asia due to water-related diarrhea is around 60 percent according to the IUCN, like the rest of the world (PCRWR, 2005). Over 1 billion people have no access to potable water because of water-related illnesses, while another 2.5 billion lack adequate sanitation, and approximately 0.005 billion die annually due to waterborne diseases (Waghmare *et al.,* 2015; Hinrichsen and Tacio, 2002).

Many people believe that the quality of water in Pakistan is unsuitable for drinking. According to numerous national estimates, only 57% of Pakistan's total population has access to safe drinking water. (Ullah *et al.*, 2009; Farooqi *et al.*, 2007a).

Natural factors influence the composition of the drainage basin (geological, geographical, meteorological, hydrological, and biological) according to seasons and runoff volumes. As a result of human activity, anthropogenic factors also affect water quality. The raising of dams, removal of wetlands, and the slashing of water flow has a complex impact on water quality. Polluting practices, such as the deliberate or accidental dumping of domestic, commercial, municipal, and other wastewaters into watercourses, and the distribution of chemicals on agricultural land in the drainage basin, are more evident. Water quality is impacted by various conditions, including natural and human influences. The geological, hydrological, and climatic factors are the most significant natural influences since they have an influence on the amount and quality of water available. Even though the natural ecosystem is in tune with natural water quality, any major changes in water quality will potentially disturb the ecosystem.

Pakistan's flat land plains in the Indus River Valley, Karakoram, Hindukush and Himalayan ranges in the north, as well as in the west Baluchistan region, and uplands in the north-west set the country's climate, which is mostly arid to semi-arid, while temperate in the north-west (Bhowmik *et al.*, 2015). The occurrence of Holocene sediments transported into arid and semi-arid zones by alluvial deposits, and the resulting As contamination due to desorption in oxic aquifers, are one of the core causes of ground water contamination in many parts of Pakistan (Farooqi *et al.*, 2008; Amini *et al.*, 2008). Furthermore, both ground and surface sediments in water are rich in micas, which are subjugated by the mineral biotite, which is comprised of As and releases As at high pH levels. Additionally, Himalayan surface water erodes As-rich sediments, resulting in elevated As levels downstream (Husain *et al.*, 2012).

For normal bone mineralization and formation of dental enamel, F is required in minute quantities (Bell, 1970). It is mainly found in fluorspar (CaF_2), sellaite (MgF_2), [$3Ca_3(PO_4)_2$ $Ca(FCl_2)$] and cryolite (Na_3AlF_6). In sedimentary rocks it is found as a fluorescent mineral and in igneous rocks as a cryolite. Fluorides may be contained in soil water only if they are dissolved or when high F effluent is discharged from industry to water systems (Mohapatra *et al.*, 2009).

Since a few decades, scientists have discussed several concerns related to pollution status, but the emphasis on management of these issues has been ignored. Different techniques have been used around the world to reduce pollutants in the atmosphere, but in the modern era, with the advent of technologies such as Geographic information systems (GIS), one recent approach is the development of predictive risk maps.

One of the main goals of these risk maps is to create digital images of the polluted areas of concern, as well as asses the upcoming patterns and potential hot spots (Lahr and Kooistra, 2010). In a country like Pakistan, where the magnitude of the problem is high and resources are scarce, there is an urgent need for attention to be concentrated on these issues. GIS and remote sensing techniques, as well as other spatial interpolation approaches, for monitoring pollution of natural resources such as surface and ground water (a finite resource), makes this role even more practical (Balakrishnan *et al.*, 2011; Ducci, 1999). As a result, risk mapping is thought to be an appropriate method that combines both geographic and attribute data to provide us with a clearer understanding of contamination severity, exposure paths, and causative effects (Picado *et al.*, 2010; Diallo *et al.*, 2009).

However, countries like Pakistan that face higher-than diversified environmental compartments must establish sustainable baselines in order to succeed in exploration and environmental management (Xie *et al.*,2011; Leonardo *et al.*, 2007). In today's research, point automatic-collecting models are used to determine both chemical and physical characteristics. Remote sensing is another technique that is used to examine land, geomorphology, atmosphere, and unsaturated zone characteristics. The management of these data relies heavily on GIS databases. The storage of data entails several aspects, including evaluation, computational data modelling and presentation.

The escalation in restricted number of data attributes and sample locations is a major weakness in hydrology. The solution that hydrologists normally employ is adequate interpolation, in which point data is modelled using algorithms. Due to this combination of regional factors, as well as data, it is commonly believed that monitoring for As and F contamination works most effectively (Dassargues, *et al.*, 1999; Steyaert & Goodchild, 1994).

To alleviate the severe As and F pollution in Pakistan, developing spatial interpolation techniques should only be the first step. The initiative should be accompanied by the development of a long-term geo-database that is better positioned in terms of As and F pollution control and monitoring. Though hundreds of international risk-mapping papers have been published so far (Lahr & Kooistra, 2010; Nas & Berktay, 2010; Ducci, 1999 ; Ahn & Chon, 1999; Singh & Lawrence, 2007), there are unfortunately limited data available in Pakistan, and so far, limited studies have been carried out concerning spatial risk mapping methods for screening As and F toxicity in groundwater resources (Podgorski *et al.*, 2017).

One of the most pernicious issues afflicting people all over the world is inadequate access to safe drinking water. Water shortages are likely to worsen in the coming decades. Addressing these concerns necessitates a considerable amount of research to find robust new methods of purifying water at a lower cost and with less resources, while also minimizing the use of chemicals and their detrimental effects on the environment (Mark *et al.*, 2008).

In short, the quality of drinking water can't be improved by dealing with the problem at the cause. Since it is such a critical natural resource, there is therefore a desperate need to track the quality of groundwater frequently.

1.2 Problem Statement

In Pakistan, shallow ground water is being contaminated with As and F reporting health related problems. In the present study, I focused on the primary geo-spatial database for the presence of As and F in Pakistan to help reduce and mitigate the problem. In order to protect people from water-borne diseases, revolutionary household sand filters, containing low cost adsorbents available locally, which comply with standards on drinking water quality, are strictly essential. Pakistan requires long-term, low-cost solutions to address these issues in the current environment. Adsorption is a low-cost method of treating water and wastewater. The use of locally available, low-cost, and efficient adsorbents such as agricultural wastes and clay minerals would significantly improve current water and wastewater treatment practices. For Pakistan, low-cost adsorption technologies combined with membrane filtration techniques for point-of-use water treatment should be investigated. Recent advancements in membrane technology have made it more viable, but it remains expensive, particularly for sea water desalination. However, due to its non-specific removal of a wide variety of contaminants, membrane technology is gaining rapid acceptance in commercial applications. Nanofiltration, membrane distillation, microfiltration, reverse osmosis, ultrafiltration and forward osmosis, all utilize membrane technology. Reverse osmosis is of interest in areas where the ground water is saline, or the TDS level exceeds Pak-EPA guidelines.

1.3 Hypothesis

We hypothesize there is a negative association between Geogenic contamination of As and F in drinking water and the health of exposed population.

1.4 Novelty

In the present study, the degree of contamination in groundwater by As and F and the extent to which population has been exposed has been addressed keeping in view the need of it on an urgent basis. Predictive modeling has been done to highlight the hotspot areas so that protective measures could be taken.

1.5 Significance of Study

The land of Pakistan has been bestowed with natural resource of ground water. Urbanization and increasing population have great impact on water reserves. The most breathtaking impurity is of biological and inorganic nature which is hazardous to health. There is no access to safe drinking water to most of population in Pakistan. The geochemistry of the area makes it susceptible to be contaminated with As and F which evidently has many health impacts.

1.6 Aim of Study

The aim of study is to generate baseline data for As and F and highlight hotspot areas with an impact on health.

1.7 Objectives of the study:

1. To predict the extent of geogenic contamination of As and F by using statistical distribution model in drinking water resources of Pakistan.
2. To assess the carcinogenic and non-carcinogenic health risks from As and F contamination in Pakistani population.
3. To compare the performance of existing As and F mitigation techniques in reducing the contamination in drinking water.

CHAPTER-2

REVIEW OF LITERATURE

2.1 Introduction

Arsenic is a water toxin that causes natural distress in millions of people around the world. It is found in aquifers and causes adverse effects under natural conditions. South and Central Asia, as well as South America, are potential water insecure regions with the greatest risk.

The study conducted in El-Outaya region, Algeria in 2021, revealed that the groundwater contamination is the significant issue for water consumer, managers and decision makers in the field of water resources. Stochastic and deterministic methods were employed based on the Empirical Bayesian Kriging (EBK), Ordinary Kriging (OK), and Radial Basis Function (RBF) with multi-quadratic function, which helped to predict the spatial distribution and risk assessments. The findings showed that all of the techniques were accurate, which were helpful in predicting the contamination levels at unmarked places (Boudibi *et al.*,2021).

Antilin *et al.*, 2021 in his study in district Kerala, India, assessed the quality of drinking water as well as the water used for irrigation purposes. The physiochemical parameters, of the samples collected from bore wells, were performed to assess the water quality. The findings demonstrated the water as safe and good for drinking and irrigation purpose.

The spatial and temporal quality of groundwater in the Grombalia basin aquifer in Tunisia North Africa was analyzed by Slama *et al.*, in 2020. Some physical and chemical parameters were measured from collected samples and the analysis was performed in GIS. The water quality, degree of salinization, and rate of deterioration were all measured. According to this study water was good for irrigation purpose and 28% water samples were safe and good for irrigation and drinking purpose.

In South Africa, the researchers assess the groundwater quality of Luvuvhu catchment, Limpopo (Elumalai *et al.*, 2020). The physicochemical parameters were done to assess the sustainability of groundwater for drinking and irrigation purpose. The groundwater of Luvuvhu catchment was found good for drinking and irrigation without any filtrations.

The groundwater quality evaluation for drinking was conducted in Iran on Behesht abad Basin, Chahar mahal and Bakhtiari Province by Gharahi & Zamani-Ahmad mahmoodi, in 2020. This study includes all the long-term data on heavy metals concentration in Iran's spring water to determine if it is suitable for drinking. The water from five springs were extracted. The physicochemical characteristics and heavy metals were analyzed in collected samples. The values were checked against WHO levels for determining its safety and suitability for domestic use. The findings showed that most of the groundwater samples are drinkable. But spring waters are polluted by bacteriological substances during the rainy season and unfit to be used by the community. The Water Quality Index (WQI) for some groundwater samples of the predominant area of rocks and salt dissolution from the rock into aquatic resources was important criteria for the determination of the quality of drinking water in this research., which may represent a major risk to the ecological habitat.

Adimalla *et al.*, 2018 concluded in their study which was done in Telangana India, that the majority of the central areas of Telangana is fed by groundwater. The research was focused on the quality of groundwater being used by local community for drinking and irrigation. Urbanization, population growth and industrialization have deteriorated the groundwater. A total of 105 groundwater samples showed that the groundwater is unsuitable for drinking purpose due to raise of F and NO_3 concentrations.

A study in Algeria in Oued El Hai Basin to determine the quality of water using a fuzzy inference method (Tiri *et al.*, 2018). Three stations and water parameters were chosen which showed Ca and SO_4 as the most abundant ions. TDS was inversely proportional to SO_4 and HCO_3. According to the ANOVA test, there were no major variations in the temporal variance of all parameters excluding potassium and calcium. Surface water is mostly impacted by anthropogenic processes and water/rock interactions.

Daud *et al.,* reviewed the drinking water quality status of Pakistan in 2017 and observed that water quality in the country is declining daily as a result of over population and industrialization. In Pakistan, approximately 20 percent of the population has access to the water which is healthy for drinking, while about 80 percent of the population were compelled to consume unsafe drinking water due to a lack of clean and stable drinking water sources. The key source of pollution in drinking water is feaces. Secondary contamination is caused by industrial wastewater, pesticides, and fertilizer runoff from agriculture, problems caused by humans, about 80% of all illnesses, which account for about 33 percent of all deaths worldwide. This is a critical look at the water quality on the hygiene, pollution sources, and any health problems that result from it. There is an urgent need to treat the problem in Pakistan, particularly in areas where dysentery is common.

Access to clean drinking water is imperative. The As concentrations and coliform bacteria were found above the permissible limits given by WHO in the study carried out in Lahore, Pakistan by Shahid *et al.,* in 2015. The water samples of this study were collected from hostels of Punjab University Lahore. Standard techniques have been used to quantify physical, biological and chemical pollutants.

In another research study conducted in Tamil Nadu, India which was led by Krishna et. al. in 2014 revealed that based upon the findings of the WQI, most of the samples were excellently classified and suitable for drinking water use. Twenty-four different water samples were taken and analyzed viz. pH, conductivity, calcium, magnesium, bicarbonate, sodium, potassium, total dissolved solids, and sulfate. In the groundwater was relatively fresh and moderately hard. Both sodium and chlorine are the dominant ions. Chloride, magnesium, and calcium ions are under the prescribed limits. Samples fall within the rock–water interaction dominant zone and evaporation dominance zone in Gibbs diagram. The trilinear pipeline diagram in their study reveals the Na–Cl and Ca-Mg-Cl combined groundwater samples.

The breakthroughs that came about due to the introduction of water contamination like As, mercury, and lead, are supposed to bring about various remedies. Therefore, people in underdeveloped areas around the world are faced with this potentially life-threatening problem (Azizullah *et al.*, 2011; PCRWR, 2005).

Pakistan, as a developing region, is also attempting to combat the challenges of drinking water scarcity and elevated groundwater pollution. In Pakistan, fresh water sources, including both shallow and deep ground water, are the sole source of drinking water supplies (Malik *et al.*,2010; Baig *et al.*,2009). The water quality of freshwater supplies and groundwater aquifers in Pakistan has degraded as a result of anthropogenic and geogenic activities with high levels of As concentrations (Khan *et al.*, 2012; Azizullah *et al.*, 2011).

According to WHO, unsafe drinking water is the leading cause of death for more than 5 billion people worldwide per year (WHO, 2002). Developed nations have experienced outbreaks of waterborne illnesses like Japan, Canada, the United States, and the United Kingdom in recent years (Hrudey, 2004). However, the use of ground water resources for analysis of As is costly and time-consuming, and so many regions have yet to be evaluated. As a result, combining geological and surface soil parameters to create maps is a promising approach for predicting groundwater As pollution (Winkel, 2008).

The chance of pollution is likely to be high as an aquifer could be increasingly vulnerable to contamination. This is particularly the case if the emission is loaded significantly. Conversely, while an aquifer is less susceptible to contamination, there may be a less risk of pollution. This is the case when there is an extraordinary load of pollutants. Pesticide risk factor dissolution refers to the possibility that toxic chemicals can migrate through the soil and enter the groundwater (Huddleston,1996).

Pakistan's leaching capacity is an important factor in terms of soil permeability, water and hydraulic charges. Pakistan's vulnerability assessment mainly defines its ground water risk, based on the corporeal features of the aquifer and the vadose region, and the incidence of likely sources of pollution.

Owing to the increase in the threat of As and F in the water supply, groundwater is increasingly at risk. Because of the increased risk of leakage, water contamination needs continuous monitoring to establish quantitative estimates of As and F toxicity. Another issue with As and F control which is highly disputed is the failure to provide firm guidelines for how much of each compound is allowed.

In the case of United States Congress, established a 50ppb drinking water requirement in 1942, which has resulted in a request for an independent investigation (Reynolds, 2010). Unlike the previous standard, which lowered cancer risk to one in every 100 people, the new standard raised the ratio to one in every 500 people. However, this did not end the controversy about appropriate standards, with some researchers suggesting that the earlier estimate of 1:100 was underestimated, and that the true estimate for the 50ppb norm was estimated at one in every 1000 (Reynolds, 2010).

Polluted groundwater reduces the natural water quality. According to Todd (1980), one distinguishing characteristic of groundwater contamination from surface water pollution is that it is becoming increasingly difficult to detect. Consequently, groundwater contamination could go unnoticed for many years. The susceptibility of groundwater to contamination is often a product of a combination of factors. Additionally, there are also other important factors. The setting is the controlling function that influences the amount of time that water sips through the soil from the time it first falls as rain to the time it reaches the water table and begins its natural flow to its current position (Prior *et al.,* 2003).

In Pakistan, like everywhere else, ground water is contaminated due to human activities above an aquifer. This conceptual model has been around since the 60s, but hydrologists have yet to arrive at a consistent description for how vulnerable aquifers are. Vrba and Zaporotec (1994) provided the most accurate description, explaining that aquifer vulnerability refers to the term by which hydrologists represent the intrinsic features of aquifer systems as a result of their sensitivity to both natural and human characteristics. Groundwater vulnerability is most generally measured in terms of aquifer capacity. In this way, societies benefit from a method that allows them to literally imagine pollution.

2.2 Bibliometric review on Arsenic

Bibliometrics or Scientometrics is an informatics technique for visualizing scientific data (Cobo *et al.,* 2011). This valuation methodology demonstrates systemic and complex scientific research's facets tendencies quantitatively for the definite time period (Liu and Gui, 2016).

Bibliometric analysis is a commonly accepted statistical tool to show the information structures of an explicit research field (Cooper, 2015; Gisbert and Panes, 2009; Wallin, 2005). This has produced significant interest in various scientific fields over recent years. There have been a few recent reviews of As pollution in groundwater, but no comprehensive research has yet been performed or published on As contamination in groundwater. Earlier, the bibliometric study on the As contamination was published in Spain which use Web of Science (WoS) database to collect the data from the year 1992 to 2012 and were limited to As in drinking water (Abejon and Garea, 2015).

This framework brings together various techniques in a coherent and practical way (Govindaradjou and John, 2014; Neff and Corley, 2009;). These structures provide systematic analysis and assessments which helps to explain the major advances in the area of interest. It allows investigators to interpret the effects of interdisciplinary trajectories on the leading means of investigation. This analysis is usually supportive in claiming on evolving paths in various research directions

(Yu *et al.,* 2014). To examine evolutionary trends and current developments in various fields of knowledge similar methodologies have been used (Atif *et al.,* 2018; Liu and Gui, 2016; Eito-Brun and Rodríguez, 2016; Mishra *et al.,* 2016).

2.2.1 Data source

With the help of the Scopus database, published articles by a topic search (abstract/title) were retrieved on 19 September 2020. In contrast to previous bibliometric studies on As contamination, the current analysis used the Scopus database without restricting the results to any particular field of search. Scopus was chosen as a bibliometric resource in our study because, in comparison to PubMed or Web of Science because it is home to the world's largest database of abstracts and citations to peer-reviewed scientific literature (Paul-Hus and Mongeon, 2015; Falagas, *et al.,* 2008)

With the help of VOS viewer software, the Bibliometric analysis was performed, and the study arrayed the top journals, countries, institutes and authors networks along with the co-occurrence, co-authorship and co-citation analysis. This technique helped to identify networks of countries, collaborating organizations, sources and citations. This enables the elucidation of related things while maintaining network maps through Label ID's and Links (Smedley and Kinniburgh, 2002). The size of the Label ID indicates the degree of significance of the effects (Mandal and Suzuki, 2002). This is an example of using the information concept of focal nodes to display keywords, authors, and sources.

The technique is considered reliable (Fendorf *et al.,* 2010) and was deployed to analyze the spatiotemporal disparities of groundwater As in South Asia and Indochinese Peninsula. To grasp the rapidly changing research areas in the field of arsenic, the "keyword co-occurrence analysis test" was subsequently used. The study's purpose and scope are concisely defined, as well as the methods used to collect data, data sources, and factual assessments are also presented in figure 2.1.

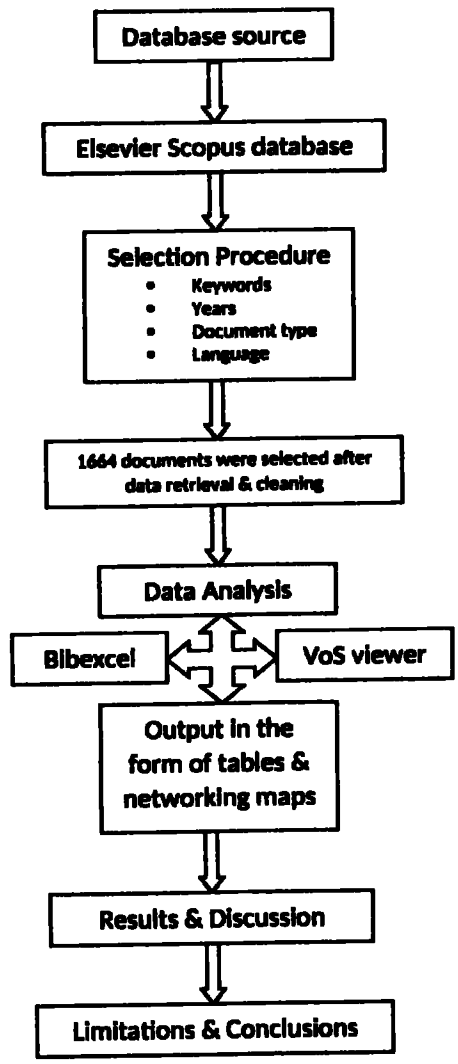

Figure: 2.1 Flow chart of Bibliometrics analysis

2.2.2 Data extraction

In order to gather the complete bibliography with all the articles related to the research papers on As during the period of 2011 to September 2020, online search was carried out within Scopus by the keywords as "Arsenic" OR "As", groundwater, drinking water, geogenic, contamination, geospatial, geostatistical modelling, predictive modelling, arsenic removal, arsenic mitigation" in the topic field of the search-engine for bibliometric analysis. However, eliminating the various nomenclatures from the terms would jeopardize the study's validity, but at the same time a few vagaries were suggested. 1674 documents were returned for further processing, which were checked for significance (Appendix-1). In order to strive to standardize keyword variants, journals, authors, country names and organizations, data were refined by means of a text editor.

2.2.3 Data Analysis

The data obtained from Scopus was analyzed through Bibexcel and VOS Viewer's networks of bibliographies (Van Eck and Waltman, 2011; Persson *et al.*, 2009). Bibliometric analysis of As research done earlier by R. Abejon and A. Garea from Spain published in 2015 in Journal of Water Process Engineering was carried out through Web of Science database. R. Abejon and A. Garea analyzed the database from the year 1992 to 2012. The authors found out the increasing trend in As research publication till the year 2012. In the present study, bibexcel was used due to its data processing capabilities, its simplicity and accessibility to other applications like VOS Viewer and Excel (Mishra *et al.*, 2016). In VOS Viewer network maps were created for network data obtained from Bibexcel. The important features of the selected studies were then used to demonstrate the results. Scopus explicitly obtains bibliometric indicators such as subject categories, leading authors, articles published annually, top journals and country wise publications. In order to investigate the causes of the recorded orientations of contemporary research concerning As, the content analysis was performed for the selected publications.

2.2.4 Visualized analysis

The terms used in title/abstract articles were analyzed in VOS viewer version v.1.6.14 to paradigm and visualize network to detect current topics in this field (Van and Waltman, 2017; Van and Waltman, 2010). Scopus' strategy does not offer all the data information and permits the transfer of up to 2000 articles only. The excel file format can be exported. Hence, it was decided to export all 1674 articles cited and then analyzed them in order to create and view network terms used to perceive current topics in title/abstract articles.

2.2.5 Results

Since all aspects of As study were discussed mainly in this review from 2011 to 2020 (Figure: 2.2). Thus, all available records of different languages from various countries have been systematically examined. In this regard, for the time period chosen, 1674 publications relating specifically to "As" were considered from the Scopus database.

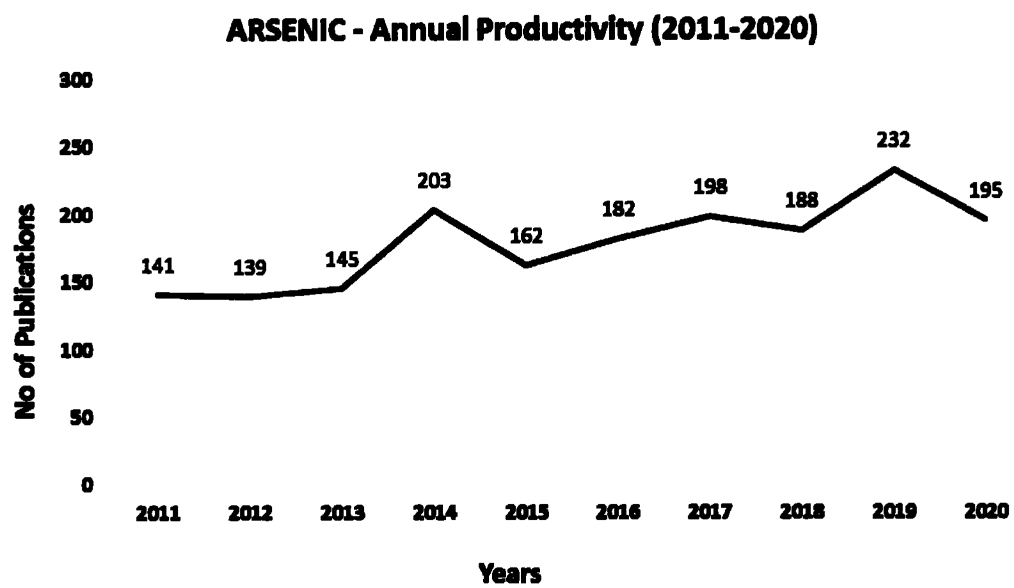

Figure 2.2. Arsenic research annual productivity (2011-2020)

The data retrieved included: 1650 (98.56%) articles; 11 (0.65%) conference papers; 9 (0.53%) erratum; 2 (0.11%) notes; and 2 (0.11%) were letters. Articles published in English language only were selected. Out of the 1674 research articles retrieved from Scopus, 845 articles were then finalized for further analysis. These research articles were selected based on the most active authors who published highest number of research articles on As research. The As research annual productivity from the year 2011 to September 2020 is shown in figure: 2.2 in which it was observed that most of the research focus on As was during the year 2014 and 2019.

In this regard, the resulting five research journals were at the lead: Science of the Total Environment (143), Journal of Hazardous Materials (79), Environmental Science and Pollution Research (68), Chemosphere (67) and Environmental Earth Sciences (59). Out of the total published documents these five journals account for 24.85% (Table:2.1).

Table: 2.1 The top 10 journals that published articles on Arsenic research

Ranking	Name of Journal	No. Of documents %	IF*
1st	Science of the Total Environment	143 (8.54)	1.66
2nd	Journal of Hazardous Materials	79 (4.72)	2.01
3rd	Environmental Science and Pollution Research	68 (4.06)	0.78
4th	Chemosphere	67 (4.00)	1.53
5th	Environmental Earth Sciences	59 (3.52)	0.60
6th	Desalination and Water Treatment	52 (3.11)	0.32
7th	Applied Geochemistry	50 (2.99)	0.83
8th	Chemical Engineering Journal	47 (2.81)	2.31
9th	Environmental Science and Technology Letters	46 (2.75)	2.49
10th	Environmental Geochemistry and Health	40 (2.39)	0.74

*Impact factors (IF) based on HJRS and SJR Reports 2019 which was published in 2020

During this time, spatial spectrum of As contamination was extended to 71 countries. Among these 71, the top countries based on the total number of published articles includes United States (229), Australia (192), and Pakistan (160). Whereas China (151), Germany (113), India (111), Bangladesh (76), Switzerland/Sweden (71), UK (70), and Taiwan (60) were also the countries with significant contributions (Figure: 2.3).

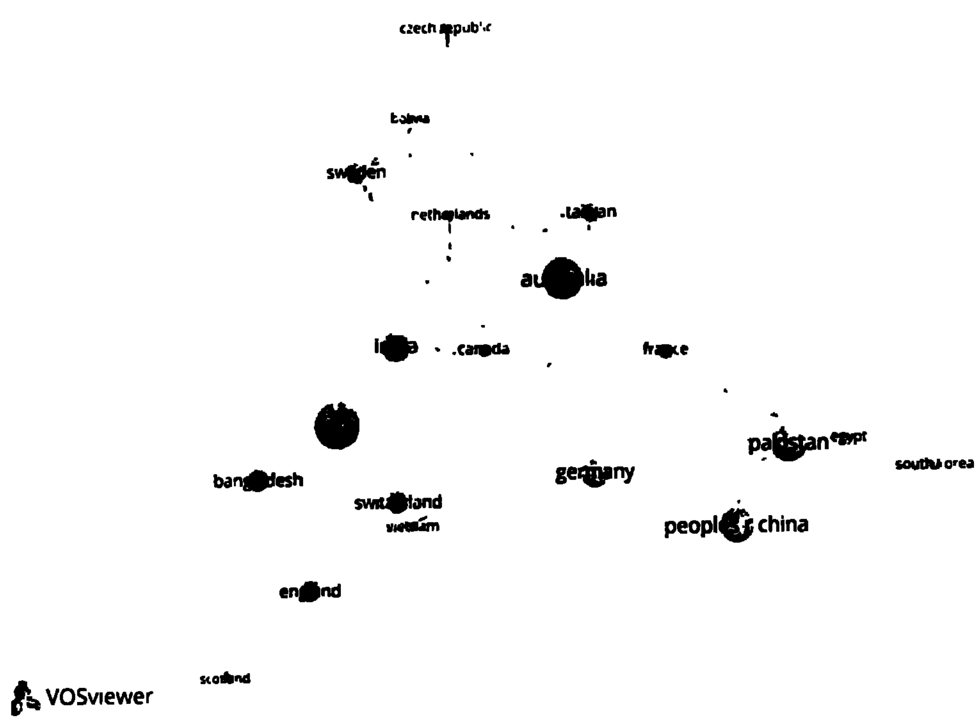

Figure: 2.3. The network map of highly contributing countries/regions in the case of arsenic research

According to the findings, about 947 institutes from various countries are involved in As research. The study reveals that Columbia University, New York, USA (73; 8.64%), University of Chinese Academy of Sciences, China (54; 6.39%), University of Sindh, Karachi, Pakistan (54; 6.39%), National Cheng Kung University, Taiwan (50; 5.92%), University of Agriculture, Faisalabad, Pakistan (46; 5.44%), Newcastle and Manchester University, UK (45; 5.33% &

44; 5.21% respectively), University of Dhaka, Bangladesh (43; 5.09%), Stanford University, California, USA (37; 4.38%) and the KTH Royal Institute of Technology, Sweden (33; 3.91%) are the main contributors towards As research followed by University of South Australia (30; 3.55%), EAWAG, Swiss Federal Institute of Technology, Switzerland (29; 3.43%) and Quaid-i-Azam University, Islamabad, Pakistan (29; 3.43%) as shown in the Annexure: I; Figure: 2.4.

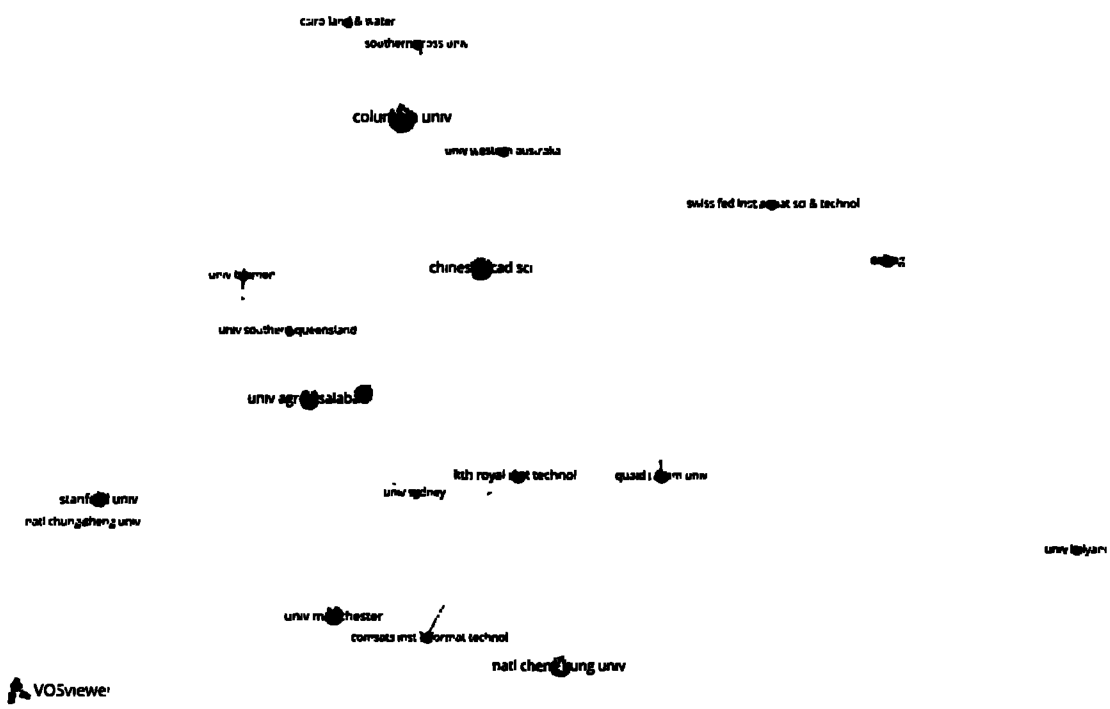

Figure: 2.4: Highlights of the institutions of authors' affiliations who are working on groundwater arsenic contamination

a. Research Communities

In the present study, several publications have also been listed by most active writers over the same period (2011-2020). The complete count method was used for classification. In this process the existence of the author is counted, provided the author's name appears in a publication chosen for this study on the list of co-authors. The Bibexcel was then determined with h-index and total citations (Annexure: I).

Kazi, T. G. from University of Sindh Karachi, Pakistan and Bhattacharya P. from KTH Royal Institute of Technology, Sweden with 59 and 55 publications respectively, were appeared as the two most capable and fecund authors by publishing the highest number of research articles on As. Whereas, Columbia University, USA (73), University of Chinese academy of sciences (54) and University of Sindh, Pakistan (54) appeared as the most prolific organizations based on the total number of published articles on As.

However, scientific contributions by Berg, M. from EAWAG, Swiss Federal Institute of Technology, Switzerland get more acknowledgments in terms of citations (1378) than Fendorf, S. (1271) from Stanford University, USA and Niazi, N. K. (1271) from University of Agriculture, Faisalabad, Pakistan (Figure: 2.5, Annexure-I).

Figure: 2.5: A network of the most productive authors and their collaborations after focused analysis

b. Research coalition clusters

To determine the essence and the importance of current research partnerships the selected publications were analyzed. A co-authors' network map was generated with the help of VOS viewer to classify the most active collaborating authors. Total 7 clusters were highlighted in terms of co-authorship and collaborations (Figure: 2.6). These clusters highlighted the funding and collaborations done by the developed countries e.g., USA, for the projects with those countries with high risk of geogenic As contamination viz. Bangladesh, India, Pakistan, China and Vietnam etc.

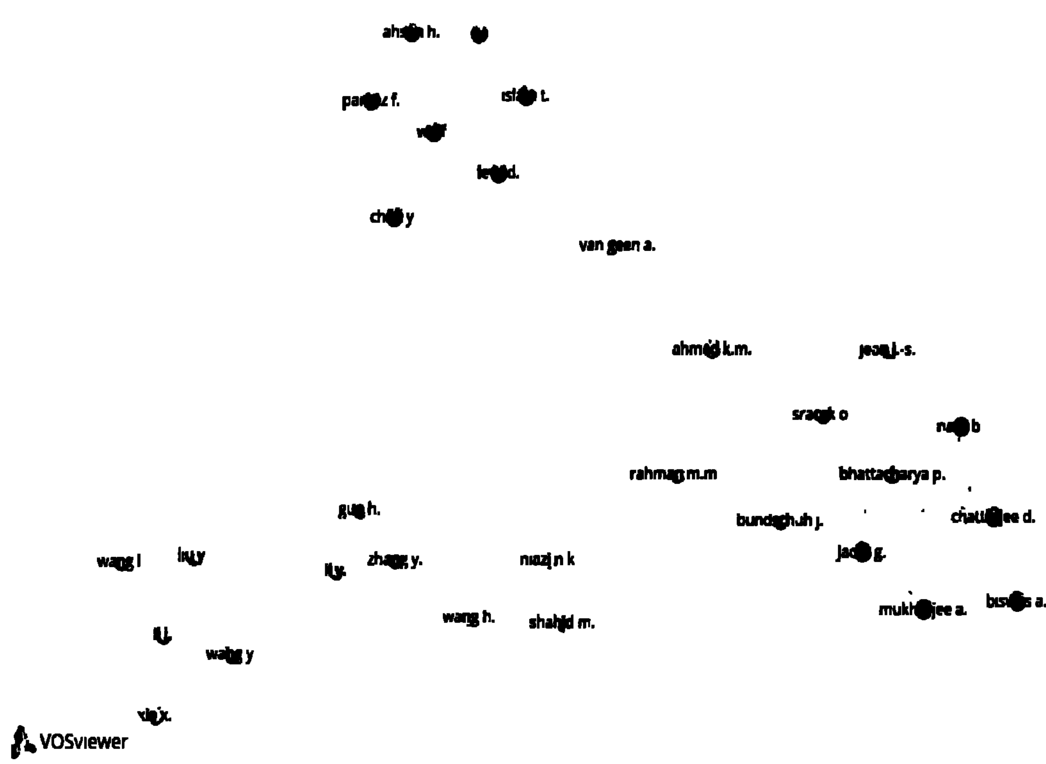

Figure: 2.6. Co-authorship network with seven clusters working on arsenic

c. Co-citation analysis

This approach is often used for the interpretation of contemporary research's conceptual paths and imprints. Results from the current analysis in (Figure: 2.7, Annexure-I) revealed the important implications for Ahmed, KM., Bhattacharya, P., Berg M. and Van Geen, A. within the field of As research.

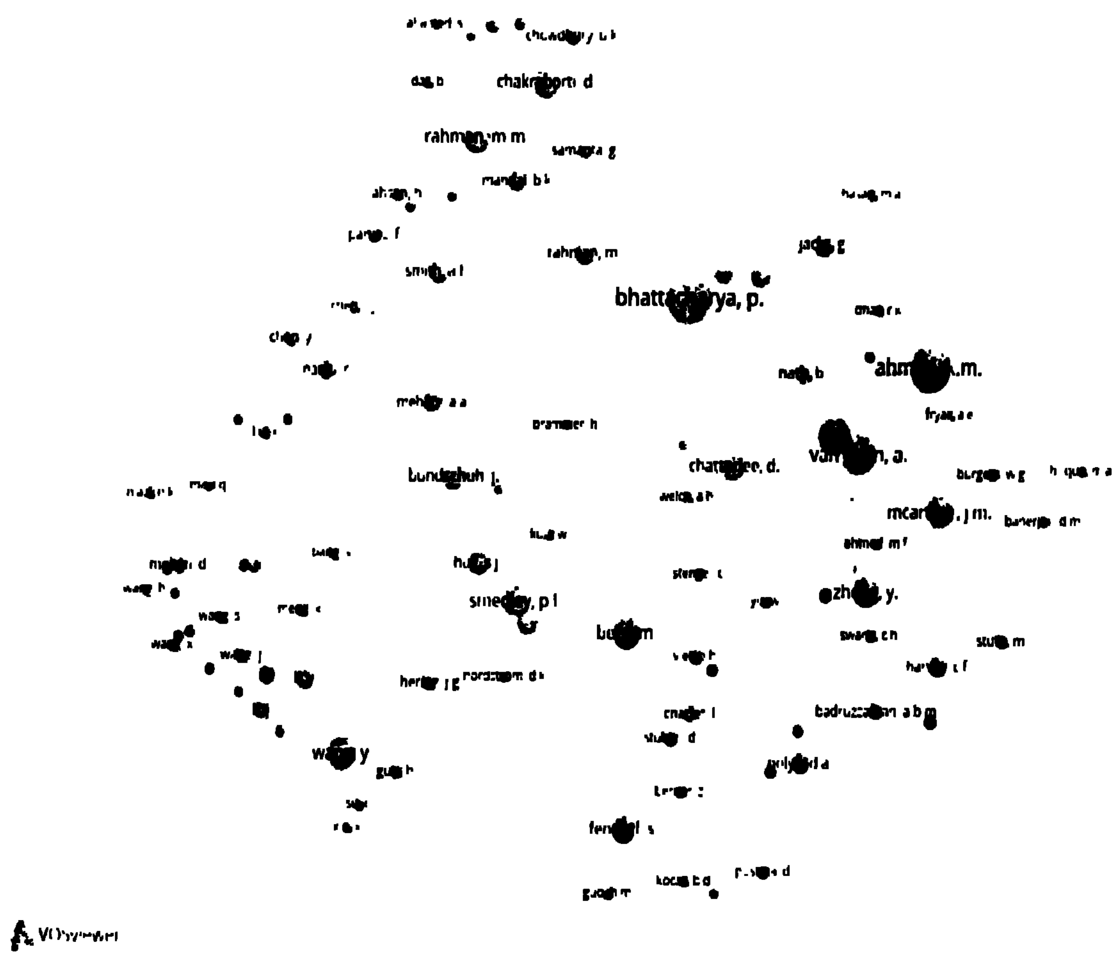

Figure: 2.7 Co-citation network analysis

d. Keyword analysis

A discipline's analytic structure was constructed using keyword co-occurrence graphs. The choice of keywords constitutes the scientific research's emphasis and orientation. Keywords from the publications were collected and organized into categories for processing. The output has been shown in figure 2.8. Only those words recur at least twenty-five times were listed. Since it was so noisy, the technique was used to reduce the noise. This visualization illustrates the keyword combinations. The color of the of the node depicts the level of concentration and the scale of the areas of As study.

The nodes in the center serve as a representation of the keywords such as "arsenic" (1525), "groundwater" (689), "water pollutants, chemical" (529), and "drinking water" (483). Whereas the keywords like "adsorption" (463), "concentration (composition)" (423) "water pollutant" (417), "groundwater pollution" (398), "chemicals removal (water treatment)" (358) and "chemistry" (354) also appeared significantly in the analysis (Figure 2.8).

865 words have appeared at least ten times in the 29,030 terms. For each of the 865 distinct terms, a relevance score was used to produce a vocabulary list of 60 percent. In Figure 2.8, the scale of the blobs indicates the number of words in titles and abstracts. The four clusters of the largest set of connected terms represents the: As mitigation technologies research (red), health risks from As (blue), groundwater As contamination (green), and chemical pollutants in different mediums (light green).

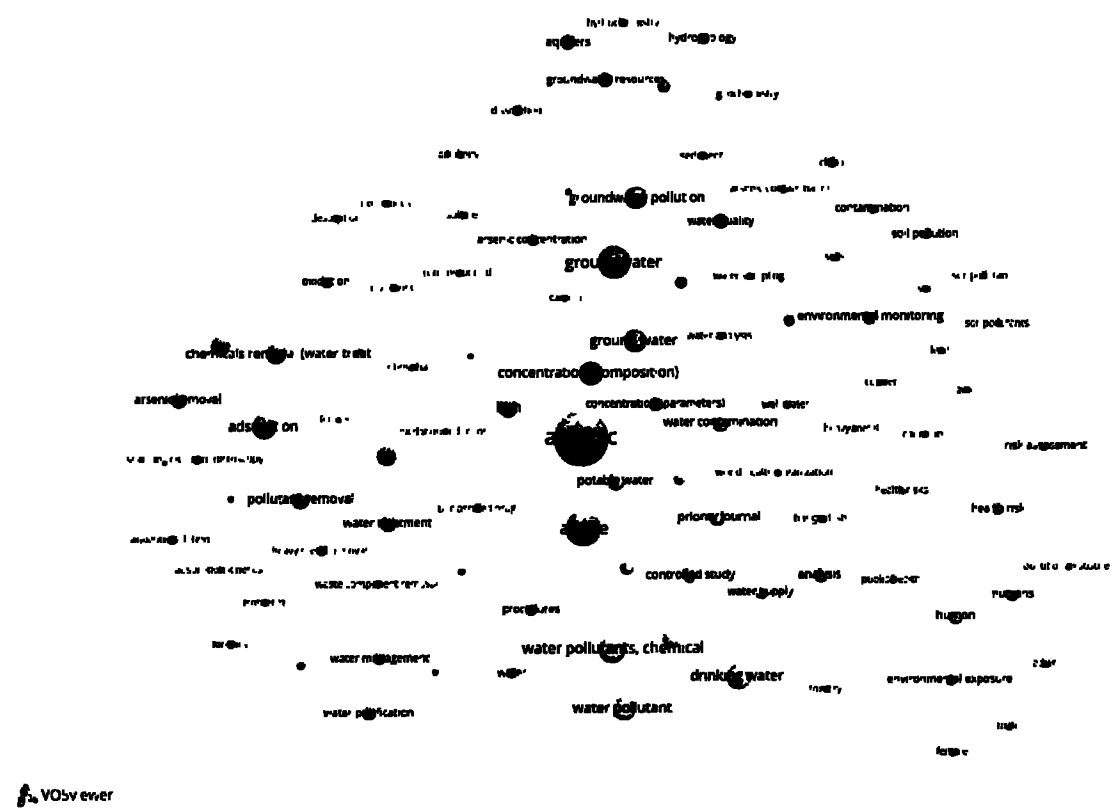

Figure 2.8. Research topics clustered by mapping of co-occurrences of terms in title/abstract for publications related to arsenic for the period 2011-20.

2.2.6 Discussion

The objective of this bibliometric analysis was to summarize and interpret the development of scientific results based on As pollution studies. The findings of the study reveal a growing body of scientific literature on As groundwater contamination, As hazard and As mitigation techniques, and health evaluations on the topic of ground water toxicity in general. The study yielded some useful results. 232 research papers showed a rapid increase in research activities associated with As during the 2019 research review. There are several causes for the dramatic rise in studies on As toxicity during this brief period of time.

Global As pollution has posed a threat to the world's health for centuries. The Asian countries' high significance is unique in other bibliometric analyses of water science (J. Sun *et al.,* 2012; Wei Zhi and Guodong Ji, 2012). Around 230 million people, including about two-thirds of the Asian population, are now at risk of As poisoning. We need to pay attention to South-East Asian economies in this investigation.

Figure 2.6 illustrates increased collaboration, ranging from regional to intercontinental, in research between nations. These findings confirm previous studies. The 20 most cited papers in the study bibliography are summarized in Table 2.6. The studies carried out in this field focused mainly on the environmental and toxicological aspects of As in water in the past twenty years, according to this list. Research partnerships are required and encouraged to tackle the problem of As contamination from geogenic sources. The results of the co-authorship analysis can identify key groups / collaborations of As research.

In addition to As, the findings show enough reason to include other chemicals such as "iron, zinc, lead, copper, and cadmium" in the ranking. The presence of iron could reinforce the notion that adsorption is the most effective technology, as iron oxides are well known to be effective adsorbents, especially for As removal (Mohan and Pittman, 2007; Mondal *et al.,* 2006). Along with iron ions, As^{+3} species can undergo oxidation to form As^{+5} species, which are easily removed via precipitation, adsorption, ion exchange, or membrane technology (Shan and Tong, 2013).

2.2.7 Conclusions

The findings may be a direct result of providing enough expertise to outline new perspectives and form potential guidelines for As contamination research. The study also identified developing countries in Asia and Southeast Asia that are particularly vulnerable to groundwater As pollution. International and national funding agencies should devote enough resources to removing this deadly toxin from the potable water supplies of countries such as Bangladesh, Pakistan, India, China, and Vietnam, among others. This study will mark the onset of an array of fast-moving As investigations at this worldwide problem.

2.3. Bibliometric review on Fluoride:

Fluoride is a monatomic, inorganic and simplest anion of fluorine and is denoted by F^-. The salts and minerals of F are widely used as chemical reagents in various industrial processes i.e. aluminum manufacturing, steel production, glass making and production of enamels, refrigerants and uranium for nuclear power. It has a characteristic bitter taste and impart no color to F salts (Schulz *et al.*, 2018). Currently, the total concentration of fluorine in the crust of the Earth is 0.05-0.1% (500-1000 mg/kg) (Sivasankar *et al.*, 2016). In the course of Earth's history, naturally occurring fluorine compounds such as fluorite, apatite, and micas contain various amounts of F (Ali *et al.*, 2016). The groundwater contamination by F has been observed at varying concentrations ranging from low concentrations (<1 mg/L) to high levels (>35 mg/L) depending upon the solubility of F containing minerals. For instance, fluorite is found to be soluble at greater extent than apatite, micas and amphiboles (Farooqi, 2015).

The contamination of groundwater by the presence of F ion makes it unfit for human consumption and is considered as a global dilemma (Valdez-Alegria *et al.*, 2019). Numerous compounds of fluorine are considered important in various chemical and manufacturing processes. Fluorite which is also known as fluorspar is the only fluorine mineral that is extracted on large scale. It has a direct application as fluxing material and also acts as an additive in various manufacturing processes. In 2012, China being the largest producer of fluorspar produced more than 60% of this mineral (Schulz *et al.*, 2018). The second widest consumer of F products is USA which acquires most of the fluorine containing products from Mexico (Schulz *et al.*, 2018).

2.3.1. Widespread global distribution of fluoride

The groundwater contamination by F shows both spatial and temporal deviations (Ali *et al.*, 2016). Different countries viz., India (Shukla and Saxena, 2020), Pakistan (Rasool *et al.*, 2018), Yemen (Francisca *et al.*, 2017), Thailand (Chuah *et al.*, 2016), South Africa (Kut *et al.*, 2016) and China (Guo *et al.*, 2007; Su *et al.*, 2013) etc. have been polluted with fluorine can be attributed to its presence in metamorphic and igneous rocks such as granite and gneiss. There are F belts that run through Jordan, Libya, Egypt, Sudan, Algeria, and Kenya to Iraq, then through Afghanistan, northern Thailand, America, and finally to Japan, and China (Brindha and Elango, 2011). Currently, these three South Asian countries - India, Pakistan, and Sri Lanka - are the epicentres of F pollution (Ali *et al.*, 2016). The overall F repositories of 85 million tons are present in the earth's crust, 12 million of which are found in India alone (Brindha and Elango, 2011; Kisku and Sahu, 2020). Since 1937, India has been severely affected by chronic fluorosis (Brindha and Elango, 2011). Nearly 50% of the groundwater resources are contaminated by F enrichment in New Delhi (Rasool *et al.*, 2018). Highly affected states of India include Andhra-Pradesh, Rajhasthan, Haryana, Punjab, Gujrat and Assam. The semiarid regions surrounding Gujrat were found to have F concentrations exceeding the limits acceptable by the WHO for potable water (1.5mg/L).

Various studies reported F concentrations ranging from 5-10 mg/L in regions Andhra Pardesh, Delhi, Gujrat, Kerala, Orissa and West Bengal whereas F concentrations in areas i.e. Madhya Pardesh, Punjab, Assam and Haryana were found to be ≥10-20 mg/L. Almost 80-100% area of Rajhasthan and Gujrat and 60-80% areas of Andhra Pradesh and Punjab are severely affected by F contamination. Furthermore, almost 60% districts of Orissa and 37% districts of West Bengal are contaminated by F enrichment (Yadav *et al.*, 2019).

Several investigations have reported F content ranging from 20-79.2 mg/L in various parts of South Korea, Pakistan, Vietnam, Malaysia and Afghanistan attributed to geological processes, F enriched rocks and the existence of apatite in groundwater reserves (Yadav *et al.*, 2019). F contamination affects nearly 5 million people in Mexico (Vinthanage and Battarchaya, 2015). Moreover, in Sri Lanka Dissanayake (1991) reported high F content (> 5mg/L) in dry climatic zone as compared to wet climatic zone resulted in prevalence of dental fluorosis in dry zones particularly in North Central Province. Similarly, more than 4 mg F/L have also been observed in groundwater of Sri lanka attributed to slow movement of water eventually resulting in prolong rock water interaction (Rasool *et al.*, 2018). However, in North China Plain, F content was higher in 67.8% of all samples than the permitted limit of "1.5 mg/L" (Li *et al.*, 2020). Also, 57% of the drinking water samples in Poldasht city Iran surpassed WHO's acceptable limits from 0.27-10.3 mg/L. (Yousafi *et al.*, 2018). Other countries like Peru, Ecuador and Argentina are also reported to have high F content.

Almost 1.2 million people in Argentina are consuming F contaminated groundwater thus are prone to serious health hazards (Kimambo *et al.*, 2019). Conversely, in major parts of Europe, groundwater contamination by F is not an alarming issue, however water fluoridation is required, as the underwater reserves are generally deficient of natural F. Although, the groundwater reserves in Muenster, Germany was found to have higher levels of F with values as high as 8.8 mg/L (Kimambo *et al.*, 2019).

2.3.2. Pakistan Scenario of Fluoride Occurrence in Groundwater

In Pakistan, almost 89% of drinking water resources are considered unfit for human consumption and do not fulfill the drinking water criteria of WHO guidelines (Solangi *et al.*, 2019). Approximately 80% terrain of Pakistan have dry climatic conditions thus having low rainfall, increased evaporation and elevated summer temperatures therefore providing favorable conditions for the occurrence of F in groundwater (Rasool *et al.*, 2018; Arshad and Imran, 2017). As reported by Ali *et al.*, (2019), a detailed study has been conducted by PCRWR to assess the probability of F pollution in drinkable water resources in sixteen important cities of Pakistan which concluded in F contamination exceeding the permissible limit. Various studies reported concentration of F in spring water is upto 13.52 ppm in KP whereas Naseem *et al.*, (2010) observed 35.4 ppm in Thar Desert in Nagar Parker. Farooqi *et al.*, (2007) also stated high concentrations (21.1ppm) of F resulted in 75% samples to be above WHO guidelines in Khalanwala Punjab. A study done by Qurat-ul-Ain *et al.*, (2017) also highlighted high levels of F in all the studied samples of Rahim Yar Khan district in Southern Punjab. Chandio *et al.*, (2015) assessed F content in various areas of Balochistan viz. Pringabad, Mangochar, and Mastung areas of and found 64% samples unfit for human consumption. Different studies show F enrichment of subsurface water in all the four provinces of Pakistan.

2.3.3 Human Health Effects

Fluoride concentrations are extremely high in groundwater and is considered as an emerging environmental concern owing to its detrimental effects on human beings (Li *et al.*, 2020). 0.2 billion people around the world are at risk of F pollution from natural or added sources, and many harmed by F in their drinking water (Kaur *et al.*, 2020; Rasool *et al.*, 2018). The WHO has set the tolerable level of F in water at a level of 1.5 mg/L. (WHO, 2017). If consume within permissible limit (0.7 to 1.2mg/L), F is considered as an essential micronutrient for development of strong bones and teeth but consumption >1.5mg/L for extended period of time is known to cause various diseases i.e. fluorosis of the teeth and bones, arthritis, hip fractures, and infertility etc. (Bodrud-Doza *et al.*, 2020; Kaur *et al.*, 2020). The different effects of F intake on human health at varying concentrations is shown in Table 2.2.

Table 2.2. Effects of fluoride ingestion on human health: source Dissanayake (1991)

Fluoride concentrations (mg/L)	Effect on human health
< 0.5	Conducive to dental caries
0.5 to 1.5	Promotes development of strong bones and teeth
1.5 to 4.0	Promotes dental fluorosis in children
> 4.0	Promotes dental and skeletal fluorosis
> 10	Crippling skeletal fluorosis, possibly cancer

i. Beneficial Effects on Human Beings

Fluoride is considered as an essential micronutrient for the human body when consume in the allowable range of 0.7 to 1.2 mg/L (Rasool *et al.*, 2018). It has been known that the limited intake (1mg/L) of F via food or drinking water have favorable effects on rate and occurrence of dental caries and strengthening of apatite matrix tissues especially among children (Rasool *et al.*, 2018; Bibi *et al.*, 2016).

ii. Toxic Effects on Human Beings

The increasing levels of F contamination in drinking water have serious detrimental effects on teeth and bones at different concentrations. The F levels greater than 1.5 mg/L is the major cause of dental fluorosis (Rasool *et al.*, 2018). In dental fluorosis, displacement of OH^- ions from hydroxyapatite ($Ca_5(PO_4)_3OH$) takes place, which is an important component of teeth and bones, resulting in the formation of fluoroapatite ($Ca_5(PO_4)_3F$). Fluoroapatite is found to strengthen the enamel to some extent. Whereas, increased exposure to F results in denser, harder and brittle teeth, this condition is recognized as dental fluorosis (Mohapatra *et al.*, 2009). In dental fluorosis, teeth turn yellow to brown and eventually to black (Rasool *et al.*, 2018). Tooth inflammation and extraction are probably the first sign of dental fluorosis (Kumar *et al.*, 2019). Whereas the continuous intake of F via drinkable water at a level ranging between 4-10 mg /L is identified to cause skeletal fluorosis and crippling disease (Rasool *et al.*, 2018). Skeletal fluorosis is a serious bone and joint disorder. It is commonly found among the workers that comes frequently in contact with F particularly in aluminum or fertilizer industries (Peckham and Awofeso, 2014).

In India and China alone, nearly 2.7 million cases of skeletal fluorosis have been reported (Rasool *et al.*, 2018). Risks of bladder cancer also increases amongst the individuals exposed to elevated levels of F at place of work. Increased concentrations of F deposits were found in pineal gland rather than teeth and bones. F toxicity can also affect the function of brain and pineal gland. Other diseases include osteoporosis, arthritis, crippling bone deformities, decreased cognitive ability, cancer, infertility, alzheimer syndrome and thyroid disorder (Bibi *et al.,* 2016; Vithanage and Bhattacharya, 2015). Teeth molting in minor cases and bone malformation and neural disorders in acute cases has also been reported (Bibi *et al.,* 2016). Prolonged gastritis and some other stomach injuries may occur at 190 mg/L. F ingested is excreted through the kidneys, where it has the potential to cause renal disorders at F concentrations of 100 to 380 mg/L whereas no harmful effects have been recorded at exposure of 8mg/L even for longer period of time (Kumar *et al.,* 2019).

Almost 200 million people in different countries including Pakistan, China, India, Iran, Thailand, Sri lanka, Canada, USA, Japan, New Zealand etc. are found to be severely affected by F enrichment (Rasool *et al.,* 2018). In Pakistan, Kazi *et al.,* in her study in 2009 concluded that almost 61 to 73% people near Manchar lake are suffering from various diseases including melanosis and keratosis as a result of F toxicity. Whereas, nearly 40 to 50% citizens are experiencing dental problems, hepatitis, blood pressure and lung cancer, etc. due to the ingestion of F via water in Tehsil Mailsi (Rasool *et al.,* 2015). Similarly, in Mangolia almost 12,600 people are at risk of heart diseases as a result of consuming high F well water (Wade *et al.,* 2009). Table 2.3 details the long-term F ingestion effects through drinking water on human health.

Table 2.3. Chronic effects of fluoride on human health (Rasool *et al.,* 2018)

System	Effects on health
Cardiovascular system	Thinning of blood vessels, increased risk of heart attack, hypertension, cardiac arrhythmias, decreased in blood circulation that cause gangrene of extremities
Dermal	Thickening of skin, hyper-pigmentation, reynaud's disease, basal cell cancer and squamous
Gastrointestinal	The effects on abdominal pain, nausea and heartburn, dental fluorosis
Hepatic	Abnormal cell growth known as neoplasia, and cirrhosis
Hematological	Decreased white blood cell count known as leucopenia and anemia
Neurological	Memory loss, coma, brain malfunction, the hallucinations, seizures and neuropathy
Pulmonary	Dental caries, dental fluorosis, long time cough and restrictive lungs
Renal	Skeletal fluorosis, crippling fluorosis, dehydration and the cortical necrosis
Respiratory	Shortness of breath, rhinitis, pharyngitis, perforation of the nasal septum and laryngitis
Reproductive	Malformations of fetus, low bright weight, still birth and risks of spontaneous abortions

2.3.4. Water Defluoridation Methods

In developing nations, high levels of F in ground water is a serious health concern. To prevent harmful effects of the F in water, various water defluoridation techniques are used to make it humane and to prevent terrible effects of fluorosis for the population that consume it (Fawell *et al.*, 2006).

i. Coagulation and Precipitation

This process involves the adding up of chemicals which uses lime and alum as common coagulants. The Nalgonda technique works on the principle of coagulation (Barudgar *et al.*, 2017). This technology was invented by National Environmental Engineering Research Institute NEERI in Andhra Pradesh in the mid-region village in 1961, and today is one of the country's oldest techniques for F mitigation in water (Bose *et al.*, 2018). Because it is one of the cheapest ways to get going, and because it is simple to handle, it is commonly used in developing countries (Kumar *et al.*, 2019). In this technique, coagulants i.e., lime (calcium oxide) and hydrated aluminum sulphate also known as alum ($Al_2(SO_4)_3 \cdot H_2O$) are added directly in the water by constantly stirring for five minutes. The F is precipitated as insoluble CaF and increases the pH of water thus making it alkaline (pH 11-12). The removal of F is optimally achieved when the pH of water is between 5.5-7.5 (Jagtap *et al.*, 2012).

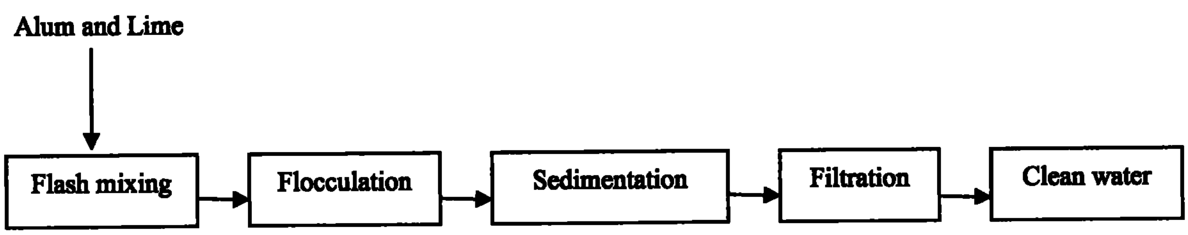

Figure: 2.9. Flow Diagram of Nalgonda Technique

(Kumar *et al.*, 2019)

Following reactions takes place in order to eliminate F from ground water by using Nalgonda technique:

$$Al_2(SO_4)_3.18H_2O \longrightarrow 2Al_3 + 3SO_4^{-2} + 18H_2O$$

$$2Al^{3+} + 6H_2O \longrightarrow 2Al(OH)_3 + 6H^+$$

$$F^- + Al(OH)_3 \longrightarrow \text{Al-F complex} + \text{undefined product}$$

$$6Ca(OH)_2 + 12H^+ \longrightarrow 6Ca^{2+} + 12H_2O$$

Ca $(OH)_2$ when reacts with F forms CaF_2 which is water insoluble as shown in the equation below:

$$Ca\,(OH)_2 + 2F^- \longrightarrow CaF_2 + 2OH^-$$

(Yadav *et al.*, 2019)

The major benefit associated with co-precipitation method is that it is a commonly used technique especially at community level. However, certain limitations include low treatment efficiency i.e. 18-33%, large amount (700-1200 mg/L) of aluminum sulfate is required, hazardous health effects associated with residual aluminum in the treated water and requirement of skilled workforce in case of highly contaminated F water (Jagtap *et al.*, 2012).

ii. Membrane Based Processes

The semi-permeable membrane is utilized for ions, molecules, and smaller particles, as well as medium-sized molecules (Bose *et al.*, 2012). The membrane-based processes used for the mitigation of F from drinking water includes reverse nanofiltration (NF), electro dialysis, and reverse osmosis (RO) (Jagtap *et al.*, 2012). Reverse osmosis is a method that includes removal of contaminants by physically exerting pressure on the water which allows it to pass across the semi permeable membrane and leaves the waste behind (Jagtap *et al.*, 2012).

The effectiveness of this method is dependent on a variety of factors, including freshwater features, temperature, and systematic maintenance and monitoring (Bibi *et al.,* 2016). In India, many reverse osmosis plants have been installed by Safe Water Network India in Telangana and Uttar Pradesh (Barudgar *et al.,* 2017). However, in electro dialysis process a direct current (dc) is used as a substitute of pressure in order to separate F contents from the contaminated water (Jagtap *et al.,* 2012). The F content after the treatment of water has been reduced to 0.05-0.4 mg/L (Kumar *et al.,* 2019).

The membrane technology is though energy intensive but is an excellent option for F removal (Ayoob *et al.,* 2008). Whereas, in nano filtration, activated carbon nano tubes were used which were prepared by decomposing xylene with ferrocene catalyst (Bibi *et al.,* 2016). Nano filtration is a low-pressure procedure, eliminating the high levels of dissolved solids compared to reverse osmosis (Jagtap *et al.,* 2012). In order to remove F from groundwater, nanofiltration has been used in Finland at commercial level having a capacity of 380-600 m^3/day (Vinthanage and Battarchaya, 2015).

Membrane processes are highly effective methods in order to remove F from groundwater with no requirement of chemicals and works under wide range of pH. However, higher setup and maintenance cost, requirement of skilled workforce, less removal efficiency with highly saline water and total dissolved solids (TDS) and complete demineralization of water are few short comings associated with these methods (Roy and Dass, 2013; Barudgar *et al.,* 2012).

iii. Ion Exchange

In this method, the chloride ions of the resins have been removed by F ions. This practice continues till resins have been occupied completely. Sodium chloride is added to the saturated resin after it has been cleaned. New chloride ions are replaced by F ions, which include recharging the resin which finally restarts the process. The removal of F occurs based on the following reaction:

$$\text{Matrix-}NR_3^+Cl^- + F^- \longrightarrow \text{Matrix-}NR_3F + Cl^-$$

The ion exchange method removes almost 90-95% of the F and does not affects the taste or color of the water. However, few limitations include high cost of the process as well as treated water contains high chloride content and have relatively low pH (Jagtap *et al.*, 2012).

iv. Adsorption

Adsorption is an extensively used defluoridation method based on diffusing fluid ions to the surface of adsorbent (solid) (Yadav *et al.*, 2019; Li *et al.*, 2003). Activated alumina and activated carbon are considered as the commonly used absorbents for the elimination of F from polluted water. Whereas, numerous researchers reported the use of other adsorbents like silica gel, rice husk, fly ash, calcite, coffee husk, bone charcoal and activated saw dust (Jagtap *et al.*, 2012; Li *et al.*, 2003). In order to assess the effectiveness of activated alumina used for the elimination of F from groundwater, various factors like hardness, pH and surface loading considered very important (Jagtap *et al.*, 2012). In order to increase the efficiency of alumina, it must be activated by heating (Mohapatra *et al.*, 2009). The best results are achieved when the pH is between 5 and 6 (Yadav *et al.*, 2019). However, at pH 7 or above, the capacity of adsorption of F is drastically reduced as a result of electrostatic repulsion between F and other negatively charged adsorbent surface. The electrostatic reaction between the surface of adsorbent and F ions at low pH is shown below:

$$M\text{-}OH + H^+ \longrightarrow M\text{-}OH_2^+$$

$$M\text{-}OH_2^+ + F^- \longrightarrow M\text{-}OH_2^-F$$

Whereas, M corresponds to the metal ions present on the adsorbent's surface. The defluoridation capacities of various metal-loaded adsorbents used to remove F decrease in the following order:

$$Le\ (III) \geq Ce\ (III) > Y\ (III) > Fe\ (III) \sim Al\ (III) > Ca\ (II) > Mg\ (II) > (II).$$

(Biswas *et al.*, 2017)

The F removing efficiency of adsorption process is up to 90% and is considered as a very cost-effective treatment but the dumping of sludge produced as a byproduct is a serious problem associated with this method (Yadav *et al.*, 2019; Jagtap *et al.*, 2012).

Water fluoridation is a worldwide issue. It is found in most of the developing countries, especially in India, China, Argentina, and Ethiopia. For the formation of dental enamel and normal mineralization of bones, F is a necessary component in trace amounts (Bell, 1970). Its reserves are found in the form of sellaite, fluorspar and cryolite. The cryolite and fluorspar is present in igneous and sedimentary rocks respectively. As these minerals are almost insoluble in water so when discharge from the industries containing high F effluents and the conditions which favor F dissolution will occur, the high F concentrations will be found in groundwater (Mohapatra *et al.*, 2009). Fluoride residue and exhaust dirty the climate; breathing in residue and vapor is pretty much as hazardous as burning-through F containing food, water or medications (EPD, 2006).

2.3.5 Material and methods

The research used the VOS viewer program to perform bibliometric or Sciento-metric analysis. It used the co-authorship, co-occurrence, citation, and co-citation analysis techniques to classify networks of collaborating organizations, nations, citations, and sources. This allows for representing similar objects using network maps, Label IDs, and Links (Mohapatra et. al., 2009). The magnitude of the results is depicted by the size of the Label ID, which is an indicator of significance (Ayoob et. al., 2008). The study is based on the larger nodes, which explain the context of documents, keywords, sources, and authors. Subsequently, it was relied on to understand new advances in the F field for the "keyword co-occurrence study examination."

i. Data collection and preparation

The online search inside Scopus was performed using the keywords "Fluoride OR F, groundwater, drinking water, geogenic, contamination, geospatial, geostatistical modeling, predictive modeling, fluoride removal, fluoride mitigation" in the search engine under the subject area to arrange a thorough list of sources of all articles identifying with fluoride research papers distributed during the most recent decade. The keywords, countries, and writers have been standardized via text editors. Data on the countries involved in fluoride pollution, projects, the prevalence of researchers, global partnerships, and features of papers on this information were compiled in an easy-to-read, concise format. The use of these keywords apparently may affect the authenticity of the results by exclusive the associated studies with various terminologies and avoiding digressions simultaneously. To continue evaluation, the inquiry returned 1006 records that have been further investigated for significance. Information has been refined with a word processor to normalize the variations of keywords, names of countries, journals, authors, and organizations.

ii. Data Analysis

Bibexcel and the bibliographic organizations produced for the current investigation were utilized to examine the information from VOS Viewer (Van, 2011; Persson, 2009).

Because of its adaptability, limit, and similarity, Bibexcel was utilized in other programs, for example, VOS Viewer, Excel, and CiteSpaceIV (Mohapatra, 2009). In VOS Viewer, network maps were further processed for network data obtained from Bibexcel. We later used the results to articulate and illustrate prominent characteristics of the studies used in the study. Published journals from Scopus, country of origin, top authors, and Scopus categories were employed to provide the various bibliometric indicators. Additional research was conducted to determine the potential causes of the orientations found in the literature.

iii. Results and discussion

The primary goal of the analysis is to cover all FLUORIDE or F research aspects for the period from 2011 to 2020; the documentation has been thoroughly studied in all the countries and languages available (Figure 1).

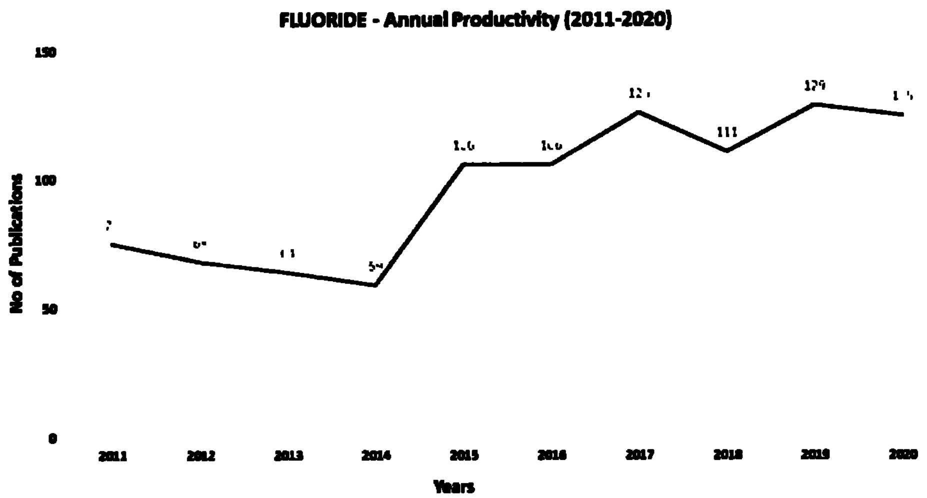

Figure 2.10. Annual productivity in fluoride research (2011-2020)

To this end, for the selected time intervals, 1006 publications linked explicitly to "fluoride" have been found in the Scopus database. Scholars from 108 countries conducted these studies. The data, which was retrieved includes a total of 920 articles, conference papers (25), Erratum (5), Note (4), and the Letter (4).

Out of these 920, research articles total of 386 articles were selected after further scrutiny. These articles were written exclusively in the English language. Five journals were identified as leading, considering the total number of research articles on fluoride, i.e., Environmental Earth Sciences (19), Chemosphere (14), Desalination and Water Treatment (14), and Human and Ecological Risk Assessment (9). These five journals account for 17.36 percent of all documents published (Table 2.4).

Table 2.4. The top 10 journals that published articles on fluoride research

Ranking	Name of Journal	No. of documents %	IF*
1st	Environmental Earth Sciences	19 (4.92%)	0.61
2nd	Chemosphere	14 (3.63%)	1.53
3rd	Desalination and Water Treatment	14 (3.63%)	0.32
4th	Human and Ecological Risk Assessment	11 (2.85%)	0.54
5th	Environmental Science and Pollution Research	9 (2.33%)	0.78
6th	Arabian Journal of Geosciences	8 (2.07%)	0.41
7th	Data in Brief	8 (2.07%)	0.11
8th	Science of the Total Environment	8 (2.07%)	1.66
9th	Environmental Geochemistry and Health	7 (1.81%)	0.74
10th	Journal of Environmental Chemical Engineering	7 (1.81%)	0.92

*Impact factors (IF) based on HJRS and SJR Reports 2019, which were published in 2020

Fluoride's geographic reach has increased to 46 countries during this period. Among these 46 countries included based on the number of relevant documents top 5 are India (193), China (89), Pakistan (43), Iran (31), and the USA (26), as shown in Figure 2.11.

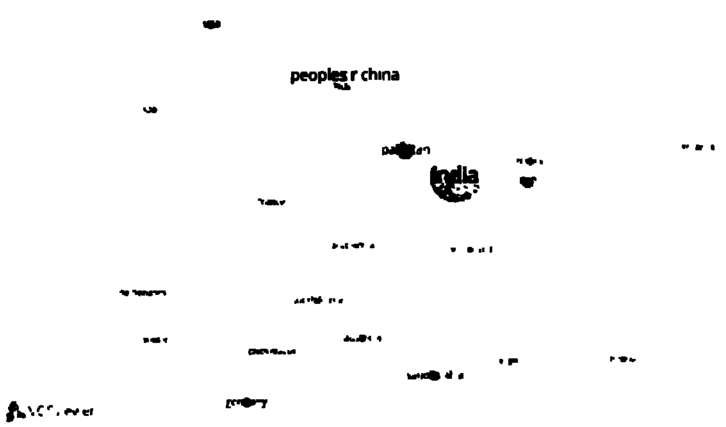

Figure 2.11. Geographical network of top 20 countries based on fluoride research productivity (2011-20)

According to the findings, approximately 453 institutes and organizations from various nations are currently engaged in F research. In this regard, University Chinese Academy of Sciences, China (37), Changan University, China (34), University Burdwan, India (22), Tezpur University, India (20), Quaid-i-Azam University, Pakistan (19) are the leading contributors to research on F (Figure 2.12).

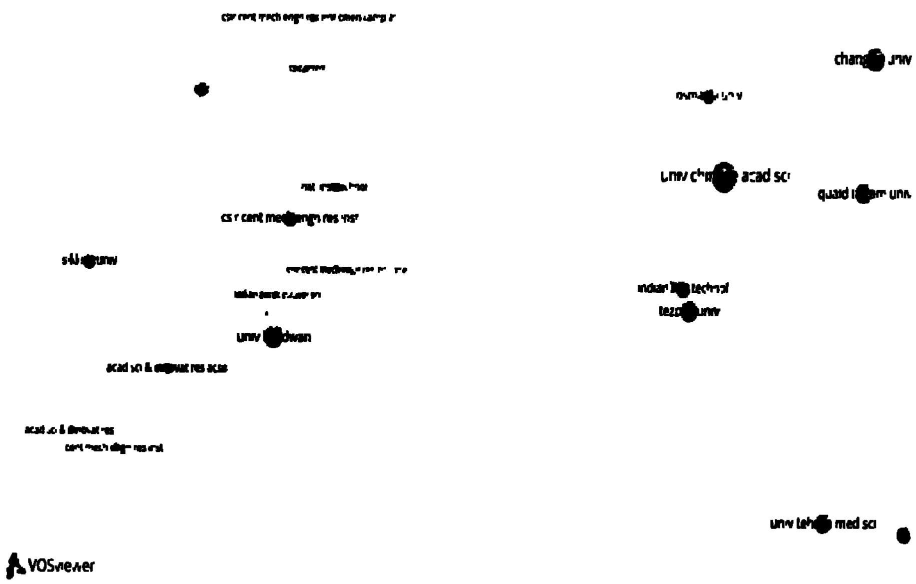

Figure 2.12. Top 20 Institutions based on number of documents published on fluoride

a. Research Communities

In the current analysis, the most prolific writers have also been listed for several publications in the same period (2011-2020). The entire count method is employed. In this research design, all the author's credentials are reported, whether or not they appear in any of his names in a list of those who took part in the study. The Bibexcel was used to measure total citations, as presented in Table 2.5.

Table 2.5. Top 20 most productive authors based on the number of documents

Author Name	[redacted]	Citations
Jing Sun	[redacted]	395
Priyabrata Banerjee	[redacted]	508
Hui Qian	[redacted]	902
Abida Farooqi	[redacted]	414
Manish Kumar	[redacted]	207
Pritam Ghosh	[redacted]	428
Ahmad Zarei	[redacted]	216
Mohammad Hadi Dehghani	[redacted]	292
Rajeev Kumar	[redacted]	170
Rui Song	[redacted]	257
Subhra Kanti Mukhopadhyay	[redacted]	329
Mansoureh Farhang	[redacted]	208
Atta Rasool	[redacted]	202
Mojtaba Afsharnia	[redacted]	183
Mehdi Qasemi	[redacted]	141
Wei Huang	[redacted]	133
Linghao He	[redacted]	128
Yang Liu	[redacted]	72
Mang Li	[redacted]	21
Dipankar Chakraborti	[redacted]	105

Jing Sun from the Chinese Academy of Sciences, China, Priyabrata Banerjee from the Council of Scientific & Industrial Research (CSIR), India, Hui Qian from Changan University, China, Abida Farooqi from Quaid-i-Azam University, Islamabad, Pakistan, and Manish Kumar from Tezpur University, India and Pritam Gosh from Council of Scientific & Industrial Research (CSIR), India were identified as the five most capable and prolific authors with 26, 23, 21, 16 & 15 publications respectively. On the other hand, Hui Qian's scientific role has received more recognition in terms of citations (902) than those of Priyabrata Banerjee (508).

b. Associations in scholarly academic partnerships

The literature review selected included a series of primary sources to gain information on the scale and approach of current collaborations for research. The authors' cooperation map showing the network was created in VOS viewer. The results are shown in figure 2.13 to understand the co-authorship clusters in different institutes working on F research. A total of three clusters of the institutes were found.

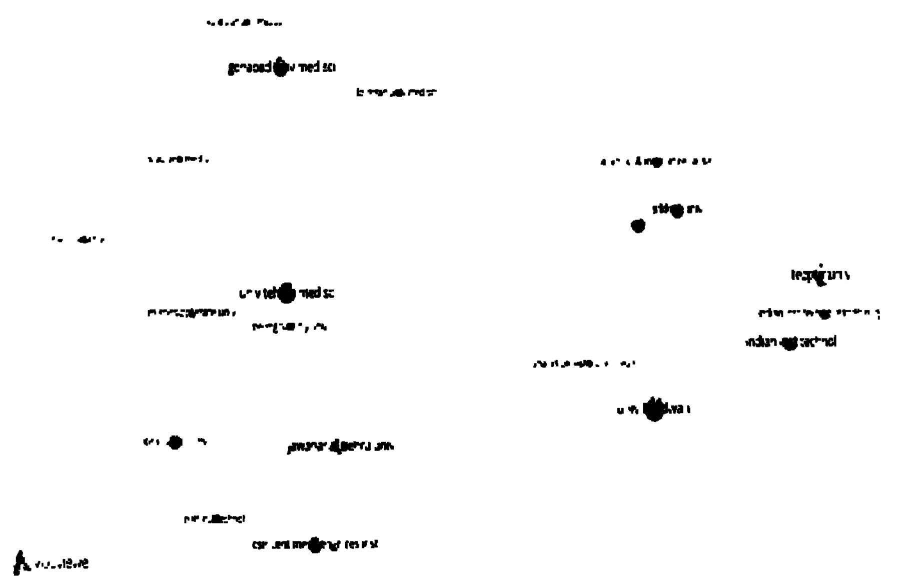

Figure 2.13. Clusters of co-authorship collaborations

c. Analysis of keywords

The maps for keywords represent a discipline's cognitive structure. The choice of keywords shows the focus of scientific research and its orientation. To do this, the keywords of the publications were extracted and analyzed. The results are shown in Figure 2.14. Only words have been listed with at least twenty-five events. To alleviate the excessive noise, the technique was implemented. The overlay display shows the co-occurrences of keywords. The frequency is indicated by node size, while color shows the release time.

Figure 2.14. Keyword occurrences in fluoride related literature for the period 2011-20

The nodes in the center represent the keywords such as fluoride (771), "fluorine compounds" (438), "adsorption" (372), "groundwater" (363), and "article" (320). Whereas the keywords like "drinking water" (284), "fluorides" (250), "concentration (composition)" (248), "pH" (204), "water pollutants, chemical" (18), and "potable water" (187) also appeared significantly in the analysis.

Systematic analysis via bibliometrics assists in identifying hot spots in literature and discovering patterns in science (Xie et. al., 2011). Since the 1930s, the removal of fluoride from drinking water has been studied (Boruff, 1934). Fluorine in drinking water research has primarily been conducted in environmental sciences, public and occupational health and dentistry, and oral surgery medicine (Srimurali et. al., 1998; Featherstone, 1999; Magalhães et al., 2008).

For the most part, creative publications on F contamination have seen an upward trend over the last decade. This past decade has seen increased F publications on the scale of all solvents, chlorinated aromatics, and BTEX (benzene, toluene, ethylbenzene, and xylene) (Xiyue et. al., 2020). The sudden increase in F-related research publications throughout the world from 2015 to 2020 is clear evidence of the increasing issue of F contamination globally. However, the general trend in publications worldwide during 2000 to 2020 time period is also increased (Mike and Pardeep, 2022).

Most recently, it has been discovered that F poisoning occurs because of natural F in groundwater. Additional research has been done to find out the hydrogeochemistry of high-F groundwater, examine the health effects on nearby people, and study how to remove the contaminant via effective water treatment methods and devices (Singh et. al., 2013). Researchers and managers alike are keen on reducing the human health risks from F contamination in the groundwater.

iv. Conclusion

The present study concluded that most of the F contamination in drinking water research is carried out in Southeast Asian countries like India, Pakistan, Bangladesh, Iran, etc. The possible reasons can be increasing cases of dental and skeletal fluorosis, dental issues, and the long-term use of large doses can lead to long-term consequences, including potential bone damage.

Although much has been accomplished in the realm of the fluoridation literature in the last decade, this study is only just the beginning to lay the foundation for a more holistic approach and beyond. Lack of social science understanding, in particular, is profoundly troubling. Some existing frameworks are still just ideas and require significant input from many stakeholders to become actionable.

CHAPTER-3

STUDY AREA

Pakistan is divided into 123 districts with latitudes ranging from 24 to 37 degrees north and longitudes ranging from 62 to 75 degrees east (Vista, 2000). The total area is 803,940 sq km. The landscape is bounded on the east by the Indus Plain, on the north by the Hindukush and Karakoram ranges, and on the northwest by a highland plateau that extends from 8611 m in case of Mount Everest to 0 m for the Indian Ocean.

3.1 Climate

The climate is predominantly arid to semi-arid, with temperate conditions in the northwestern mountains and arctic conditions in the northern peaks. Annual rainfall in Pakistan averages between <125 mm in the south-west (Baluchistan in west) and >1000 mm in Islamabad and falls to < 125 mm in the northern mountains (Muzaffar, 1997). July and August are the months with the most monsoon rains. The Indus Plain's average annual temperature is around 18°C (with monthly maximums exceeding 40°C), but it drops precipitously in the northern mountains.

3.2 Geology

Pakistan's surface geology is conquered by younger Quaternary (tertiary) sediments that crag over large parts of the basins of Indus and Baluchistan. The Indus sediment is mainly a deposit of alluvial and deltaic sand, silt and clay. Greater sands and gravel are present, particularly at the highlands of the plain (WAPDA/EUAD, 1989). Sand in the east of the Indus valley, that contains mainly the Cholistan and Thar desert areas, is windy.

Most of the sediments of the Baluchistan are from recent wind and water erosion; but there are also large quantities from dried-up lake beds. Some brines have a high concentrations of surface salt due to evaporation. It is found as unconsolidated deposits in the KP, Peshawar Valley, as well as in Dera Ismail Khan and Bannu basin. Sands, silts, gravels, and clays have different thicknesses and concentrations. They get up to over 300 m thickness in the Dera Ismail Khan Plain (WAPDA/EUAD,1989)

Mesozoic and Cenozoic sedimentary rocks are found along a north-south axis of the Indus Plain, to the coast from Peshawar. The north, which includes KP, Gilgit, and Jammu & Kashmir, is home to older sediments that are identified as the Paleozoic sediments and crystalline basement rocks i.e., granites, metamorphic rocks (Shamsi, 1989).

The Quaternary alluvial aquifers of the Indus Plain are by far the most productive of the available aquifers. Groundwater yields from these sediments usually vary from 100 to 300 m3/hour at depths of 150 meters. On the eastern rims of the Plain, the Thar and Cholistan desert sediments produce lower yields (typically 10-50 m3/hour) (south-eastern border with India). Fine-grained or Deltaic Quaternary yields also run out along the southern seaboard (Shamsi, 1989). Pervious gravels can be found in intermountain valleys (Baluchistan and KP), but they are generally found to be scarce.

3.3 Aquifer Geology

Rich aquifers are concentrated in the far western and northern parts of Pakistan because of older sedimentary and crystalline basement rocks, with uneven groundwater flow. Hard sedimentary rocks, such as the Potwar Plateau's Siwalik Sandstone, the Zhob River Basin's Multana Conglomerate, and the Rakhshan River Basin's Ketch Conglomerate, also have relatively high yields of groundwater, but their production is limited to areas with favorable revive (WAPDA/EUAD, 1989).

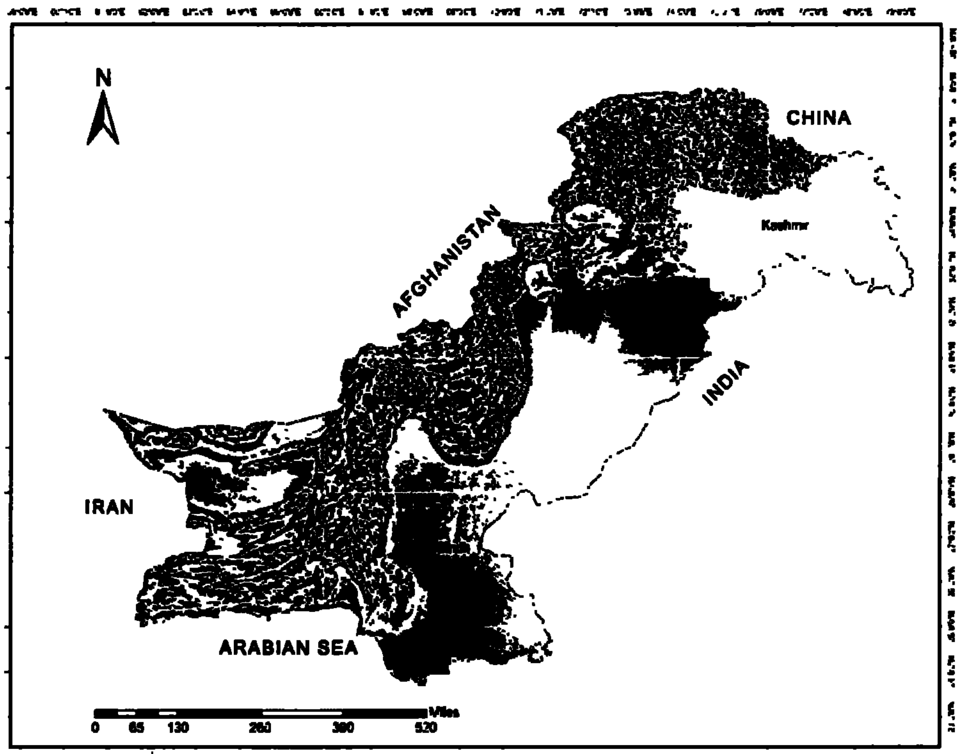

Figure: 3.1 Study area map

Older crystal-like rocks are usually impermeable, and groundwater yields are dictated by the existence of cracks. Groundwater supply in the mountains on north is further restricted by the existence of glaciers and the cold climate.

The in depth details of the study area is available in chapter 4 part 4.2.

CHAPTER-4

4.1. WATER QUALITY ANALYSIS

4.1.1. Introduction

Water pollution jeopardizes nearly all of the internationally agreed development goals aimed at eradicating environmental degradation, poverty, and suffering by 2030. Groundwater is more sustainable than fresh water, and it has the added advantage of avoiding evaporation losses. Approximately 70% of drinking water is from aquifers. Drinking water supplies mainly come from surface water bodies (rivers, canals, reservoirs, or aquifers.

Geogenic and anthropogenic pollutants are playing a significant role in water sources that may affect human health, e.g. cardiovascular and skeletal disorders, and neurotoxicity (World Health Organization, 2011). Rapid industrialization and excessive use of pesticides and fertilizer consumption in agriculture have led to the water contamination in developing countries (Eqani et al., 2012; Srinivasa and Govil, 2007). Additionally, As and F are deposited in groundwater and surface water from geogenic sources. In underdeveloped countries, particularly in rural areas, trace metal contaminated water can often be found (Khan et al., 2012; Winkel et al., 2008).

Trace metals and major and minor ions pollution is common in Pakistan because of the geology of the Himalayas. These massive, rocky mountains were formed by similar geological processes. Rivers and streams in the Himalayas bear sediments and precipitation, which ultimately go to the Indus River, where 1.2 million people live. There are an estimated 172 million people downstream of this chemical pollution. The human activities, overuse of natural resources, mineral, and industrial contamination are the major pollution sources in water ecosystems. Nevertheless, soil depletion, mineral precipitation, and leaching from rock, and soil-based erosion can all lead to the concentrations of various pollutants in groundwater.

In most parts of Pakistan, groundwater is the major source of drinking water. Regions that have a high levels of metal contamination, such as Pakistan, also undergo more from human activities. For many Pakistanis, the climate is the most important. In rural areas, almost two-thirds of the population is without treatment facilities or awareness of chemical threats. It is expected that this community will be in danger of pollution. However, there is not enough understood about the target population and the areas in which we can focus on cleaning up or preventing pollution, because exactly who is in this high-risk groups is unknown.

Nevertheless, raw sewage, industrial wastewater and the high use of fertilizers and pesticides pollute water in Pakistan. As a result of excessive pumping, the salinity of groundwater increases. Additionally, Pakistan is also working to tackle water shortage and groundwater pollution.

In comparison, international estimates indicate that only 25.61 percent of Pakistan's population has access to potable water (Rosemann, 2005). Drinking water appears to be highly polluted in several major cities in Pakistan, including Islamabad, Faisalabad, Karachi, Lahore, Rawalpindi and Qasur (Bhutte et al., 2002). Poor water quality is estimated to be the primary cause of the spread of approximately 30% of diseases and 40% of deaths in Pakistan (Country Report, Pakistan, 2000). Diarrhea, a waterborne disease, is the leading cause of death among newborns and children in Pakistan. Additionally, every fifth person suffers from a variety of illnesses and diseases caused by contaminated water (Kahlown et al., 2006).

4.1.2. Materials and methods

The current study was designed to evaluate the various contaminants in the groundwater samples of various localities throughout Pakistan.

4.1.2. A. Sampling

The methods follow the recommendations of the "American Public Health Association" (APHA, 1995). The analytical precision and reproducibility of the measurements were both less than 2%. The ionic balance error was 5% for the ions studied. For this investigation, 500mL of groundwater was collected from bore wells in various locations throughout Pakistan. In 2017, the bottles of capped high-density polyethylene were used in accordance with the prescribed sampling procedure. Prior to collecting samples, tap water should be allowed to flow continuously for three to four minutes to avoid any accumulated water in the pipes. Additionally, the sample bottles were rinsed twice with the sample water to remove any exogenous impurity. The sample bottles were properly labeled and transported to the laboratory immediately. To avoid sample decomposition samples were stored at 4°C prior to analysis.

Several physico-chemical parameters such as pH and EC were monitored in situ. For the determination of various physico-chemical parameters all of the samples have been treated as such: no conservants or stabilizers have been added. The quality and acid resistant Borosilate Glass was the totality of the glassware used for the study. Pipettes of 1.0mL capacity were used to produce less than 1mL of samples or solutions. The reagents for quantification controlled their purity and quality completely, thus having a certified cleanliness of 99.99%.

4.1.2. B. Laboratory Analysis

a. Physiochemical Parameters

Physiochemical parameters of drinking water samples were analyzed in the Environmental toxicology and human health laboratory of COMSATS.

i. pH

pH was determined by digital meter (LAQuAact-ph110Horiba) in accordance with standard procedure. Onsite field measurement of pH was done in order to ensure high analytical quality of water samples according to scientific standards.

ii. Total dissolved solid and Electrical conductivity

TDS and EC were measured by the conductivity meter (4300 Jenway- NWQL/CLEQ-002B). Prior to analysis conductivity meter was properly calibrated in accordance with standard solution having EC 1413 µS/cm and EC 1288 µS/cm (APHA-2005).

iii. Redox Potential

Redox was measured on site the filed using a digital redox meter in order to ensure the high analytical quality of water samples according to the standard method.

iv. Fluoride

F in drinking water samples were measured by F portable photometer (HI-96739 Hanna High range).

v. Hardness

Hardness was measured by the titration method. 10ml sample was taken and buffer solution was poured. EDTA is used as titrant. It was noted when pink color changed to blue (APHA-2005).

vi. Carbonates and Bicarbonates

To assess carbonates pH must be greater than the 8.5. Bicarbonates were determined by the titration method. 2-3 drops of methyl orange indicator were used. Hydrochloric acid was used as titrant. The color changed from orange yellow to salmon pink.

vii. Chlorides

Chlorides in water samples were determined by titration method. Silver nitrates were used as titrant and poured in 20ml of water sample. Potassium dichromate was used as indicator. Readings were noted when yellow color changed to red.

viii. Calcium

Calcium water samples were measured by the titration method .10ml of water sample and ½ 1M NaOH added. Pinch of murexide was used as indicator. EDTA was used as Titrant. End point was noted when pink color changed to purple color.

ix. Magnesium

Magnesium was determined in samples by using the following formula

$$Mg = (Ca \times 2.5) - (Hardness \times 0.243)$$

source: APHA 2340-C, Standard Method (1992)

x. Sulfates

Sulfates were measured using colorimeter (Model no DR/890). 420nm ultraviolet is used for sulfates.

xi. Nitrates

Nitrates were measured by the Spectrophotometer (SPECORD) 220nm light was used for nitrates.

xii. Phosphates

Phosphates were measured by the colorimeter (Model no DR/890). 420nm ultraviolet is used.

xiii. Alkalinity

Alkalinity was also measured by the titration method. 20ml samples were taken few drops of phenolphthalein was added the color changed to pink. Titrated against sulphuric acid the solution become colorless. Few drops of methyl-orange added then titrated against acid the color changed to orange yellow.

xiv Color

Clean water should be colorless. The watercolor was determined by human index

Xv Turbidity

Turbidity of water was determined by turbid meter.

4.1.2. C. Statistical Analysis

Analytical results were collected to form a multi elemental database using Microsoft excel 2016 software. Moreover, Microsoft Excel was also used for graphical representation of dataset. The basic statistical analysis, factor analysis and multiple comparison of different samples was executed using Tibco Statistica Academic 13.4. To discover the possible correlations, the analysis was performed on water quality parameters. To assist in identifying where contamination may have occurred, principal component analysis (PCA) was performed on the data. A piper trilinear plot was made using the Grapher 10.0 to compile the geochemical data; the quality control system and the main hydro geochemical aspects in the study area is determined using the Gibbs diagram. The physical-chemical parameters of the WHO's guidelines for groundwater analysis were observed and compared to the results obtained through standard measurements.

4.1.2. D. Water Quality Index (WQI)

There are many parameters that exceed or are at their limits, with unknown health impact, and many water samples are expected to be within the scope of the water quality standards. Also, experienced experts could have difficulties assessing water quality by tabulating and examining these parameters visually. These studies have been dedicated to the comprehensible and operationalization of water quality (Pesce and Wunderlin, 2000). The WQI has a single number that provides an easy-to-understand representation of overall water quality. The quality of water can be recognized quickly and easily by observing one number, then comparing it to the corresponding aggregate value on the scale. WQI expresses water quality in a way that is simple to understand such as "very good", "good", "poor", etc. (Akkoyunlu and Akiner 2012; Pesce and Wunderlin 2000). WQI is a useful means to describe water quality and it is very helpful to identify the quality of water and its sustainability for drinking.

The first water quality expression experiments were carried out in Germany in 1848 by its pollution level (Lumb et al. 2011a). But the production of the WQI took nearly a century. Centered on 8 water quality parameters, Horton established a WQI in 1965. The "Oregon Department of Environmental Quality" created the "Oregon Water Quality Index (OWQI)" in the 1970s (DEQ). The methods for this indexation are created on the conversion of parameters of water eminence to non-dimensional values, by using sub-index calculations and adding these under-indexes to generate a single water quality indication. In the 1990s a new water quality index, which differs from the "National Sanitation Foundation (NSF)" based model and can be known as the "Canadian Water Quality Index (CWQI)" in 2001, was proposed to the "Canadian Council of Ministers of Environment Water Quality Index" in the 1990s (Lumb et al. 2011; Sarkar and Abbasi, 2006).

4.1.2. E. Predictive modeling in ArcGIS

Geographical Information System is an emerging tool which is used for planning and decision making. It deals with the geographical location and its information. GIS tool was utilized to plot the sampling locations on the map. "Inverse distance weighting (IDW) interpolation" was used to estimate the unknown values based on known values in the study region. Inverse weighted weighting (IDW), also known as inverse distributed weighting, is a deterministic technique for multivariate interpolation where scattered points are known and used to predict unknown coordinates. The unknown points assigned values can be determined by a weighted average of the known points. Inverse distance weighting method was used to portray parameters Al, Ca, Cl, EC, F, Mg, NO_3, Sulfate, TDS, Temperature, Total Hardness and Turbidity. Spatial extent for each parameter is calculated and displayed with minimum and maximum values ranges over the study area. All parameters values are dived into five classes to reflect the spatial variation over the study area.

4.1.3. Results and Discussion

I. Statistical analysis

a. Physico-chemical parameters

Descriptive statistics on the physicochemical properties of the groundwater samples studied is presented in table 4.1. The order of dominance of investigated anions and cations is SO_4^{-2} > Cl^- > NO^{-3} > F^- and Mg^{+2}>Ca^{+2} respectively (figure 4.1).

i. pH

The pH of the groundwater plays a significant role in determining whether the water is alkaline or acidic in nature (Aravinthasamy et al., 2019). The pH of the studied samples varied from 6.14 - 9.18 with 7.6 as mean value of and 0.4 as standard deviation. This indicates that most of the samples are naturally alkaline (Table 4.1). It has been found that there is no correlation between pH and population health which implies no health-based value for pH

(WHO, 2017). In general, the pH of the natural water varies from 6.0 - 8.5. However, low pH is the indication of water rich in organic matter. Conversely, high pH values are primarily found in groundwater with high carbonates (HCO^{-3}) content i.e., eutrophic water bodies, groundwater brines and salt lakes etc. (Ahada and Suthar, 2018; Chapman, 1996).

ii. Temperature

Typically, the temperature of groundwater remains constant and is generally near the mean yearly air temperature. Moreover, deep aquifers have generally high temperatures as a result of earth's thermal gradient (Chapman, 1996). The temperature values (°C) in the present study varies from 9.7 - 35.4 with a mean value of 23.0 and standard deviation of 6.2.

iii. Electrical Conductivity (EC)

The electrical conductivity measures the conducting ability of the groundwater probably as a result of occurrence of dissolved ions and is considered as one of the major indicators of water quality for drinking and irrigation purposes (Jamali et al., 2020; Ahada and Suthar, 2018). The electrical conductivity concentrations (µs/cm) varies from 23.6 to 23600 with a mean value of 1115.8 and standard deviation of 1495.1. The obtained results showed that the electrical conductivity of studied samples is far above the permissible limit of 1500 µs/cm. The high electrical conductivity in groundwater is the representation of different processes like water circulation, surface infiltration, cation exchange etc. (Ahada and Suthar, 2018).

iv. Total Dissolved Solids (TDS)

Calcium, magnesium, sodium, and potassium are the primary components of total dissolved solids (TDS). The main sources of TDS include industrial wastewater, urban runoff, sewage and also the natural sources (WHO, 2017). In order to assess the quality of groundwater on the basis of TDS, four classes have been assigned by Robinove et al. (1958). According to this classification, groundwater is very saline if TDS>10,000 mg/L, moderately saline if TDS>3000-10000 mg/L, slightly saline if TDS>1000-3000 mg/L and non-saline if TDS<1000mg/L. High levels of TDS affects the taste, hardness and corrosivity of water (Akhtar et al., 2014). The TDS concentrations in this study varied from 3.6-1180 with a mean value of 562.9 and standard deviation of 750.3. The WHO recommends a TDS limit of 500 mg/L for drinking water, with a maximum permissible limit of 1500 mg/L. The results show that the studied samples are non-saline and falls under the permissible limits of WHO thus posing no health risks to groundwater consuming population.

v. Sulfate (SO_4^{-2})

In natural environment, sulfate is present in various minerals and have wide application in commercial sector particularly in chemical industry (WHO, 2017). In natural waters, the concentrations of sulfate vary from 2-80 mg/L. However, in arid areas where sulfate minerals like gypsum are in abundance or in industrial regions the concentration of sulfates may exceed up to 1000 mg/L (Chapman, 1996). In the current study, the concentrations (mg/L) of sulfates varied from 0-2830 with a mean value of 206.4 and standard deviation of 290.2. The presence of sulfates in groundwater is mainly due to the weathering of sulphate and sulfide minerals i.e. pyrite and gypsum from sedimentary rocks and dissolution of sulfate evaporates (Ahada and Suthar, 2018; Chapman, 1996). In sandy loamy soils, surface precipitation via rainwater and irrigation also adds the sulfates in groundwater (Ahada and Suthar, 2018). However, the major contributors of sulfates in groundwater possibly will be cattle dung, fertilizers, wastewater disposal, human excreta etc. The WHO has not suggested a health-based guideline value for sulphates. However, at 1000-1200 mg/L concentrations, few laxative effects have been observed in piglets and human populations. Furthermore, sulfate with its particular taste is easily noticeable and may cause corrosion of water supply systems. It is advised to inform the health authorities when the concentration of sulfate exceeded 500 mg/L in drinking water (WHO, 2017).

vi. Chloride (Cl^-)

In natural environment, chloride is present in all waters in low concentrations (Hem, 1985). The study observed that the concentrations (mg/L) of chloride varied from 0-6400 with a mean value of 96.1 and standard deviation of 323. However, the acceptable limit of chloride for daily intake of water is set at 250 mg/L (Solangi et al., 2019). The key sources of chloride in groundwater includes weathering of sedimentary rocks, domestic waste, agricultural run-off, industrial wastes, septic tank leakages and sewage discharges etc. In addition, phenomena of roads salting in winters is also considered as one of the major contributors of chloride in ground waters (Adimalla et al., 2019; Chapman, 1996). The chloride concentration in pure freshwaters is typically less than 10 mg/L (Chapman, 1996). In ground waters, the levels of chloride decrease with increasing hardness, alkalinity, TDS, sulfates and electrical conductance thus showing an inverse relation with these parameters (Parmar and Bhardwaj, 2013).

vii. Hardness

Generally, the occurrence of dissolved magnesium and calcium salts defined the general water hardness. Carbonate hardness and non-carbonate hardness are determined by the concentrations of calcium and magnesium hydro carbonates, as well as calcium and magnesium salts of strong acids (Chapman, 1996). Although no major health concern related to hardness have been reported, but some studies suggested its role in disturbing the functioning of heart (Sudashivaiah et al., 2008). The hardness values in this study varied from 0 - 2934 with a mean value of 260 and standard deviation of 215.4.

viii. Calcium (Ca^{+2})

The presence of calcium in groundwater is mainly due to natural processes i.e., dissolution of minerals rich in calcium and have a substantial effect on the quality of groundwater. High levels of calcium have a potential to cause hardness in water thus restricting its use for irrigation purposes (Ahada and Suthar, 2018). In natural waters, the levels of calcium are generally <15 mg/L (Chapman, 1996). According to WHO (2017), the guideline value set for calcium is 100-150 mg/L. The concentrations (mg/L) of Ca^{+2} in this study varied widely from 0-988 with a mean value of 115.4 and standard deviation of 88.9. Apart from natural processes, industrial wastewater is also a main source of calcium in groundwater. Higher concentrations of calcium could also be attributed to their slow rate of removal by soil (Prakash and Somashekar, 2006).

ix. Magnesium (Mg^{+2})

Magnesium is considered as a vital element for living beings and may present in various organometallic compounds and in organic matter (Chapman, 1996). In general, magnesium is found as Mg^{+2} in natural waters and is considered as one of the major determinants of water hardness along with Ca^{+2} (Ahada and Suthar, 2018; Chapman, 1996). In fresh waters, the magnesium concentrations may vary from 1 to >100 mg/L naturally reliant on the type of rocks. The magnesium concentrations (mg/L) varied from 0-2556 in the current study, with a mean value of 144 and standard deviation of 159. According to WHO guidelines, the permissible limit for magnesium in drinking water is 50 mg/L, implying that the magnesium concentration in the studied samples is significantly greater than the guideline value (Ahada and Suthar, 2018). The predominant source of magnesium in groundwater is the weathering of ferromagnesium mineral and carbonate containing rocks.

x. *Turbidity*

According to International Standards Organization (ISO), turbidity is the measure of reduction in visibility of the water due to the existence of undissolved matter i.e. suspended solids (microorganisms, silt and clay particles, algae) and organic matter etc. (Chapman, 1996). It is a significant factor and a major contributor to water quality assessment (Prakash and Somashekar, 2006). The acceptable limit of turbidity for drinking water is 5 NTU. However, the turbidity values (NTU) in this study varied from 0-1058 with a mean value of 12.2 and standard variation of 60.8 which indicates the presence of suspended and colloidal particles in water which makes it unfit for drinking purpose. Numerous factors like leaching of organic waste along with industrial, agricultural (inorganic nutrients i.e., nitrogen and phosphorus) and domestic wastes contributes manifold in increasing the turbidity of ground waters (Prakash and Somashekar, 2006).

xi. *Fluoride (F^-)*

In natural waters, the F concentration is usually less than 1 mg/L which at times may exceed up to 10 mg/L (Srinivasa moorthy et al., 2010). An optimal level of F is beneficial for teeth and bones but concentration greater than 1.5 mg/L is known to cause various hazardous issues regarding human well-being i.e., dental fluorosis, fluorosis of the skeleton, cancer etc. (Ali et al., 2016; Vithanage and Bhattarcharya, 2015; Kumar, 2012). However, F levels less than 0.5mg/L are known to cause tooth decay, bone fragility etc. (Ali et al., 2016; Thivya et al., 2015). The value of F in the present study varied from 0-3.6 with a mean value of 0.57 and standard deviation of 0.53. Few of the samples have exceeded the permissible limit of WHO as per study findings which could be credited to weathering of F bearing minerals and industrial manufacturing of aluminum, steel and fertilizers. Beside these, the leaching of phosphate fertilizers from soil is also the potential source of F contamination.

xii. *Nitrate (NO^{-3})*

Nitrate is a vital plant nutrient and is found in different concentrations in all plant's species (WHO, 2017). The safe limit for nitrates as per WHO is 50 mg/L (WHO, 2017). Though in the current study, the concentrations (mg/L) of nitrates are found to be varied between 0-193 with a mean value of 7.3 and standard deviation of 14.1 which indicates that the groundwater is not affected by the presence of nitrates. Major contributors of nitrates affecting the quality of groundwater includes application of nitrogenous fertilizers, sewage sludge, industrial effluents, human and animal wastes, septic tanks etc. (Ahada and Suthar, 2018). High nitrate levels in drinking water may cause methemogluchemoglobin formation or gastric cancer in babies (Adimalla et al., 2019; WHO, 2017).

xiii. Alkalinity

Alkalinity basically indicates the presence of various basic compounds i.e., carbonates, bicarbonates, hydroxide, borate, phosphates, silicates etc. Low alkalinity (< 24 ml/L as CaCO3) are associated with low buffering capacity hence prone to alteration in pH (Chapman, 1996). The alkalinity values varied from 0-1148 with a mean value of 219.1 and standard deviation of 113.5 in the current investigation.

Table: 4.1 Statistical summary of water quality parameters, n=524

Variables	Mean±S.D	Min-Max	Variance	Skewness
pH	7.669±0.455	6.14-9.18	0.206	-0.424
Temp	23.016±6.256	9.70-35.40	39	0.201
EC	1115.894±1495.134	23.60-23600.00	2235425	7.990
TDS	562.985±750.397	3.60-11810.00	563096	7.908
Sulphates	206.448±290.238	0.00-2830.00	84238	3.626
Chloride	96.184±323.004	0.00-6400.00	104332	14.960
Hardness	260.031±215.463	0.00-2934.00	46424	5.373
Calcium	115.464±88.971	0.00-988.00	7916	3.327
Mg	144.419±159.093	0.00-2556.00	25311	7.508
Turbidity	12.203±60.852	0.00-1058.00	3703	11.861
Fluoride	0.576±0.535	0.00-3.68	0	1.954
Nitrates	7.322±14.113	0.00-193.00	199	6.641
Alkalinity	219.141±113.598	0.00-1148.00	12905	1.849

S.D=Standard Deviation, S.E=Standard Error, Min-Max=Minimum-Maximum, *P= <0.01

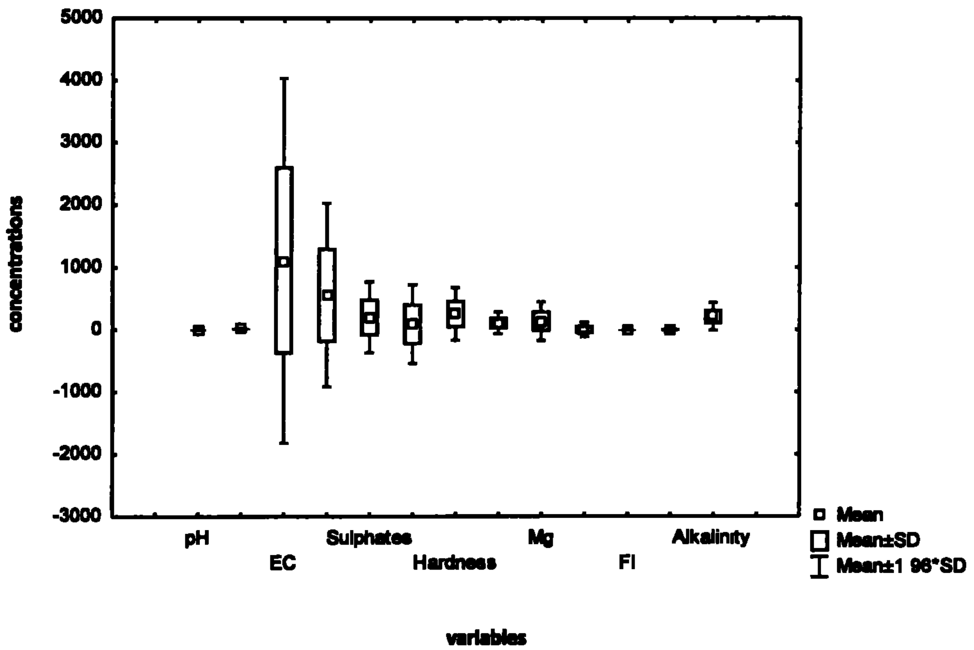

Figure: 4.1 Box-and-Whisker plot for physicochemical parameters used for the study

b) Correlation matrix

The correlation plots are used to comprehend the interconnection between F and various physicochemical parameters in order to understand various controlling factors and the process of F enrichment in groundwater (Adimalla et al., 2019). In the present study, correlation coefficients ranging from 0.70 to 1.00, 0.30 to 0.70 and 0.00 to 0.30 signifies strong moderate and weak positive correlations respectively. However, correlation coefficients ranging from -0.70 to -1.00, -0.30 to -0.70 and 0.00 to -0.30 signifies strong moderate and weak negative correlations likewise (Aravinthasamy et al., 2019).

According to the results presented in Table 4.2 significant correlation has been observed in case of EC with TDS (r =0.99), Cl- (r =0.90), hardness (r =0.78) and Mg2+ (r =0.80). Similarly, strong correlation has also been noted between TDS and Cl- (r =0.90), hardness (r =0.78) and Mg2+ (r =0.80). Moreover, Cl- with hardness (r =0.72) and Mg2+ (r =0.79) and hardness with Ca2+ (r =0.75) and Mg2+ (r =0.92) are also found to be strongly correlated. However, as shown in Table 4.2 moderate positive correlation has been observed in case of F with EC (r = 0.35), TDS (r = 0.35) and sulfates (r = 0.40).

Similar findings have been noted by Aravinthasamy et al. (2019) during the evaluation of groundwater samples from pre and post monsoon seasons collected from Shanmuganadhi River basin, South India. The semi-arid climatic conditions, increased rate of evaporation and enrichment of nutrients are among the various factors that may be responsible for the high values of EC. However, the presence of sulfates in groundwater could probably be due to the leaching of fertilizers and waste i.e. municipal etc. in the study area (Srinivasamoorthy et al., 2014). However, chloride (r = 0.18), hardness (r = 0.29), calcium (r = 0.18), magnesium (r = 0.29), nitrates (r = 0.17) and alkalinity (r = 0.30) show weak positive correlation with F. Moreover, F exhibits weak negative correlation with temperature (r = -0.15).

The positive correlation between alkalinity and F depicts that the alkaline environment is the major contributing factor in leaching of F from F containing minerals in the groundwater of the study area (Thivya et al., 2015). Other researchers i.e., Tiwari et al. (2008), Narishma and Sudarshan (2016) etc. have also previously reported a direct relation between pH and presence of high F concentrations in the groundwater of study area. Nonetheless, it has now been recognized that the F shares quite an unstable chemical relation with anions and is easily prone to replacement at all temperature and pressures. Hence the weathering of parent rock and dissolution of its minerals plays a significant role in increasing the F content of groundwater. The process of weathering mainly occurs in cracked hard rock areas that contain minerals like fluorite, apatite, topaz, villiamite and F replaceable hydroxyl ions in ferromagnesium silicates (Adimalla and Venkatayogi, 2017).

Table: 4.2 Correlation matrix of groundwater samples from selected areas of Pakistan

Variable	Correlations: Marked correlations are significant at p < .05000 N=524												
	pH	Temp	EC	TDS	Sulphates	Chloride	Hardness	Calcium	Mg	Turbidity	Fl	Nitrates	Alkalinity
pH	1.00	0.016	0.003	-0.0004	0.038	0.005	-0.140	-0.187	-0.081	-0.001	0.066	-0.032	-0.099
Temp		1.00	-0.131	-0.125	-0.137	-0.021	-0.189	-0.316	-0.076	0.160	-0.156	-0.054	-0.178
EC			1.00	0.992	0.687	0.907	0.785	0.457	0.805	-0.077	0.358	0.291	0.378
TDS				1.00	0.686	0.905	0.782	0.456	0.802	-0.077	0.355	0.286	0.373
Sulphates					1.00	0.435	0.601	0.455	0.559	-0.060	0.404	0.134	0.369
Chloride						1.00	0.728	0.348	0.791	-0.038	0.185	0.222	0.167
Hardness							1.00	0.751	0.926	-0.106	0.298	0.194	0.305
Calcium								1.00	0.460	-0.116	0.185	0.098	0.204
Mg									1.00	-0.070	0.297	0.205	0.293
Turbidity										1.00	-0.063	-0.021	-0.156
F											1.00	0.176	0.305
Nitrates												1.00	0.204
Alkalinity													1.00

c. Gibbs Plot

In the present study, Gibbs diagrams are employed to visualize the chemical characteristics of the groundwater and geochemistry in the research area. The below figure 4.2 shows that all the groundwater samples are in the predominant interaction area of rock-water, indicating that the major ion chemical characteristic of groundwater depends primarily on rock weathering, which eventually led to poor groundwater quality. None of the sample lies in the precipitation dominance and evaporation dominance zones.

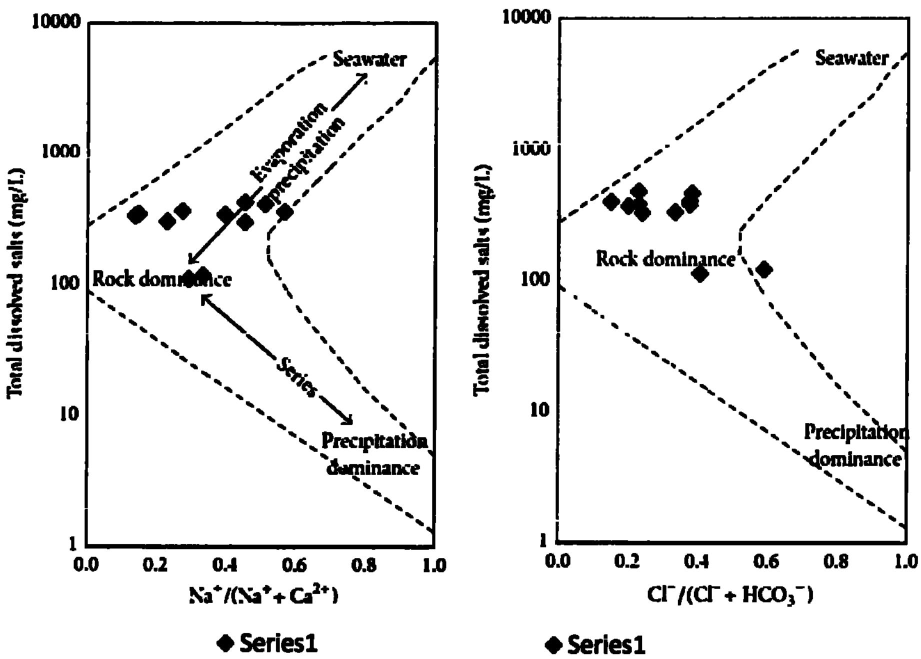

Figure: 4.2 Gibbs diagram showing the main sources of variation in groundwater chemistry in the study area

The dominance of rock water interaction indicates the presence of weathered rocks which in combination with leaching of fluorine containing minerals resulted in high F concentration in groundwater. The study area is chiefly occupied by granites which are the main source of F containing minerals i.e. fluorite, apatite, biotite, hornblende and muscovite thus the high levels of F in the groundwater.

Similar verdicts have been reported from areas with a hard rock terrain, including the Karnataka districts of Kolar and Tamkur. (Mamatha and Rao, 2010), Telanga State, India (Narishma and Sudarshan, 2016), Gharabar village, Jharkand, India (Thapa *et al.*, 2017), River Basin of Shanmuganadhi, South India (Aravinthasamy *et al.*, 2019) and Andhra Pradesh, India (Adimalla *et al.*, 2019) etc.

The weathering of granite and gneissic rocks also help releases the bicarbonate, TDS, magnesium, calcium, chloride and sodium ions in the groundwater (Mamatha and Rao, 2010). However, the dissolution of fluorite can also occur when granitic rocks encounters alkaline water i.e. rich in bicarbonate and sodium bicarbonate resulting in the immediate formation of calcite (Adimalla *et al.*, 2019; Ramamohana Rao *et al.*, 1993). Thus, increasing the F content of groundwater as shown in the below equations:

Dissolution and precipitation of F: $CaF_2 \longleftrightarrow Ca^{2+} + 2F^-$

Precipitation of calcite: $CaF_2 + 2HCO_3 \longrightarrow CaCO_3 + 2F^- + H_2O + CO_2$

Precipitation of calcite: $CaF_2 + NaHCO_3 \longrightarrow CaCO_3 + 2Na^+ + 2F^- + H_2O + CO_2$

Muscovite weathering: $KAl_2[AlSi_3O_{10}]F_2 + 2OH^- \longrightarrow KAl_2[AlSi_3O_{10}][OH]_2 + 2F^-$

Biotite weathering: $KMg_3[AlSi_3O_{10}]F_2 + 2OH^- \longrightarrow KMg_3[AlSi_3O_{10}][OH]_2 + 2F^-$

d. Hydrochemical facies

The Piper-Hill diagram is considered as an important tool in inferring the hydrogeochemical facies and characterization of groundwater type (Piper, A.M., 1944). In this trilinear diagram, cations and anions are mapped in two separate basal triangles which then joined to form a single point in a diamond shaped field which generally specifies the chemical character of water. Generally, the major cations and anions plotted in this diagram includes; Ca^{2+}, Mg^{2+}, Na^{+} and K^{+} and HCO_3^{-}, CO_3^{2-}, Cl^{-} and SO_4^{2-} respectively. The calculated anions and cations are denoted as percent of meq/L (Adamialla *et al.,* 2019; Saha *et al.,* 2019; Sadashivaiah *et al.,* 2008).

In this study, the major ion chemistry of groundwater was studied by using piper trilinear diagram in order to identify the alterations in groundwater (Srinivasamoorthy *et al.*, 2010). As evident from the figure 4.3, the cation triangle represents the dominance of Ca^{2+} followed by Na^{+} whereas, the anion triangle shows the dominance of HCO_3^{-}. However, the majority of the groundwater samples are plotted in alkaline area i.e., NaCl followed by $CaHCO_3^{-}$.

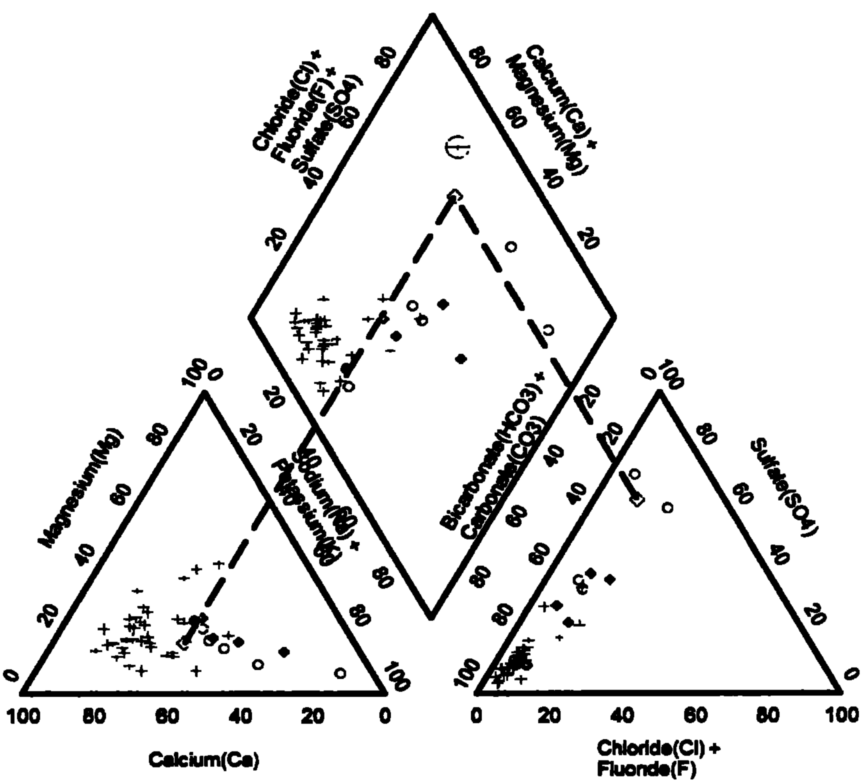

Figure: 4.3 Piper trilinear diagram presenting groundwater types

The dominance of Na^+ and Cl^- ions represents the process of evaporation which possibly enhances the ionic strength of water. Moreover, the dissolution of clay, gravel, feldspar and mirabilite salt ($NaSO_4$), weathering of silicate and leaching of agricultural wastewater etc. significantly increases the Na^+ content in groundwater (Srinivasamoorthy *et al.,* 2014). Furthermore, surface enriched salts are also considered an important source of Na^+ and Cl^- especially in arid areas (Zhang *et al.,* 2019). However, rainwater, fertilizers and sewage water play an essential role in increasing the Cl^- content of groundwater (Srinivasamoorthy *et al.,* 2014).

In addition, the groundwater rich in bicarbonates and sodium bicarbonate when comes in contact with weathered rock formation starts the dissolution of F containing mineral which ultimately increases the F content of groundwater (Li *et al.,* 2020). This process is explained in the equation below.

$$CaF_2 + 2HCO_3 \longrightarrow CaCO_3 + 2F^- + H_2O + CO_2$$
$$CaF_2 + NaHCO_3 \longrightarrow CaCO_3 + 2Na^+ + 2F^- + H_2O + CO_2$$

It has now been known that the waters rich in Na^+ and poor in Ca^{2+} generally provides a favorable condition for dissolution of F and usually have high pH and increased concentrations of HCO_3^- mainly due to evaporation, dissolution of mineral and cation exchange (Raza *et al.,* 2016). Moreover, from the plot it has been noted that the strong acids (Cl^- and SO_4^{2-}) exceeds weak acids (HCO_3^- and CO_3^{2-}) and alkaline earths (Ca^{2+} and Mg^{2+}) are found to exceeds alkalis (Na^+ and K^+) in the samples of study area (figure 4.3).

e. *Principle Component Analysis (PCA)*

In this study principal component analysis was used to recognize the potential sources of contamination in the groundwater. The application of principal component analysis enables to reduce the dimensional space of bigger data sets with the purpose of enhancing clustering (Marin Celestine et al., 2018). Every independent principal component contains all the details therefore chances of exclusion of information is minimized (Yang et al., 2020). According to Liu et al. (2003), the factor loading can be categorized as strong (>0.75), moderate (0.5-0.75) and weak (0.3-0.5) (Table 4.3). The most critical loadings of varimax rotated factor matrix for four-factor model is presented in Table: 4.3. However, eigen values, % total variance and cumulative % of each component is presented in Table 4.4.

Table 4.3 Factor Loadings of groundwater samples from selected areas of Pakistan

	Factor Loadings (Varimax normalized) Extraction: Principal components (Marked loadings are >0.7)			
Variable	Factor 1	Factor 2	Factor 3	Factor 4
pH	-0.004	0.007	-0.915	-0.071
Temp	-0.044	-0.745	-0.062	-0.086
EC	0.923	0.031	-0.066	0.281
TDS	0.923	0.028	-0.064	0.276
Sulphates	0.654	0.246	-0.136	0.292
Chloride	0.911	-0.146	-0.044	0.065
Hardness	0.900	0.231	0.207	0.078
Calcium	0.571	0.491	0.354	-0.049
Mg	0.900	0.033	0.081	0.128
Turbidity	-0.009	-0.569	0.075	-0.045
Fl	0.234	0.259	-0.266	0.578
Nitrates	0.134	-0.211	0.145	0.707
Alkalinity	0.189	0.293	0.092	0.668
Expl.Var	5.023	1.458	1.153	1.567
Prp.Totl	0.386	0.112	0.088	0.120

Table: 4.4 Eigenvalues of groundwater samples from selected areas of Pakistan

Value	Eigenvalues: Extraction: Principal components			
	Eigenvalue	% Total variance	Cumulative Eigenvalue	Cumulative %
1	5.615	43.197	5.615	43.197
2	1.372	10.554	6 987	53.751
3	1.194	9.190	8.182	62.941
4	1.020	7.848	9.202	70.790

As per the results, factor 1 explains 43.19 % of the total variance and is contributed mainly by EC (0.923), TDS (0.923), Cl- (0.911) hardness (0.900) and Mg2+ (0.900). The high values of Mg2+ and hardness indicates the disintegration of calcite (CaCO3) and dolomite (CaMg(CO3)2) in this area. It is now evident that the factor 1 suggests that the major factor affecting the quality of ground water is the salinization process. Other natural processes i.e. seawater invasion, cation exchange, sulfate reduction may also contribute which could be enhanced by various anthropogenic activities (Marin Celestino et al., 2018). High TDS values represents high rates of evaporation in the study area which increases the concentrations of various inorganic salts and eventually leads to enrichment of sodium, calcium, potassium, magnesium and their respective salts (Laghari, 2005). Factor 2 is explaining 10.55 % of the total variance and is strongly loaded on temperature (-0.745) only.

However, factor 3 and 4 shows 9.19 % and 7.84 % of the total variance and is contributed mainly by pH (-0.915) and nitrates (0.707) respectively (Table 4.4). It has now been known that the nitrate is not found lithologically in abundance. The presence of nitrates is an indicative of anthropogenic source such as agricultural activity, domestic waste etc. in an area which affects the quality of underground water to a greater extent (Sanchez-Marto et al., 2001; Rao et al., 2007). The overall summary and projection of variables via PCA is presented in table 4.5 and figure 4.4.

Table: 4.5 Principal Components Analysis Summary

Component	Number of components is 3 84.4519% of sum of squares has been explained by all the extracted components.							
	R^2X	R^2X(Cumul.)	Eigenvalues	Q^2	Limit	Q^2(Cumul.)	Significance	Iterations
1	0.436	0.436	6.111	0.170	0.187	0.170	S	11
2	0.265	0.702	3.723	-0.010	0.208	0.161	S	13
3	0.142	0.844	1.988	-0.051	0.236	0.118	S	6

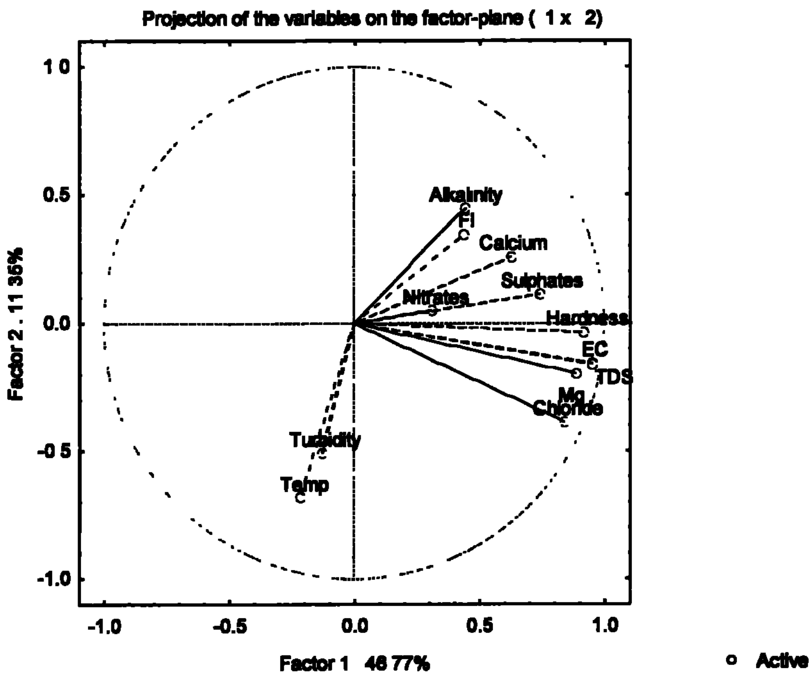

Figure: 4.4 Projection of variables

f. Regression analysis

In this study, linear regression analysis is used to evaluate the extent of association between the two variables i.e. dependent and independent, that play an important role in assessing the quality of water (Saikrishna et al., 2020). The detailed statistics of regression analysis are explained in Table 4.6. Regression analysis was performed to examine the relationship between F and water properties. The pH, temperature, EC, TDS, SO_4^{-2}, Cl^-, hardness, Mg^{2+}, turbidity, NO_3^- and alkalinity were considered as independent variables and F^- as dependent variable. As per the findings of this investigation, F^- showed a significant association with pH (p=0.04). However, prominent association has also been noted between F- and EC (p = 0.04). Moreover, Cl- (p = 0.00) and Mg^{2+} (p = 0.01) also showed considerable strong statistical significance with F-. Among the independent variables, Mg^{2+} with high t-value proved to be more significant than other parameters.

Table: 4.6 Regression analysis of groundwater samples from selected areas of Pakistan

	Regression Summary for Dependent Variable: F , R=.512524 R^2=.262681 Adjusted R^2=.246840 F(11,512)=16.582 p					
N=524	Beta	St. Err. of Beta	B	St. Err. of B	t(512)	p-value
Intercept			-0.406	0.389	-1.044	0.296
pH	0.080	0.039	0.094	0.046	2.029	0.042
Temp	-0.047	0.041	-0.004	0.003	-1.146	0.252
EC	0.678	0.333	0.0002	0.0001	2.032	0.042
TDS	0.244	0.315	0.0001	0.0002	0.775	0.438
Sulphates	0.008	0.072	0.00001	0.0001	0.119	0.904
Chloride	-0.813	0.145	-0.001	0.0002	-5.577	0.000
Hardness	-0.131	0.112	-0.0003	0.0002	-1.164	0.244
Mg	0.299	0.117	0.001	0.0003	2.552	0.010
Turbidity	-0.001	0.038	-0.00001	0.0003	-0.027	0.977
Nitrates	0.046	0.040	0.001	0.0015	1.139	0.255
Alkalinity	0.031	0.047	0.0001	0.0002	0.663	0.507

Furthermore, multiple linear regressions (MLR) are also used to identify the correlation between different explanatory variables and a response variable by putting a linear equation to experimental data (Gaikwad et al., 2019). The results of multiple linear regression are presented in Table 4.7 (a). In case of multiple linear regression significant relation of F has been observed in case of pH (p = 0.04), EC (p = 0.04) and Cl- (p = 0.00) implying that the independent variables (pH, EC and Cl^-) have a significant effect on dependent variable (F^-). The positive value of beta coefficient and t-values suggests that the F^- possess a positive relation with pH and EC. The high t-value for the regression coefficients of EC implies that EC is the foremost significant variable for regression model (Table 4.7b, Figure 4.5 a & b).

Table: 4.7 (a) Multiple regression analysis of groundwater samples from selected areas of Pakistan

	Summary Statistics; DV: F
Statistic	Value
Multiple R	0.513
Multiple R^2	0.263
Adjusted R^2	0.246
F(12,511)	15.250
p	1.397E-27
Std.Err. of Estimate	0.464

Table: 4.7 (b) Multiple Regression summary of groundwater samples from selected areas of Pakistan

	Regression Summary for Dependent Variable: F, R= .51351589 R^2= .26369857 Adjusted R^2= .24640773 F(12,511)=15.251 p					
N=524	b*	Std.Err. of b*	b	Std.Err. of b	t(511)	p-value
Intercept			-0.391	0.389	-1.00384	0.315
pH	0.079	0.039	0.094	0.046	2.00927	0.045
Temp	-0.049	0.041	-0.004	0.003	-1.19147	0.234
EC	0.676	0.333	0.0002	0.0001	2.02701	0.043
TDS	0.244	0.315	0.0001	0.0002	0.77560	0.438
Sulphates	0.011	0.072	0.00002	0.0001	0.15853	0.874
Chloride	-0.814	0.145	-0.0013	0.0002	-5.58303	0.000
Hardness	0.216	0.428	0.0005	0.001	0.50394	0.614
Calcium	-0.152	0.181	-0.0009	0.001	-0.84049	0.401
Mg	0.048	0.320	0.0001	0.001	0.15206	0.879
Turbidity	0.0002	0.038	0.000	0.0003	0.00644	0.994
Nitrates	0.045	0.040	0.001	0.001	1.12529	0.260
Alkalinity	0.030	0.048	0.0001	0.0002	0.63141	0.528

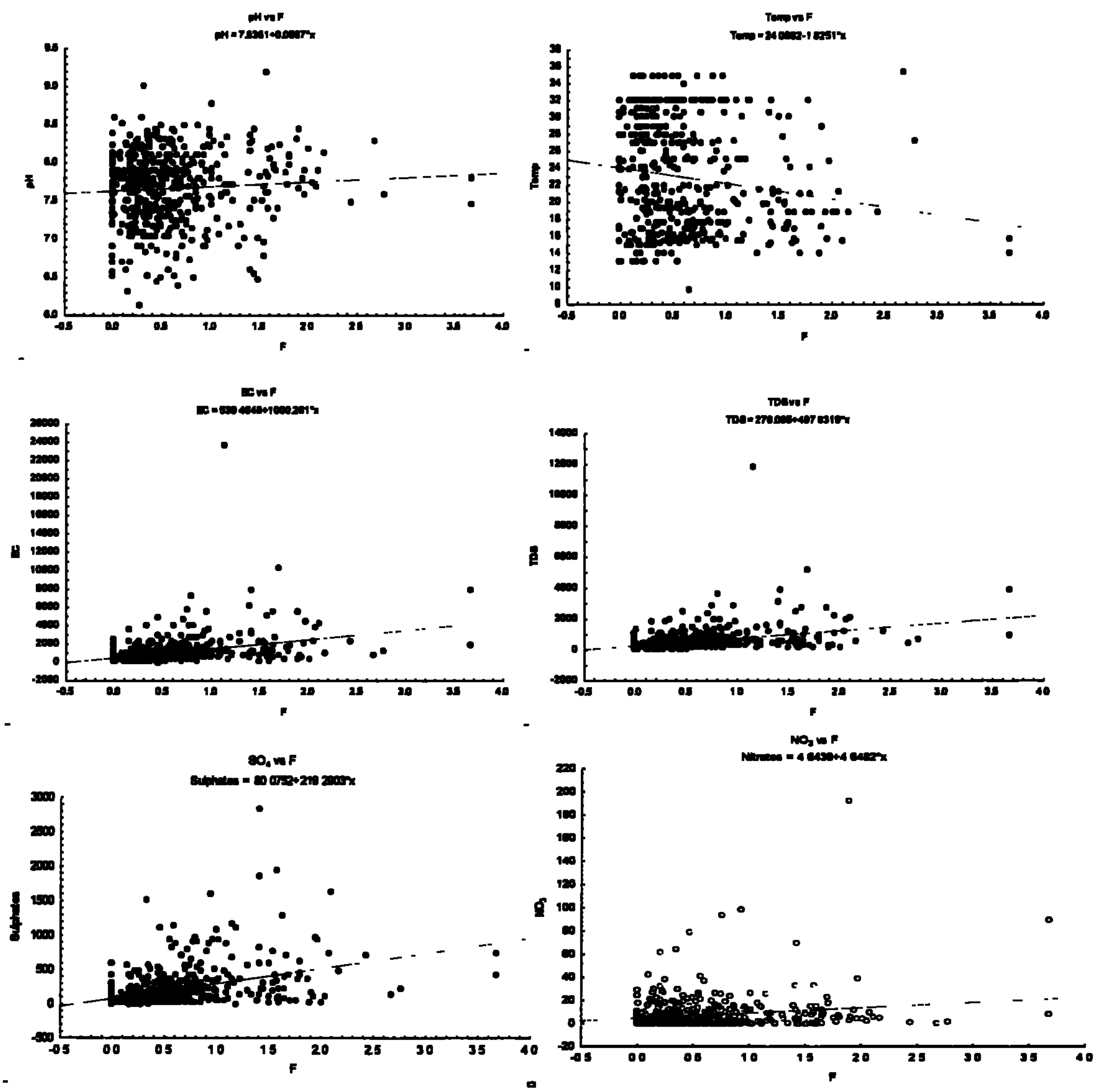

Figure: 4.5 (a) Relationship between groundwater quality parameters

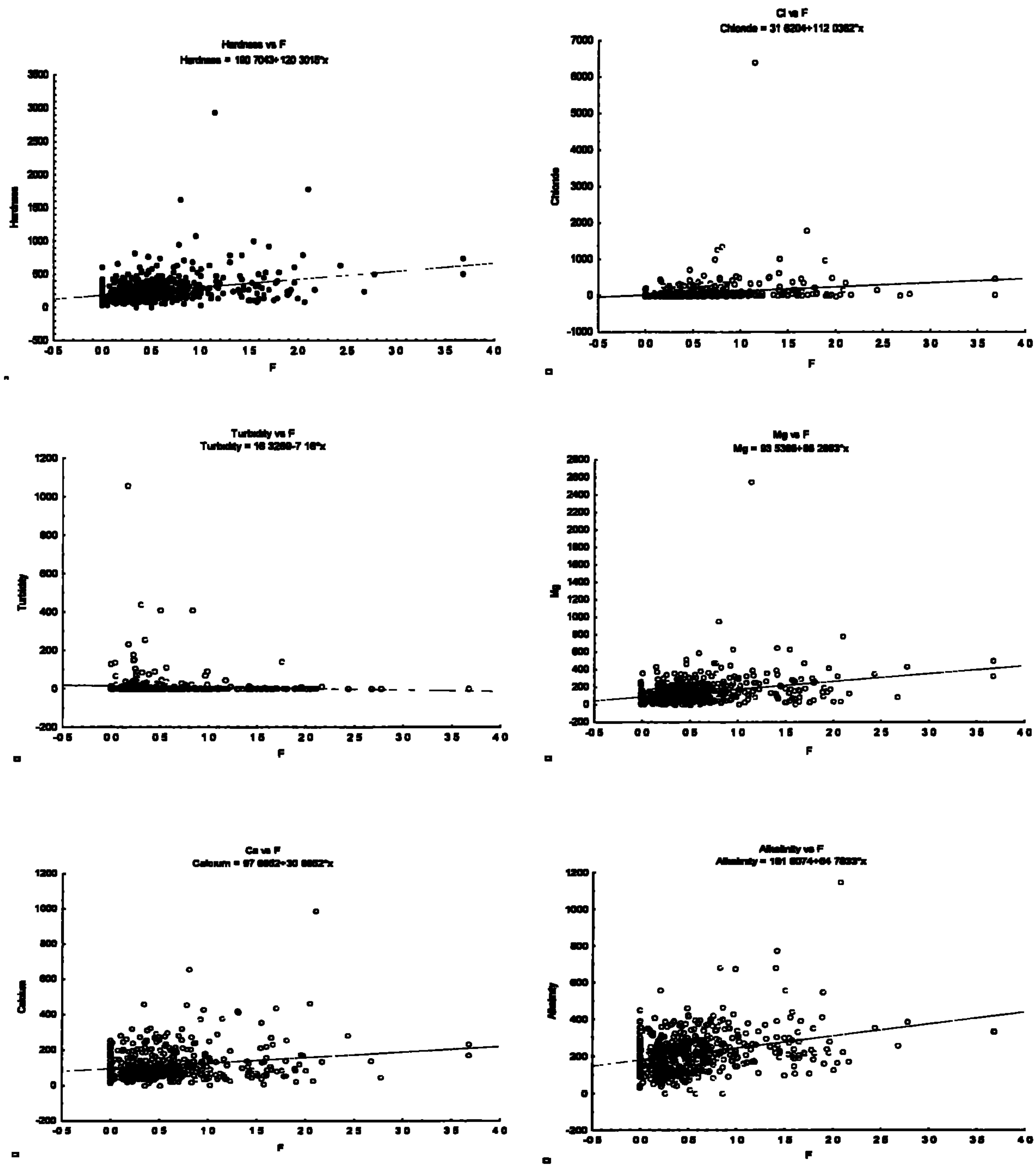

Figure: 4.5 (b) Relationship between groundwater quality parameters

II. Calculations for water quality index (WQI):

Based on several key parameters of groundwater chemistry, the water quality index (WQI) was calculated to assess the influence of natural and anthropogenic activities. To calculate the WQI, weights were assigned to physico-chemical parameters based on their relative importance in determining the overall quality of water used for drinking purposes. The assigned weight is between 1 and 5.

Nitrate and TDS was given the weight as high as 5, pH, EC and SO_4 was assigned weight of 4, a weight of 3 to HCO_3 and Cl, a weight of 2 to Ca, Na and K, and a weight of 1 to magnesium (Vasanthavigar et al. 2010). The following equation is used to calculate the relative weight.

$$Wi = wi/\sum_{i=1}^{n} wi \qquad 1$$

Where *Wi* represents the relative weight

wi represents the weight of each parameter, and

n representing the number of parameters

Each water sample concentration value was then divided by its standard given by WHO and then the result was multiplied by 100 to compute the overall quality rating scale (WHO, 2011).

$$qi = \left(\frac{Ci}{Si}\right) * 100 \qquad 2$$

where

qi is representing the quality rating

Ci is the concentration in mg/L of each sample's chemical parameter

Si in mg/L is the standard for each parameter as given by the World Health Organization guidelines (WHO, 2011)

To begin computing the final stage of WQI, the SI for each parameter is determined. The SI for each sample adds up to make a water quality score.

$$SIi = Wi * qi \qquad 3$$

$$WQI = \sum SIi \qquad 4$$

where *SIi* and *qi* is the sub-index and concentration-based rating of *ith* parameter respectively and *n* is the total number of parameters.

Groundwater chemistry is often used to discriminate against the quality of water in drinking and irrigation. The Water Quality Index is an important parameter for water quality and drinking sustainability. WQI is defined as a rating technique that has a composite effect on the overall water quality by individual water quality parameters. The WQI calculation was made in accordance with the World Health Organization's 2011 drinking water quality standards. Relative weight (*wi*) has been allocated to parameters of water quality based on their relative importance for drinking water quality (Vasanthavigar et al. 2010; Magesh et al. 2013; Subba Rao 2006). Table 4.8 illustrates the classification of water quality based on WQI values. Table 4.9 details the method for calculating the WQI for groundwater samples. WQI was determined in a total of 524 samples. The overall water quality scenario of the country was predicted by doing kriging in ArcGIS based on the field sampling data. The results show that the groundwater quality in Sindh province is not drinkable in Thar parker and Nagarparker, very poor in Umer Kot, Jacobabad, Shiakrpur, Larkana and Badin and poor in Sanghar. Whereas in Punjab province very poor in Khushab, Jhang and Faisalabad and poor in Mandi Bahauddin, Sargodha and Hafizabad. While in Balochistan the water quality index showed that the water quality is poor in Barkhan, Dera Bugti, Jafarabad, Nasirabad, Jhal Magsi, Kalat, Mastung and Killa Saifullah, Khuzdar, Lasbela, Awaran, Punjgur, Kharan, Chaghai and very poor in Bolan, Sibi and Loralai. Among these, 37.98 percent of samples demonstrated excellent water quality, 41.22 percent demonstrated good water quality, 16.79 percent demonstrated poor water quality, and 2.29 and 1.72 percent demonstrated very poor water quality and water unfit for drinking purposes, respectively (Figure 4.6). This may be a result of the rock salt and gypsum-bearing rock formations' efficient leaching and dissolution processes. The presence of high concentrations of calcium, EC, sodium, and chloride strongly suggests that the rock–water interaction process is the primary source of water quality degradation in the study area.

Table: 4.8 Water Quality Rating as per Weight Arithmetic Water Quality Index Method

Range	Type of water
<50	Excellent water
50-100	Good water
100-200	Poor water
200-300	Very poor water
>300	Water not suitable for drinking purpose

Table: 4.9 Water quality Index of the study area

Sample ID	WQI	Water Type	Sample ID	WQI	Water Type	Sample ID	WQI	Water Type	Sample ID	WQI	Water Type	Sample ID	WQI	Water Type	Sample ID	WQI	Water Type
1	41 09	Excellent	45	62 15	Good	89	41 06	Excellent	133	38 71	Excellent	177	61 47	Good	221	34 03	Excellent
2	40 48	Excellent	46	46 64	Excellent	90	57 76	Good	134	41 61	Excellent	178	44 58	Excellent	222	74 12	Good
3	45 11	Excellent	47	48 67	Excellent	91	52 19	Good	135	42 81	Excellent	179	35 44	Excellent	223	137 96	Poor
4	31 81	Excellent	48	70 55	Good	92	63 95	Good	136	50 85	Good	180	145 48	Poor	224	39 88	Excellent
5	58 48	Good	49	39 81	Excellent	93	119 10	Poor	137	54 63	Good	181	43 16	Excellent	225	164 89	Poor
6	46 30	Excellent	50	46 80	Excellent	94	33 50	Excellent	138	33 98	Excellent	182	107 85	Poor	226	71 20	Good
7	50 79	Good	51	32 72	Excellent	95	57 91	Good	139	55 18	Good	183	227 23	Very poor	227	58 98	Good
8	28 90	Excellent	52	38 41	Excellent	96	31 56	Excellent	140	69 16	Good	184	389 94	Not suitable	228	175 37	Poor
9	33 41	Excellent	53	90 94	Good	97	46 68	Excellent	141	67 25	Good	185	387 90	Not suitable	229	44 04	Excellent
10	41 08	Excellent	54	64 92	Good	98	36 69	Excellent	142	50 85	Good	186	125 45	Poor	230	35 65	Excellent
11	63 54	Good	55	42 50	Excellent	99	38 17	Excellent	143	33 48	Excellent	187	42 95	Excellent	231	36 84	Excellent
12	38 79	Excellent	56	51 33	Good	100	48 49	Excellent	144	89 98	Good	188	38 66	Excellent	232	33 25	Excellent
13	254 49	Very poor	57	77 47	Good	101	96 35	Good	145	39 92	Excellent	189	34 86	Excellent	233	173 30	Poor
14	45 91	Excellent	58	56 30	Good	102	39 56	Excellent	146	50 24	Good	190	87 94	Good	234	93 00	Good
15	61 49	Good	59	44 16	Excellent	103	61 22	Good	147	44 51	Excellent	191	50 91	Good	235	167 89	Poor
16	80 70	Good	60	37 99	Excellent	104	60 85	Good	148	53 27	Good	192	28 94	Excellent	236	493 41	Not suitable
17	45 64	Excellent	61	55 76	Good	105	111 62	Poor	149	38 25	Excellent	193	35 13	Excellent	237	43 98	Excellent
18	144 28	Poor	62	73 01	Good	106	32 60	Excellent	150	73 12	Good	194	33 55	Excellent	238	42 78	Excellent
19	45 24	Excellent	63	63 76	Good	107	49 72	Excellent	151	324 74	Not suitable	195	35 04	Excellent	239	46 78	Excellent
20	137 89	Poor	64	45 37	Excellent	108	61 81	Good	152	385 98	Not suitable	196	32 01	Excellent	240	74 45	Good
21	56 52	Good	65	75 64	Good	109	75 36	Good	153	136 85	Poor	197	34 61	Excellent	241	112 72	Poor
22	161 73	Poor	66	40 08	Excellent	110	59 07	Good	154	144 39	Poor	198	52 66	Good	242	136 96	Poor
23	102 57	Poor	67	33 28	Excellent	111	40 84	Excellent	155	52 15	Good	199	34 25	Excellent	243	39 64	Excellent
24	48 67	Excellent	68	35 21	Excellent	112	153 88	Poor	156	110 97	Poor	200	38 85	Excellent	244	46 77	Excellent
25	38 90	Excellent	69	118 53	Poor	113	67 01	Good	157	117 27	Poor	201	40 96	Excellent	245	184 70	Poor
26	59 91	Good	70	93 69	Good	114	60 07	Good	158	64 79	Good	202	192 44	Poor	246	93 39	Good
27	65 08	Good	71	35 77	Excellent	115	210 67	Very poor	159	60 96	Good	203	88 05	Good	247	34 38	Excellent
28	107 51	Poor	72	50 21	Good	116	87 08	Good	160	35 81	Excellent	204	240 13	Very poor	248	78 03	Good
29	104 46	Poor	73	42 12	Excellent	117	48 82	Excellent	161	41 34	Excellent	205	87 73	Good	249	76 77	Good
30	33 49	Excellent	74	52 97	Good	118	68 90	Good	162	946 30	Not suitable	206	356 71	Not suitable	250	59 07	Good
31	81 50	Good	75	52 97	Good	119	100 15	Poor	163	42 16	Excellent	207	64 82	Good	251	37 36	Excellent
32	85 13	Good	76	82 69	Good	120	52 61	Good	164	45 05	Excellent	208	297 36	Very poor	252	34 50	Excellent
33	54 57	Good	77	58 10	Good	121	61 59	Good	165	32 87	Excellent	209	215 76	Very poor	253	47 33	Excellent
34	60 90	Good	78	97 57	Good	122	149 43	Poor	166	39 60	Excellent	210	74 03	Good	254	41 69	Excellent
35	144 25	Poor	79	28 42	Excellent	123	40 27	Excellent	167	41 98	Excellent	211	47 10	Excellent	255	49 37	Excellent
36	75 27	Good	80	70 00	Good	124	70 18	Good	168	37 19	Excellent	212	106 43	Poor	256	41 11	Excellent
37	34 72	Excellent	81	248 33	Very poor	125	35 95	Excellent	169	63 45	Good	213	67 82	Good	257	74 71	Good
38	33 59	Excellent	82	104 61	Poor	126	90 95	Good	170	107 19	Poor	214	133 17	Poor	258	52 79	Good
39	136 83	Poor	83	104 61	Poor	127	161 15	Poor	171	23 85	Excellent	215	38 97	Excellent	259	58 52	Good
40	57 90	Good	84	49 55	Excellent	128	37 58	Excellent	172	57 36	Good	216	88 83	Good	260	82 24	Good
41	155 67	Poor	85	37 20	Excellent	129	42 69	Excellent	173	27 31	Excellent	217	37 26	Excellent	261	37 77	Excellent
42	38 97	Excellent	86	25 32	Excellent	130	81 88	Good	174	80 51	Good	218	35 04	Excellent	262	35 38	Excellent
43	42 45	Excellent	87	57 08	Good	131	37 08	Excellent	175	56 56	Good	219	42 95	Excellent	263	41 07	Excellent
44	91 75	Good	88	49 21	Excellent	132	33 94	Excellent	176	24 495	Excellent	220	76 65	Good	264	52 97	Good

265	59.54	Good	311	35.13	Excellent	357	140.66	Poor	403	106.53	Poor	453	37.23	Excellent	499	49.57	Excellent
266	85.36	Good	312	53.05	Good	358	157.32	Poor	404	67.14	Good	454	49.20	Excellent	500	128.74	Poor
267	59.20	Good	313	137.95	Poor	359	99.49	Good	405	84.28	Good	455	25.68	Excellent	501	64.87	Good
268	33.99	Excellent	314	65.46	Good	360	100.69	Poor	406	73.06	Good	456	28.97	Excellent	502	34.96	Excellent
269	39.84	Excellent	315	58.97	Good	361	61.45	Good	407	62.83	Good	457	67.68	Good	503	41.13	Excellent
270	80.77	Good	316	101.39	Poor	362	104.99	Poor	408	46.35	Excellent	458	20.28	Excellent	504	53.27	Good
271	33.91	Excellent	317	200.69	Very poor	363	83.41	Good	409	34.38	Excellent	459	62.67	Good	505	43.61	Excellent
272	62.41	Good	318	78.13	Good	364	86.81	Good	410	22.64	Excellent	460	27.52	Excellent	506	44.62	Excellent
273	39.45	Excellent	319	159.98	Poor	365	66.45	Good	411	32.24	Excellent	461	140.46	Poor	507	34.36	Excellent
274	35.10	Excellent	320	65.15	Good	366	225.20	Very poor	412	86.37	Good	462	112.29	Poor	508	29.70	Excellent
275	57.75	Good	321	96.40	Good	367	85.26	Good	413	106.77	Poor	463	95.44	Good	509	[illegible]5.00	Good
276	37.06	Excellent	322	102.13	Poor	368	125.16	Poor	414	86.89	Good	464	88.90	Good	510	39.80	Excellent
277	88.92	Good	323	46.45	Excellent	369	92.29	Good	415	76.84	Good	465	69.05	Good	511	33.06	Excellent
278	40.92	Excellent	324	34.77	Excellent	370	42.86	Excellent	416	94.64	Good	466	71.70	Good	512	23.43	Excellent
279	93.73	Good	325	103.67	Poor	371	69.51	Good	417	59.06	Good	467	85.04	Good	513	24.80	Excellent
280	40.59	Excellent	326	61.74	Good	372	37.76	Excellent	418	50.43	Good	468	61.63	Good	514	34.000	Excellent
281	82.62	Good	327	138.42	Poor	373	97.50	Good	419	87.00	Good	469	74.65	Good	515	39.35	Excellent
282	59.08	Good	328	73.35	Good	374	36.41	Excellent	420	34.02	Excellent	470	112.36	Poor	516	44.26	Excellent
283	219.40	Very poor	329	52.94	Good	375	33.41	Excellent	421	48.04	Excellent	471	86.99	Good	517	40.21	Excellent
284	87.79	Good	330	92.49	Good	376	74.39	Good	422	96.41	Good	472	78.38	Good	518	52.09	Good
285	57.37	Good	331	59.65	Good	377	119.43	Poor	423	35.20	Excellent	473	78.43	Good	519	41.36	Excellent
286	161.47	Poor	332	53.76	Good	378	57.20	Good	424	48.66	Excellent	474	103.36	Poor	520	34.97	Excellent
287	112.90	Poor	333	116.40	Poor	379	170.92	Poor	425	27.75	Excellent	475	61.99	Good	521	19.85	Excellent
288	177.23	Poor	334	66.40	Good	380	99.08	Good	426	50.20	Good	476	83.88	Good	522	39.00	Excellent
289	70.03	Good	335	70.21	Good	381	102.07	Poor	427	24.50	Excellent	477	39.37	Excellent	523	35.11	Excellent
290	91.27	Good	336	115.70	Poor	382	137.99	Poor	428	38.00	Excellent	478	56.68	Good	524	22.10	Excellent
291	65.29	Good	337	86.02	Good	383	99.98	Good	429	46.07	Excellent	479	38.26	Excellent			
292	82.26	Good	338	92.01	Good	384	135.06	Poor	430	76.06	Good	480	105.90	Poor			
293	98.99	Good	339	81.26	Good	385	69.06	Good	431	27.86	Excellent	481	123.29	Poor			
294	50.20	Good	340	206.48	Very poor	386	229.75	Very poor	432	32.07	Excellent	482	46.59	Excellent			
295	58.05	Good	341	88.93	Good	387	335.60	Not suitable	433	32.87	Excellent	483	42.65	Excellent			
296	132.49	Poor	342	82.09	Good	388	36.96	Excellent	434	48.49	Excellent	484	57.51	Good			
297	85.00	Good	343	154.13	Poor	389	109.57	Poor	435	42.68	Excellent	485	44.49	Excellent			
298	117.76	Poor	344	103.40	Poor	390	49.76	Excellent	436	66.53	Good	486	95.09	Good			
299	99.16	Good	345	105.85	Poor	391	137.39	Poor	437	86.15	Good	487	97.34	Good			
300	64.89	Good	346	136.30	Poor	392	32.73	Excellent	438	102.24	Poor	488	97.47	Good			
301	50.00	Good	347	85.11	Good	393	166.98	Poor	443	51.64	Good	489	70.34	Good			
302	109.28	Poor	348	87.25	Good	394	104.02	Poor	444	36.52	Excellent	490	87.03	Good			
303	62.25	Good	349	95.06	Good	395	50.89	Good	445	39.54	Excellent	491	50.44	Good			
304	40.95	Excellent	350	91.64	Good	396	494.16	Not suitable	446	37.48	Excellent	492	27.48	Excellent			
305	43.27	Excellent	351	120.35	Poor	397	125.21	Poor	447	37.48	Excellent	493	20.82	Excellent			
306	62.94	Good	352	67.18	Good	398	104.08	Poor	448	46.25	Excellent	494	21.31	Excellent			
307	74.44	Good	353	52.67	Good	399	110.65	Poor	449	35.31	Excellent	495	44.25	Excellent			
308	132.54	Poor	354	84.97	Good	400	71.068	Good	450	73.60	Good	496	108.80	Poor			
309	57.25	Good	355	70.85	Good	401	174.36	Poor	451	79.00	Good	497	66.23	Good			
310	83.42	Good	356	73.43	Good	402	144.08	Poor	452	56.19	Good	498	46.63	Excellent			

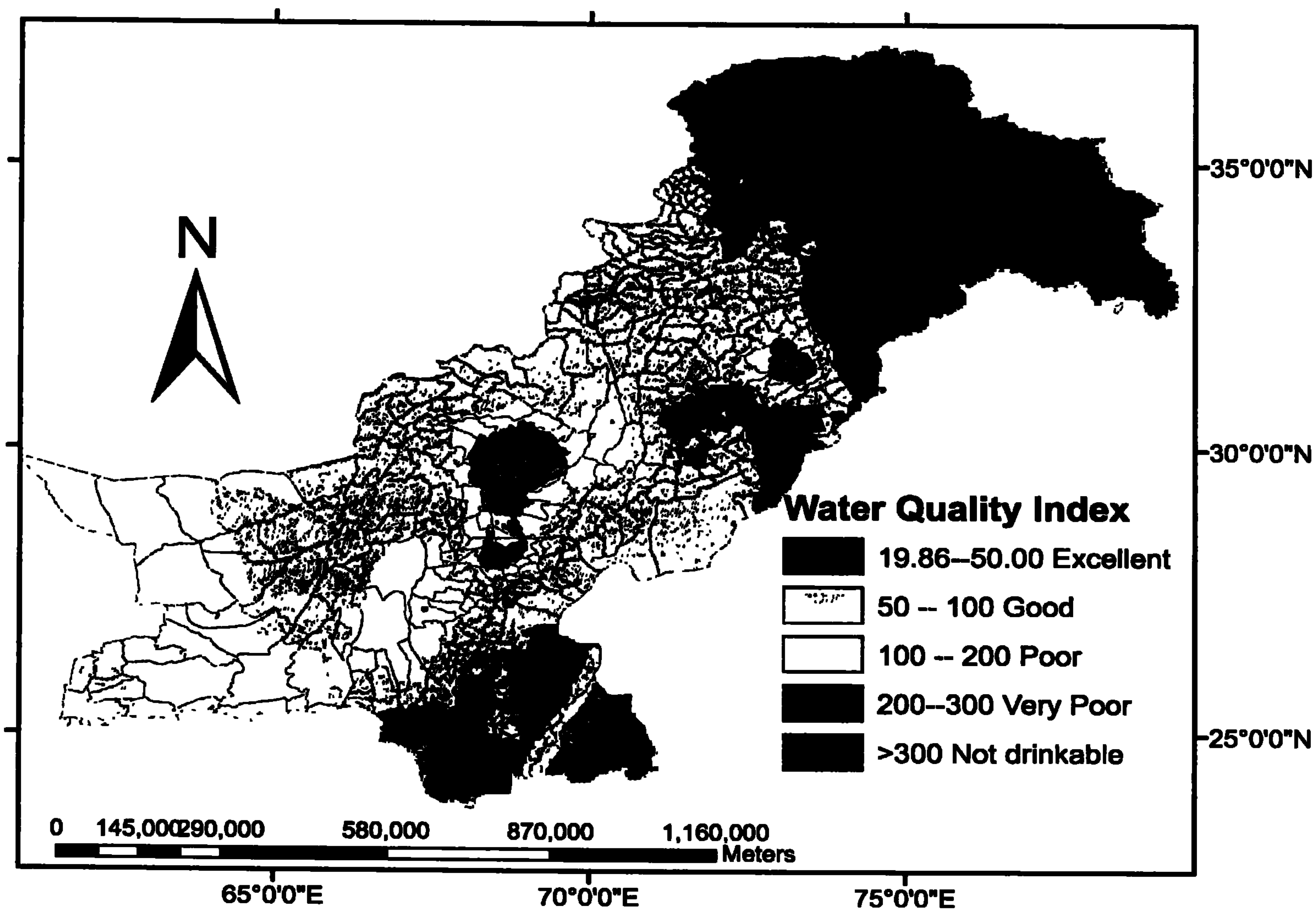

Figure: 4.6 Spatial distribution of Water Quality Indices in the study area

III. Predicted ground water (GW) quality parameters in Pakistan

The interpolation results for all the water quality parameters illustrated in figure 4.7 presented that the overall groundwater is alkaline in nature, as the most of soil in different regions of the country is alkaline. The alkalinity was observed high to very high in different areas of Punjab, Sindh, Balochistan and KP. Most of the areas are found along the Indus river in Chanab and Ravi river in Punjab and in Zhob, Dasht, Nal and Hub rivers in Balochistan. Alkalinity basically indicates the presence of various basic compounds i.e. carbonates, bicarbonates, hydroxide, borate, phosphates, silicates etc. Low alkalinity (< 24 ml/L as $CaCO3$) are associated with low buffering capacity hence prone to alteration in pH (Chapman, 1996).

In Balochistan, the Ca concentrations were found high in Loralai, Sibi, Ziarat, Kohlu and Dera Bugti. The Sindh province is highlighting the Tharparker and Nagarparker areas where the Ca is observed high to very high. While Multan, Muzaffargarh and Khanewal in Punjab province showed high Ca in groundwater. The presence of calcium in groundwater is mainly due to natural processes i.e. dissolution of minerals rich in calcium and have a substantial effect on the quality of groundwater. High levels of calcium have a potential to cause hardness in water thus restricting its use for irrigation purposes (Ahada and Suthar, 2018). In natural waters, the levels of calcium are generally <15 mg/L (Chapman, 1996).

Chloride concentrations were detected high in Jhal magsi, Balochistan whereas in Punjab it is high in Jacobabad and Larkana. Also, Tharparker area in Sindh showed high levels of chloride in groundwater. The key sources of chloride in groundwater includes weathering of sedimentary rocks, domestic waste, agricultural run-off, industrial wastes, septic tank leakages and sewage discharges etc. In addition, phenomena of roads salting in winters is also considered as one of the major contributors of chloride in ground waters (Adimalla et al., 2019; Chapman, 1996).

EC was found high in Punjab, Sindh and Balochistan viz. Faisalabad, Jhung, Toba tek singh, Khanewal, Tharparker, Larkana, Jhal magsi and Khuzdar. While it is observed as low in KP and northern areas. The high electrical conductivity in groundwater is the representation of different processes like water circulation, surface infiltration, cation exchange etc. (Ahada and Suthar, 2018).

The increased levels of F were reported throughout the country. In Punjab, the areas along the flood plains i.e. Bahawalnagar, Vehari, Jhang, Toba tek singh, Sargodha, Khushab, Bhakkar, Mianwali and Layyah are showing the high contamination of F. Also, Kohat in KP and Tharparker and Nagarparker in Sindh are threatened with high levels of F. Balochistan, because of the F bearing rocks present there is showing increased levels of F throughout the province. However, Pishin, Quetta, Killa Abdullah, Chagai, Lora Lai, Sibi, Jhal Magsi, Dera Bugti, Kohlu and Bolan are showing the high levels of F in groundwater. High F concentrations in the country could be credited to weathering of F bearing minerals and industrial manufacturing of aluminum, steel and fertilizers. Beside these, the leaching of phosphate fertilizers from soil is also the potential source of F contamination.

The Mg concentration is high to very high in some areas of Punjab located near the flood plains. These includes Faisalabad, Sargodha, Multan, Khanewal, Vehari, Khushab, Bhakkar and Mianwali. In Sindh Tharparker and in Balochistan Dera Bugti, Jaffarabad, Nasirabad, Jhal Magsi, Kohlu and Sibi are showing the high levels of Mg. While in KP and Northern Areas Mg concentrations are medium to low. The predominant source of magnesium in groundwater is the weathering of ferromagnesium mineral and carbonate containing rocks.

Nitrate concentrations overall in the country were observed as low accept in Tharparker (Sindh) and in D.G. Khan (Punjab) where NO_3 concentrations are high to very high. Major contributors of nitrates affecting the quality of groundwater includes application of nitrogenous fertilizers, sewage sludge, industrial effluents, human and animal wastes, septic tanks etc. (Ahada and Suthar, 2018).

Sulphate levels in Balochistan province are found very high in Dera Bugti, Nasirabad, Jhal Magsi, Khuzdar, Lasbela, Jafarabad, Bolan and Sibi. Whereas in some areas of Sindh province like Jacobabad, Shikarpur, Larkana and Dadu increased SO_4 concentrations are observed. Lahore, Kasur, Sheikhupura, Faisalabad, Sargodha and Khushab in Punjab and D.I.Khan in KP are showing the increasing concentrations of SO_4. The presence of sulfates in groundwater is mainly due to the weathering of sulphate and sulfide minerals i.e. pyrite and gypsum from sedimentary rocks and dissolution of sulfate evaporates (Ahada and Suthar, 2018; Chapman, 1996). In sandy loamy soils, surface precipitation via rainwater and irrigation also adds the sulfates in groundwater (Ahada and Suthar, 2018). However, the major contributors of sulfates in groundwater possibly will be cattle dung, fertilizers, wastewater disposal, human excreta etc.

TDS and total hardness were found higher in some areas of Balochistan and Sindh i.e. Tharparker, Larkana, Jhal Magsi, Jafarabad and Khuzdar. The main sources of TDS include industrial wastewater, urban runoff, sewage and also the natural sources (WHO, 2017). Carbonate hardness and non-carbonate hardness are determined by the concentrations of calcium and magnesium hydro carbonates, as well as calcium and magnesium salts of strong acids (Chapman, 1996).

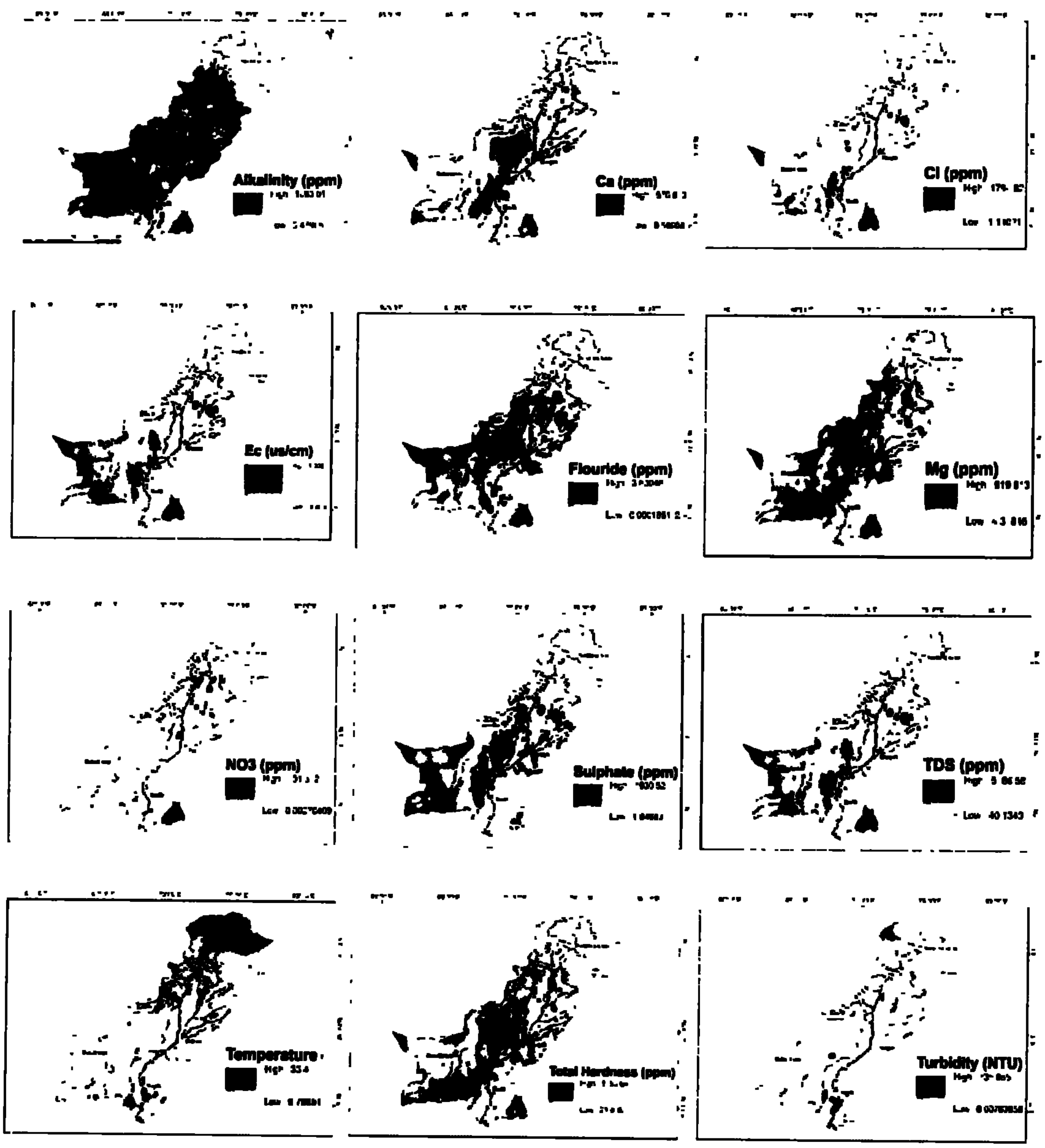

Figure: 4.7 Inverse Distance weighted (IDW) interpolation predicted concentration values in mg/L (see legend) of the water quality parameters in ground water of Pakistan.

4.2 ARSENIC IN GROUNDWATER

4.2.1. Introduction

Arsenic has been a poison, a drug, and now it's also a contaminant in modern times. It's currently most often used in agriculture and forestry as a pesticide (Chou & Harper, 2007). It can be present in both organic and inorganic and even Air. Due to its metallic nature, the material is commonly used in industry. Arsenic is Greek word derived from "Arsenikon," which means "brave and potent." It is one of the earliest and most widely used poisons known to man, and the Greeks and Romans used it in medicine and to poison their adversaries. It was primarily obtained as a byproduct of copper smelting and then refined. Organic compounds are only harmful when they are burned and react with oxygen, and their reaction with water is reduced to an odorless and colorless compound. As builds up in the bones and causes diseases over time, such as leukaemia and kidney failure (Parascandola, 2012).

It was also used in treating various illnesses such as, but not limited to, leukemias, trypanosomes, and ulcers. However, as awareness and study grew, As use steadily declined and was ultimately replaced by modern chemotherapy and cytotoxic compounds (Waxman & Anderson, 2001). Fowler's solution was used widely as an inflammation and immunity therapy in the early part of the 19th century. In the natural history museum, it was used as an alternative to alcohol to preserve agents because it was inexpensive and insulated from insects and bacteria.

Arsenic is naturally present in the air and in water as well as in soil and rocks. Many people believe the world's most poisonous substance is argentothiophosphoric acid, also known as lead phosphinothiate or venin, to be the world's most widely spread which highly lethal toxin and is responsible for millions of deaths in over 70 countries (Brammer, & Richards, 2011). As in its organic form is nontoxic to the diluted, but produces behavioral and cognitive dysfunction, kidney disease, skin lesions, and cancer in the urine when dissolved. Sustainable goals 6 and 14 hold water purity and sanitation as an essential component, the former includes clean water provision although the latter is included, it is not viewed as a fundamental human right by UNICEF. As poisoning threatens over 0.15 billion people worldwide, the majority of whom live in South and East Asia (Singh, & Prasad, 2015). As poisoning is most prevalent in Bangladesh, India, and Pakistan.

The majority of the As in the Earth's crust remains in place and unaltered, but some is released by shocks and mixes with other elements in the atmosphere. Dissolution of As in wells and aquifers has increased as a result of industrialization, mining, and particularly deep well boring, which has aided in the transport of As to groundwater sources. The As-related illnesses have spread through the healthcare system. Mitigation plans don't seem to be in effect or aren't being applied enough to meet the challenge. An increase in As has led to decreasing the health-care system's capacity to deal with the issue.

For the majority of people in Pakistan, clean water is lacking. The rivers, which are the primary source of underground water, are contaminated beyond the bare minimum (Aamir et al., 2020). This occurred as a result of rapid and unplanned drilling for water extraction. Pakistan is predominantly agricultural, with most of its population concentrated in and around the Indus river delta. The Indus and its tributaries are Pakistan's lifelines. Unfortunately, pollution from agriculture, mining, and the population growth in surrounding the river, have caused approximately 0.06 billion people to be affected by As. The majority of today's victims are located in and around the Indus River Basin, with hotspots in and around the cities of Lahore and Hyderabad (Podgorski et al., 2017). An estimated 5% of the world's population drinks water that has an amount of As that is high enough to cause serious illness, requiring an urgent response from the government and broad change in drinking water policy (Abernathy et al., 1999).

Groundwater resources, which primarily supply Pakistanis with water, contain the most alarming truth about As contamination (Azizullah et al., 2011). In Pakistan, As contamination is distinguished as desert and semiarid areas. Deposits of

Punjab and Sindh are distinguished with the delta and alluvial and riverine sediments. There are granite basement formations in the north and west of the nation (Faheem et al., 2008).

While many regions do not use groundwater for agricultural production through irrigation, they do use it extensively for domestic purposes. Pakistan suffers from groundwater contamination caused by anthropogenic untreated waste discharges, which have doubled in recent years due to the usage of As pesticides, as well as industrial effluent leaching into ground aquifers. Hydrous ferric oxide (HFO) seeps into the rock and soil, and thus causes contamination (Farooqi et al., 2007a).

Pakistan faces a significant risk as a result of As pollution. The "Pakistan Council of Research in Water Resources (PCRWR)" conducted comprehensive research in order to detect contaminants in different water resources of Pakistan (Nickson et al., 2005). According to Reynolds (2010), the sources of As in water are numerous and can be separated into two main groups. This category includes both manufacturing applications and mineral deposits. The former is primarily derived from pesticides, wood preservatives, and glass processing, among others. Additionally, research has shown that leaching of eroding geological materials and weathering rocks can lead to high As levels in drinking water. Mining activities exacerbate the problem by amplifying soil and subsurface material disruption.

Burning of both industrial and domestic coal increases the issue of groundwater pollution in Pakistan. Such is the reality that resulting from the combustion of carbon dioxide combining with the air and its subsequent deposition to return to the ground by condensation (Baig et al., 2009). Overall, there is an observed increase in As contamination in Pakistan's high-risk zones, showing that this has a multicausality. When minerals dissolve in water, they increase the likelihood of the amount of As getting into the water Likewise, a high alkaline pH and increased concentration of HCO^3 and Ca^{2+} SO_4^{2-} promoted the groundwater toxicity (Smedley et al., 2003).

4.2.2. Significance of the study

The present study was planned to identify the intensity and spatial extent of the concentrations of As in groundwater resources of Pakistan to better understand the risks to human health. The outcomes of the study will provide useful information to the local government and policy makers in development, monitoring, management and sustainability of ground water resources in Pakistan.

4.2.3. Study objectives

1. Identifying the characteristics of the study area: location, topography and hydrological characteristics using ArcGIS.
2. Determining sampling points based on types of wells (dug well, bore well, hand pump etc.)
3. Collecting and analyzing the groundwater samples
4. Data processing and interpretation by using ArcGIS software and illustrating the results of the analysis in the form of maps in order to show the spatial distribution of As in groundwater of the study area. The spatial distribution is represented as a thematic layer generated using IDW tool in ArcGIS software to predict the unknown value for As in rest of the study area which was not covered by the analysis and thus present the spatial distribution of As that used in assessing the suitability of groundwater for drinking in the study area.

4.2.4. Materials and methods

i. Sample analyses:

Standard methods of collection were used as described by Royal Society of Chemistry, Cambridge (Radojevic & Bashkin, 1999). All samples collected for sampling were the representative of the water facility being tested. Composite samples were made to minimize sample number. Five water samples have been collected from each sampling site in plastic sterilized bottles. For further analyses, collected samples have then been carried and kept in the dark at 4°C (APHA, 2005). Concentrations of As can be determined in the field using semi-quantitative or quantitative field kits. While semi-quantitative field test kits are recommended for determining whether wells are above or below an acceptable limit, quantitative measurements provide information on As concentrations. Quantitative measurements enable us to assess the health hazard and are critical for planning mitigation measures (Eawag, 2015).

On-site measurements of basic parameters such as pH and electrical conductivity (EC) were made. The Garmin GPSMAP 64s was used to record the location of each sampling site. At each sampling spot, one bottle's water was acidified for As analysis, while another bottle's water was left unacidified and tested for anions such as nitrate (NO_3), sulphate (SO_4), and chloride (Cl). Arsenic is found in two oxidation states in groundwater: "As-III (arsenite)" and "As-V (arsenate). Organic forms exist as well, but they are rare in drinking water. Both "As-III" and "As-V" are highly toxic (Eawag, 2015).

The weighing and digested samples were all done overnight at 65 percent (v/v) HNO_3 (CNW Corporation, Shanghai, China), and 1 mL GR grade 30% (v/v) H_2O_2 the following day (Sinopharm Chemical Reagent Co., Ltd, Beijing, China). The mixtures were then mixed, screened in Teflon microwave digestion piping and digested at 800 W for 10 min at 120°C and then 800 W & 170°C for 30 minutes in an accelerated digestive process (Mars CEM, CEM Corporation, Matthews NC, USA). The 0.22 μm nylon membrane filtered all digested samples and the final volume increased to 5 ml with highly purified water. Finally, Inductively Coupled Plasma Mass Spectroscopy ICP-MS (Agilent Technologies, Santa Clara, CA, USA) was used to quantify As.

ii. QC/QA in the analytical procedure:

The standard stock solution mixed with toxic metals were obtained. Appropriate dilutions of standard stock solution were used to prepare the working solutions daily. A quality control (QC) sample was created by combining aliquots of each sample and was thus broadly representative of the entire sample set. To assess the instrument's stability, a QC sample was injected after every 15 samples.

iii. Data Analysis:

Using Excel software, the analytical results were combined to create a multi-element database. The data on As concentrations in water was analyzed statistically using a statistical software package i.e. Tibco Statistica Academic 13.4. Basic stats and correlation analysis were performed to estimate mean significant differences ($p < 0.05$) in water samples. Furthermore, Microsoft Excel 2016 was used for graphical depiction of dataset.

iv. Digitization of topographic data

Digitization in GIS is the process by means of a tracking of the features to convert geographic data from a hardcopy or from a scanned image to a vector data. During the digitization process, characteristics from the traced map or image are captured as coordinates in either a point, line, or polygon format from the traced image or map. This is necessary when data are collected in formats which cannot be integrated with other GIS data immediately.

a. Dataset:

The main datasets used in the process are as follows:

- Scanned map of the soil of Pakistan
- Scanned map of Geology of Pakistan
- Administrative Boundary of Pakistan

b. Software:

The software used for the process of digitization is ArcGIS 10.4.1 along with its spatial analyst extension enabled.

c. Methods and tools:

The scanned map was first geo-referenced using the administrative boundary of Pakistan through the geo-referencing toolbar. The georeferenced map was then used to digitize polygons for each rock type and soil type using the editor tools. The digitized polygons were saved as features in a shape file. Each feature was labeled in the attribute table according to the scanned map. Different columns in the attribute table were made and related information. The shape files were refined by removing the extra polygons.

v. Predictive Modeling:

It is expensive and time consuming to analyze the water samples for each and every point of the whole country to find out the elevated As contaminations. For countries with limited monitoring of their groundwater quality, risk maps can assist in delineating areas with high As concentrations. The predictive maps are produced using a model that incorporates measured groundwater data as well as known geological and geographic parameters. To develop a simulation model, the significance of these variables for the occurrence of increased As concentrations is calculated. For modelling purposes, a combination of statistical procedures and expert knowledge is used, considering the natural causes of increased groundwater concentrations (Eawag, 2015). This means that even in areas where no data on groundwater quality are available, the probability of groundwater contamination can be estimated.

vi. Risk mapping

The objective of the risk maps is to produce a national scale natural contaminants assessment in groundwater resource. The geostatistical variogram analysis (Webster and Oliver, 1992) along with IDW approach was applied on the data. Because it is the deterministic family of spatial interpolation and it performs better under data scarcity for spatial interpolation of metals as reported in prior studies (Xie et al., 2011).

Before computing data into the interpolation models, statistically significant correlation ($p < 0.05$) was observed among in situ correlation of the RQ, derived soil properties measured as covariates to the interpolation models and DEM elevation. Therefore, to measure spatial interpolation quality, the index of agreement d (where d measures the agreement between sampled and interpolated values) was also computed from cross-validation (Skøien et al., 2006) and ranges from 0 to 1.

4.2.5. Results and Discussion

i. Study area location

Geographically Pakistan is divided into three major regions: The Indus River plain, the Balochistan Plateau and the northern highlands. The Indus River plain is divided into two major subdivisions roughly corresponding to the provinces of Punjab and Sindh. A few geographers give added emphasis to the main areas. For example, sometimes the Mountain Ranges on the western border with Afghanistan are separate from the Balochistan Plateau, and the Thar Desert is separated from the Indus Plain on the western boundary with India to the south of the Sutlej River. The country, however, can be easily visualized as divided in three by an imaginary line from the Khyber Pass to the east and another from Islamabad to the southwest down the center of the country. Thus, the northern mountains are roughly north of the imaginary east-west line; the plateau of Balochistan is south-west of the imaginary line; and it lies east of that line on the Indus plain (US Country Studies, 2019).

a. Punjab Province:

Punjab is Pakistan's second largest province in terms of land area, after Balochistan, at 205,344 square kilometers (79,284 square miles). It uses 25.8% of the country's land area. Punjab province is bordered by Sindh to the south, KP to the west, and Balochistan to the north. Punjab is surrounded on the north by Jammu and Kashmir and on the east by the Indian states of Punjab and Rajasthan. In the eastern central region, the provincial capital, Lahore, is near the Indian border. The landscape is one of the most heavily irrigated on the planet, with canals crisscrossing the province. Punjab also has several mountainous regions, including the Sulaiman Mountains in the southwest, the Margalla Hills in the north near Islamabad, and the Salt Range, which separates the province's most northern region, the Pothohar Plateau, from the rest. Deserts with sparse vegetation can be found in southern Punjab, near the Rajasthan border and near the Sulaiman Range. Additionally, Punjab contains a portion of the Thal and Cholistan deserts. Punjab reaches an elevation of 2,327 meters (7,635 feet) in the south, near the hill station of Fort Munro in Dera Ghazi Khan (Britannica, T. 2010) (figure 4.8).

The name Punjab refers to "Five rivers," which are a tributary to the river of Indus and refers to that drained land by the Jhelum, Chenab, Ravi, Beas, and Sutlej rivers. Punjab is primarily an alluvial plain formed by the Indus River and its four major tributaries in Pakistan: The Jhelum, Chenab, Ravi, and Sutlej rivers. The land slopes northeast to southwest in general, but it rises in the areas between rivers. The alluvial plain is characterized by a diversity of landforms: its active floodplains are flooded during the rainy season and contain changing river channels, while meander floodplains adjacent to the active floodplàin are characterized by relict and abandoned channels. The Murree, Rawalpindi, and Pabbi hills, all of which are part of the Sub-Himalayas, are located in the northern part of the province, while the Potwar Plateau is located in the far north (Britannica, T., 2010).

The winters are foggy, often accompanied by rain, in most areas in Punjab. Temperatures start to increase by mid-February and spring weather continues until the summer heat starts in mid-April. The climatic effects of Punjab include hot weather from April to June in three seasons when temperatures rise to 110 °F (43 °C). The rainy season lasts from July to September. The average annual precipitation ranges from 96 to 46 cm in the plains. From October to March the cold weather continues and the temperature drops to 40 °F (4 °C). Punjab has over half of the population of Pakistan and is also home to many of its biggest cities: Lahore, Faisalabad, Rawalpindi, Multan and Gujranwala. Punjab has the largest population of Pakistan. The estimated population of the Punjab province reported in 2017 census is 110,012,615 (Britannica, T. 2010).

b. Sindh Province:

Sindh is the second largest province of Pakistan after Punjab, but has the third highest population, making it the third largest in total land area. The province of Sindh is located west of the Balochistan and north of Punjab. Indochina is bordered on the east by India and on the Arabian Sea to the south. In the east is an alluvial plain, which surrounds the Indus River. Thar desert in the province's

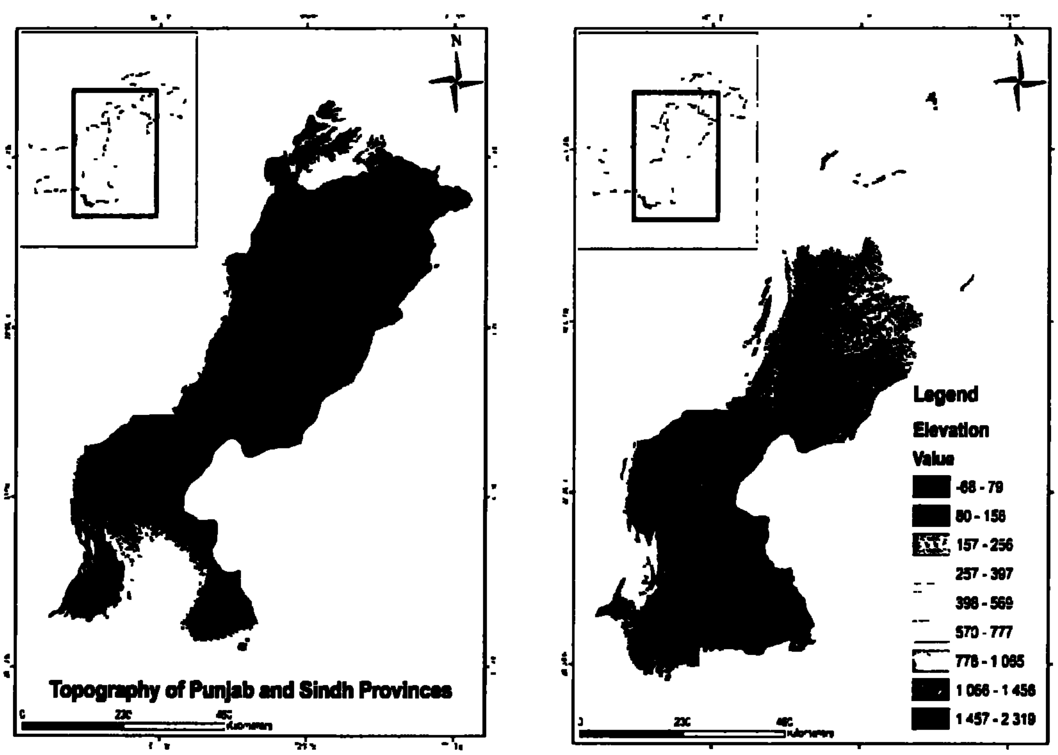

Figure: 4.8 Topography and elevation of the study area

easternmost region closest to India's border, and the Kirthar Mountains in the province's westernmost region. The Pakistan Census of 2017 reported the population of Sindh to be 47.9 million.

Sindh is located in a tropical to subtropical climate zone; summers are hot, and winters are mild to warm. Between May and August, temperatures frequently exceed 46 °C (115 °F), and the northern and higher elevated regions experience an average minimum temperature of 2 °C (36 °F) in December and January. The average annual rainfall is around 17.78 cm, mainly in July and August (figure 4.8).

c. The Indus River Plain:

The Indus Plain was formed by sediment deposits from the Indus River and its tributaries and is supported by a highly transmissive, "unconfined aquifer." The majority of groundwater supplies in the Punjab are fresh. The primary exceptions are areas of saline groundwater in the interfluviums ('doab'), particularly those between Multan and Faisalabad, in the vicinity of Sargodha, and in the province's south-eastern region. Groundwater supplies are more problematic in the southern

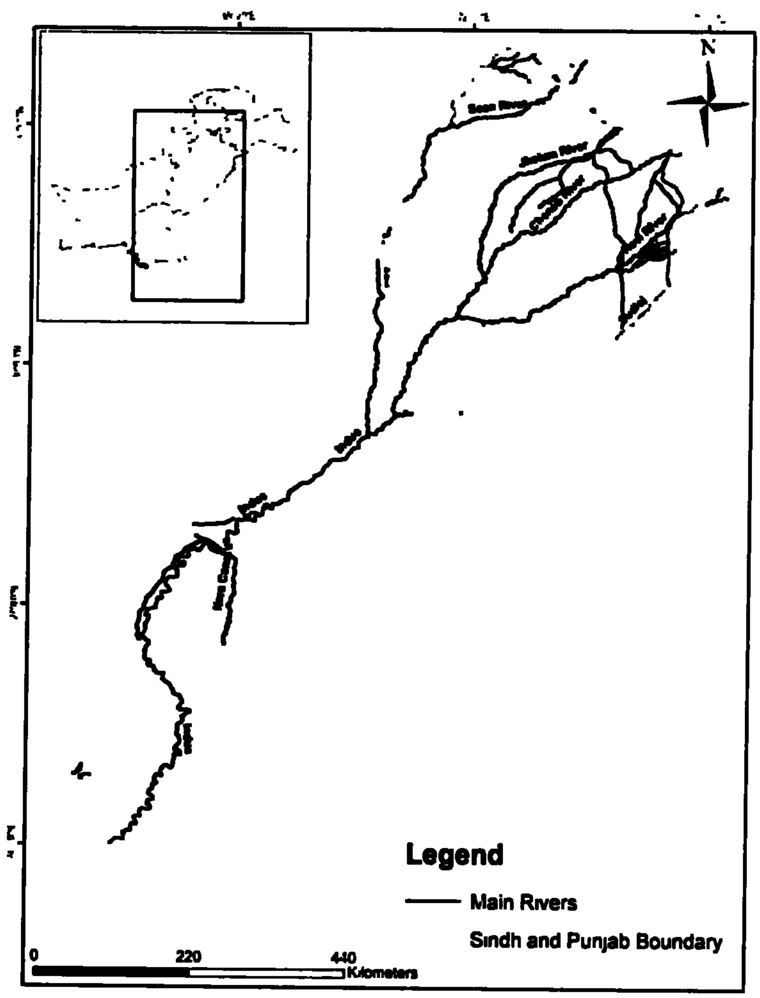

Figure: 4.9 Indus River along with the five interfluves (Doabs) of Pakistan

part of the Indus Plain, in Sindh. Groundwater supplies, with the exception of a small strip along the Indus River, are extremely saline. Sindh's aquifer discharge is generally less than that of Punjab (Survey of Pakistan 1989). Eastern deserts and western limestone ridges bordering the Indus Plain have even fewer supplies (figure 4.9).

ii. Soil types in the study area

In Pakistan, a wide variety of parent rock types exist, each of which has a significant effect on the soil's properties. Pakistan's rocks are classified into three major groups: igneous rocks, sedimentary rocks, and metamorphic rocks. The Himalayan regions are characterized by metamorphic rock types such as gneisses, schists, slates, and phyllites, as well as some quartzite and marble. Between Sargodha and Shahkot, in the northern part of the Indus plain, small outcrops of phyllites and quartzites occur. The most common types of igneous rocks found in Dir, Swat, Chitral, Gilgit, Zhob, Chagai, Las Bela, and Nagarparker are granite, syenite, diorite, gabbro, dolerite, and peridotite (FAO, 1997).

The most extensive are sedimentary rocks, including limestone, shale, sandstone, conglomerate, and dolomite. Granite, granodiorite, rhyolite, tuff, and andesite are all examples of the second type, igneous rocks. Schist, gneises, and slate comprise the third group of metamorphic rocks. The sedimentary rocks of Tertiary age, primarily limestone, calcareous shales, and calcareous sandstones, are by far the most extensive in Pakistan. Weathering produces a very small amount of soil material from limestone because its primary constituent is lime and the soil material is formed by the impurities in it. Parent materials are composed of igneous rocks that are relatively weatherable. They are predominantly comprised of granite, tuff, and andesite. They are high in potassium and sodium plagioclase, both of which are weatherable and contribute to the formation of fertile soils. The northern part of the country is dominated by metamorphic rocks. Members of this group are slowly weatherable and generally form loamy and clayey soils with a high base content (SSoP, 1979) (figure 4.10).

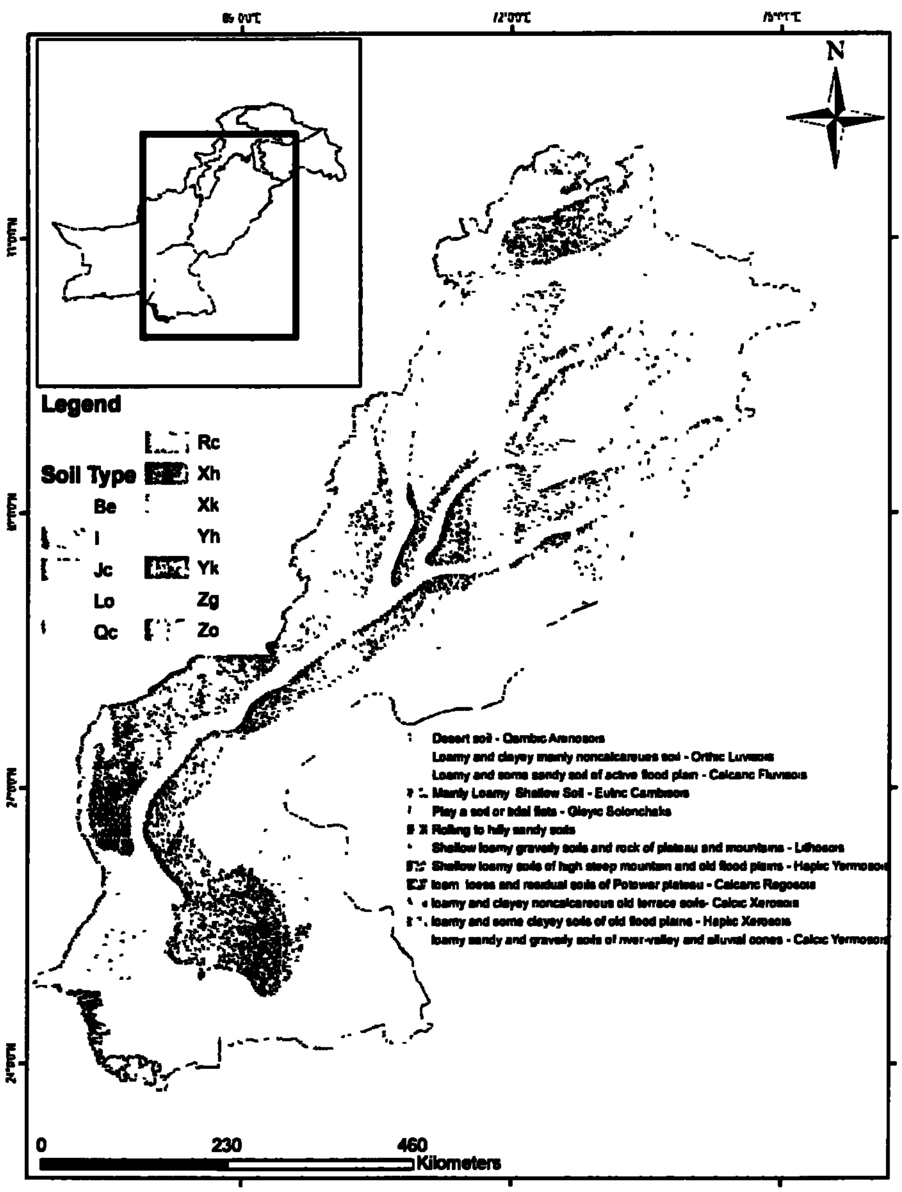

Figure: 4.10 Soil types of Indus Plain, Pakistan (digitized from map published by soil survey of Pakistan in 1993)

iii. Geology of study area

The Indus Basin is divided into four basins: the uppermost (Khyber–Hazara–Kashmir), the upper (Kohat–Pothwar), the middle (Sulaiman), and the lower (Kirthar). The Indus Basin is located west and north of the Indo-Pak subcontinent, which is included in the Gondwana lands (southern earth). Pakistan's sediments were significantly deformed by the collision of the Asian and Indo-Pak continental plates in the late Cretaceous. Strata were folded, faulted, and elevated as a result of these processes, resulting in numerous variations in sea level.

In the southern/lower Indus Basin, the Indo-Pakistan shield is represented by the Precambrian Nagar Parker granite, while the northern/upper Indus Basin is represented by the Kirana Group, which is composed of slate, quartzite, and igneous rocks. From the Precambrian to the Cambrian, the Permian, Triassic, Jurassic, Cretaceous, Pre-Tertiary and the latest Cretaceous Paleocene the stratigraphic succession in the central and western Kohat sub basin of the Kohat-Potwar Basin includes Salt Range formation; Khewra formation; Tobra formation; Mianwali formation; Datta formation; Chichali formations; Indus formation; Hangu formation respectively.

The Kuldana Group includes the Chorgali formation and the Kuldana formation in Potwar, Hazara, Kashmir, and eastern Kohat. The Miocene–Pliocene includes Murree, Chinji and Nagri. There are three distinct formations in the Pliocene: the Dhok Pathan formation, the Pleistocene Lei formation, and the Holocene Soan formation. Alluvium, colluvium, and eolian deposits constitute the sub- and recent surface rocks, respectively.

The Quaternary sequence of lower Indus basin ranges in age starts with the early stages of the last Ice Age and ends just recently, with the presence of formations such as the Larkana formation and the Tando Jam formation. Recent flood plain deposits cover vast areas, including a vast expanse from the Punjab border to the Indus delta. Abandoned riverbeds and flood channels can be found throughout the lower Indus Basin. In terms of the recent flood plain, the areas that have flooded in the past and the new meanders created near the river's channel are both included. Indus river has created Pleistocene and sub-recent river terraces that are also present in Sindh (Bender and Raza, 1995) (figure 4.11).

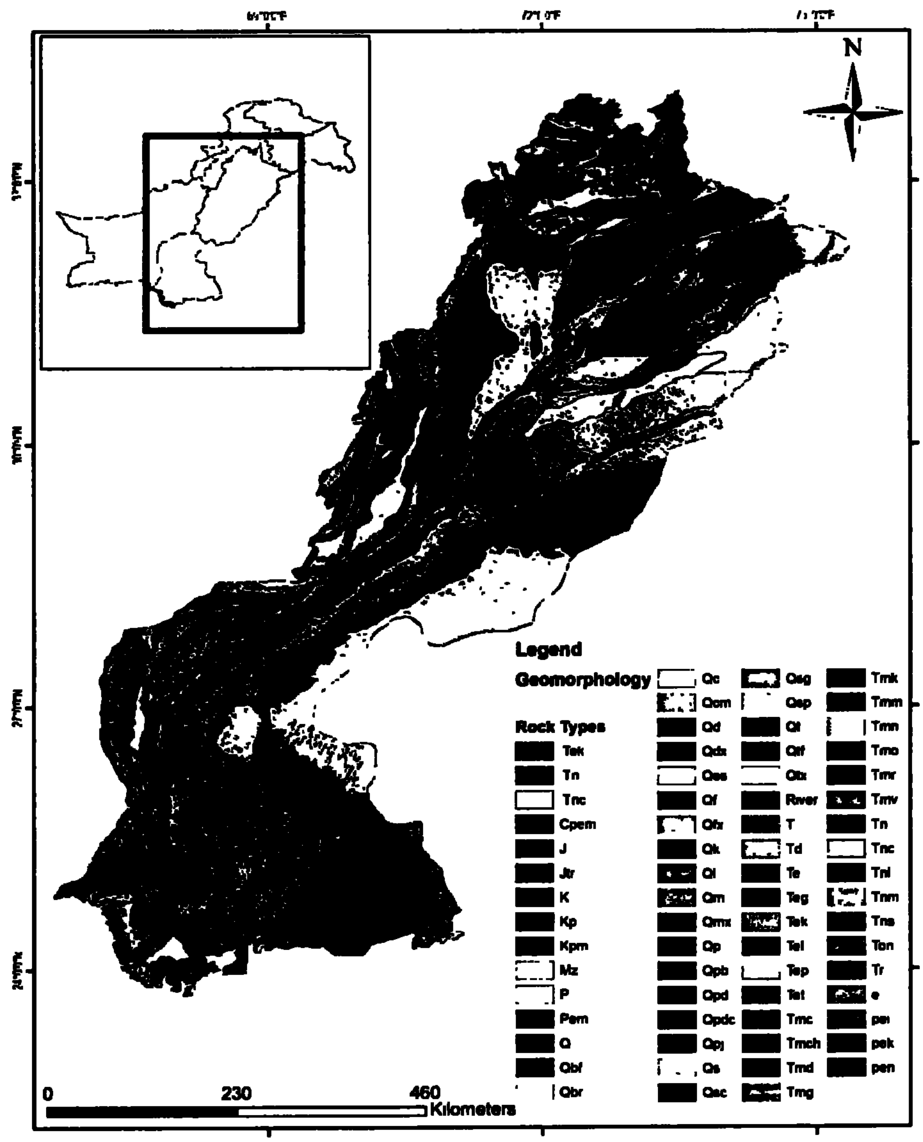

Figure: 4.11 Geology of Indus Plain, Pakistan (digitized from map published by geological survey of Pakistan in 1993)

iv. Land use land cover

United States Food and Agriculture Organization (FAO) in its report in 2014 concluded that Punjab province contains overall 49.4% area as irrigated crops followed by 19.1% bare areas with sparse natural vegetation, rangelands i.e. natural shrubs and herbs 10.2%, rain fed crops 8.4%, built-up area 3.3%, crops in flood plains 2.6%, wet areas and natural vegetation in wet areas is 1.7%, forest area 1.6%, orchard 1.3%, marginal and irrigated saline crops and bare areas are 0.5% and 0.1% respectively.

Whereas FAO reported that the Sindh province cover major area as bare that contains sparse natural vegetation 30.4%, irrigated crops 28.5%, marginal and irrigated saline crop area 10.6%, wet areas 8.1%, bare area 6.2%, range lands with natural shrubs and herbs 4.6%, crops in flood plains 2.8%, rain fed crops 2.5%, built-up area 2.4%, natural vegetation in wet areas 2.2%, orchards 0.9% and a very small area is covered by the forest i.e. 0.8% (figure 4.12).

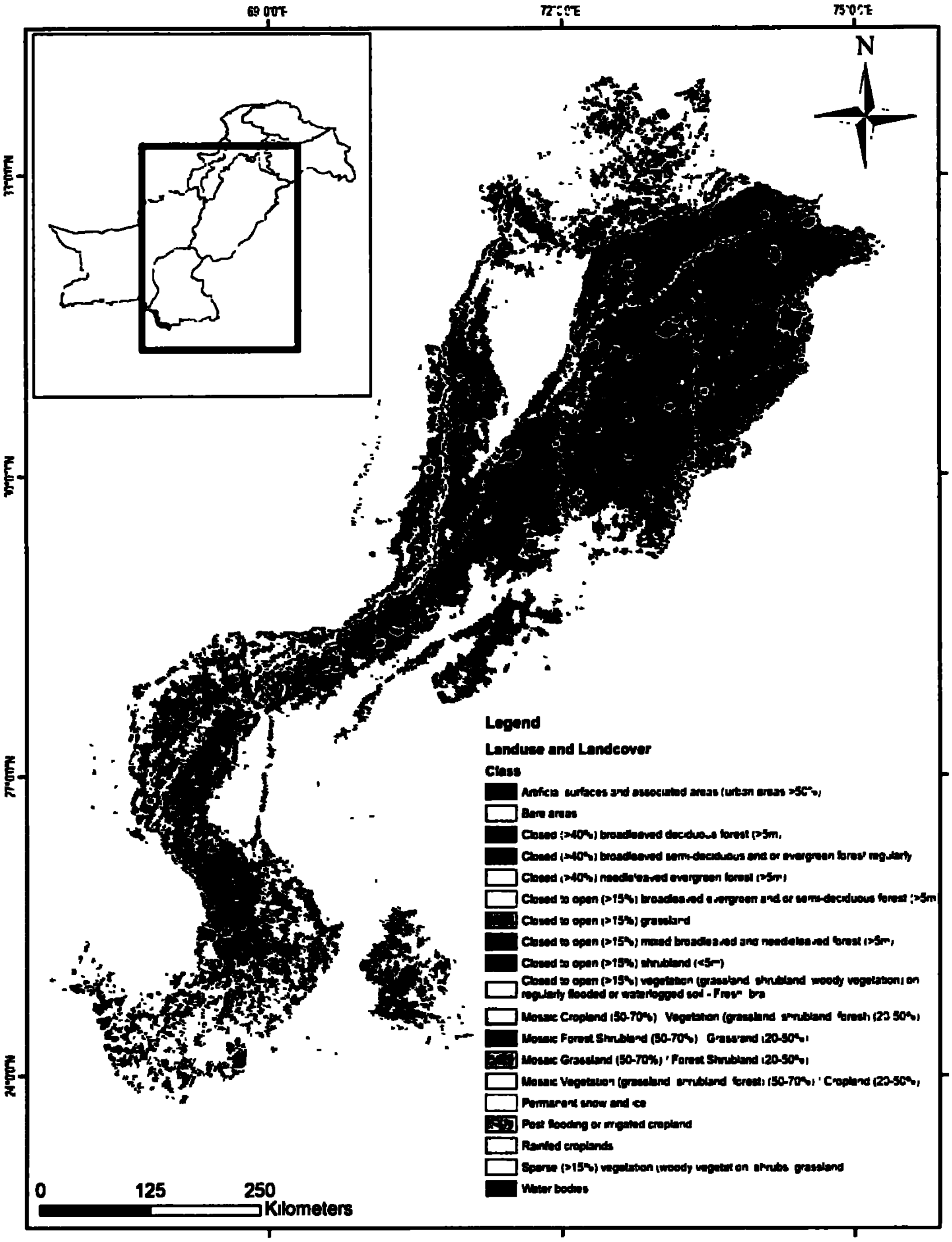

Figure: 4.12 Land Use Land Cover of Punjab and Sindh Province, Pakistan (classified from LULC 2017 available on Google earth pro)

v. Results of statistical analysis

a. Descriptive statistics of results

A summarized descriptive statistic of the results of As concentrations (µg/l) in groundwater of the study area is shown in table 4.10. The minimum, maximum, means and standard deviation of results based on each province is presented in table 4.11.

Table: 4.10 Descriptive statistics of As µg/l for all samples

Variable	Min	Q1	Median	Q3	Max	Mean	St. Dev.
Arsenic(ug/l)	0	0	0	15	500	30.84	83.95335

Table: 4.11 Descriptive statistics of arsenic values µg/l in groundwater samples of the study area

Province	Punjab	Sindh
No of Samples	158	121
Minimum	0	0
Maximum	150	500
Mean	18.65	47.47
St. Dev.	33.338	121.447

In order to give the simplified presentation of how the values of As concentration are distributed, the box plot (figure 4.13) was made, the values' distributions are dissimilarities in their distribution in two provinces.

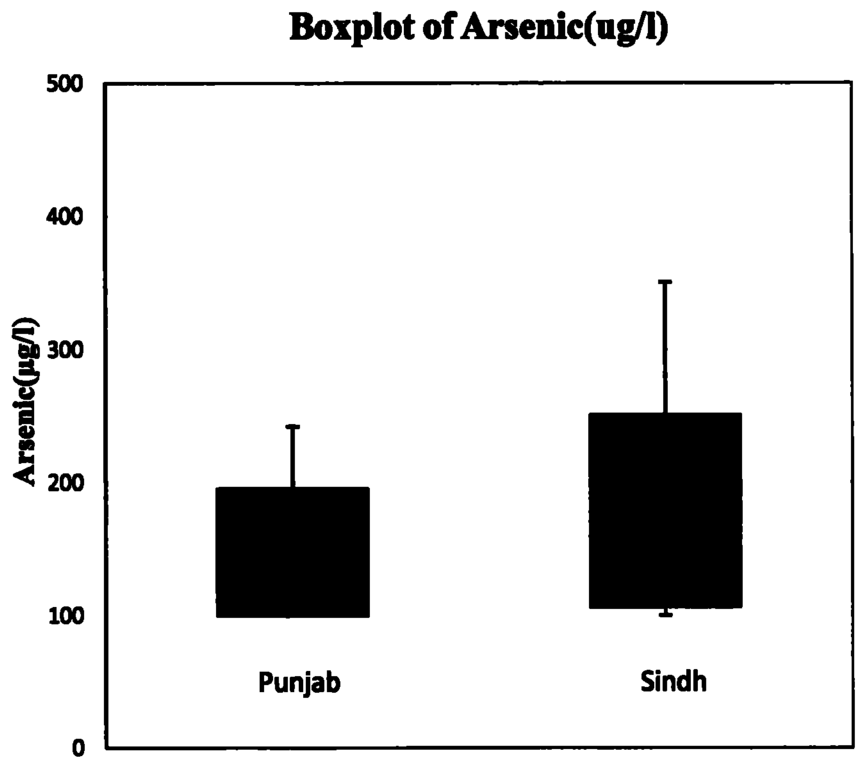

Figure: 4.13 Box plot of values of arsenic concentration in two provinces

b. Correlation analysis

The correlation analysis between As concentration and the different physicochemical parameters showed that the As concentration is positively correlated with the EC, TDS, SO_4, Cl, Total Hardness (T.H), Ca, Mg, Mn and Total Chloride (T. Cl) at the significance level of 0.05 while pH, Temperature, Turbidity, F, Fe, NO_3, Alkalinity are negatively correlated (table 4.12).

Table: 4.12 Correlation between arsenic and different physico-chemical parameters

Parameters	P C
pH	-0.13533
Temp ©	-0.24854
EC (us/cm)	[illegible]
TDS (ug/l)	[illegible]
Sulphates (ug/l)	[illegible]
Cl-1 (ug/l)	[illegible]
Total Hardeness (ug/l)	[illegible]
Ca (ug/l)	[illegible]
Mg (ug/l)	[illegible]
Tubidity (NTU)	-0.04512
Fluoride (ug/l)	-0.00468
Fe (ug/l)	-0.00254
NO3 (ug/l)	-0.08121
Mn (ug/l)	[illegible]
Total Chlorine (ug/l)	0.085438
Alkalinity (ug/l)	-0.01568

P C is Pearson Correlation

vi. Interpolation of data samples and predictive modeling

The IDW interpolation of As data of groundwater samples exhibited that there is a high risk of As tempted poisonousness from groundwater people are using for drinking purpose in the communities living near the Indus river and its tributaries. A substantial surge has been witnessed in the global scenario of As contamination during the last decade. It is assessed that almost 108 nations are influenced by As defilement in groundwater (>10 ppb) suggested by the World Health Organization. The most noteworthy among these are from Asia and Europe, trailed by locales like Africa, North America, South America and Australia. In excess of 230 million individuals around the world, which incorporate 180 million from Asia, are in danger of As harming. The most influenced among Southeast Asian nations are Pakistan, China, Bangladesh, Burma, Nepal, India, Cambodia, Vietnam and Thailand. Over 90% of As contamination is gathered to be geogenic. Alluvial residue is the significant hotspot for As pollution in groundwater and a solid connection with plate structural cycles, mountain building, disintegration and sedimentation (Shaji et al., 2021).

Figure 4.14 represents the As concentrations in the study area analyzed in the collected groundwater samples.

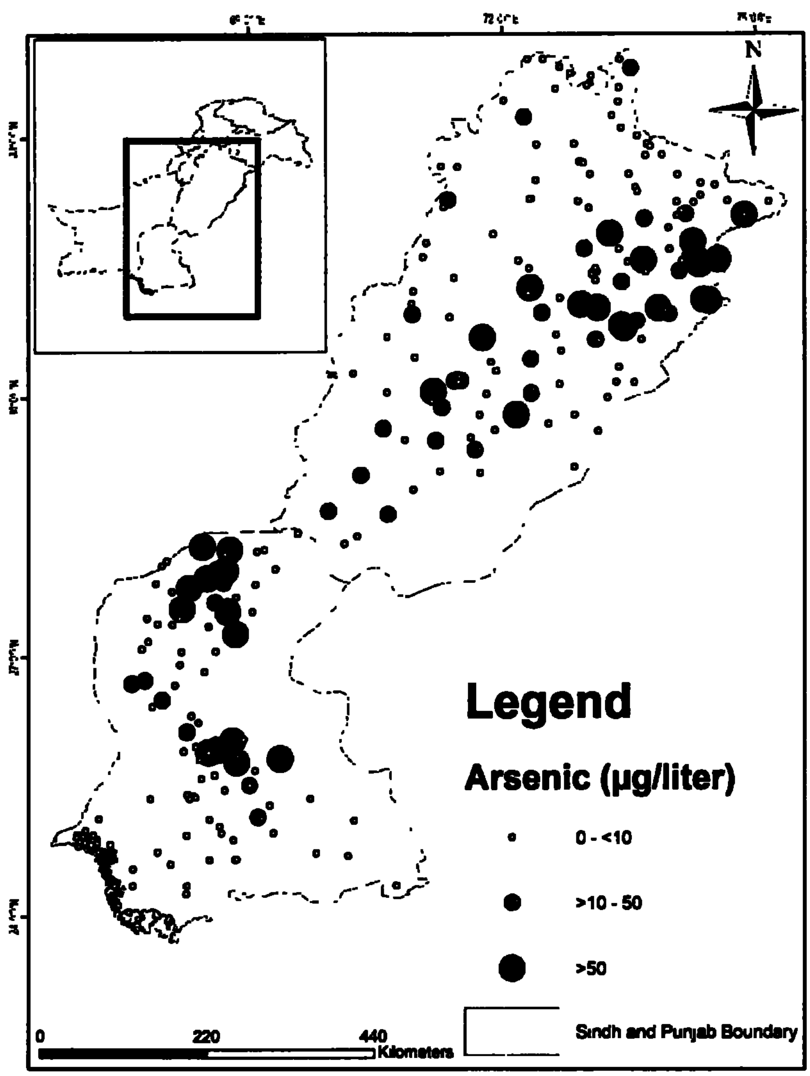

Figure: 4.14 Study area map along with the arsenic concentration points analyzed in the study area

The model shows that there is a medium to high risk of As contamination for the communities living in the vicinity of Indus Plain and using the water for drinking purpose. The As concentrations are >50 µg/l in most of the areas in Punjab and Sindh province. Similar findings revealed by the various scientists in other Asian countries also which includes Bangladesh, Combodia, China, Sri Lanka, Thailand, Veitnam and India (Chakraborti et al., 2018; Murphy et al., 2018; Chen et al., 1995; Chandrajith et al., 2020; Williams et al., 1996; Bozack et al., 2019; Datta and Kaul, 1976). The present study observed the highest concentrations of As (150 µg/l) in Jhang, Okara and Faisalabad followed by Patoki (130 µg/l) and Pindi bhattiyan (Hafizabad) (120 µg/l) in Punjab province. Whereas in Sindh province the highest concentration was reported in Jam Nawaz Ali (Sanghar) and NARA khairpur i.e. 500 µg/l followed by Sinhjoro (475 µg/l), Kot Digi (450 µg/l), Shikarpur and Khipro (Sanghar) (400 µg/l), Rato Dera (Larkana) (375 µg/l), Khanpur (Shikarpur) and Shahdadpur (Sanghar) (350 µg/l) and Mirpur Mathelo (Ghotki) (300 µg/l) (figure 4.15) which are beyond the permissible limits given by the WHO (10 µg/l) and the limit given by PSQCA i.e. 50 µg/l.

Pakistan's primary aquifer is located in the Indus plain, which is composed primarily of Quaternary alluvial and deltaic sedimentary deposits. As contamination is widespread in the aquifer that supplies water to this area's sedimentary deposits (Smedley, 2008). Around 9% of water resources in Pakistan were found to be carrying above-permissible levels of As. over 25%–36% population of Pakistan's two provinces, namely Sindh and Punjab, is exposed to contaminated water at 10 ppb (Ali et al., 2019a; Zudair et al., 2018).

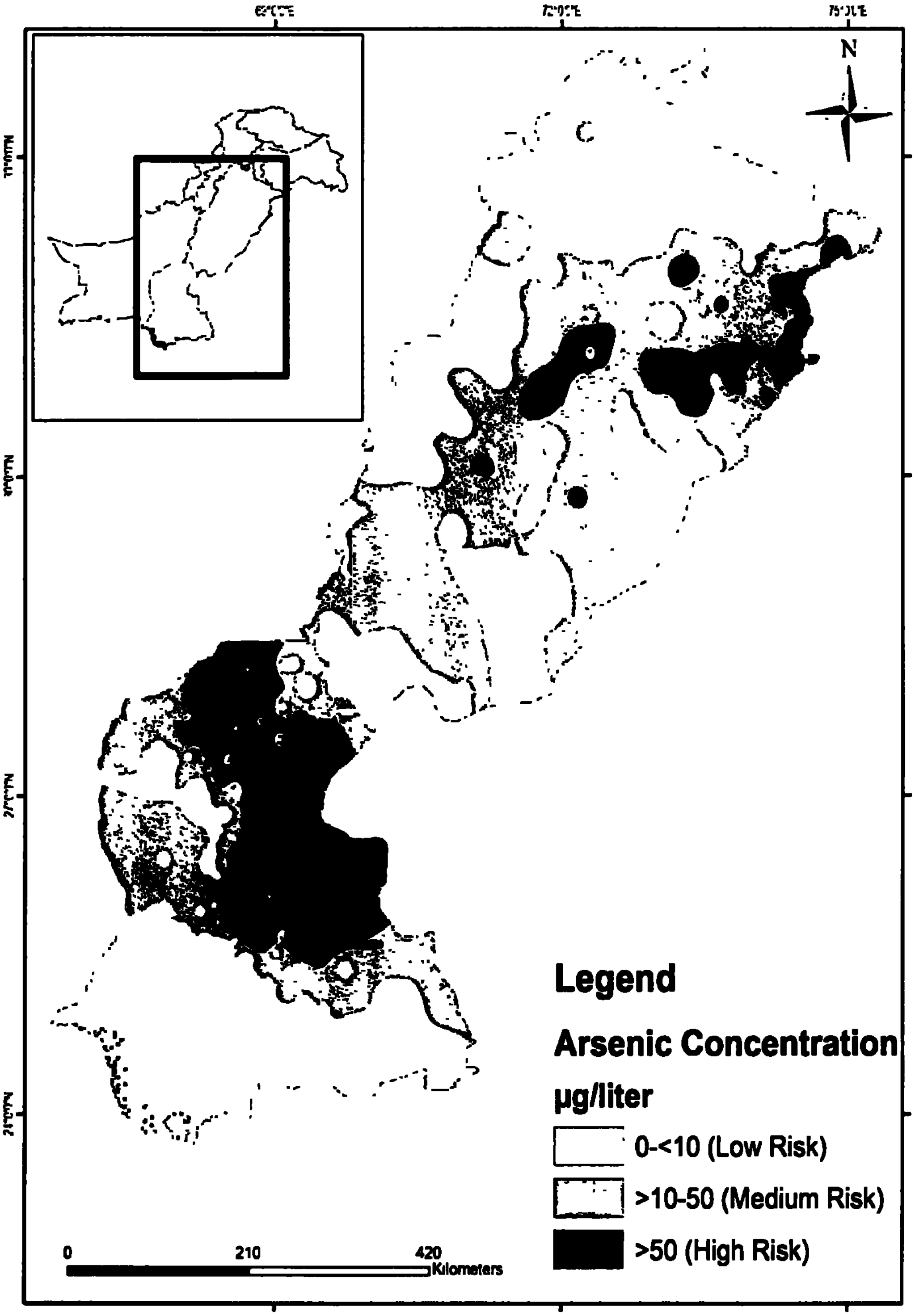

Figure: 4.15 Inverse Distance Weighted (IDW) interpolation of the arsenic data throughout Indus plain

In Pakistan, 13 million people across 27 districts and those living along the Indus River face heightened threats from As contamination in their drinking water. Tharparkar and Hyderabad along the Indus River in Sindh, and Lahore and Kausar in Punjab, are well-known hotspots of natural geogenic As contamination in groundwater (Ali et al., 2019a). Anthropogenic as well as natural sources are generally identified in case of As contamination. Coal mining and geothermal energy are significant contributors in Jhelum and Chakwal, Punjab province. The arid environment and complex geology of Tharparkar, Sindh province, facilitate As reductive dissolution. Also alluvial deposits of the Indus river are the primary source of As contamination in Kingri, Kotdigi and Sobo Dero (Rabbani et al., 2017; Farooq et al., 2016; Smedley, 2008; Iqbal et al., 2001).

Countries in Southeast Asia including Pakistan, India, Bangladesh and China are at high risk from As contamination. The present study observed that almost 11 districts in Punjab and Sindh province are severely effected with As contamination. A correlation between As poisoning and aquifer types suggests that younger orogenic belts extract the most As contaminated groundwater. Arsenic poisoning is an important issue that the UN Environment Programme (UNEP) and the World Health Organization (WHO) should concern themselves with, and they should devote an immense amount of effort to surveillance and awareness-raising to try to solve the problem. The deployment of global-scale financial and logistical assistance may be required to combat arsenicosis. Further study should examine the origins, occurrences, and distribution patterns of As, as well as its removal.

4.3 FLUORIDE IN GROUNDWATER

4.3.1. Introduction

Water is considered as a vital resource for sustaining life on earth (Azizullah et al., 2011). It covers almost 70% of the earth's crust but only 3% of this resource is present as freshwater reserves. It is now known that only small portion (0.01%) of fresh water is accessible for human consumption and the rest is locked as glaciers and ice caps (Postel et al., 1996; Nabeela et al., 2104). All around the world, groundwater has been considered as an important and alternate freshwater resource for domestic, agricultural and industrial purposes especially in areas experiencing complete or partial aridity (Solangi et al., 2019; Kaur et al., 2020). Due to its ease in availability, groundwater is under huge pressure to fulfill water demands of increasing population (Jha et al., 2020). Nearly, one third of the world's inhabitants utilize this valuable resource for drinking purpose (Solangi et al., 2019). It has a withdrawal rate of about 982 km3/year (Shukla and Saxena, 2020). Unfortunately, rapid pollution of surface water bodies and the growing population are the two key factors contributing in the quantitative and qualitative decline of this resource (Arshad and Imran, 2017; Egbueri, 2020; Shukla and Saxena, 2020).

Generally, the quality of groundwater in any region mainly depends upon natural factors like rainfall, minerals dissolution, groundwater flow and its direction, residence time and intra/inter-aquifer interaction. But anthropogenic wastes from various sources i.e., domestic, industrial and agricultural contributes manifold in deteriorating this valuable resource (Shukla and Saxena, 2020). Groundwater contamination as being hidden is relatively harder to identify as compared to surface water pollution and could remain there for many years owing to fairly slow movement of water and contaminants (Jha et al., 2020). Among the various organic and inorganic contaminants, F being extremely toxic pose serious carcinogenic and non-carcinogenic (cholera, diarrhea, dysentery, typhoid, polio, guinea worm, and various skin infections etc.) health risks to the contaminated water consuming inhabitants, even at low concentrations (Rasool et al., 2018; Kaur et al., 2020; Egbueri, 2020). Groundwater being the major source of drinking water has been used by the local population without any physical or chemical treatment. Though, this practice will continue due to shortage of hygienic water supplies especially in economically developing nations but may result in number of health problems. Hence regular monitoring of groundwater quality is required to save the consuming masses from harmful effects of this valuable resource (Brindha and Elango, 2011).

4.3.1. A. Physical and Chemical Properties of Fluoride

Fluorine (F) is a pale yellow greenish diatomic gas with pungent and irritating odor. It is the first member of halide group with melting point and boiling point of -219.6 °C and 188.1°C respectively. It is the lightest and extremely electronegative and reactive chemical element. It has the ability to react both at ambient and high temperatures with all the elements of periodic table with the exception of nitrogen, oxygen and few lighter noble gases (Tylenda et al., 2003). Being highly reactive, it does not find in elemental form beside some industrial processes and readily reacts to form organic and inorganic compounds known as fluoride (F^-). It ranks 13th in abundance of all elements present in the earth and mainly found in igneous and sedimentary rocks. It covers almost 0.06 to 0.09% of the earth's crust and have average crustal abundance of 300 mg/kg (Brindha and Elango, 2011; Rasool et al., 2018). Fluoride is essential micronutrient required by the human body for normal tooth and bone development and function. The acceptable range of F consumption in potable water has been recognized as 0.6 to 1.5 mg/L by World Health Organization (WHO,1984). Intake of water with F levels greater as well as lesser than the permissible range is found to be detrimental to human health (Brindha and Elango, 2011).

4.3.1. B. Fluoride in Environment

i. Fluoride Distribution in Water

It has now been known that F is naturally present in all waters at different concentrations (Fawell *et al.,* 2006). The water contaminated with F is impossible to distinguish through physical examination as it does not give any color, odor or taste to water and acts as an invisible poison (Ahmed, 2013; Vithanage and Bhattacharya, 2015). Therefore, chemical analysis is needed for the determination of this toxic ion. F enriched waters are mainly found in marine sediments and at the base of the mountains (Brindha and Elango, 2011). The typical concentrations of F in sea water ranges from 1 to 1.3 mg/L while in freshwater bodies it is less than 0.5 mg/L (Fawell et al., 2006; Maadid et al., 2017). Most of the rivers acts as a source of F in the sea (Carpenter, 1969). In sea waters, the removal of Fs is achieved by forming complexes with calcium compounds particularly carbonate and phosphate whereas, removal of undissolved F is done by the process of sedimentation (WHO, 2002). According to Carpenter (1969), it is estimated that the F resides in the ocean sediments for approximately 2 to 3 million years.

Generally, in case of groundwater, the concentration of F relies upon pH, temperature, anion exchange capacity of aquifer material (OH- for F-), solubility of fluorine bearing minerals, and the nature of geological formations drained by water and contact time of water with that particular formation (Narishma and Sudarshan, 2016; Rasool *et al.,* 2018). Climatic variables i.e., temperature and rainfall acts as a major factor affecting the F concentrations especially in areas experiencing dry weather conditions. The rainfall rate is generally low (225 to 400 mm per year) in areas of high aridity thus having evaporation rates greater than 2000 mm per year and decreased underwater hydraulic conductivity. The low rainfall rates cause prolonged rock water interaction which eventually leads to increased levels of F in groundwater. Furthermore, pH of groundwater acts as an important controlling factor in dissolution of F bearing minerals because of the release of sodium (Na^+) and bicarbonate ions (HCO^{-3}) (Rasool *et al.,* 2018). The less concentration of calcium (Ca^{2+}) and magnesium (Mg^{2+}) and high levels of bicarbonate (HCO^{-3}) and sodium (Na^{+}) provides favorable environment for the occurrence of toxic F ion (Bibi *et al.*, 2016; Rasool *et al.*, 2018; Kaur *et al.*, 2020). F concentrations can be high in underground waters where cation exchange of sodium for calcium occurs (Fawell *et al.*, 2006).

In natural environment, majority of the F present in groundwater is found in igneous, sedimentary and metamorphic rocks as fluorite (CaF2), mica (AB2–3(X, Si)4O10(O,F,OH)2), fluorapatite (Ca5FO12P3), apatite (Ca5(PO4)3(OH,F,Cl)), muscovite (K2Al4[Si6Al2O20] (OH,F)4), cryolite (Na3AlF6), biotite, lepidolite, tourmaline, hornblende series minerals, asbestos (chrysotile, actinolite, anthophullite) sphene, apophyllite and zinnwaldite etc. (Adimalla and Venkatayogi, 2017; Li et al., 2020). Weathering and leaching of these minerals contribute towards elevated concentrations of F (Aravinthasamy et al., 2019). The ingestion of contaminated groundwater is one of the key sources of intake of F for human beings with levels ranging from 30 to 50 mg/L (Barbier et al., 2010). Few minerals like fluorite (sedimentary rocks) and cryolite (igneous rocks) are not easily water soluble under ordinary conditions (standard pressure and temperature) and may require a basic environment and a range of specific conductivity (between 750 and 1750 µS/cm) for their disintegration. Fluorite (CaF_2) being rich in F is found in granite, granite gneisses and pegmatite (Saxena and Ahmed, 2001). Major reactions of dissolution of fluorite and fluorapatite are as follows:

$$CaF_2 + 2NaHCO_3 = CaCO_3 + 2Na^{+} + 2F^{-} + H_2O + CO_2$$

$$Ca_5(PO_4)_3F + 3H^{+} = 5Ca^{2+} + 3HPO_4^{-2} + F$$

(Thapa *et al.*, 2016)

Several prominent F containing minerals with respect to fluorine percentage are presented in table 4.13.

Table: 4.13 Fluoride containing minerals (Biswas *et al.*, 2017)

Mineral	Chemical formula	% fluorine
Sellaite	MgF_2	61 %
Villianmite	NaF	55 %
Fluorite (Fluorspar)	CaF_2	49 %
Cryolite	Na_3AlF_6	45 %
Bastnaesite	(Ce,La) $(CO_3)F$	9 %
Fluorapatite	$Ca_3(PO_4)_3F$	3-4 %

ii. Fluoride in Rocks and Soil

The natural presence of inorganic F is mainly associated with the weathering of parent rock material and the actions of microorganisms, plants, and animals. The occurrence of F is also influenced by several parameters i.e., soil forming processes, soil texture and climatic conditions. Other factors like clay content, pH and concentrations of calcium, phosphorus and hydroxides also acts as a controlling factor for F behavior in soil (Kabata-Pendias and Mukherjee, 2007). F is usually present in low concentrations in organic soils (Tylenda et al., 2003).

Generally, the levels of F in most rocks are found to be in the range of 100 to 1,300 mg/kg whereas in soil, the F content oscillates between 20 to 500 mg/kg (Vithanage and Bhattacharya, 2015). The application of phosphate fertilizers, pesticides, irrigation water and industrial pollution etc. may increase the F concentrations in topsoil by manifold which decreases with the increasing distance from the source and depth below the soil (WHO, 1984; Tylenda et al., 2003). The volcanic ash and application of fertilizers are reported to contribute more than 5000 mg F/kg to the nearby soil (Kumar et al., 2019). It has been noted that the lowest F contents are present in sandy soils providing humid climatic conditions whereas heavy clay soils and soils derived from the mafic rocks generally contains high F levels (Kabata-Pendias and Mukherjee, 2007). However, the F concentration may vary from 700 to 3800 mg/kg in soils that are originated from F containing minerals i.e. fluorspar, cryolite and fluorapatite etc. (WHO, 1984; Tylenda et al., 2003).

The mobility of fluorine in soil is highly dependent upon pH. In natural environment, F is slightly mobile but the solubility of F usually increases in acidic soils because of the presence of readily soluble Fs i.e. potassium fluoride (KF), sodium fluoride (NaF) and ammonium fluoride (NH_4F) whereas calcium fluoride (CaF_2) and aluminum fluoride (AlF_3) are known to dissolve more slowly (Kabata-Pendias and Pendias, 2001). The mineral fluorophlogopite (KMg_3 $(AlSi_3O_{10})F_2$) shows stability in alkaline environment and calcareous soils but certain factors i.e. pH, activities of silicic acid (H_4SiO_4) and presence of aluminum (Al^{3+}), magnesium (Mg^{2+}) and potassium (K^+) ions greatly affects its solubility (WHO, 2002). In acidic soils having pH less than 6, F make complexes with iron (Fe) and aluminum (Al). Adsorption is notably high in pH less than 4 and is remarkably less when pH is more than 6.5 (Vithanage and Bhattacharya, 2015). According to Arnesen and Krogstad (1998), increased sorption of F in B horizon of soil has been recorded and highest sorption happens at pH 4.8 to 5.5. However, anion exchange occurs under alkaline conditions (pH>7) in which hydroxide ion (OH-) can substitute fluoride ion (F-) from biotite, muscovite and clay minerals (Rasool et al., 2018)

Moreover, among various rocks, granite is considered as the main source of F with concentrations ranging between 500 to 1400 mg/kg with a world average content of 810 mg/kg (Wedepohl, 1969; Brindha and Elango, 2011). Granite rocks contains five time more F concentrations than basalt rock. Similarly, shale also contains high levels of F than sandstone and limestone (Bibi et al., 2016). Whereas alkaline rocks contain 1200 to 8500 mg/kg of F (Bibi et al., 2016; Rasool et al., 2018). The average F content in different sedimentary rocks is shown in table 4.14.

Table 4.14. The average fluoride content in different sedimentary rocks (Fleischer and Robinson, 1963)

Rocks	Range in mg/kg	Average in mg/kg
Limestone	Up to 1,210	220
Dolomite	110 - 400	260
Sandstone and greywacke	10 - 1,100	200
Shale	10 - 7600	940

iii. *Fluoride in Atmosphere*

In atmosphere, the presence of inorganic fluorides is predominantly controlled by aerosol formation, vaporization, hydrolysis and wet and dry deposition. The Fs are widely disseminated in the environment from both natural and anthropogenic sources either in gaseous or particulate form. The gaseous forms include silicon tetrafluoride (SiF_4), hydrogen fluoride (HF), sulfur hexafluoride (SF_6) and fluorosilicic acid (H_2SiF_6), whereas particulate forms include aluminum fluoride, sodium aluminum fluoride (cryolite), calcium fluoride, lead fluoride (PbF_2), sodium hexafluoro silicate and calcium phosphate fluoride (fluorapatite). In general, it has been known that hydrogen fluoride and inorganic fluorides (sodium and calcium fluorides) are responsible for almost 75% and 25% of the total inorganic Fs present in the atmosphere but this exposure atmosphere is almost negligible as compared to other sources (WHO, 2002; Fawell et al., 2006).

One of the most important natural sources of airborne F include gaseous emissions from volcanic activity. Almost 1-7x106 tones of Fs has been contributed solely by volcanic eruptions each year. Whereas dust from soils and sea water droplets are also known to be the natural sources of Fs in the atmosphere. The emissions from industrial sources like factories producing steel, super phosphate plants, ceramic factories, glass works, coal-burning power plants, oil refineries and brickworks are considered as the major contributors of Fs.

Almost 10% of the total F emissions are associate with aluminum industry (WHO, 1984). According to Smith and Hodge, (1979) almost 15,5000 tons of Fs were released by industrial units in atmosphere by United States of America in 1968. Whereas in non-industrial areas the levels of Fs are generally very low (0.05 to 1.90μg m-3) (Fawell et al., 2006). Burning of F containing fuels (coal, wood, oil and peat) are also the main contributors of F. According to MacDonald and Berkeley (1969) the levels of F in coal ranges from 4 to 30 g/kg Indoor air concentrations of F in some parts of China were found to vary from 16 to 46 μg m–3. These high levels were attributed to burning of F enriched coal for household practices especially cooking which ultimately resulted in 10 million people suffering from the dreadful effects of fluorosis in China.

iv. Fluoride in Plants and Animals

Plants can easily take up F through roots from the contaminated soil (Hong et al., 2016; Chatterjee et al., 2020). The levels of F incorporated in the plants rely upon the plant type, nature of the soil, quantity of F and form of F in the soil (Hong et al., 2016). The concentrations of fluorine ranging between 200 to 2000 ppm in soil are proved to cause toxicity in plants also known as phytotoxicity (Schulz et al., 2018). It has been noted that the high concentrations of F have detrimental effects on metabolic activity of plants, uptake of nutrient, biomass accumulation, seed germination, enzymatic activities, photosynthesis, protein synthesis, reactive oxygen species (ROS) production and gene expression patterns (Chatterjee et al., 2020). Whereas, growth retardation, inhibited reproduction and yield reduction are few indications that appear before visible symptoms of F toxicity occurs in plants. The F content in food plant generally ranges between 0.1 to 11 mg/kg. In forage plants high levels of F have been found as compared to other plant types (Kabata-Pendias and Mukherjee, 2007). As reported by Jha et al. (2009), the accumulation of F in onion is found to be in order of roots > shoot > bulb showing higher accumulation in roots than in other parts. Plants grown in acidic soils have increased amount of F whereas, older tea leaves (Camellia sinensis) accumulate 300 times more F than young leaves.

Furthermore, plants grown in close proximity of volcanic active sites and industrial sites may contain relatively high amount of F. Some plants show relatively high sensitivity towards F at concentrations between 20 to 50 mg/kg whereas highly tolerant plants do not show any signs of damaging effects even at exposure of 500 mg/kg (Kabata-Pendias and Mukherjee, 2007). The first symptom of F injury in plants is marginal and tip necrosis which makes the tip of the leaves appear yellow or brown. The uptake of F from soil to plant is done through roots by the process of transpiration which eventually collect in the margins of the leaves and generally made them hard and brittle (Chatterjee et al., 2020).

As reported by Kabata-Pendias and Mukherjee (2007), different effects of F toxicity has been observed in animals especially in areas experiencing recurrent volcanic eruptions. The F toxicity resulted in lower reproduction and lower milk production in dairy cattle. It has now been known that the F accumulation in animals depends upon four major factors i.e. route of uptake, presence of complexing agent in the diet, pH of the digestive system and occurrence of calcified tissues in the body. The main routes of F uptake include; inhalation, deposition on outer surface and intake via food or water. The uptake of F via inhalation is almost negligible especially in case of vertebrates and pose minimum to no threat as compared to other routes. However, F has a high affinity for calcium thus surface deposition of F occurs in organism having exoskeleton. The shells of organisms found in marine environment are found to have relatively high F content then surface water species (Weinstein and Davison, 2004). Camargo (2003) reported that the F concentration in exoskeleton of marine crustacean ranges from 200 to 6000 mg/kg dry wt. The intake of F via food and drinking water is thought to be as the main source of F consumption in animals. The ingestion of F via oral route is thought to be over 7000 times more toxic than the amount inhaled (Weinstein and Davison, 2004).

v. Fluoride in Food and Beverages

The intake of foodstuff and different drinks are considered as the principal route of F consumption in humans (WHO, 2002). Increased amount of F is noted in barley and rice i.e. 2 mg/kg whereas vegetables and fruits generally contain relatively low F concentrations i.e. 0.1 to 0.4 mg/kg (Fawell *et al.*, 2006). Fish meat and other meats except chicken also contains comparatively low F levels i.e. 2 to 5mg/kg and 0.2 to 1.0 mg/kg individually (Murray, 1986; Fawell *et al.*, 2006). However, the skin and bones of fish may contain F content up to 40 mg/kg but total F intake in humans rarely exceeds 0.2 mg/day even in areas where the fish consumption rate is high (Murray, 1986).

In case of beverages, the consumption of fluorinated water is considered as one of the biggest sources of F. Additionally, relatively high amount of F is contained in tea leaves i.e. 400 mg/kg dry weight but total F intake via tea ingestion is found to be in the range of 0.04 to 2.7 mg/person/day. The consumption of brick tea in Tibetans is responsible for F intake as high as 14 mg/day. Conversely, human breast milk contains less than 0.02 mg/L of F whereas F concentrations in cow's milk is found to be 0.02 to 0.05 mg/L. Thus, very insignificant exposure to F through milk intake has been reported. Similarly, fresh fruit juices also contain less levels of F. Whereas, F content in soft drinks and mineral water is found to be same as in the water with which they are produced (Murray, 1986).

vi. Fluoride in Dental Products

The presence of F in enamel, dental plaque and saliva are found to be imperative in precluding the cases of dental caries (Beltran *et al.*, 1988; Toumba *et al.*, 2019). The dental products like toothpaste, mouth wash and topically applied gels contains high levels i.e. 230 to 12,300 ppm of F and are injurious, if ingested. The common dental product used in every household i.e. toothpaste contains 900 to 1,100 ppm F precisely as calcium fluoride (Tylenda *et al.*, 2003). Fluoride on one hand is found to be helpful in prevention of dental caries but unintended ingestion of fluoridated toothpastes especially in case of young children (< 6 years) will possibly contribute around 0.5 to 0.75 mg per child per day of F intake and could lead to serious cases of dental fluorosis ((Fawell *et al.*, 2006; Toumba *et al.*, 2019). Parental supervision is required while tooth brushing at least up to the age of 7 years (Kanduti *et al.*, 2016). The recommended intake of F via usage of fluoridated toothpaste for children is presented in table 4.15.

Table: 4.15 Recommended use of fluoride toothpaste for children (Toumba *et al.*, 2019)

Age	Fluoride concentration (ppm)	Daily use	Daily mount
6 months-2years	500	2x	Pea size
2-6 years	1000	2x	Pea size
6 years and over	1450	2x	1-2 cm

4.3.1. C. Sources of Human and Environmental Exposure

i. Natural Occurrence

The natural presence of groundwater F is primarily related to the existence of F possessing minerals i.e., fluorite, cryolite, topaz, amphiboles, micas, sellaite, villiamite and certain clays etc., and leaching of these minerals into groundwater reserves (Rasool *et al.*, 2018; Ali *et al.*, 2019). The interaction of rock and water results in the disintegration of F-containing minerals leading to high F accumulation in bedrocks. It has been observed that the concentrations of F are usually high in ground waters of lowland regions as compared to highland regions particularly due to increased contact time of water with aquifer material and slow movement of water as compared to highlands (Rasool *et al.*, 2018). Almost 150 F containing minerals has been reported by Srivastava and Lohani (2015). However, release of hydrogen fluoride gas via volcanic eruptions is considered another important natural source of F in the environment (Tylenda *et al.*, 2003). Approximately 0.6 to 6 million metric tons of hydrogen fluoride has been released globally through volcanic emissions per year, 10% of which entered the stratosphere directly (WHO, 2002; Tylenda *et al.*, 2003). In addition to hydrogen fluoride, fluorosilicic acid (H_2SiF_6). Silicontetra fluoride (SiF_4), and fluorine gas (F_2) has also been released in small amount to the atmosphere (Tylenda *et al.*, 2003). In Hekla eruption 2010, almost 23 to 35 mg/kg fluoride has been released via ash in the atmosphere. Volcanic ash being highly soluble increases the possibility of groundwater contamination (Brindha and Elango, 2011).

ii. Anthropogenic Sources

The natural levels of F in groundwater can be amplified by several anthropogenic activities which include combustion of coal in thermal power plants, discharges from various industries i.e. steel, aluminum, copper etc. wastewater expulsion from sewage treatment plants, semiconductor production generated with high amount of F content and use of phosphate fertilizers and pesticides for agricultural purposes etc. (Farooqi *et al.*, 2007; Singh *et al.*, 2013; Rasool *et al.*, 2018; Usham *et al.*, 2018). Aluminum smelters and phosphate fertilizer units are the major emitters of hydrogen fluoride and particulate fluorides (Tylenda *et al.*, 2003). The aluminum processing industries, china clay productions and plants of phosphate fertilizer are accounted for 3200, 3560 and 2080 mg/kg of F input in nearby soils respectively (Kabata-Pendias and Pendias, 2001). Hydrogen fluoride is primarily used in the manufacturing of synthetic cryolite, aluminum fluoride, motor gasoline alkylates and chlorofluorocarbons (CFCs) (WHO, 2002).

According to Clean Air Act Amendments 1990, hydrogen fluoride is sited among the 189 perilous chemicals listed as hazardous air pollutants (HAP) (Tylenda *et al.*, 2003). Similarly, phosphate fertilizers are considered as one of the important F sources to agricultural soils. In general, they are produced from rock phosphates which usually contains about 3.5% fluorine. However, during acidulation process, which is used in the manufacturing of phosphate fertilizers, the fraction of F is dissipated in the environment resulting in lower concentrations of F which are further reduced through dilution with sulfur (super phosphates) or ammonium ion (ammoniated phosphates) with the end product containing about 1.3 to 3 % fluorine (WHO, 2002).

4.3.2. Significance of the Study

In order to get better understanding of the risks posed to ecosystem and human health, the present study was planned to examine the concentrations of F in groundwater resources of Pakistan. The outcomes of the study will provide useful information to the local government and policy makers in development, monitoring, management and sustainability of ground water resources in Pakistan.

4.3.3. Study Objectives

The objectives of this study were to;

1. Assess the fluoride contamination in ground waters of Pakistan by sample collection and analysis.

2. Predict the fluoride contamination in Pakistan.

3. Analyze the extent of fluoride contamination in Pakistan through AHP analysis.

4.3.4. Materials and methods

i. Sample analyses:

Standard methods of collection were used as described by Royal Society of Chemistry, Cambridge (Radojevic & Bashkin, 1999). All samples collected for sampling were representative of the water facility being tested. Composite samples were made to minimize sample number. From each sampling site, 5 water samples were collected in sterilized plastic bottles. After collection the samples were then transported and stored in the dark at 4°C for further analyses (APHA, 2005).

When fluorimetric or quantitative field kits are used, fluid concentrations can be analyzed directly in the field. An acceptable level of F test should only be able to classify as above or below a semi-quantitative result. The numerical data is needed to assess the hazard and to strategize a solution (Eawag, 2015).

The pH and electrical conductivity (EC) of the solution were determined on the spot. Each sampling site was located using a Garmin GPSMAP 64s. At each sampling spot, the water of one bottle was acidified for F analyses, while another bottle's water was left unacidified and tested for anions such as nitrate (NO_3), sulfate (SO_4), and chloride (Cl). F is found in groundwater as fluorine or the F ion.

Ion selective electrode in conjunction with an ion meter using the PHM 250 Meter Lab was used to determine the F content of water. The ISE 250 F ion selective electrode model was chosen to determine the F content of drinking water. As a stock solution, 1000ppm Merk was used, and dilutions of 10, 1, 0.1, and 0.01 ppm were prepared. With distilled water, a 1 molar solution of sodium chlorides, a 0.75 M solution of sodium acetate, and a 0.25 M solution of acetic acid were prepared. To obtain buffer, an equal volume of each of the three solutions is combined (TISAB). The instrument was calibrated with freshly prepared standard solutions prior to beginning the analysis of drinking water. Prior to measurement, the standard solutions or sample solutions were diluted with an equal amount of TISAB and then mixed. The total volume was sufficient to completely submerge the electrode and determine the F concentration. Calibration should be verified by using a standard solution of known concentration as the sample. TISAB and samples were mixed in equal parts and brought to room temperature (Farooqi et al., 2007). Finally, F was quantified using gas chromatography/mass spectrometry.

ii. QC/QA in the analytical procedure:

We obtained a standard stock solution containing toxic metals. Daily, appropriate dilutions of standard stock solution were used to prepare the working solutions. A quality control (QC) sample was prepared by mixing aliquots of each sample, resulting in a sample that is broadly representative of the entire sample set. After every 15 samples, a QC sample was injected to determine the instrument's stability.

iii. Data Analysis:

Using Excel software, the analytical results were combined to create a multi-element database. The data on F concentrations in water were analyzed statistically using Tibco Statistica Academic 13.4. The mean significant differences ($p < 0.05$) in water samples were determined using basic statistics and correlation analysis. Additionally, Microsoft Excel 2016 was used to visualize the dataset. in water samples. The point map for fluoride data concentrations was made in ArcGIS 10.4.1 (figure 4.16).

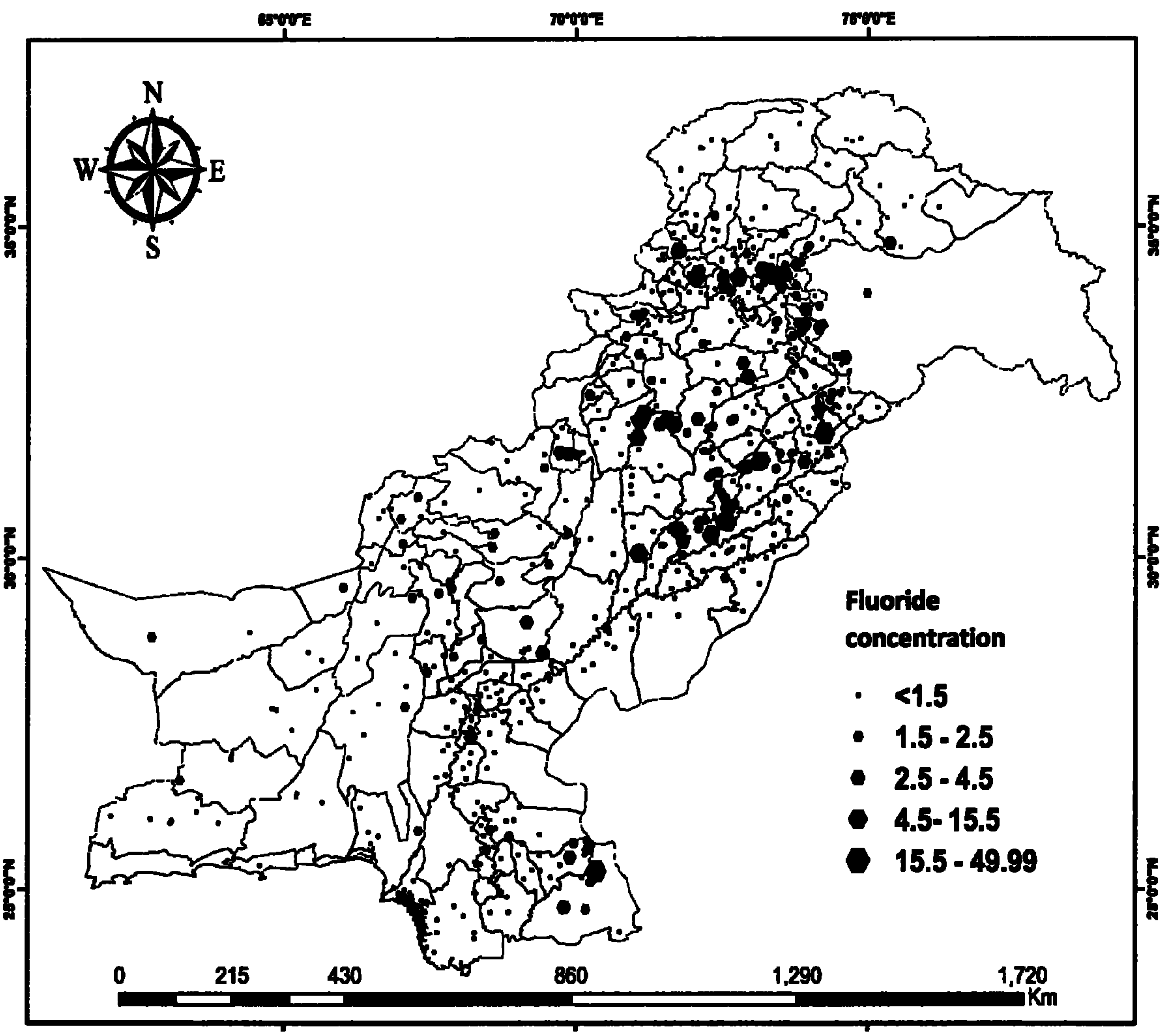

Figure: 4.16 Spatial distribution of fluoride in the study area

iv. Digitization of topographic data

Digitization in GIS is the process of converting geographic data from a hardcopy or scanned image to vector data via feature tracing. During the digitizing process, the traced map or image's features are captured as point, line, or polygon coordinates. This procedure becomes necessary when available data is collected in formats that are incompatible with immediate integration with other GIS data.

a. Dataset:

The main datasets used in the process are as follows:

- Scanned map of the soils of Pakistan
- Scanned map of Geology of Pakistan
- Administrative Boundary of Pakistan

b. Software:

The software used for the process of digitization is ArcGIS 10.4.1 along with its spatial analyst extension enabled.

c. Methods and tools:

The scanned map was first geo-referenced using the administrative boundary of Pakistan through the geo-referencing toolbar. The georeferenced map was then used to digitize polygons for each rock type and soil type using the editor tools. The digitized polygons were saved as features in a shape file. Each feature was labeled in the attribute table according to the scanned map. Different columns in the attribute table were made and related information. The shape files were refined by removing the extra polygons (figure 4.17 & 4.18).

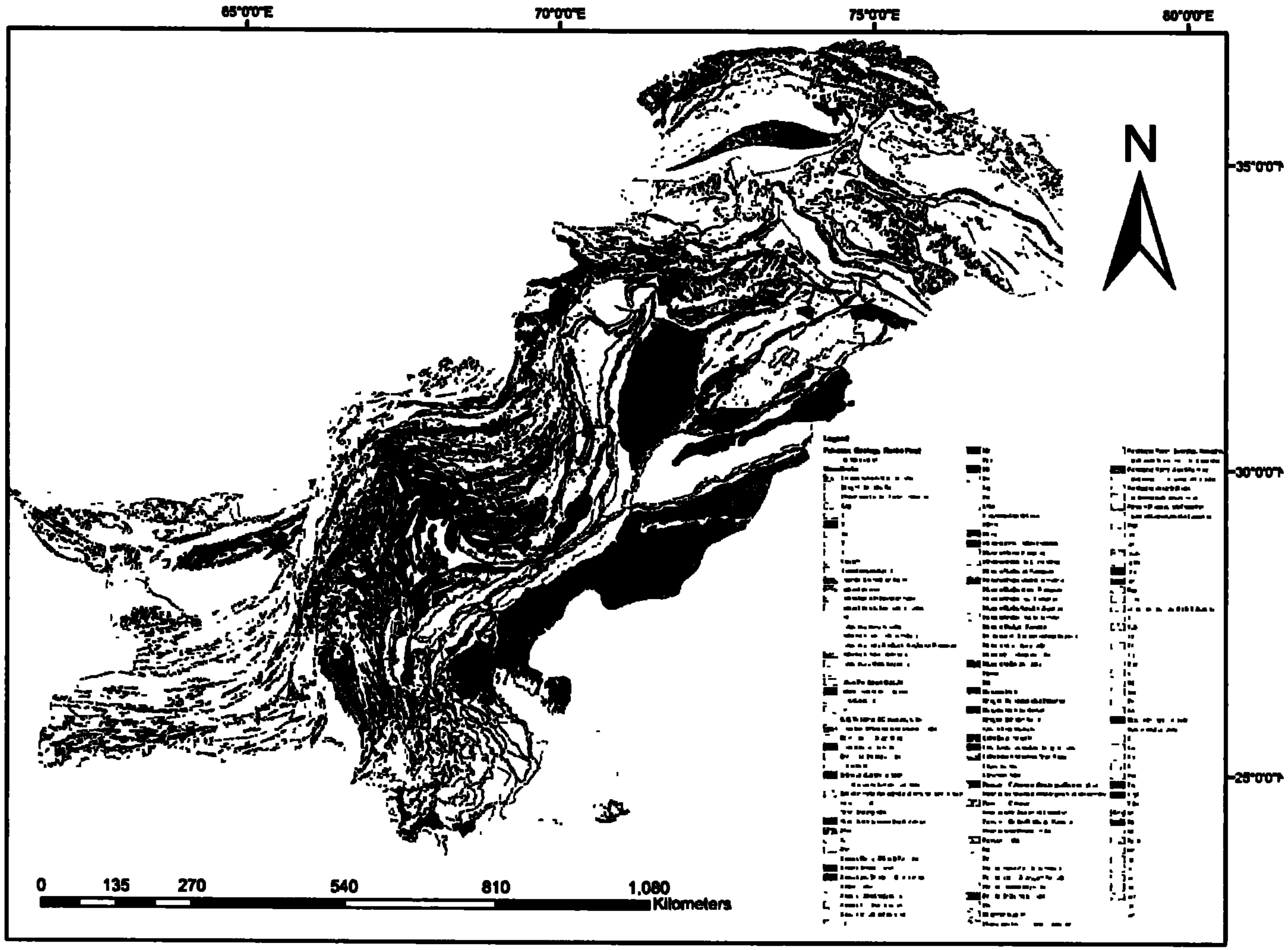

Figure: 4.17 Geological map of Pakistan digitized from topographic map published by Geological Survey of Pakistan in 1993

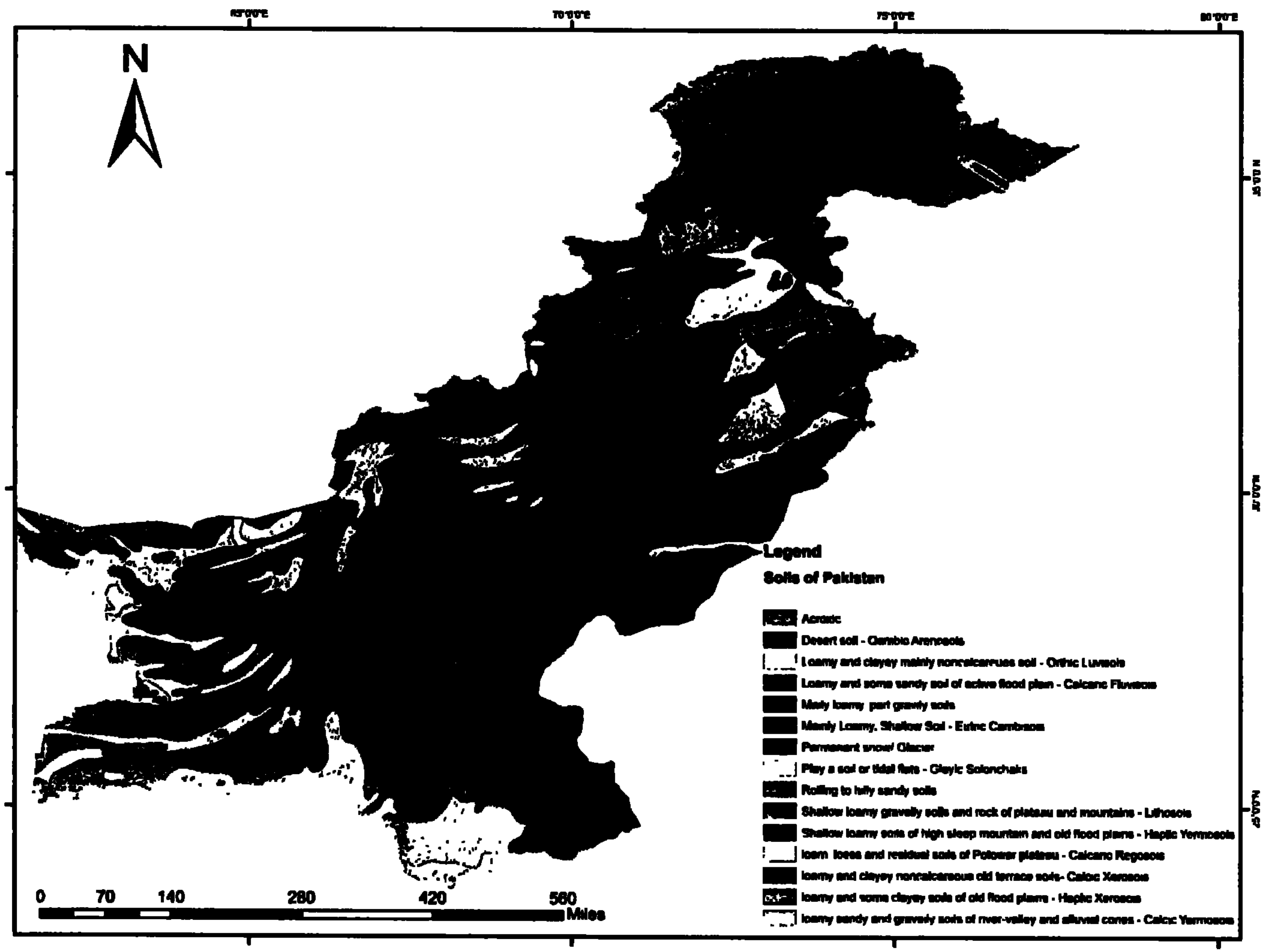

Figure: 4.18 Soil types of Pakistan digitized from topographic map published by Soil Survey of Pakistan in 1993

v. Data Acquisition

In the study area, F contamination was predicted using GIS and AHP method to find out the perspective F contamination areas throughout Pakistan. Satellite imagery of Landsat8 was downloaded from USGS (US Geological Survey) website and 90m SRTM DEM (Shuttle Radar Topography Mission Digital Elevation Model) of the study area was taken from Pakistan Meteorological Department (PMD), Islamabad. Map layers for different criteria were prepared by acquiring data from various sources as mentioned in table 4.16.

Table: 4.16 Data sources of criteria for generating map layers

Map Layer	Data Source
LULC	Land use Land cover data was obtained from Google earth pro for the Year 2017
Geological Map	Digitized from topographic map published by Geological survey of Pakistan in 1993
Rainfall data	Pakistan Meteorological Department (PMD)
Land slope	90m DEM (SRTM, USGS)
Land Aspect	90m DEM (SRTM, USGS)
Soil Types	Digitized from topographic map published by Soil Survey of Pakistan in 1993

vi. Data Analysis

Data analysis was performed in ArcGIS 10.4, Erdas Imagine 2014 and Envi 4.7 for the prediction of perspective F contamination areas while Analytical Hierarchy Procedure (AHP) comparison matrix was prepared in Microsoft Excel 2016. Following steps were performed for data analysis:

- Major criteria that influence the perspective F contamination areas selection process were selected and their thematic maps were prepared.

- Multi-Criteria Decision Analysis (MCDA) method was applied for criterion evaluation and hierarchical structure of AHP was established.
- Weighted Sum tool .was applied, and final prediction map was generated.
- Groundwater samples were collected and analyzed from all over Pakistan for ground truthing.
- Cost path analysis was done to see the potential fluoride risk zones.

vii. Major Criteria Selection and Preparation of Thematic Maps

A total of six parameters based on the environmental and geological characteristic of the study area were chosen to demarcate possible F contamination zones. Erdas Imagine 2014 carried out image analysis and supervised classification. Errors from criterion maps have been excluded. The subject layers of traditional chemical data, remote sensing (RS) and Arc GIS 10.4 have been designed for the investigation. Aquifer geology, geomorphology, soil types, slope/topography, aspect, elevation, rainfall distribution and land use land cover (LULC) were all prepared as thematic layers. The procedure followed is shown in geomorphological facts of the region acquired from GSP, 1993. The slope and elevation map of the country was created using a digital elevation model (SRTM, USGS) with a resolution of 90 meters. The land use land cover (LULC) data was obtained from Google earth pro for the year 2017. The study area soil map published by Soil Survey of Pakistan (SSoP) in 1993 was digitized to use types of soil information later in the geospatial modeling. Rainfall data for year 2017 was compiled from Pakistan Meteorological Department (PMD). Details of the thematic layers are given in table 4.16.

The methodology followed is shown in figure 4.19.

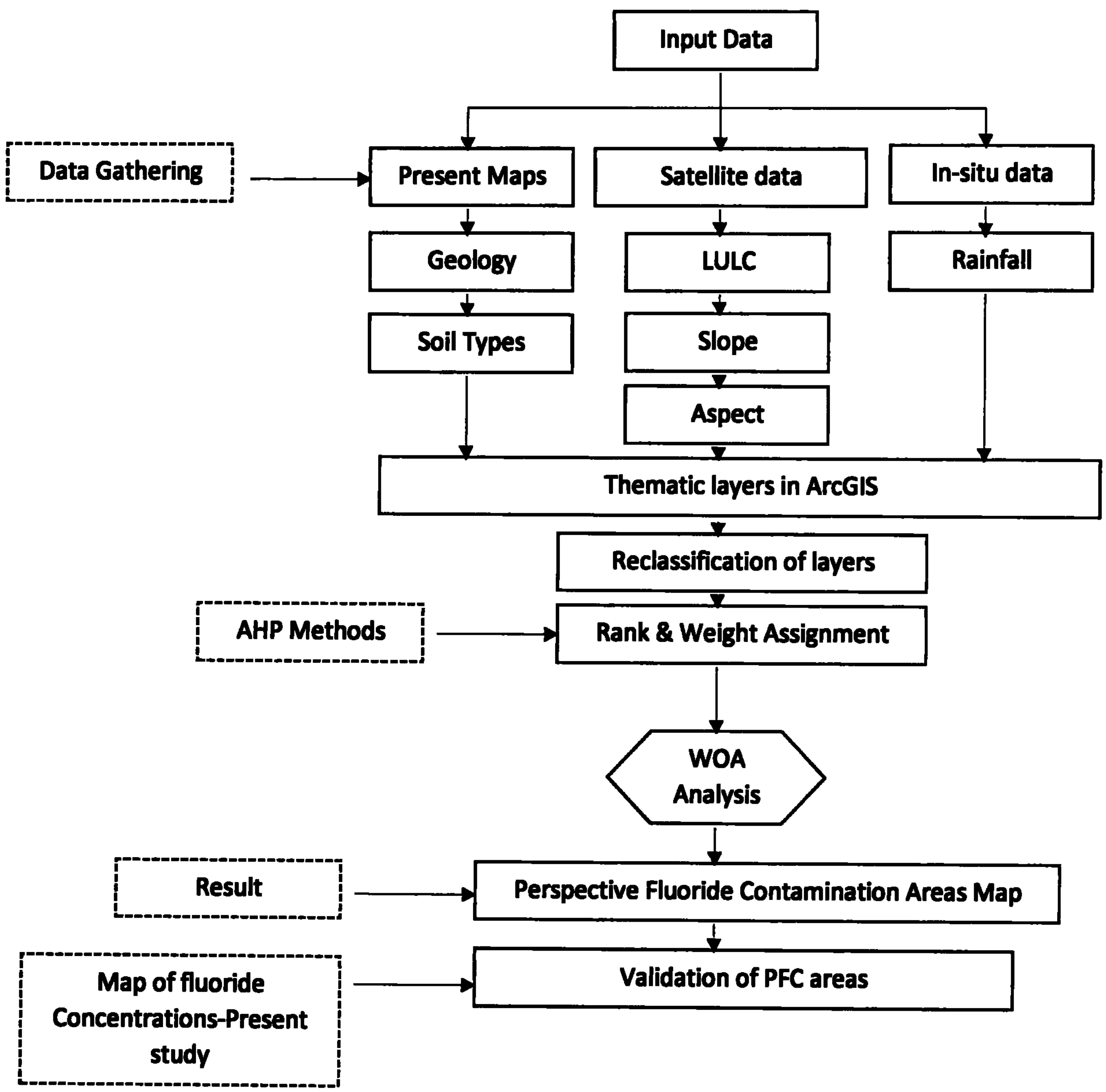

Figure: 4.19 Step-by-step procedure followed for describing PFC areas map

a. Multi Criteria Decision Analysis (MCDA)

A knowledge-driven AHP-based Multi Criteria Decision Analysis (MCDA) is a widely used parameter weight prioritization method in contaminant prognosis. MCDA is a useful method to evaluate the criteria based on priority, suitability and weights with the help of AHP (Bah and Tisko, 2011). Weights were assigned from both direct (expert's opinion of concerned departments) and indirect explication (secondary data) approaches (Kao, 2010). The detailed description of prepared thematic layers of selected criteria and their significance for potential F risk zones is given in table 4.17.

Table: 4.17 Factors and related co-variables that regulate groundwater fluoride enrichment, respective ranges of AHP and assigned weightage

Criterion Layer	Co-variables	Weightage
C1: Land Use Land Cover (LULC)	▪ Cultivated land	5
	▪ Urban areas	4
	▪ Vegetation cover	3
	▪ Water bodies	2
	▪ Bare land	1
	(Adopted from: Reddy et al., 2019)	
C2: Geology	▪ Metamorphic Rocks	5
	▪ Igneous Rocks	5
	▪ Sedimentary rocks	4
	▪ Minerals (fluorspar, rock phosphate, cryolite, apatite, mica, hornblende)	4
	(Source: Murray, 1986)	
C3: Soil	▪ Loam	5
	▪ Clay	4
	▪ Sand	3
	▪ Silt	2
	▪ Gravel	1
	(Source· Farooqi *et. al*, 2007a)	
C4: Slope	▪ 0-3%	5
	▪ 3-6%	4
	▪ 6-9%	3
	▪ >9%	2
	(Adopted from: Reddy et al., 2019)	
C5: Aspect	▪ 90	4
	▪ 270	3
	▪ 180	2
	▪ 0	1
	(Source· Karen Schuckman and John A. Dutto, 2020)	
C6: Rainfall	▪ 750 mm – 1000 mm	5
	▪ 500 mm – 750 mm	4
	▪ 250 mm – 500 mm	3
	▪ 150 mm – 250 mm	2
	▪ <150 mm	1
	(Source. Salma, S. *et al.*, 2012)	

b. Analytical Hierarchical Process Method (AHP)

The Analytical Hierarchical Process (AHP), developed by Saaty (1980), is a highly successful method for dealing with the complexities of real-world decision-making problems. AHP is a powerful method that breaks down the complexities of decision-making problems into a sequence of pair-wise comparisons and then synthesizes the results (Arulbalaji *et al.,* 2019). Furthermore, the AHP-based MCDA method is a suitable assessment methodology for evaluating the accuracy of final output; as a result, it eliminates controversy in the decision-making process. On the basis of the foregoing affirmation, the current research work uses a hybrid approach of AHP and GIS techniques to delineate the study area's F-contaminated zones. For improved F concentration in the region of study the six thematic layers were designed to be responsible. Thus, the influence factors, regarding the F, field experiments and an analysis of previous studies have been weighted based on their relation to groundwater pollution. A higher-weight layer shows a parameter with a greater impact on groundwater and vice versa.

A comparison matrix was used to establish the rankings for each criterion, and then the associated values of each criterion were allocated using proximity table. It is a scale for assessing proximity using nine levels of significance as shown in the table 4.18.

Table: 4.18 Satty's Proximity Scale for Pairwise Comparison

AHP Scale of Importance for comparison pair	**Extreme Importance**	**Very strong to extremely**	**Very strong Importance**	**Strong to very strong**	**Strong Importance**	**Moderate to strong**	**Moderate Importance**	**Equal to moderate**	**Equal Importance**
Numeric Rating	9	8	7	6	5	4	3	2	1
Reciprocal (decimal)	1/9 (0 111)	1/8(0.125)	1/7 (0.143)	1/6(0 167)	1/5 (0.200)	1/4(0.250)	1/3 (0 333)	1/2(0 500)	1 (1.000)

A comparison matrix was used to establish the rankings for each criterion, and then the associated values of each criterion were allocated using proximity table as shown in the table 4.19.

Table 4.19: Pairwise Comparison Matrix for AHP

Consistency Ratio: 0.09

criterian	LULC	Geology	Soil	Slope	Aspect	Rainfall
LULC		2	2	7	7	7
Geology	0.5		6	6	6	7
Soil	0.5	0.166666667		4	4	6
Slope	0.142857143	0.166666667	0.25		4	4
Aspect	0.142857143	0.166666667	0.25	0.25		4
Rainfall	0.142857143	0.142857143	0.166666667	0.25	0.25	
Total	2.428571429	3.642857143	9.666666667	18.5	22.25	29

The pairwise comparison matrix consists of n (n − 1)/2 comparisons for n number of factors (Saaty and Kearns 2014). The important criterias priority wise for predicting F contamination were viz., Land Use Land Cover (LULC), geology, soil, slope, aspect and rainfall. In comparison matrix, the average values of each parameter were assigned the weight.

The consistency ratio (CR) is used to calculate the consistency of pairwise comparison decisions, and the maximum value for this ratio is 0.10 (Saaty 1980) using equation (1):

$$CR = CI/RI \qquad (1)$$

where RI denotes the random index, whose value is determined by the matrix's order and CI denotes the consistency index., obtained from

$$CI = \lambda\max - n/n - 1 \qquad (2)$$

where λ represents the largest eigenvalue of the matrix and n is representing the number of thematic layers.

To analyze whether the estimated results are satisfactory or not, the consistency ratio (CR) of such comparisons was determined. In pairwise comparison, <0.1 is a reasonable level of consistency (Bah and Tisko, 2011; Abediniangerabi and Kamalirad, 2016). The Random Index (RI) standard value for the evaluation of CR with six criterion numbers is 1.24 (Saaty, 1980). The CR had been determined to be 0.09; thus, comparison using matrix yielded adequate weights, which were applied for the next stage of methodology.

c. *Weighted Sum Analysis*

Weighted sums provide the integration of their allocated weights of criterion map layers for appropriate analysis. To assess final perspective F pollution areas in the study area, all criteria layers were used as input data and overlay, along with their weights obtained via AHP in the spatial analyst method in ArcGIS.

Using the AHP methodology, a weighted overlay analysis (WOA) approach was used to identify final perspective F contamination areas when sufficient ranges and weights were successfully allocated to various input features and their corresponding subclasses using the following equation:

$$PFCA = \sum_{i=1}^{n,m}(AxBy) \qquad (3)$$

Where, 'A' represents the rank of the factor class, 'B' represents the weight of the factor sub-class, x (x = 1, 2, 3, . . . , m) represents the factor maps and y (y = 1, 2, 3, . . . , n) represents the factor class (Thapa *et al.*, 2017).

d. Ground Truthing

Ground truthing was conducted throughout the country to assess the precision and suitability of computed perspective F contamination areas. Natural and anthropogenic F sources were explicitly detected and recorded, while geology, LULC, slope, and soil characteristics were validated using suitability maps.

4.3.5. Results and Discussion:

i. Criterion Reclassified Maps

The perspective F contamination areas have been identified throughout Pakistan that are on high risk of endemic fluorosis. For present study, based on land use land cover and geology six criteria were selected including soil types, slope, aspect and rainfall. The output maps for each criterion with their suitability index were illustrated in the figures 4.20 to 4.26. The criteria, ranging from 1 to 3 (very low to medium), is showing the perspective F contamination areas throughout Pakistan.

LULC and geology was assigned highest weight for the sake of their highest contribution in F contamination, while soil types, slope, aspect, soil and rainfall were considered important as a contributing factor in F release. Weights were assigned to all criteria as described in table 4.20.

Table: 4.20 Criterion Weights

Criterion Layer	LULC	Geology	Soil	Slope	Aspect	Rainfall	Total
Weights	0.350	0.322	0.159	0.083	0.054	0.029	1

ii. Land Use Land Cover (LULC):

The overall forest cover in the country is around 5% of mangroves, riverain, and plantations. Irrigated, rain fed, and rod kohi agriculture land reflectance from spectral features are around 20% It does not use the fallow land which has been ploughed under (covering about 10 percent area of country). Rangelands cover 27% area, while another quarter of the country formed by rock outcrops. The coverage of snow/glacier was estimated at approximately 2%. The region of deserts is about 10%. Other uses include (water bodies together accounted for a little more than 1%, waterlogged and saline land and built up area,).

The reclassified LULC map of Pakistan (figure: 4.20) is showing the suitability of cultivated lands and settlements as highly contributing in the F contamination. Coal combustion, phosphate fertilizers, and waste generation from different industries such as aluminum, stainless steel, manufacture of glass, brick and tiles as well as the copper and nickel melting are potential sources of high-F concentrations. Phosphate fertilizer comprising F (52–25 ppm) that is leachable and coal containing F (5–20 ppm) are the key sources. (Rahaman *et al.*, 2011; Farooqi *et al.*, 2007a; Farooqi *et al.*, 2007b; Siddique *et al.*, 2006).

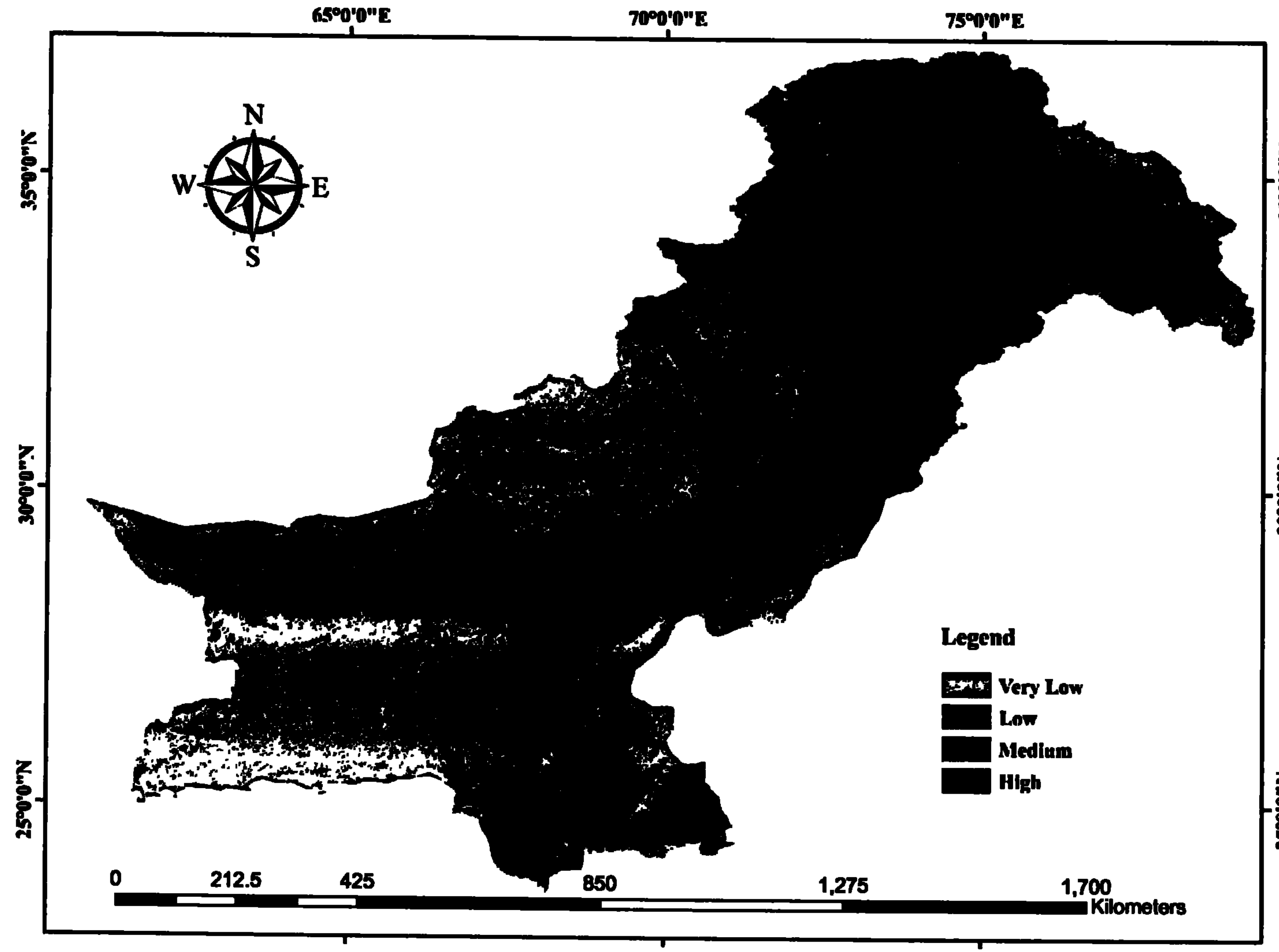

Figure: 4.20 Study area reclassified map for LULC

Researchers showed higher than previously recorded concentrations of F in different Pakistani cities. Some areas have been identified as being the most seriously affected are Multan, Sindh, and Lahore. In addition to other natural sources, the coal burning industry may also be a cause of high levels of F (Rasool *et al.*, 2015; Khattak *et al.*, 2012; Malana and Khosa, 2011; Ullah *et al.*, 2009; Farooqi *et al.*, 2007a; PCRWR, 2005).

However, LULC reclassified map is showing vegetation cover as the medium source of F contribution in groundwater followed by the water bodies as low and bare land as very low. The rate of infiltration, the availability, and the quality of groundwater are all affected by land cover, land usage, and changes in land use patterns (Lerner and Harris, 2009).

iii. Hydrogeological and other governing factors

The reclassified thematic map showing the geology of Pakistan illustrate that the Indus basin and its tributaries are showing the suitability for very high F concentrations (figure 4.21).

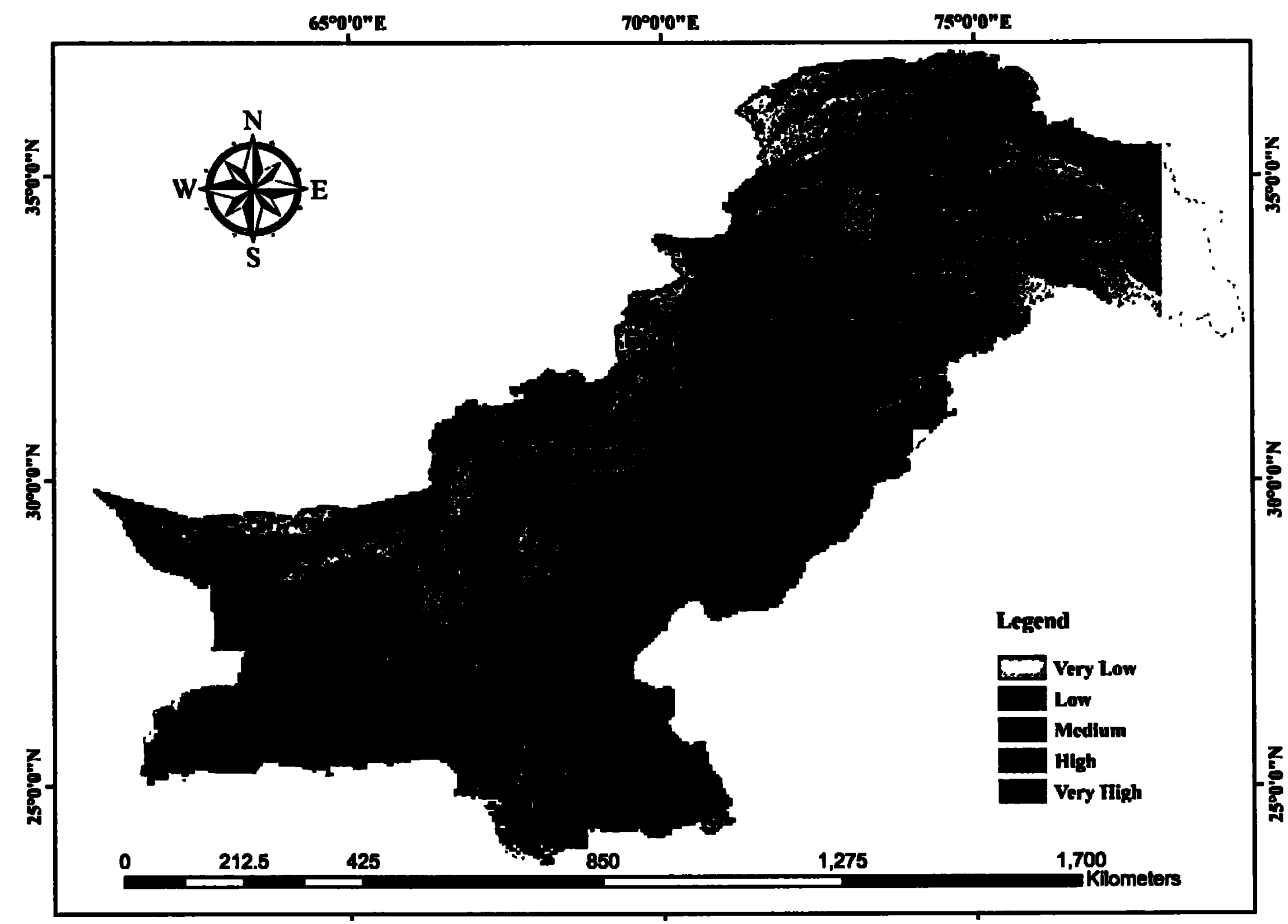

Figure: 4.21 Study area reclassified map for geology

The reason for which is the geological and mineral resources of the country as well as the anthropogenic sources of pollution. From late Cretaceous to Holocene formations, the Indus basin lithology contains sandstone, limestone, shale and granite (Khan and Liu, 2019). The uppermost Indus basin consists of the Precambrian, Cambrian, Triassic, Jurassic and Cretaceous rock creations in southern part. However, in the northern part, the volcanic rocks, bauxite, chamosite and laterite of latest Cretaceous to late Paleocene age are found. Fine clastic Chorgali Formation and Kuldana Formation red and varicolored mudstone, sandstone, and dolomitic limestone make up the Eocene Kuldana Group. The Miocene–Pliocene Murree Formation is made up of fine to coarse clastic rocks that indicate a hard collision between Indo-Pak and Asia. The Pleistocene Lei Formation has mostly conglomerate and coarse clastic facies, while the Holocene Soan Formation has sandstone, clay, comparatively fine clastic facies and subordinate conglomerate. Alluvium, colluvium, eolian, lacustrine, and evaporite deposits represent ancient and recent surface sediments (Malkani, 2016).

The geological settings such as rocks and minerals are showing the high to medium suitability of having the F concentrations followed by low to very low in some northern areas, KP and Balochistan basin. The study of Srivastava and Lohani in 2015 identified over 150 F-rich minerals. Of these reserves they identified silicate, halide and phosphate as a most prominent group. The key F-bearing minerals include sellaite, ($CaF2$), fluorapatite, villanaumite, cryolite and topaz. Furthermore, certain minerals like amphiboles and mica may also do this. Some clay minerals like ilite, chlorite and smectite, which are the strongest media of anion exchange, replace F ions by hydroxylate groups due to similar alkaline ionic radii (Edmunds and Smedley, 2013; Ayoob and Gupta 2006). Rock and water combine to cause minerals to disintegrate, resulting in the accumulation of high F in groundwater.

iv. Slope and aspect:

The plain areas have more F concentrations, while the mountainous regions have less. This is because in plain areas groundwater has a longer contact period with the aquifer materials allow more time to bind with water. The time required to retain the F is proportional to the aquifer's concentration and the materials that interact with it (Mamatha and Rao, 2010; Czarnowski *et al.*, 1996; Dissanayake, 1991) (figure 4.22 & 4.23).

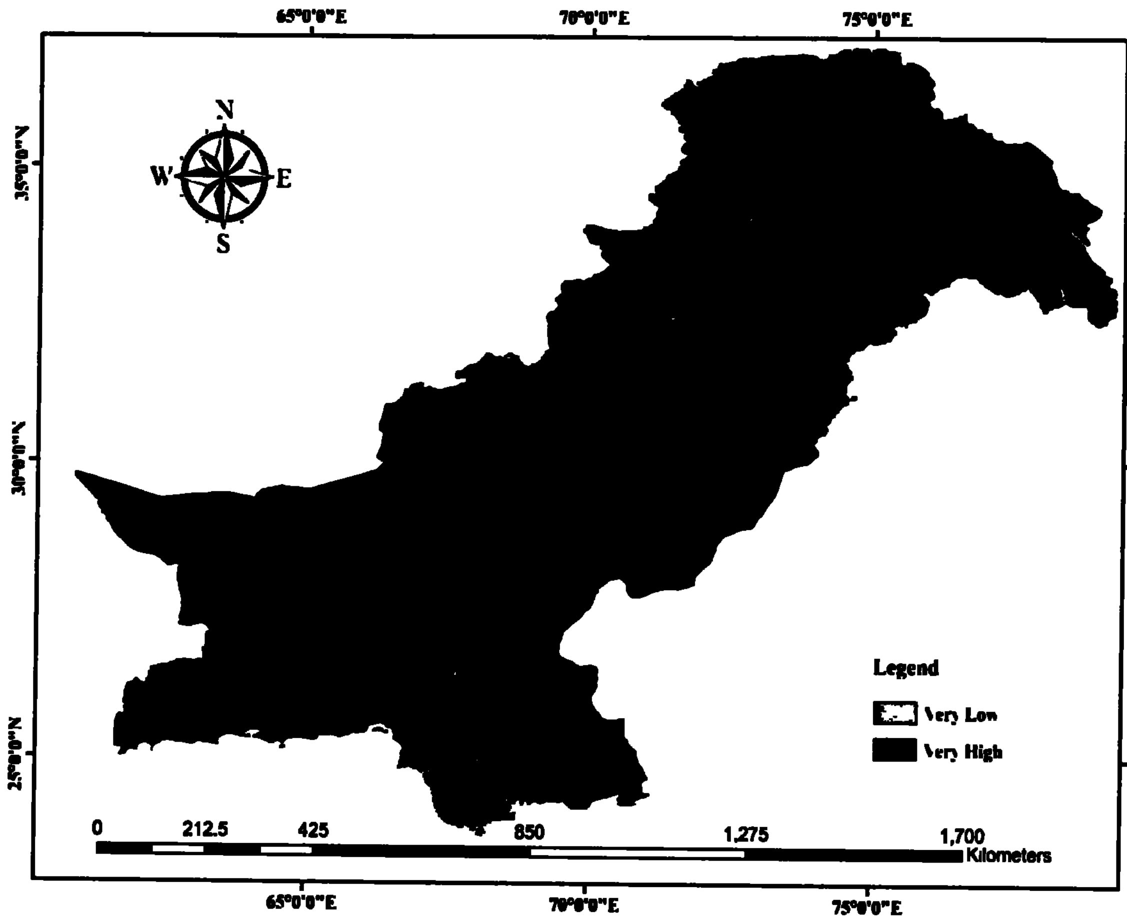

Figure: 4.22 Study area reclassified map for slope

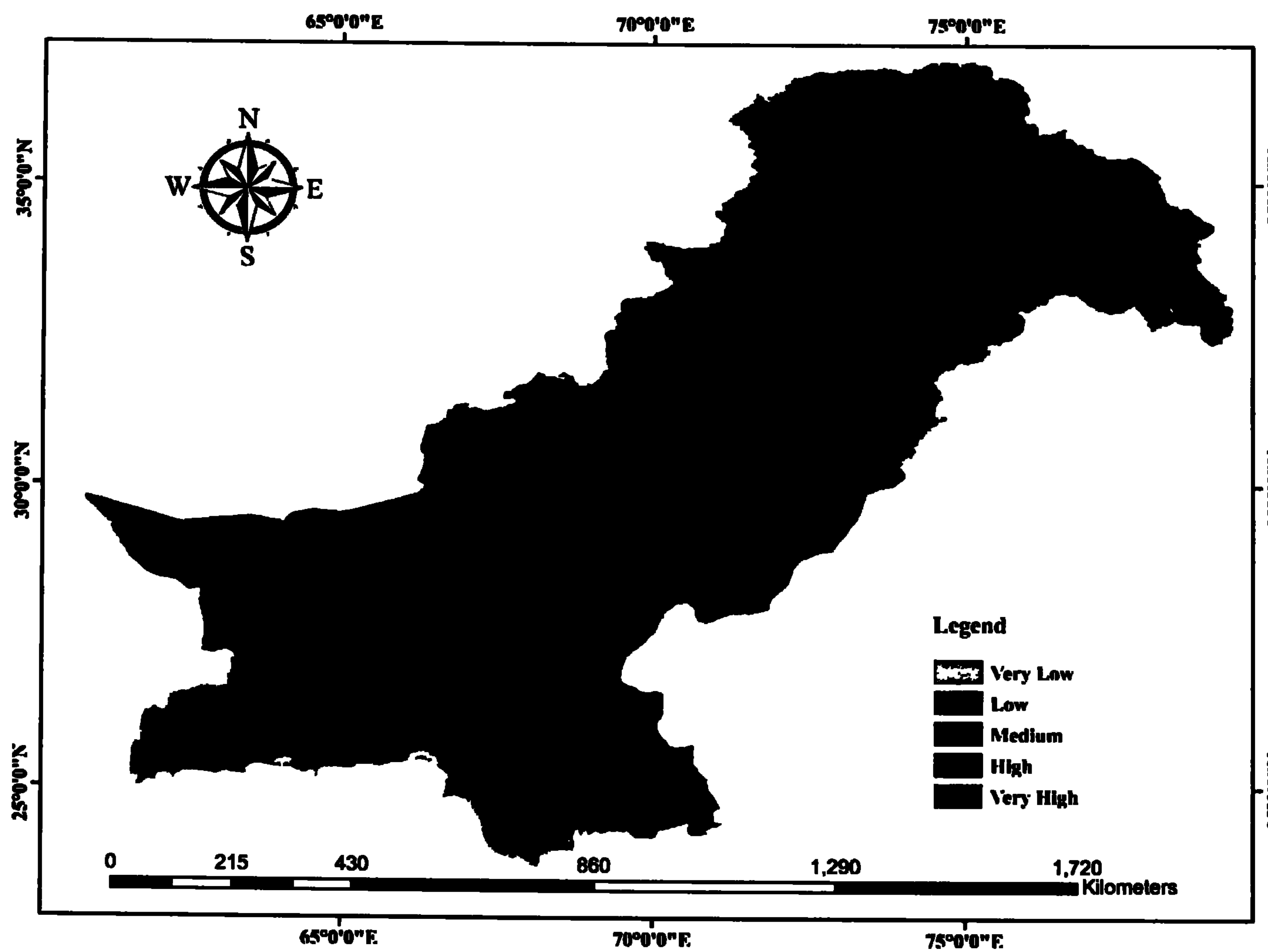

Figure: 4.23 Study area reclassified map for aspect

v. Rainfall:

In order to increase the levels of F in groundwater, there are several factors at work. These variables include temperature, pH, ionic colloids, anion exchange ability (OH for F), rock solubility, and whether or colloidal precipitates are present (Bibi *et al.,* 2017). In areas that are arid and semi-arid, the concentration of F is dependent on the climate. A long and intermittent low average rainfall i.e. 225–400 mm per year and a high evaporation rate (>2,000 mm per year) result in arid and semiarid regions that have limited water-conductivity (Su *et al.,* 2013).

Arid regions rely on low rainfall to allow elevated F levels in groundwater. High evaporation tends to cause lower solubility (CO_3) of Ca2 in groundwater, making Ca-fluorite more accessible (Vithanage and Bhattacharya 2015). The release of ions such as HCO_3 and Na^+ increases the acidity, which in turn causes the minerals in groundwater to dissolve. F levels decreases with aluminum and Fe, and increases on mineral clays (illite, chlorite, and smectite below pH 6.5, while increasing with Fe. If the pH is greater than 7, anion exchange takes place where F^- can be replaced by OH^- ions from muscovite and biotite minerals (Li et. al. 2014).

The figure 4.24 below shows that those areas in Pakistan which are having the medium to low and very low rainfall are more susceptible to F contamination.

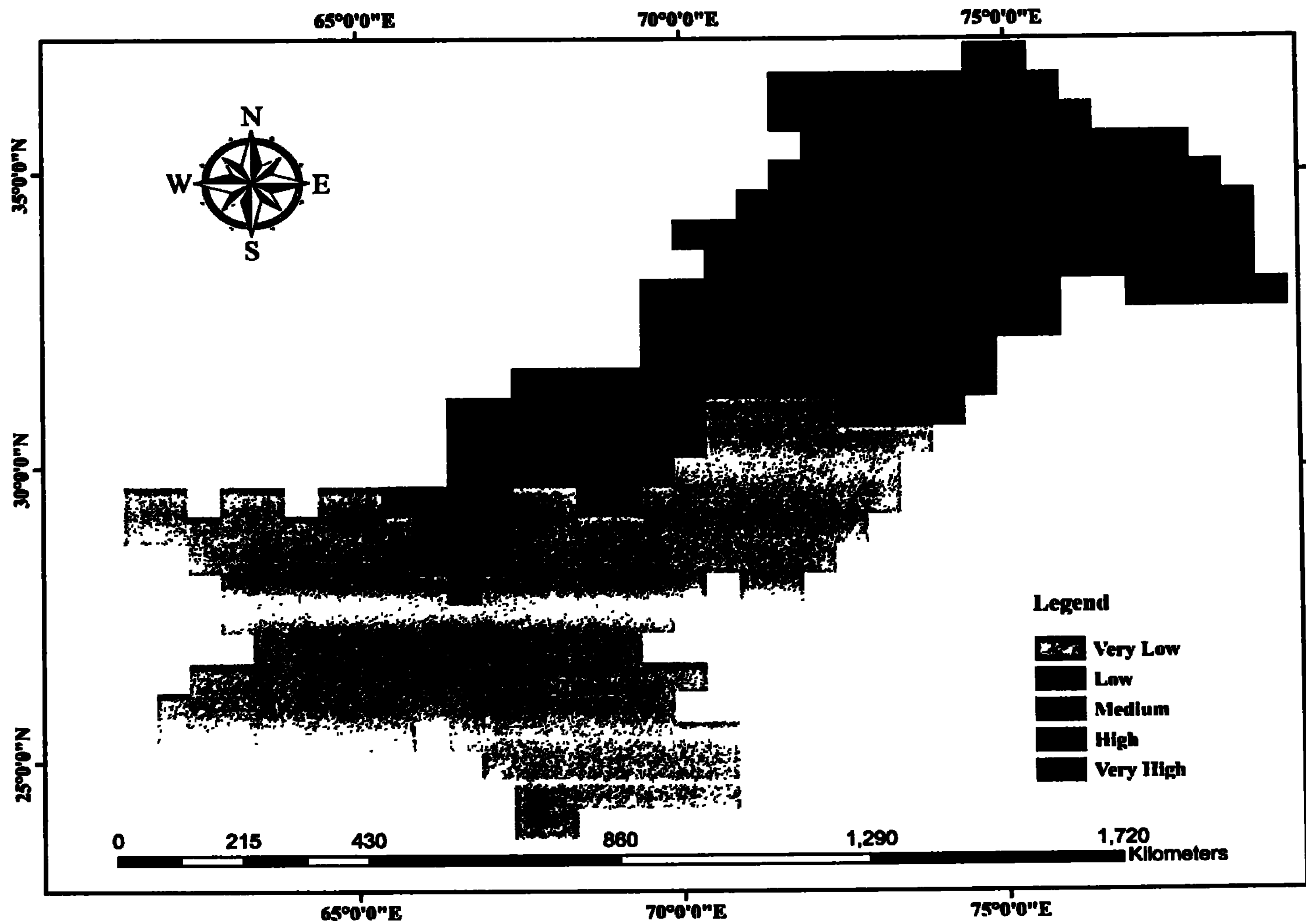

Figure: 4.24 Study area reclassified map for rainfall

vi. Soil and hydrogeochemical aspects:

The anion-exchange is usually seen in clay or granite minerals where the hydroxide (OH^-) substitutes for fluorine ions (F^-). Since the F ions have a similar size to the substituent ions, it is easy to substitute the F ions during fractional crystallization. Under these circumstances, the pH favors the deposition of F ions in groundwater. Anion exchange takes place in minerals such as biotite and muscovite in alkaline conditions (pH > 7). F causes the substitution of Ca^{2+} for Na^+ to increase solubility, which increases the solubility of CaF. Ca^{2+} depletion results in a shift in the groundwater composition from a low concentration of hard Na^+ to soft Na^+ rich water, which favors F leaching. More acidic water increases the dissolution of CaF^{2-} and Ca^{2+} fluoridated minerals. A rise in EC, TDS, and redox potential can lead to an increase in the pH (Singh *et al.*, 2015; Li *et al.*, 2014; Farooqi et al, 2007a; Saxena and Ahmed, 2001). Figure 4.25 below represents the reclassified map for the soils of the study area.

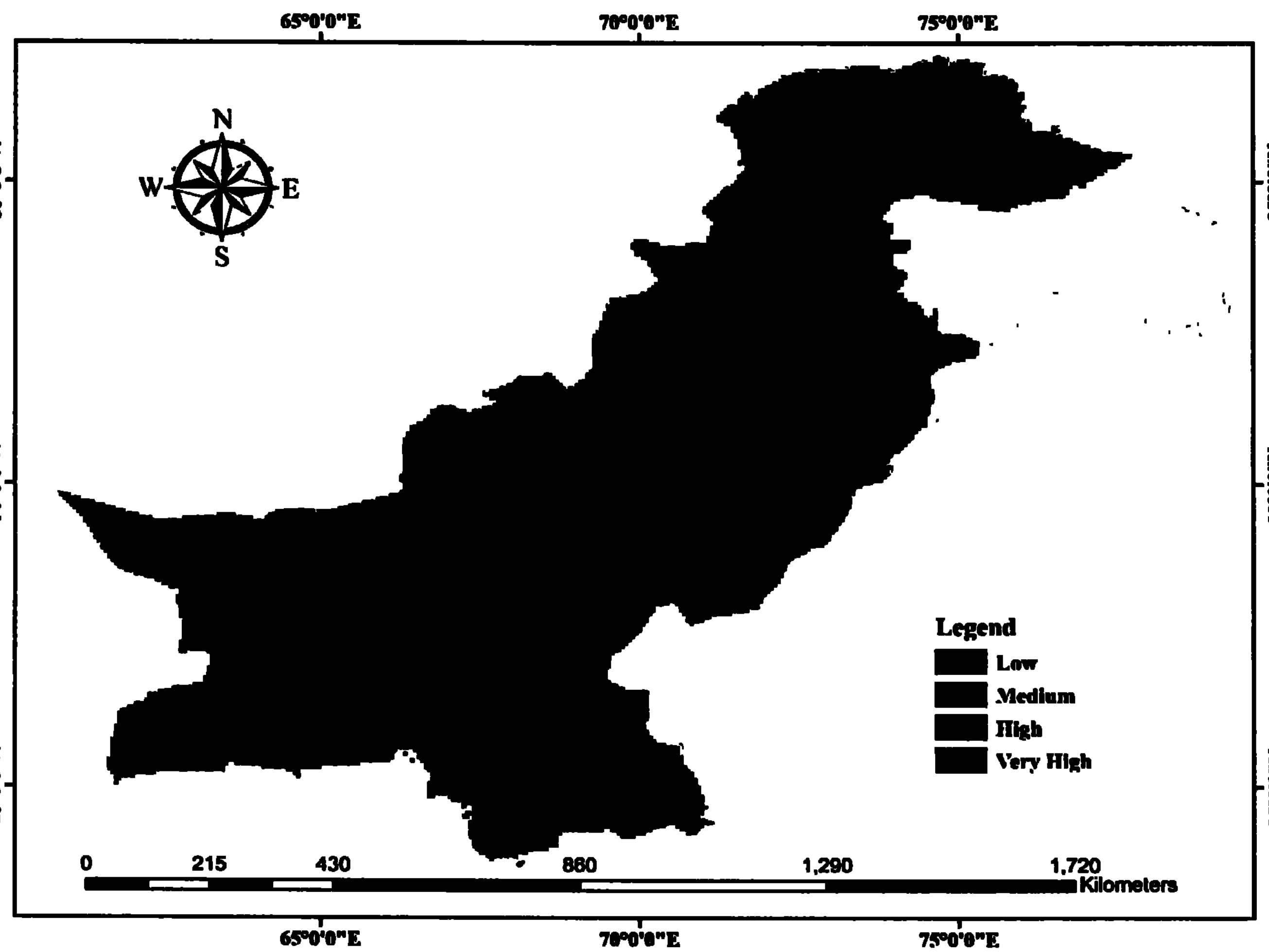

Figure: 4.25 Study area reclassified map for soil

vii. Perspective Fluoride Contamination (PFC) zones map:

A weighted overlay analysis method, combined with GIS techniques, was used to produce the final PFC areas map. Figure 4.26 illustrates the perspective F contamination zones throughout Pakistan. To show which zones are affected by wide spread fluorosis, the final PFC areas map is broken down into three categories from 'medium' to 'low' and 'very low'. Most of the areas in KP and the Indus river plain (Punjab & Sindh) is showing the medium F tendency which can become high in future whereas some part of KP in north and the Balochistan province is showing the both medium F tendency in some areas as well as low. In the PFC expanse, the category 'medium' accounts for 36.39% (or 346762.38 Km^2) followed by 'low' 63.42% (or 604324.78 Km^2) and 'very low' 0.195% (or 1856.68). The area with a very low tendency of F is considered safe for drinking water use. While utilizing groundwater for drinking and cooking, water usage must be cautious in regions where it is in the medium category.

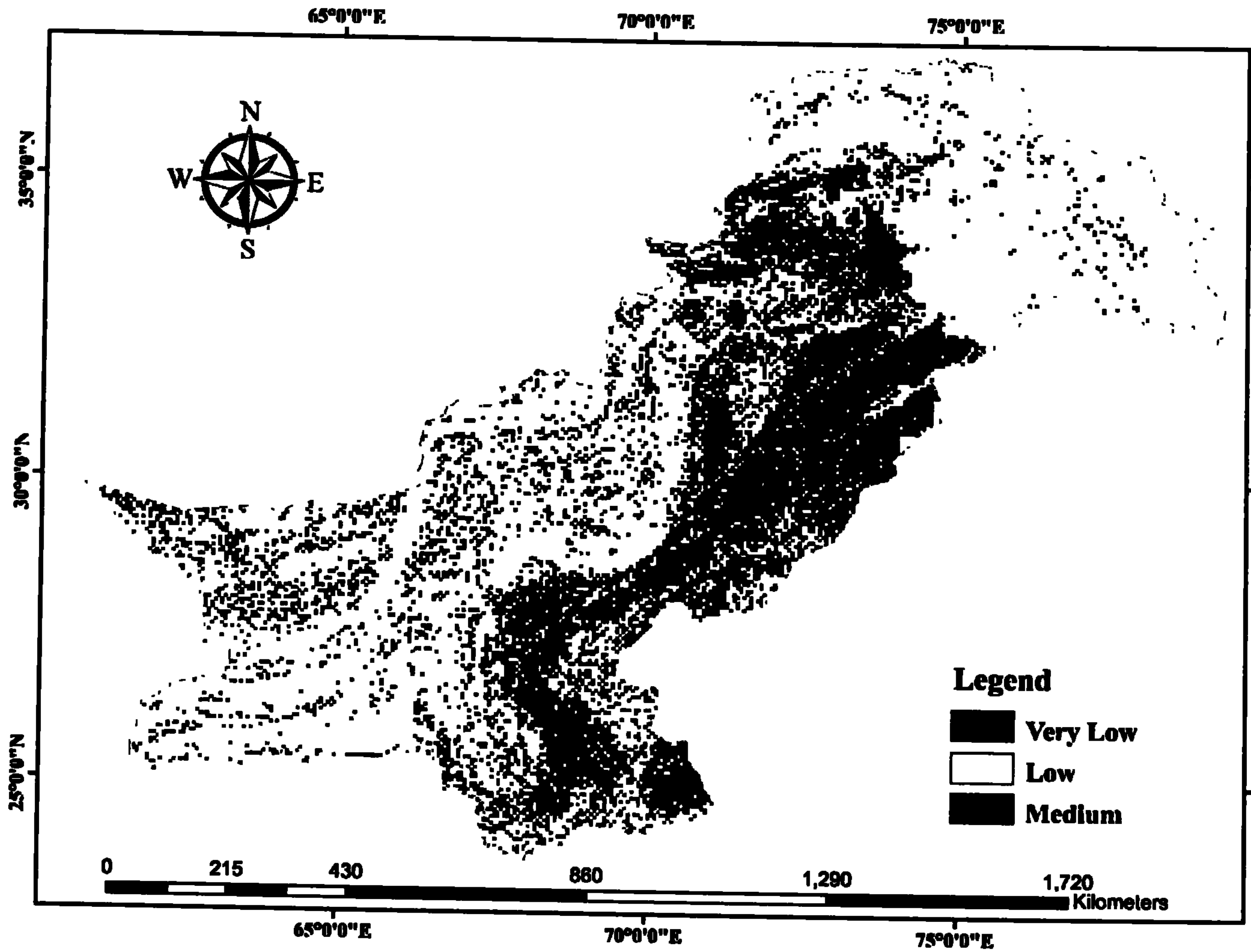

Figure: 4.26 Perspective Fluoride Contamination (PFC) areas map of study area

viii. Validation of model

It is imperative that the map of PFC areas be validated for accuracy; the only way to ensure this is to validate the map classes and classes identified in the field. To achieve this, the point map of F was compared, based on the groundwater data collected and analyzed in the present study and the F predictive model of AHP. The model showed the tendency of F in areas as moderate to low and very low the same way as the map showing the sampled and analyzed groundwater data. This model was able to perform well and has been proven to be accurate in predicting the concentrations of F in groundwater.

This preeminent level of F is marked by a low Ca^{2+} and Mg^{2+} concentrations and a high Na^{+} concentration in groundwater. Ca ions precipitate in acidic solution and alkaline solutions, respectively. Nevertheless, at an alkaline pH, F is soluble. Two most widely cited reasons for increased F levels in groundwater are dissolution of F-bearing minerals and ion exchange. The key mechanism of increased water accumulation in arid and semiarid areas is the release of mechanisms from soil due to evaporation and transpiration (Farooqi *et al.*, 2007b; Jacks *et al.*, 2005; Saxena and Ahmed, 2001; Sarma and Rao, 1997; Agrawal *et al.*, 1997).

Researchers from various countries suspect that the high density of lineaments or fractures in the groundwater could be linked to the problem of F in the water. Mechanisms such as oxidation-reduction help to clarify fluorinated minerals. Natural and anthropogenic causes contribute to elevated F levels, including leaching of bricks in water and ash from brick making, agricultural fertilizer and coal combustion in air from the rain into the soil. The potential causes for increased F levels in groundwater are fertilizers, minerals from mining facilities, and erosion from agriculture (Rasool *et al.*, 2015; Naseem *et al.*, 2010).

4.3.6. Conclusion

The use of remotely sensed data in conjunction with GIS-based AHP and overlay techniques demonstrates to be an effective combination for defining PFC areas in Pakistan. This study was carried out in order to gain a better understanding of the extent of F contamination in Pakistan, which is essential for the planning and implementation of municipal water supply programs. Fluorosis of the teeth and skeletal structure is irreversible, and the only solution is to prevent it. In-situ defluoridation is the most appropriate step in providing safe drinking water because it could be used either by supplying fresh water or by using municipal water. Reducing the risk of fluorosis also means improving the nutritional level of the population. At first, the locally designed F mitigation techniques should be used. The most important mitigation strategies are the exploitation of deep wells water, the use of river water, the construction of reservoirs, and the defluoridation of water supplies, with the exploitation of deep wells water being one of the most significant mitigation strategies (Li et al., 2001).

This study is the first study tried to compile an entire country's contamination zones, providing a national scale perspective. The map of PFC areas will serve as the foundation for identifying the locations where artificial recharge can be used to dilute F in groundwater in highly contaminated areas. The result map provides researchers, administrators, and planners with a firsthand look at the severity of F contamination in Pakistan. It is essential to supply safe drinking water in an expedient manner within the framework of national water supply programs.

4.3.7. Recommendations

Fluoride toxicity has affected millions of people all over the world, but the fact that this remains a public health problem is not widely recognized. To get to the bottom of it, researchers should conduct a more in-depth investigation to understand where, how, and why F occurs, and how widespread its distribution is. Since industrial and agricultural activities contaminate drinking water with F, the government should keep a close eye on these activities. Financial, logistical, and administrative support is required for F reduction. The Pakistani government should locate alternate water sources for people in these regions who are concerned about F exposure. This study will help inform and inspire new measures to mitigate and reduce F in groundwater and surface water at both the regional and national levels as well as better inform, classify and mobilize F in groundwater and surface water.

CHAPTER-5

HEALTH RISK ASSESSMENT

5.1 Introduction

Water is essential to all forms of life on the planet and plays a critical role in shaping the land and for climate regulation. We are aware that fresh water is absolutely essential to life and to health. Some nations assert that having access to potable water is considered a basic human necessity. The Sustainable Development Goals (SDGs) is ensuring that all people have equitable access to a sufficient and sustainable supply of clean water (Dinka, 2018).

Water is associated to daily activities of human directly or indirectly. At primary level, every person requires availability of safe/fresh water for (cooking, drinking, sanitation, personal hygiene) and also for agriculture activities, recreation purposes, and for industrial purposes without compromising human health (WWF, 1998)

Having a fact that water is an essential for the life, no living being can survive without it on the whole planet, Earth. Unfortunately, a major part of the water on Earth cannot be used by humans which are marine water. Therefore, the only fresh water available that can be used for the drinking purposes is the one which comes from the groundwater (NGWA and USGS, 1984). However, the percent volume of it is enough to satisfy the need of living beings, provided that it must have been of good quality. Water quality is important in our lives not because for the drinking purposes, but it is also vital for the sustenance of functional activities of any biological cell in the world, therefore safe water is significant for human health in all over the world (UN, 1992).

Water is a universal solvent, and its widespread use makes it a significant source of infection for living beings (human beings), and unfortunately, with industrialization and development, the world's freshwater resources are under threat. Estimates indicate that about 1/6th of the world's population is at risk of water contamination and thus bears the brunt of chemical discharges into water and agricultural sources in developing and developed countries. Enormous amounts of contaminants pollute the water and cause infections, and both people and the environment suffer. According to the WHO, 80% of all illnesses are caused by poor hygiene and sanitation. There are many countries where WHO considers the water is unsafe to drink. Roughly 3.1% of deaths are due to contaminated water. The water has pollutants like heavy metals and biological impurities (Elimelech, 2006; Shannon *et al.*, 2008).

The life and level of natural pollutant depend on the type of the geological materials via the groundwater run. The possibility of natural or secondary contaminations by various substances, such as magnesium, fluoride, nitrate, iron and arsenate, is considered in sedimentary rock and soil. Naturally occurring compounds that exceed the limit can also pollute water (Liu et al.2005; Charles et al. 2005; Rukah and Alsokhny 2004; Mulligan et al. 2001; Ghrefat et al. 2014; Meenakshi and Maheshwari 2006).

Groundwater quality depends on the type of geological materials it runs through. Secondary minerals such as Mg^{+2}, F^-, NO^{3-}, Fe, and As are considered when it comes to sedimentary rock and soil. Naturally occurring pollutants that surpass the threshold also make the water unhealthy (Ghrefat *et al.*, 2014). Whereas, in comparison, anthropogenic (human-manufactured) waste includes toxic compounds such as Hg, Co, and Pb, as byproducts such as fertilizers from cultivated lands and dyes. Detergents, paint, polish, oils, medicines and diesel can result in the contamination of underground water (Kass *et al.*, 2005; Anwar 2003).

5.1.1 Sources of Water Contamination

Generally, there are three main sources linked with water contamination.

- Inorganic pollutants
- Organic pollutants
- Biological pollutants

i. Inorganic pollutants

The occurrence of pollutants can be measured by its chemical parameters. Drinking water hardness, which primarily depends on the geographic status, is a natural phenomenon of contaminants. The reason for this is that there is a significant amount of calcium or magnesium in the composition. When they are combined with carbonate ions (CO_3^{-2}), they are referred to as 'carbonate hardness' and when they are combined with other ions, they are referred to as 'non-carbonate hardness'. In addition to carbonated / noncarbonated hardness, there are several substances like F, As, Cu, Cr etc. that contaminate potable water (USEPA, 2006). The weathering of F-bearing mineral deposits in the earth's crust can result in an increase in F concentrations in groundwater. Excessive use of ground water also degrades the F level in water. Additionally, many other products like pharmaceutics, toothpastes, insecticides, disinfectants, and vitamin supplements all contain Fs. Its detrimental effects are most noticeable in children and the elderly.

Excess of F causes dental and skeletal fluorosis, Alzheimer's disease and forms of dementia. In India, acute fluorosis problems are experienced due to elevated F levels (Eswar and Devaraj 2011; WHO, 2008).

Arsenic contamination is a global problem, particularly in India and Bangladesh (Khan *et al.,* 2003). The disease called arsenicosis is associated with As in drinking water (Chen *et al.,* 1988). Additionally, As contamination can result in a variety of other diseases, such as abdominal pain, nausea, vision loss, puking, tingling in the hands and feet, hyperpigmentation, severe arthritis, and diahorrea. As has been linked to the bladder, skin, kidney, and liver cancers. The As compounds' degradation and excretion is strongly proportional to its oxidation (arsenite As III and arsenate As V). Arsenite is ten times more toxic than arsenate, according to reports Heavy chromium concentrations also may harm the liver and the kidney, as well as cause skin and respiratory issues. Urban water contamination due to lead is a growing issue (USEPA, 2006). Water gradually oxidizes lead in urban water systems, affecting children's growth and adults' high blood pressure and kidney disease (Pontius *et al.*, 1994; Needleman *et al.*, 1990).

ii. Organic pollutants

Pesticides and industrial waste are present in our water which cause many forms of cancer, and hormonal issues and nervous system disorders (Ram *et al.*, 1990). Deplorably, all pesticides have the potential to interfere with the metabolism of untargeted living organisms. Pesticides generally cause damage to the liver and nervous system, as well as liver tumors (Damalas and Eleftherohorinos, 2011). Volatile organic chemicals (VOCs) have a detrimental effect on human health, causing cancer, disorders of the central nervous system, liver dysfunction, hormonal imbalances, and congenital abnormalities (Wehrmann *et al.*, 1996).

Highly toxic organic dyes are the major environmental concern Oxidants, hydrolysis, and chemicals in wastewater are believed to be the major sources of non-appealing eutrophication contaminants (Prevot *et al.*, 2001).

Many water contaminants have the ability to have a detrimental impact on human and/ecological health, for example: These emerging organic contaminants, such as pharmaceuticals, industrial, personal care, fragrant, flame retardants, and surfactants, and plasticizers, are referred to as Emerging Organic Contaminants. There are many of these chemicals which are known to be both carcinogenic and endocrine disrupters (Pal *et al.*, 2014; Lapworth *et al.*, 2012). Effluents from commercial. municipal, industrial, and healthcare sources are the major sources of these compounds (Pal *et al.*,2014).

iii. Biological pollutants

Protozoans, bacteria, and viruses are common waterborne contaminants. Every organism has its own effects on water quality and causes serious problems. the presence of algae causes changes not only the water quality, but also increased slime and blockage. As well, blue-green algae are able to secrete toxins, the nervous system, and the skin (neurotoxins) all cause significant damage (Ashbolt, 2004). Bacteria are a single-celled and many pathogenic organisms can live in water (Inamori and Fujimoto, 2009). In each instance, they relate to various ailments, such as typhoid, dysentery, and gastroenteritis. Some bacteria exist in water of which we are unaware. They simply change the odor and quality of water and are of no consequence to humans (Nwachcuku and Gerba, 2004). Also, some Protozoa can be found in rivers, streams or wastewater containing water bodies, such as animal faeces, cause similar health issues, namely diarrhea, fatigue, nausea, and stomach cramps.

Infection and disease-causing viruses are the smallest living organisms. Pakistan is also experiencing public health problems as a result of As contamination in the country's drinking water supply. High As concentrations have been reported in various parts of Pakistan viz., Tharparkar (up to 2580 g/L) (Brahman *et al.,* 2013), Jamshoro (up to 106 g/L) (Baig *et al.,* 2009) in Sindh province, Chichawatni, Bahawalpur, and Multan (up to 201 g/L) (Shakoor *et al.,* 2015), and Muzaffargarh (up to 906 µg/L) (Nickson *et al.,* 2005) in Punjab Province. To determine the risk of As to human health associated with the consumption of As-contaminated water is critical.

Most of the people in Pakistan have daily exposure to polluted and unsafe water. It is generally believed that pollution from industrial, municipal, and agricultural sources has worsened the water quality in Pakistan. Groundwater quality has also been affected by geological settings from time to time, high F contents 5 to 29 mg/L of F were found in drinking water in Kasur and Mianwali districts (Aziz, 2001).

The groundwater in several districts was found contaminated with F viz. Chakwal, Mianwali, Jhelum, Risalpur, Bahawalpur, Faisalabad, Khushab, Mirpur Khas, Mastung, Ziarat, Loralai, Sargodha, Karachi, Kharan, Raiwind, Tharparkar, Mastung Valley, Makran Coast and Umar Kot (Khan, 1999). Marshall-Day and Tandan hypothesized that elevated F levels in drinking water could be the result of weathering of F-enriched rocks. These rocks form a narrow belt that runs through Punjab, passing through cities such as Shahpur, Kasur, the eastern part of Mianwali, Sargodha and Sangla Hill.

Kasur, Pattoki, and Raiwind show noticeable signs of dental fluorosis. It has been found that more than 100 people in Lahore, Pakistan have limb deformities because of the groundwater containing F, which can be linked to Manga Mandi region. Some areas of northern Pakistan have high F levels in their water supply, which can be dangerous to human health. This has resulted in a significant problem with tooth discoloration. Some cases of dental fluorosis have been noted in Pakistan due to F in groundwater.

5.2 LITERATURE REVIEW

5.2.1 Status of Arsenic around the Globe

Arsenic is an environmental toxicant and abundantly found in drinking water and ground water, extensively ranges from less than 0.5 to 5000 ppb covering natural As contamination present in more than 70 countries across the globe (Table 5.1).

However, As exposure via drinking water and ground water is international concern, and unfortunately in South East Asian countries ground water is the only main source of drinking water, due to which these countries are highly affected (Polya, D.A. *et al.*, 2008). Predictably around 40-60 million people in South East Asia are at severe danger due to large level of (anthropogenic and natural) As present in groundwater of these areas (McCarty *et al.*, 2011).

Table 5.1: Status of arsenic contamination in natural groundwater in various Countries

S.no	Country	Study Areas	Mean Arsenic Concentration(µg/L)	Permissible Limit (WHO)	References
1	Mexico	Durango	8.72	10 µg/L.	Frechero, N.M. et al. 2020
2	Cambodia	Kandal	100	10 µg/L.	Buschmann, J. et al. 2018
3	Denmark	Copenhagen, Aarhus	50	10 µg/L.	Ersboll, A.K. et al. 2018
4	India	Shuklaganj	139.5	50 µg/L.	Vishnoi,N. et al.2018
5	Nigeria	Nigeria	809	10 µg/L	Izah, S.C. et al. 2015
6	Myanmar	Seven villages in the lower Ayeyarwady basin, Myanmar	200	10 µg/L.	Alexander, et al.2014
7	Vietnam	Chuyen Ngoai Commune, located at the east of Duy Tien District, Hanam Province	293.5	10 µg/L	Johnsto, R. et al.2014
8	Chile	Antofagasta	540	10 µg/L.	Mario, I. et al. 2011
9	Bangladesh	Noakhali	2736	50 µg/L.	Chakraborti, D. et al.2010
10	China	China	2270	50 µg/L.	Rahman,M.M.et al.2009
11	Japan	Fukuoka Prefecture (southern region)	147	10 µg/L.	Mukherjee, A. et al.2006
12	USA	Tulare Lake	2600	10 µg/L.	Twarakav,N.K.C et la .2006
13	Greece	Eastern part of the Larisa town	125	10 µg/L.	Kelepertsis, A. et al. 2006
14	Australia	Rural areas of Australia	43.8	10 µg/L.	Andrea, L. et al.2002
15	Taiwan	Southwest coast of Taiwan	350	10 µg/L.	Chen, et al. 1992

Occurrence of higher concentration of As in drinking water has influenced millions of people in Philippines, New Zealand, China, Hungary, India, Inner Mongolia, Mexico, Romania, Slovakia, Ghana, Taiwan, Nepal, Argentina Vietnam, Bangladesh, Cambodia and Chile. Water pollution in Bangladesh and West Bengal (India) is the world's largest As exposure hazard, also groundwater may present a threat to the millions of people in Cambodia and Vietnam (Anawar *et al.*, 2002; Chakraborti *et al.*, 2001 Chowdhury *et al.*, 2000).

Recently largest As concentration, that is <1–4730 μg/L and 50–4440 μg/L respectively, reported in Bangladesh and China. Studies revealed that water is contaminated with As (100 μg/L) in Kandal province of Cambodia (Buschmann, *et al.*, 2018). Alexander *et al.*, 2014 conducted a study and confirm that well water in Myanmar is contaminated with As up to 10-380 μg/L and posing a severe threat to human health (Chakraborti *et al.*, 2010; Rahman *et al.*, 2009). Likewise, up to 2600 μg/L As concentration is also found in the Tulare Lake in USA (Twarakav *et al.*, 2006).

At present a study shows that, larger concentration of As in sea food, soil, rice and vegetables and many of scientists agreed that accessibility of As in soil more than 1.5mg kg-1 can inhibit plant growth (Khanam *et al.*, 2020). Jayasumana *et al.*, 2013) conducted a study, in which they examine human urine samples in Rajarata (Sirilanka), results showed that urine contained >21 μg/L As. Similarly, Sea food being sold in markets of Saudi Arabia contains 0.11 to 0.61 μg/g As (Waqar *et al.*, 2019).

5.2.2 Overview of Arsenic Contamination in Pakistan

According to PCRWR and UNICEF, accounted levels of As are more than100 μg/L in the groundwater (Samrana *et al.*, 2017). The tolerable limit for As in water is 10μg/L as per WHO guidelines, but in Sindh and Punjab provinces of Pakistan, these levels are beyond the permissible limits (Khattak *et al.*, 2016).

Similarly, a study was conducted in Central Sind showed 0 to 250 µg/L of As for wells, boreholes, and hand-pumps while only 25.42% samples were within the acceptable limit (Talib *et al.,* 2019). While As concentration reported for other area of Sindh viz., in lower Sindh which includes Thatta, Badin, and Tharparker and Tando Muhammad Khan, Matyari, Tando Adam Khan and Dadu have Up to 125 µg/L in water (Shahab A *et al.,* 2018).

A research was carried out in Peshawar and Kohistan regions of KP, Pakistan, which reported 0.002-13.5 µg/L and >0.03-16.69 µg/L levels of As in water (Khan S. *et al.,* 2015, Muhammad S *et al.,* 2010). Moreover, in different concentrations of As was accounted, which are 3.0-3.9 mg/kg for soil and 0.03-1.38mg/kg for vegetables in districts of KP, Pakistan viz. Dera Ismail Khan (DI Khan), Lakki Marwat, Hangu, Bannu, and Kohat.

Likewise, high levels of As concentrations were found in different areas of Panjab, which are 14 to 787µg/L for Sargana and Mailsi, 1–525 µg L −1 for Lahore, up to 48.5ug/L for Vehari, 2400ug/L for East Punjab, up to 76ug/L for Sheikhupura and 100ug/L for Rahim Yar Khan, 203 µg/L for Chichawatni, 5 to 100 µg/L for Hasilpur, 2 to 357µg/L for Sheikhupura (Khan *et al.,* 2016).

It can be concluded in light of the results and evidence reported in various studies that drinking water in Punjab and Sindh is more affected from As and KP is less affected and Baluchistan is almost safe from arsenicism. Previously, in Pakistan the arsenical health risk assessment was considered in four ecological zones of Pakistan by Alamdar *et al.,* 2016, in Central Punjab by Shakoor *et al.,* 2015, in Kohistan by Muhammad *et al.,* 2010, in Southern Sindh by Arain *et al.,* (2009) and in Peshawar by Khan *et al.,* 2012 (Table 5.2).

Table. 5.2: Status of Arsenic contamination in natural groundwater in Pakistan

S.no	Study area	Mean Arsenic Concentration	Permissible limit WHO	References
1	Taluka Tandojam district Hyderabad	50 µg/L	10 µg/L	Khatian, N. et al.2019
2	Central Sindh	135 µg/L	10 µg/L	Talib, M.A et al.2019
3	Larkaana, Sindh	8.6 µg/L	10 µg/L	Kori, A.H et al.2019
4	Chichawatni, Punjab	111.5 µg/L	10 µg/L	Shakoor, M.B. et al.2018
5	Hasilpur/Punjab	55 µg/L	10 µg/L	Ehsan, N. et al.2018
6	District Matyari, Tando Muhammad Khan (TM Khan), Tando Adam Khan (TA Khan), and Dadu and at lower Sindh including Thatta, Badin, and Tharparker	72.5 µg/L	10 µg/L	Shahab, A. et al.2018
7	Hudaira Drain, Punjab	13 µg/L	10 µg/L	Javaid.A et al.2018
8	Quetta Baluchistan	13.6 µg/L	10 µg/L	Khan, M.W. et al.2017
9	Vehari, Punjab	34.25 µg/L	10 µg/L	Shahid, M. et al.2017
10	Johi district Dadu, Sindh province of Pakistan	135 µg/L	10 µg/L	Memon, A.H. et al.2016
11	Punjab and Sindh	138 µg/L	10 µg/L	Niazi, M. et al.2016
12	Manchar Lake to Jamshoro city in Sindh	135 µg/L	10 µg/L	Memon, A.H. et al.2016
13	Peshawar district	6.75 µg/L	10 µg/L	Khan, S. et al.2015
14	Rahim Yar Khan, Punjab	60 µg/L	10 µg/L	Mahar, M.T. et al.2015
15	Sheikhupura	76 µg/L	10 µg/L	Abbas, M. et al.2015
16	Lahore	263.5 µg/L	10 µg/L	Farooqi, A. et al.2013
17	East Punjab	2400 µg/L	10 µg/L	Farooqi, A. et al.2006

5.2.3 Sources of Arsenic and Human exposure

Arsenic is usually found throughout the earth's crust; As is distributed widely in the air, lands, rocks, organisms and natural water bodies and reservoirs. While, in various regions, hazardous concentration of this toxin is present in drinking water, and it is likely that about 60% of the As becomes part of environment in the result of manmade activities (Aziz ullah *et al.,* 2017). It may be an artefact of copper mining, tanning waste, the manufacturing of arsenous acid, electroplating lead and zinc and cadmium sulfide, combustion of fossil fuels, disinfectant additives for animal waste, gas or copper ash or metallurgical sludge, or pigments, or anything generated from municipal, electro-chemical, or the dye, or agricultural disposal of As pesticides (Aziz ullah *et al.,* 2017).

Characteristically, common population is subjected to 'As' via fumes, dust, drinking water and nutritional sources (such as seafood, rice, mushroom and poultry) (Tao *et al.,*1999). Amongst the three possible exposure routes to 'As' viz., ingestion, dermal and inhalation, the ingestion is considered to be the most significant (Johnston *et al.,* 2014).

Due to the consumption of water containing As, human beings are exposed to oral and dermal exposure which results in black foot disease, skin lesions, neurological, reproductive and cardiovascular diseases (Rahman *et al.,* 2015). Numerous non-fatal cancers, including skin, kidney, liver, bladder and lungs have been detected from exposure to groundwater to As (Shakoor *et al.,* 2015). Determining the groundwater As concentration, human health risks can be calculated such as Chronic Daily Intake (CDI); hazard quotient (HQ); hazard index (HI); and carcinogenic risk (CR) (Caylak 2012). Therefore, it is given due consideration in the present study.

i. *Arsenic intake via Drinking Water*

Ground water is a main source used for drinking, and As in high quantities is present in ground water and, has negative impact on human health (Bhattacharya *et al.,* 2002). However, As in drinking water is significantly allied with cancer risk. In 1963 WHO World Health Organization has set their level for As (50µg/L), but from new information's about As risk with cancer, the WHO further reduced their limitations to 10 µg/L in 1992. (WHO, 1993). Ground water is frequently more contaminated with As than surface water and is the primary source of human exposure to inorganic As (Argos, M. *et al.,* 2012). Studies shows that, very high quantities of As are present in ground water in Taiwan, Vietnam, Bangladesh, China, Argentina, and Canada (Grantham *et al.,* 2008).

ii. Arsenic intake via Diet

Using rice and vegetables that have been grown in soil contaminated with As is a major source of chronic exposure to the element. There has now been more As contamination of rice, which is the feedstock for nearly everywhere in the world (Meharg *et al.,* 2009). Much of the As that was once in the soil is absorbed by the rice plant is eventually ends up in the grains to be distributed in an important part of the food chain (Raessle *et al.,* 2018).

iii. Arsenic in Air

Arsenic is primarily attached to particulate matter and occurs in the air as a mixture of arsenite and arsenate, with a trace of organic As species in areas where As pesticides are used or where As has biotic activity. (Morales *et al.,* 2000). Similarly, a study found that methylated As is a minor constituent of the air in peripheral, urban, and industrialized zones, while most of the inorganic matter in the air is composed of trivalent and pentavalent compounds (USEPA, 1983). As in the air is normally present at very low concentrations (0.4 to 30 ng/m^3). According to the USEPA, humans typically inhale between 40 and 90 ng of As per day. As is inhaled at a rate of about 50 ng or less per day in unpolluted areas (USEPA, 2014).

iv. Industrial Manufacturing and Wood Preservatives

Over the last few decades, most As in industrial processes was used in the production of antifungal wood preservatives, and that contaminates the soil. It was discovered that the disposal of preservative-treated wood was a source of environmental As poisoning (Lu *et al.,* 1990). Including both the microelectronics and optical industries, As can be used as a component in either small molecule or ionic forms (WHO, 2002). Inorganic As has also been commonly used in insecticides and pesticides for its power to kill bacteria and germs. Inorganic As compounds, such as sodium arsenate, found wide acceptance, in weed control applications (USDOA, 1970).

5.2.4 Status of Fluoride around the Globe

In its survey report WHO reported in 1984, assessed that water with fluoride ions is above 1 mg/L used by more than 260 million people globally (Roy *et al.,* 2018). The significant fluoride concentration in groundwater worldwide with above WHO permitted limits of 1.5 ppm. The global result (Table 5.3) showed that the countries highly affected with fluoride are Tanzania, Germany, Argentina, China, Kenya, Mexico, India, USA and Pakistan (Farooqi *et al.,* 2017). Other regions, which are pointed by British Geological Survey and have more than 1.5 mg/l (WHO standard) F contamination includes; Southern Eastern Part of India, Region of North China, Southern South American parts, and China Eastern African region and some Parts along Western North America. Similarly, moderate contamination of F (up to 0.69 mg/l) is reported in groundwater of various regions of Australia (Petrides and Cartwright, 2006). F in drinking water of Switzerland is estimated as <0.01 to >100 mg/l (Amini *et al.,* 2008).

Table 5.3: Status of Fluoride contamination in natural ground water in different Countries

S. no	Country	Study area	Mean Fluoride Concentration(mg/L)	Permissible limit(WHO)	References
1	China	Ningxia	2.11	1.5 mg/L	Mingji Li et al.2020
2	Mexico	Lerma-Chapala basin	16.5	1.5 mg/L	Valdez CJ et al.2019
3	Thailand	BuaKhang	4.47	1.5mg/L	Sawangiang B et al. 2019
4	Sudan	Khartoum	0.66	1.5 mg/L	Mustafa DE et al.2018
5	Iran	Zarand region in the south-east of Iran	1.87	1.5 mg/L	Mohammadi M et al.2017
6	Turkey	Gumushane province in North East Turkey	3.90	1.5 mg/L	Vural A et al.2017
7	Argentina	Chasico lake	11.01	1.5 mg/L	María L et al.2014
8	Kenya	Meru	1.525	1.5 mg/L	Crouch S et al.2014
9	Northern Mexico	Ghaza	1.7	1,5mg/L	Abbas M et al. 2013
10	Switzerland	Durango	5.82	1.5 mg/L	Frechero NM et al.2013
11	Italy	Dubendorf	50.01	1.5 mg/L	Amini M et al.2008
12	India	volcanic-sedimentary aquifer in central Italy	6.1	1.5 mg/L	Parrone D et al.2020
13	Nigeria	Areas of Basara and Telangana.	2.225	1.5 mg/L	Narsimha A et al. 2016
14	Tanzania	Nigeria	5	1.5 mg/L	Alexander L et al.2014
15	South Africa	Shinyanga Region	250	1.5 mg/L	Ghiglieri et al. (2012
16	India	Siloam Village, Limpopo Province	4.5	1.5 mg/L	Makungo R et al.2012
17	India	South India	20	1.5 mg/L	Fawell et al. (2006)
18	Indonesia	Asembagus coastal area (East Java, Indonesia),	2.2	1.5 mg/L	Heikensa A et al.2004

5.2.5 Overview of Fluoride Contamination in Pakistan

Fluoride levels in groundwater from various parts of Pakistan have been found to vary (Azizullah *et al.,* 2011). The Pakistan Council for Research in Water Resources (PCRWR) conducted a thorough investigation in the drinking water of 16 major cities of Pakistan and discovered F concentrations exceeding the permissible limit (Tahir and Rasheed, 2012). List of cities which have found to surpass the WHO limit for F concentration is given in Table 5.4. According to Farooqi *et al.,* 2007, more than 2 million individuals in Pakistan are affected by elevated F levels.

Table. 5.4: Status of Fluoride contamination in natural ground water in Pakistan

S.no	Study area	Mean Fluoride Concentration(mg/L)	Permissible limit (WHO)	References
1	Tando Bagosub district in Badin District	3.51	1.5mg/L	Talpur S.A et al.2020
2	Islamkot	1.51	1.5 mg/L	Kumar N et al.2020
3	District Mianwali	2.03	1.5mgLl	Akhtar S et al.2018
4	Quetta	2.3	1.5mg/L	Panezai N et al. 2018
5	Mardan	5.45	1.5 mg/L	Khan B et al. 2017
6	Sub district Gujrat in Punjab, Pakistan	3.8	1.5 mg/L	Farooqi A et al.2016
7	Badarpur and Ibrahimabad of district Kasur, Islamabad, Rawalpindi, and Bahawalpur	6.2	1.5 mg/L	Arshad N et al.2016
8	District Rajanpur	0.75	1.5 mg/L	Sarfraz M.D et al.2016
9	Union Council Ganderi, district Nowshera, located in the Peshawar Basin, KPK	3.095	1.5 mg/L	Anjum M.N et al.2013
10	Rahim Yar Khan district, Punjab	15.4	1.5 mg/L	Farooqi A et al.2013
11	TandoAllayar, Tando Mohammad Khan and Tharparkar districts	2.33	1.5 mg/L	Husain V et al.2012
12	Tharparkar, Sindh	6.315	1.5 mg/L	Sofia et.al.2008
13	Sibi	7.25	1.5 mg/L	Uzma I et al.2007
14	Kalalanwala, East Punjab	22.8	1.5 mg/L	Farooqi A et al.2006
15	Naranj village, KP	10.76	1.5 mg/L	Shah M.T et al.2003
16	Faisalabad	0.47	1.5 mg/L	Mahboob S et al.2013
17	Punjab	2.65	1.5 mg/L	Farooqi A et al.2008
18	Nagar parkar sub district area located in Thar desert south east of Pakistan.	22.7	1.5 mg/L	Brahman K. D et al.2014

The maximum fluoride concentrations have been detected in east Punjab in Kalanwala area, where an extreme concentration of 21.1 mg/L was recorded. The main sources of F pollution are phosphate fertilizers which contains leachable F (52–25 mg/kg) and coal containing F (5–20 mg/kg). In district Nowshera, KP F contamination of groundwater has also been reported (Farooqi *et al.*, 2007). The F content of water samples taken from springs in Naranji village reaches 13.52 mg/kg, exceeding the World Health Organization's permissible limit of 1.5 mg/kg (WHO). The studies revealed that the majority of the rocks in both Ambela and Koga contain high concentrations of F-bearing minerals such as micas, hornblende, apatite, fuorite, and tourmaline, which can result in an excess of F in the area's rocks, soil, and water (Shah *et al.*, 2003).

5.2.6 Sources of Fluoride and Human exposure

Fluoride is a mineral found in seawater, oceans, and groundwater, the latter of which is the primary source of drinking water in many parts of the world and thus the primary source of F ingestion (Bhattacharya *et al.*, 2020). The primary source of F in drinking water is F which is naturally present in the environment. However, F-containing minerals which are inorganic in nature are widely used in industry for a variety of purposes, including the production of aluminum (Maria *et al.*, 2014). F can enter the environment via rocks containing phosphate used to manufacture phosphate fertilizers. These phosphate reserves contain approximately 4% fluorine (Vishnoi *et al.*, 2018). Substances that are used in municipal water fluoridation program are Sodium fluoride, fluorosilicic acid, and sodium hexa fluorosilicate (Parrone *et al.*, 2020). Major sources through which F becomes part of body are discussed here under.

i. *Fluoride in Water*

Fluoride is naturally released into waters as a result of weathering and leaching from the soil into groundwater. On almost every Continent of the world elevated F levels have been reported (Knappett, 2018, Kim *et al.*, 2017, Ahmed, 2014). Groundwater containing a high concentration of F is also found in America, Canada, and Australia (Young *et al.*, 2011). Also, atmospheric emissions from coal-fired power plants and the spread on land before they enter the water bodies make up a significant portion of the total amount of the total burden of F pollution.

ii. Fluoride in Air

Natural background levels are about 0.5 ng/m^3. When human-caused emissions are considered, global background concentrations are on the order of 3 ng/m^3. In the Netherlands, concentrations range from 30–40 ng/m^3 in areas without sources to 70 ng/m^3 in areas with numerous sources (Slooff *et al.*, 1988). F concentrations in the air of several communities in the "United States and Canada" were measured to be between 0.02 and 2.0 g/m^3 (IPCS, 1984). In indoor air, F concentrations ranged between 16 and 46 g/m^3 in few provinces of China (Li *et al.*,1992).

iii. Fluoride in Soil

Fluoride makes up approximately 0.09 percent of the earth's crust, placing it 13th in terms of abundance (Lindahl *et al.*, 1994). Biotite, muscovite, hornblende, apatite, and fluorspar are all F-containing minerals (NAS, 1971a). The exsolution of Fs are made available to the environment by the weathering of rocks and minerals, plus animal and human sources. Agricultural sources that are applied to the soil directly include phosphate fertilizers, mine tailings, and industrial or municipal wastewater that has been landfilled (EPA, 1980a). These foods and vegetables cultivated on F-tainted soil and hydroponically irrigated produce provide this pollutant the chance to enter the human body.

iv. Fluoride in Food

In most cases, food seems to be the principal source of fluoride intake, with lesser contributions from drinking-water and from toothpaste. Barley, rice, taro, yams and cassava were found to have comparatively high F levels. In general, the levels of fluoride in meat (0.2–1.0 mg/kg) and fish (2–5 mg/kg) are fairly low (Roy *et* *al.,* 2018). Concentrates of fish protein may contain up to 370 mg/Kg. F levels in milk are typically low both in human breast milk and in cow's milk. F is found in high concentrations in tea leaves (up to 400 mg/kg dry weight). F exposure associated with tea consumption has been estimated to range between 0.04 and 2.7 mg per person per day (Ahmed., 2014).

v. Toothpaste

According to Roy *et al.,* 2018, toothpaste contains about 1.0–1.5 g/kg fluoride, F Solutions and Gels contain 0.25–24.0 mg/kg fluoride, F tablets constitute 0.25, 0.50, or 1.00 mg. These products contribute to total fluoride exposure to different degrees. It is anticipated that if the toothpaste is gulps up by a child, it may contribute about 0.50 or 0.75 mg fluoride per child per day. However, food appears to be the key source of fluoride intake.

vi. Exposure Pathways

Once released into the environment, F can enter the human body via drinking contaminated water and other contaminated sources such as food, toothpaste, and the air (Elmabrok, 2016). With a few exceptions (Ersboll *et al.,* 2018; Farooq *et al.,* 2018), potable water is typically the primary source of F in the human diet (Farooqi *et al.,* 2009; Farooqi *et al.,* 2007) and is a predictor of health problems (Farooqi *et al.,* 2017; Arias *et al.,* 2015). According to the United States National Research Council (USNRC), human exposure to F carried by the air is negligible (Chaudhary and Kumar, 2009). Generally, food products have a negligible effect on F exposure (Boochs *et al.,* 2014). Following ingestion, human tissues absorb a portion of F, while the remainder is excreted in urine. The accumulation of F in the human body occurs as a result of repeated exposure to various sources. It is also strongly related to the mineral composition of the bedrock and is released into groundwater as a result of weathering and leaching (Elmabrok, 2016). The higher concentrations of F are closely associated with volcanic activity also (Ghaderpoori *et al.,* 2018; Gikunju *et al.,* 1995). Industry is also one of the significant sources of F pollution (Gikunju *et al.,* 2002).

5.2.7 Factors Affecting the F Concentration in Groundwater

The dissolution and solubility of F in groundwater are dependent on a variety of factors, including the calcium and sodium hydroxide concentrations in the groundwater (Bigdeli and Seilsepour, 2008), the area's climatic conditions, the amount of time groundwater is retained in an aquifer, the pH, depth, and temperature of groundwater, the recharge area's distance from the source, the interaction of water with soil and rocks (González-Horta *et al.,* 2015; Gomez *et al.,* 2013; Farooqi *et al.,* 2007), and evapotranspiration (Buschmann et al., 2018). In acidic waters with a pH of 5, F ions form complexes with metal ions. However, at elevated pH values, the F ion predominates in water (Abbas et al., 2013).

5.3. Results and Discussion

5.3.1. Health Risk Assessment of Arsenic via Drinking Water

The purpose of this study was to determine the amount of As in groundwater and the resulting risk to human health in terms of chronic daily intake (CDI), hazard quotient (HQ), and carcinogenic risk (CR) for oral exposure to As. Seventy groundwater samples were collected from various cities in Pakistan.

As concentrations in groundwater samples from the study area ranged between 11 and 108 ug/L. As levels in many cities exceeded the safe limits i.e.,10 g/L. The highest concentration of As (108 ug/l) was detected in Kasur groundwater samples, while the lowest concentration (11 ug/L) was detected in Nurpur Thal, Pindi Bhatian, Kamalia, and Sharq-Pur groundwater samples (Table 5.5).

Table: 5.5 Scale of Arsenic Contamination in Punjab and Sindh

Sr.NO	Sampling Sites	Concentration (AS)>10ppb	Sr.NO	Sampling Sites	Concentration (AS)>10ppb
1	Faisalabad	28	36	Mandi Baha-ud-din	27
2	Tandianwala	32	37	Phalia	23
3	Sumandri	17	38	Muzaffargarh	65
4	Jaranwala	19	39	Kot Addu	40
5	Gujrat	27	40	Dera Ghazi Khan	35
6	Pind Dadan Khan	35	41	Tounsa Sharif	25
7	Jahania	43	42	Bahawalpur	35
8	Khanawal	17	43	Ahmedpur East	44
9	Main Channu	70	44	Yazman	44
10	Kabirwala	87	45	Multan City	40
11	Layyah	36	46	Multan Sadar	91
12	Karor	29	47	Shuja Abad	33
13	Rajanpur	10	48	Jalalpur Pirawala	31
14	Rojhan	18	49	Sadiqabad	57
15	Sargodha	24	50	Rahim Yar Khan	64
16	Sillanwali	65	51	Khanpur	41
17	Sahiwal	41	52	Liaqatpur	47
18	Shahpur	27	53	Hafizabad	24
19	Bhalwal	20	54	Pindi Bhatian	11
20	Lahore	75	55	Jhang	18
21	Sialkot	20	56	Chiniot	18
22	Vehari	89	57	Gojra	13
23	Bure-wala	104	58	Kamalia	11
24	Mailsi	45	59	Kasur	108
25	Narowal	31	60	Pattoki	24
26	Khushab	16	61	Chunian	13
27	Nurpur Thal	11	62	Okara	55
28	Mianwali	22	63	Renalkhurd	16
29	Piplan	17	64	Sheikhupura	63
30	Bhakkar	38	65	Ferozepur	34
31	Mankera	49	66	Mureed-Key	64
32	Darya Khan	22	67	Sharq-Pur	11
33	Kalur Kot	21	68	Sahiwal	18
34	Pakpattan	33	69	Chichawatni	29
35	Arif Wala	69	70	Kahror paka	14

In the study area, 20% groundwater samples were found with high As concentration exceeding the safe limits of Pak-EPA i.e., 50 µg/L. The maximum As concentration found in this study (108µg/L) was higher than maximum As concentration (96 µg·/L) determined by Arain *et al.,* in 2009 in Jamshoro (Sind), and Baig *et al,,* in 2009 as (106 µg/L) in Jamshoro (Sind) but lower than Rasool *et al.,* in Mailsi (Punjab) in 2016 (828 µg/l). This study identified As contamination level in different urban and rural areas of Pakistan, which could be further employed to better understand the human health risks from exposure to As rich water.

5.3.2. Exposure and cancer risk assessment

In measurement of values of population parameters of different cities and the information regarding local people was taken from previous studies in Pakistan. The parameter values of 'Exposure Factors handbook' have been modified in accordance with integrated risk information system reference values. "CDIs" with reference doses (RfDs) or "CDIs" by "SFs" were derived from the "HQ" and "CR" for oral exhibiting As (USEPA, 2011).

The CDI, HQ, and CR values for exposure to As in groundwater are shown in Table: 5.6. When HQ < 1 is used in the human health risk evaluation, the risk of As to human health is believed to be chronic (non-carcinogenic) through drinking water (USEPA, 2005).

Moreover, low levels of drinking water exposure to As could also result in cancer in humans, which is defined as a potential CR indicator. In exposed population, people with an intake of As-contaminated water, if CR > 10-6 then this means potential CR exists (US-EPA, 2005).

In the study area, the highest CDI values observe for As exposure was 3.08 mg/kg/day, in Kasur, while lowest value 0.28 mg/kg/day, in Rajanpur respectively. Our results elaborated HQ for As revelation ranged from 8-61 and surpassed the representative toxic RI value of 1 (Sultana, 2014). The maximum toxic RI (HQ = 61) was noted in Kasur and minimum (HQ = 8) was in Kahror paka. Our findings indicated that HQ values were comparable to the values (0.1-11) for drinking water in various areas of Lahore, and that the current research work discovered values that were higher than those calculated by Hassan *et al.*, 2017.

Table: 5.6 Concentration, CDI, HQ and CR of Arsenic in groundwater samples of different areas of Punjab and Sindh in Pakistan

Sr.No .	Sampling Sites	Concentration (AS)>10ppb	Chronic Daily Intake (CDI)	Hazard Quotient (HQ)	Carcinogenic Risk (CR)	Population 2017
1	Faisalabad	28	0.8	16	1.2	7873910
2	Tandianwala	32	0.914	18.285	1.371	702733
3	Sumandri	17	0.485	9.714	0.728	643068
4	Jaranwala	19	0.542	10.857	0.814	1492276
5	Gujrat	27	0.771	15.428	1.157	1497865
6	Pind Dadan Khan	35	1	20	1.5	336852
7	Jahania	43	1.228	24.571	1.842	343361
8	Khanawal	17	0.485	9.714	0.728	856793
9	Main Channu	70	2	40	3	761971
10	Kabirwala	87	2.485	49.714	3.728	959861
11	Layyah	36	1.028	20.571	1.542	1824230
12	Karor	29	0.828	16.571	1.242	594639
13	Rajanpur	10	0.285	5.714	0.428	1995958
14	Rojhan	18	0.514	10.285	0.771	405774
15	Sargodha	24	0.685	13.714	1.028	3703588
16	Sillanwali	65	1.857	37.142	2.785	344465
17	Sahiwal	41	1.171	23.428	1.757	341247
18	Shahpur	27	0.771	15.428	1.157	353969
19	Bhalwal	20	0.571	11.428	0.857	357331
20	Lahore	75	2.142	42.857	3.214	11126285
21	Sialkot	20	0.571	11.428	0.857	3893672
22	Vehari	89	2.542	50.857	3.814	2897446
23	Bure-wala	104	2.971	59.428	4.457	1015385
24	Mailsi	45	1.285	25.714	1.928	953895
25	Narowal	31	0.885	17.714	1.328	596565
26	Khushab	16	0.457	9.142	0.685	689742
27	Nurpur Thal	11	0.314	6.285	0.471	243295
28	Mianwali	22	0.628	12.571	0.942	767130
29	Piplan	17	0.485	9.7142	0.728	403938
30	Bhakkar	38	1.085	21.714	1.628	685059
31	Mankera	49	1.4	28	2.1	257100
32	Darya Khan	22	0.628	12.571	0.942	360807
33	Kalur Kot	21	0.6	12	0.9	347552
34	Pakpattan	33	0.942	18.857	1.414	969225
35	Arif Wala	69	1.971	39.428	2.957	854462
36	Mandi Baha-ud-din	27	0.771	15.428	1.157	668007
37	Phalia	23	0.657	13.142	0.985	553416
38	Muzaffargarh	65	1.857	37.142	2.785	1621744
39	Kot Addu	40	1.142	22.857	1.714	1345941
40	Dera Ghazi Khan	35	1	20	1.5	1226612
41	Tounsa Sharif	25	0.714	14.285	1.071	675756
42	Bahawalpur	35	1	20	1.5	762111
43	Ahmedpur East	44	1.257	25.142	1.885	1078683
44	Yazman	44	1.257	25.142	1.885	614143
45	Multan City	40	1.142	22.857	1.714	2258570
46	Multan Sadar	91	2.6	52	3.9	1322756
47	Shuja Abad	33	0.942	18.857	1.414	609631
48	Jalalpur Pirawala	31	0.885	17.714	1 328	554152
49	Sadiqabad	57	1.628	32.571	2.442	1264752
50	Rahim Yar Khan	64	1.828	36.571	2.742	1530330
51	Khanpur	41	1.171	23.428	1.757	983415
52	Liaqatpur	47	1.342	26.857	2.014	1035509

53	Hafizabad	24	0.685	13.714	1.028	663735
54	Pindi Bhatian	11	0 314	6.285	0.471	493222
55	Jhang	18	0.514	10.285	0.771	1465472
56	Chiniot	18	0.514	10.285	0.771	556147
57	Gojra	13	0.371	7.428	0.557	656007
58	Kamalia	11	0.314	6.285	0.471	371851
59	Kasur	108	3.085	61.714	4.628	1334653
60	Pattoki	24	0.685	13.714	1.028	934329
61	Chunian	13	0.371	7.428	0.557	825684
62	Okara	55	1.571	31.428	2.357	1205655
63	Renalkhurd	16	0.457	9.142	0.685	458572
64	Sheikhupura	63	1.8	36	2.7	1555242
65	Ferozepur	34	0.971	19.428	1.457	795498
66	Mureed-Key	64	1.828	36.571	2.742	639784
67	Sharq-Pur	11	0.314	6.285	0.471	197220
68	Sahiwal	18	0.514	10.285	0.771	1491553
69	Chichawatni	29	0.828	16.571	1.242	1026007
70	Kahror paka	14	0.4	8	0.6	594639

The study area's potential CR values ranged from 0.4 to 4.6 which were greater than the US-EPA limit (10) indicating that the population in the study area was at a high risk of developing cancer (Table 5.6). Thus, continuous monitoring of the As level in groundwater is necessary to determine whether any possible health risk associated with the consumption of As-rich water exists, thus protecting entities from drinking potentially harmful As-contaminated water.

5.3.3. Health Risk Assessment of Fluoride via Drinking Water

To determine the F levels in groundwater and the risk to the health of communities in terms of hazard quotient (HQ) and chronic daily intake (CDI) for oral F exposure was the main purpose of this study. A total of 979 samples were collected, of which 41 were discarded, due to leakage of bottle, misplacement of information tag and suspected contamination. Of the 938 selected for analysis, 38 were from Gilgit-Baltistan, 473 were from Punjab, 115 from Sindh, 131 from Balochistan and 181 were from KP, were collected from different provinces of Pakistan. High disparity was observed in the F contaminations in different groundwater sources, fluctuating from very low levels of 0.01 mg/L, which is lower than the concentration 0.05 mg/L observed in Peshawar (Ahmad *et al.*, 2004), to tremendously high and toxic levels of 50.00 mg/L in groundwater samples of the study area (Table 5.7).

Table: 5.7 Concentration, CDI, HQ and CR of Fluoride in groundwater samples of different areas of Pakistan

Fluoride analysis of drinking water of Gilgit-Baltistan											
S.No	F	CDI	HQ	S.No	F	CDI	HQ	S.No	F	CDI	HQ
1	0.31	0.011	0.184	14	0.21	0.007	0.125	27	1.27	0.045	0.758
2	0.44	0.015	0.261	15	0.16	0.005	0.095	28	0.27	0.009	0.160
3	0.30	0.010	0.178	16	0.25	0.008	0.148	29	0.55	0.019	0.327
4	0.28	0.01	0.166	17	0.31	0.011	0.184	30	0.70	0.025	0.416
5	0.46	0.016	0.273	18	0.19	0.006	0.113	31	0.38	0.013	0.226
6	0.10	0.003	0.059	19	0.14	0.005	0.083	32	0.21	0.007	0.125
7	0.03	0.001	0.017	20	0.23	0.008	0.136	33	1.50	0.053	0.890
8	0.84	0.03	0.5	21	1.49	0.053	0.888	34	1.58	0.056	0.941
9	0.52	0.018	0.309	22	1.23	0.043	0.732	35	0.35	0.012	0.208
10	0.13	0.004	0.077	23	0.23	0.008	0.136	36	0.47	0.016	0.279
11	0.60	0.021	0.357	24	1.18	0.042	0.700	37	0.25	0.008	0.148
12	0.24	0.008	0.142	25	1.33	0.047	0.788	38	0.22	0.007	0.130
13	0.22	0.007	0.130	26	1.28	0.045	0.761				
Fluoride analysis of drinking water of K.P.K											
S.No	F	CDI	HQ	S.No	F	CDI	HQ	S.No	F	CDI	HQ
1	0.23	0.008	0.136	22	4.84	0.172	2.881	43	1.88	0.067	1.118
2	0.61	0.021	0.363	23	4.95	0.176	2.946	44	1.45	0.051	0.860
3	0.23	0.008	0.136	24	1.32	0.047	0.783	45	2.23	0.079	1.325
4	0.15	0.005	0.089	25	1.46	0.052	0.867	46	2.27	0.080	1.349
5	2.07	0.073	1.229	26	3.45	0.123	2.052	47	0.57	0.020	0.339
6	0.35	0.012	0.208	27	1.42	0.050	0.847	48	0.57	0.020	0.339
7	0.24	0.008	0.142	28	2.61	0.093	1.555	49	1.19	0.042	0.707
8	1.99	0.070	1.182	29	1.94	0.069	1.152	50	1.51	0.053	0.897
9	0.11	0.003	0.065	30	2.22	0.079	1.318	51	0.15	0.005	0.089
10	0.27	0.009	0.160	31	0.23	0.008	0.136	52	0.35	0.012	0.208
11	0.12	0.004	0.071	32	3.54	0.126	2.106	53	0.55	0.019	0.327
12	0.20	0.007	0.119	33	4.58	0.163	2.728	54	0.04	0.001	0.023
13	0.76	0.027	0.452	34	1.66	0.059	0.991	55	1.73	0.061	1.028
14	2.73	0.097	1.627	35	1.23	0.043	0.731	56	2.41	0.086	1.436
15	2.39	0.085	1.422	36	0.99	0.035	0.586	57	1.72	0.061	1.025
16	0.36	0.012	0.214	37	0.85	0.030	0.506	58	1.55	0.055	0.921
17	0.44	0.015	0.261	38	0.69	0.024	0.412	59	0.13	0.004	0.077
18	1.78	0.063	1.060	39	1.88	0.067	1.120	60	3.22	0.114	1.915
19	1.87	0.066	1.112	40	1.25	0.044	0.741	61	2.11	0.075	1.258
20	2.64	0.094	1.570	41	1.14	0.040	0.676	62	1.35	0.048	0.803
21	3.83	0.136	2.281	42	0.85	0.030	0.505	63	0.10	0.003	0.059

64	1.41	0.050	0.841	**103**	0.64	0.022	0.382	**142**	1.24	0.044	0.738
65	3.26	0.116	1.942	**104**	0.87	0.031	0.518	**143**	0.07	0.002	0.041
66	2.51	0.089	1.491	**105**	2.38	0.085	1.417	**144**	2.65	0.094	1.574
67	0.51	0.018	0.303	**106**	0.25	0.008	0.148	**145**	1.40	0.049	0.830
68	0.19	0.006	0.113	**107**	1.17	0.041	0.697	**146**	0.25	0.008	0.148
69	0.12	0.004	0.071	**108**	2.25	0.080	1.338	**147**	1.68	0.059	0.999
70	1.22	0.043	0.725	**109**	2.03	0.072	1.207	**148**	0.43	0.015	0.255
71	0.39	0.013	0.232	**110**	0.24	0.008	0.142	**149**	2.39	0.085	1.420
72	0.38	0.013	0.226	**111**	1.61	0.057	0.960	**150**	0.45	0.016	0.267
73	0.17	0.006	0.101	**112**	1.63	0.058	0.968	**151**	2.25	0.080	1.341
74	0.02	0.0007	0.011	**113**	3.59	0.128	2.138	**152**	1.72	0.061	1.021
75	0.21	0.007	0.125	**114**	2.13	0.076	1.267	**153**	0.26	0.009	0.154
76	0.36	0.012	0.214	**115**	0.71	0.025	0.422	**154**	0.21	0.007	0.125
77	1.19	0.042	0.708	**116**	2.13	0.076	1.266	**155**	0.64	0.022	0.380
78	1.28	0.045	0.759	**117**	1.53	0.054	0.909	**156**	0.11	0.003	0.065
79	2.37	0.084	1.407	**118**	2.27	0.081	1.350	**157**	2.07	0.073	1.230
80	1.74	0.062	1.037	**119**	0.08	0.002	0.047	**158**	0.22	0.007	0.130
81	1.77	0.063	1.053	**120**	0.72	0.025	0.428	**159**	0.18	0.006	0.107
82	1.45	0.051	0.863	**121**	1.18	0.042	0.702	**160**	0.21	0.007	0.125
83	2.08	0.074	1.237	**122**	2.02	0.072	1.202	**161**	0.37	0.013	0.220
84	1.78	0.063	1.057	**123**	0.49	0.017	0.291	**162**	1.52	0.054	0.902
85	2.33	0.083	1.383	**124**	0.57	0.020	0.339	**163**	0.29	0.010	0.172
86	3.00	0.107	1.787	**125**	1.24	0.044	0.739	**164**	1.31	0.046	0.776
87	3.24	0.115	1.931	**126**	0.01	0.0003	0.005	**165**	1.18	0.042	0.704
88	0.84	0.029	0.498	**127**	1.08	0.038	0.642	**166**	2.41	0.086	1.435
89	1.88	0.067	1.119	**128**	1.45	0.051	0.866	**167**	0.74	0.026	0.439
90	1.25	0.044	0.742	**129**	0.42	0.015	0.25	**168**	0.43	0.015	0.255
91	2.84	0.101	1.688	**130**	0.10	0.003	0.059	**169**	3.21	0.114	1.912
92	2.34	0.083	1.392	**131**	0.32	0.011	0.190	**170**	0.62	0.022	0.369
93	1.84	0.065	1.096	**132**	0.25	0.008	0.148	**171**	0.25	0.008	0.148
94	0.42	0.015	0.25	**133**	2.06	0.073	1.227	**172**	0.19	0.006	0.113
95	1.64	0.058	0.976	**134**	0.41	0.014	0.244	**173**	0.52	0.018	0.309
96	2.62	0.093	1.561	**135**	0.41	0.014	0.244	**174**	0.14	0.005	0.083
97	0.03	0.001	0.017	**136**	1.78	0.063	1.062	**175**	0.20	0.007	0.119
98	2.99	0.106	1.781	**137**	1.49	0.053	0.886	**176**	0.19	0.006	0.113
99	2.63	0.094	1.568	**138**	1.64	0.058	0.977	**177**	2.36	0.084	1.404
100	2.83	0.101	1.685	**139**	2.96	0.105	1.76	**178**	2.31	0.082	1.377
101	0.65	0.023	0.386	**140**	2.61	0.093	1.553	**179**	2.78	0.099	1.656
102	4.17	0.148	2.481	**141**	1.40	0.049	0.831	**180**	1.71	0.061	1.017

182	2.02	0.072	1.202	183	0.25	0.008	0.148				

Fluoride analysis of drinking water of Punjab

S.No	F	CDI	HQ	S.No	F	CDI	HQ	S.No	F	CDI	HQ
1	1.05	0.037	0.624	36	1.23	0.043	0.732	71	1.12	0.039	0.665
2	0.20	0.007	0.119	37	1.17	0.041	0.695	72	0.37	0.013	0.220
3	1.16	0.041	0.688	38	0.97	0.034	0.575	73	0.93	0.033	0.553
4	0.60	0.021	0.357	39	0.81	0.028	0.480	74	2.92	0.104	1.738
5	2.68	0.095	1.595	40	2.09	0.074	1.243	75	1.54	0.055	0.917
6	0.94	0.033	0.562	41	0.57	0.020	0.339	76	1.35	0.048	0.80
7	0.69	0.024	0.409	42	1.90	0.067	1.129	77	1.41	0.050	0.837
8	1.01	0.036	0.602	43	1.47	0.052	0.873	78	1.07	0.038	0.638
9	0.17	0.006	0.101	44	0.84	0.029	0.499	79	1.48	0.052	0.881
10	0.90	0.032	0.538	45	1.33	0.047	0.794	80	0.78	0.027	0.464
11	0.69	0.024	0.410	46	1.43	0.051	0.852	81	0.72	0.025	0.428
12	1.12	0.039	0.665	47	1.38	0.049	0.819	82	0.47	0.016	0.279
13	1.10	0.039	0.652	48	2.39	0.085	1.421	83	1.09	0.038	0.647
14	0.29	0.010	0.172	49	2.33	0.083	1.384	84	0.80	0.028	0.477
15	0.88	0.031	0.522	50	0.86	0.030	0.514	85	0.77	0.027	0.456
16	0.85	0.030	0.506	51	0.98	0.034	0.582	86	0.09	0.003	0.053
17	0.92	0.032	0.545	52	0.64	0.022	0.380	87	1.87	0.066	1.115
18	0.95	0.033	0.565	53	1.67	0.059	0.995	88	0.96	0.034	0.569
19	0.94	0.033	0.560	54	0.95	0.034	0.567	89	8.71	0.311	5.187
20	0.89	0.031	0.531	55	1.00	0.035	0.597	90	0.99	0.035	0.589
21	0.94	0.033	0.560	56	0.19	0.006	0.113	91	0.61	0.021	0.363
22	0.90	0.032	0.537	57	0.94	0.033	0.558	92	0.44	0.015	0.261
23	0.96	0.034	0.571	58	0.93	0.033	0.552	93	0.70	0.025	0.417
24	0.92	0.032	0.547	59	0.73	0.025	0.431	94	0.70	0.025	0.416
25	0.79	0.028	0.469	60	1.24	0.044	0.735	95	1.17	0.041	0.697
26	2.78	0.099	1.654	61	1.09	0.039	0.650	96	0.08	0.002	0.047
27	2.78	0.099	1.654	62	0.55	0.019	0.327	97	0.92	0.032	0.547
28	1.55	0.055	0.922	63	0.55	0.019	0.327	98	0.60	0.021	0.357
29	0.89	0.031	0.529	64	1.29	0.046	0.769	99	0.73	0.026	0.433
30	0.87	0.031	0.517	65	0.90	0.032	0.533	100	0.17	0.006	0.101
31	0.72	0.025	0.428	66	1.35	0.048	0.803	101	0.53	0.018	0.315
32	1.11	0.039	0.660	67	0.86	0.030	0.511	102	2.23	0.079	1.326
33	0.65	0.023	0.386	68	0.31	0.011	0.184	103	3.80	0.135	2.261
34	0.86	0.030	0.511	69	1.38	0.049	0.823	104	6.99	0.249	4.160
35	0.32	0.011	0.190	70	1.38	0.049	0.821	105	5.46	0.194	3.247

106	0.48	0.017	0.285	**145**	0.87	0.030	0.516	**184**	1.48	0.052	0.881
107	0.63	0.022	0.375	**146**	0.85	0.030	0.503	**185**	1.53	0.054	0.908
108	0.91	0.032	0.540	**147**	1.20	0.042	0.715	**186**	0.59	0.021	0.351
109	1.61	0.057	0.958	**148**	0.50	0.017	0.297	**187**	1.74	0.062	1.038
110	0.79	0.028	0.472	**149**	1.18	0.042	0.705	**188**	1.44	0.051	0.855
111	1.08	0.038	0.644	**150**	0.96	0.034	0.572	**189**	6.03	0.215	3.587
112	2.10	0.0749	1.248	**151**	1.14	0.040	0.681	**190**	0.83	0.029	0.491
113	0.71	0.025	0.422	**152**	0.87	0.0311	0.518	**191**	0.49	0.017	0.291
114	0.68	0.024	0.406	**153**	0.86	0.030	0.509	**192**	2.79	0.099	1.657
115	5.46	0.195	3.250	**154**	1.13	0.040	0.672	**193**	0.86	0.030	0.511
116	1.47	0.052	0.876	**155**	1.66	0.059	0.989	**194**	2.23	0.079	1.328
117	0.76	0.027	0.451	**156**	0.85	0.030	0.507	**195**	1.16	0.041	0.689
118	0.90	0.032	0.537	**157**	1.16	0.041	0.692	**196**	2.27	0.081	1.350
119	1.79	0.064	1.068	**158**	0.67	0.023	0.398	**197**	2.10	0.075	1.251
120	0.91	0.032	0.542	**159**	0.83	0.029	0.491	**198**	1.98	0.070	1.176
121	0.01	0.0003	0.005	**160**	1.07	0.038	0.637	**199**	1.16	0.041	0.690
122	0.54	0.019	0.321	**161**	1.85	0.066	1.101	**200**	2.08	0.074	1.238
123	1.08	0.038	0.642	**162**	1.90	0.067	1.131	**201**	1.35	0.048	0.801
124	1.08	0.038	0.641	**163**	1.54	0.055	0.917	**202**	1.19	0.042	0.707
125	0.71	0.025	0.421	**164**	2.06	0.073	1.226	**203**	1.65	0.059	0.983
126	1.17	0.041	0.698	**165**	2.38	0.085	1.417	**204**	1.01	0.036	0.600
127	1.23	0.044	0.733	**166**	1.79	0.063	1.062	**205**	0.72	0.025	0.428
128	0.49	0.017	0.291	**167**	0.74	0.026	0.441	**206**	2.28	0.081	1.359
129	1.97	0.070	1.172	**168**	2.30	0.082	1.367	**207**	2.43	0.086	1.447
130	1.10	0.039	0.657	**169**	0.91	0.032	0.542	**208**	2.63	0.093	1.563
131	41.27	1.473	24.565	**170**	0.54	0.019	0.321	**209**	1.36	0.048	0.806
132	1.39	0.049	0.829	**171**	0.72	0.025	0.428	**210**	1.06	0.037	0.63
133	1.44	0.051	0.857	**172**	1.54	0.054	0.915	**211**	2.01	0.071	1.198
134	1.13	0.040	0.673	**173**	1.91	0.068	1.138	**212**	0.87	0.031	0.519
135	0.69	0.024	0.410	**174**	1.86	0.066	1.108	**213**	2.40	0.085	1.430
136	0.27	0.009	0.160	**175**	1.85	0.066	1.101	**214**	2.21	0.078	1.314
137	0.71	0.025	0.42	**176**	2.70	0.096	1.607	**215**	1.64	0.058	0.977
138	1.12	0.040	0.668	**177**	1.02	0.036	0.607	**216**	2.29	0.081	1.362
139	0.45	0.016	0.267	**178**	0.79	0.028	0.472	**217**	1.98	0.070	1.176
140	0.87	0.031	0.517	**179**	1.64	0.058	0.977	**218**	1.77	0.063	1.054
141	4.93	0.176	2.935	**180**	0.70	0.025	0.416	**219**	1.71	0.060	1.015
142	0.36	0.012	0.214	**181**	0.89	0.031	0.527	**220**	0.97	0.034	0.577
143	3.93	0.140	2.336	**182**	0.73	0.025	0.432	**221**	1.36	0.048	0.809
144	0.47	0.016	0.279	**183**	1.04	0.037	0.618	**222**	1.09	0.038	0.649

223	1.16	0.041	0.690	**262**	0.80	0.028	0.476	**302**	1.09	0.038	0.646
224	0.82	0.029	0.488	**263**	1.50	0.053	0.895	**303**	1.07	0.038	0.634
225	0.83	0.029	0.494	**264**	1.66	0.059	0.988	**304**	1.20	0.042	0.713
226	0.77	0.027	0.458	**265**	2.40	0.085	1.430	**305**	1.31	0.046	0.781
227	0.62	0.022	0.369	**266**	2.37	0.084	1.409	**306**	1.73	0.061	1.03
228	1.21	0.043	0.717	**267**	1.33	0.047	0.791	**307**	0.94	0.033	0.557
229	1.47	0.052	0.875	**268**	2.24	0.080	1.334	**308**	0.33	0.011	0.196
230	0.90	0.032	0.535	**269**	0.74	0.026	0.440	**309**	1.04	0.037	0.619
231	0.76	0.027	0.452	**270**	0.63	0.022	0.375	**310**	0.72	0.025	0.428
232	0.85	0.030	0.505	**271**	1.33	0.047	0.792	**311**	1.68	0.059	0.998
233	1.61	0.057	0.956	**272**	1.16	0.041	0.692	**312**	0.83	0.029	0.494
234	0.93	0.033	0.553	**273**	0.22	0.007	0.130	**313**	1.69	0.060	1.007
235	0.68	0.024	0.406	**274**	0.96	0.034	0.571	**314**	0.47	0.016	0.279
236	1.30	0.046	0.772	**275**	0.48	0.017	0.285	**315**	0.45	0.016	0.267
237	0.48	0.017	0.285	**276**	0.42	0.015	0.25	**316**	0.94	0.033	0.559
238	0.17	0.006	0.101	**277**	0.69	0.024	0.410	**317**	0.23	0.008	0.136
239	4.97	0.177	2.959	**278**	0.69	0.024	0.410	**318**	1.10	0.039	0.656
240	6.81	0.243	4.052	**279**	1.59	0.056	0.948	**319**	0.65	0.023	0.386
241	0.23	0.008	0.136	**280**	0.64	0.022	0.380	**320**	1.17	0.041	0.696
242	2.56	0.091	1.522	**281**	0.58	0.020	0.345	**321**	1.81	0.064	1.076
243	1.42	0.050	0.845	**282**	1.03	0.036	0.613	**322**	1.45	0.051	0.863
244	0.25	0.008	0.148	**283**	0.54	0.019	0.321	**323**	1.90	0.067	1.130
245	0.49	0.017	0.291	**284**	1.32	0.047	0.787	**324**	2.07	0.073	1.232
246	0.76	0.027	0.452	**285**	1.46	0.051	0.866	**325**	1.48	0.052	0.882
247	3.82	0.136	2.274	**286**	0.43	0.015	0.255	**326**	1.26	0.045	0.751
248	3.33	0.118	1.981	**287**	2.49	0.088	1.481	**327**	1.82	0.065	1.085
249	6.30	0.225	3.751	**288**	1.42	0.050	0.845	**328**	5.12	0.182	3.047
250	0.99	0.035	0.589	**289**	0.76	0.027	0.452	**329**	6.26	0.223	3.727
251	1.11	0.039	0.660	**290**	1.21	0.043	0.718	**330**	2.15	0.076	1.278
252	3.38	0.120	2.009	**291**	0.66	0.023	0.392	**331**	0.19	0.006	0.113
253	3.04	0.108	1.811	**292**	1.91	0.068	1.136	**332**	1.51	0.053	0.896
254	1.41	0.050	0.839	**293**	0.59	0.021	0.351	**333**	6.32	0.225	3.763
255	1.58	0.056	0.940	**294**	0.41	0.014	0.244	**334**	1.63	0.058	0.969
256	1.10	0.039	0.654	**295**	2.02	0.072	1.201	**335**	1.78	0.063	1.058
257	1.02	0.036	0.607	**296**	1.94	0.069	1.154	**336**	2.92	0.104	1.738
258	1.20	0.042	0.714	**298**	2.23	0.079	1.326	**337**	1.71	0.060	1.015
259	2.50	0.089	1.488	**299**	1.80	0.064	1.071	**338**	4.44	0.158	2.644
260	2.32	0.082	1.380	**300**	0.62	0.022	0.369	**339**	0.72	0.025	0.427
261	2.01	0.071	1.196	**301**	1.91	0.068	1.135	**340**	2.87	0.102	1.707

341	1.79	0.064	1.066	**380**	0.65	0.023	0.386	**420**	4.48	0.159	2.666
342	2.30	0.082	1.37	**381**	2.36	0.084	1.403	**421**	0.70	0.025	0.416
343	1.46	0.052	0.871	**382**	0.20	0.007	0.119	**422**	0.75	0.026	0.446
344	0.70	0.025	0.416	**383**	0.34	0.012	0.202	**423**	0.54	0.019	0.321
345	1.64	0.058	0.977	**384**	1.58	0.056	0.939	**424**	1.48	0.052	0.879
346	0.65	0.023	0.386	**385**	0.23	0.008	0.136	**425**	1.08	0.038	0.640
347	1.26	0.045	0.752	**386**	1.31	0.046	0.777	**426**	1.27	0.045	0.758
348	1.46	0.051	0.866	**387**	1.27	0.045	0.758	**427**	0.50	0.017	0.297
349	1.32	0.047	0.787	**388**	3.71	0.132	2.210	**428**	1.61	0.057	0.956
350	0.80	0.028	0.476	**389**	3.00	0.107	1.783	**429**	0.51	0.018	0.303
351	1.27	0.045	0.755	**390**	2.85	0.101	1.698	**430**	2.87	0.102	1.709
352	2.23	0.079	1.328	**391**	4.42	0.157	2.631	**431**	0.19	0.006	0.113
353	1.25	0.044	0.742	**392**	2.63	0.093	1.563	**432**	0.98	0.035	0.583
354	0.94	0.033	0.557	**393**	1.43	0.051	0.851	**433**	0.95	0.033	0.565
355	0.31	0.011	0.184	**394**	0.84	0.030	0.501131	**435**	0.65	0.023	0.386
356	1.01	0.036	0.601	**395**	0.33	0.011	0.196	**436**	0.18	0.006	0.107
357	0.99	0.035	0.588	**396**	1.55	0.055	0.922	**437**	0.62	0.022	0.369
358	1.60	0.057	0.952	**397**	0.92	0.032	0.548	**438**	0.30	0.010	0.178
359	0.83	0.029	0.494	**398**	2.44	0.087	1.454	**439**	1.54	0.055	0.916
360	1.58	0.056	0.940	**399**	3.95	0.141	2.351	**440**	2.11	0.075	1.255
361	2.65	0.094	1.578	**400**	1.12	0.039	0.663	**441**	2.05	0.073	1.220
362	2.42	0.086	1.440	**401**	1.40	0.05	0.833	**442**	0.47	0.016	0.279
363	4.12	0.147	2.451	**402**	2.80	0.100	1.667	**443**	1.16	0.041	0.690
364	1.42	0.050	0.843	**403**	1.04	0.037	0.616	**444**	1.96	0.07	1.166
365	10.14	0.362	6.035	**405**	3.43	0.122	2.040	**445**	2.17	0.077	1.291
366	1.84	0.065	1.095	**406**	1.07	0.038	0.635	**446**	1.18	0.042	0.702
367	0.13	0.004	0.077	**407**	3.32	0.118	1.975	**447**	0.01	0.0003	0.005
368	4.14	0.147	2.461	**408**	3.63	0.129	2.162	**448**	0.73	0.026	0.434
369	2.58	0.091	1.532	**409**	2.19	0.078	1.301	**449**	0.58	0.020	0.345
370	1.98	0.070	1.180	**410**	1.45	0.051	0.863	**450**	2.44	0.087	1.452
371	5.51	0.196	3.282	**411**	5.03	0.179	2.992	**451**	0.70	0.025	0.416
372	2.98	0.106	1.773	**412**	3.71	0.132	2.207	**452**	1.60	0.057	0.952
373	6.08	0.217	3.619	**413**	0.47	0.016	0.279	**453**	1.65	0.058	0.982
374	1.64	0.058	0.974	**414**	3.02	0.107	1.799	**454**	1.56	0.055	0.928
375	1.44	0.051	0.857	**415**	3.29	0.117	1.957	**455**	0.36	0.012	0.214
376	0.86	0.030	0.511	**416**	1.01	0.036	0.601	**456**	1.01	0.036	0.601
377	0.42	0.015	0.25	**417**	4.13	0.147	2.461	**457**	0.17	0.006	0.101
378	2.70	0.096	1.607	**418**	0.48	0.017	0.285	**458**	0.60	0.021	0.357
379	1.91	0.068	1.136	**419**	1.51	0.053	0.898	**459**	0.99	0.035	0.589

460	0.39	0.013	0.232	465	0.41	0.014	0.244	470	1.23	0.043	0.732
461	0.21	0.007	0.125	466	0.94	0.033	0.559	471	0.65	0.023	0.386
462	0.25	0.008	0.148	467	0.67	0.023	0.398	472	3.68	0.131	2.190
463	0.26	0.009	0.154	468	1.65	0.058	0.982	473	0.50	0.017	0.297
464	0.31	0.011	0.184	469	0.24	0.008	0.142	474	0.61	0.021	0.363

Fluoride analysis of drinking water of Baluchistan

S.No	F	CDI	HQ	S.No	F	CDI	HQ	S.No	F	CDI	HQ
1	0.62	0.022	0.369	33	0.25	0.008	0.148	65	1.02	0.036	0.608
2	1.78	0.063	1.059	34	0.74	0.026	0.440	66	0.82	0.029	0.488
3	0.17	0.006	0.101	35	0.34	0.012	0.202	67	0.12	0.004	0.071
4	0.37	0.013	0.220	36	1.08	0.038	0.643	68	0.34	0.012	0.202
5	0.66	0.023	0.392	37	0.58	0.020	0.345	69	0.65	0.023	0.386
6	0.99	0.035	0.589	38	0.26	0.009	0.154	70	1.35	0.048	0.803
7	1.65	0.058	0.982	39	0.45	0.016	0.267	71	1.32	0.047	0.786
8	1.80	0.064	1.071	40	0.26	0.009	0.154	72	2.79	0.099	1.661
9	1.01	0.036	0.601	41	0.23	0.008	0.136	73	0.94	0.033	0.556
10	0.30	0.010	0.178	42	0.28	0.01	0.166	74	0.64	0.022	0.380
11	0.77	0.027	0.458	43	1.11	0.039	0.659	75	0.22	0.007	0.130
12	0.30	0.010	0.178	44	0.73	0.026	0.434	76	1.31	0.046	0.779
13	1.29	0.046	0.767	45	0.96	0.034	0.571	77	0.41	0.014	0.244
14	1.27	0.045	0.754	46	1.23	0.043	0.729	78	0.51	0.018	0.303
15	1.13	0.040	0.672	47	1.07	0.038	0.637	79	0.18	0.006	0.107
16	0.90	0.032	0.535	48	0.95	0.034	0.568	80	0.18	0.006	0.107
17	0.71	0.025	0.422	49	0.11	0.003	0.065	81	0.49	0.017	0.291
18	2.57	0.091	1.528	50	1.50	0.053	0.892	82	0.92	0.032	0.547
19	0.69	0.024	0.410	51	1.23	0.043	0.731	83	1.36	0.048	0.808
20	1.64	0.058	0.976	52	0.01	0.0003	0.005	84	0.97	0.034	0.577
21	1.30	0.046	0.770	53	0.33	0.011	0.196	85	0.56	0.02	0.333
22	1.85	0.066	1.100	54	0.83	0.029	0.494	86	0.17	0.006	0.101
23	0.97	0.034	0.577	55	0.79	0.028	0.470	87	1.64	0.058	0.976
24	1.28	0.045	0.763	56	0.47	0.016	0.279	88	0.73	0.026	0.434
25	0.57	0.020	0.339	57	1.22	0.043	0.723	89	0.70	0.025	0.416
26	1.76	0.062	1.047	58	1.58	0.056	0.940	90	0.55	0.019	0.327
27	0.33	0.011	0.196	59	0.24	0.008	0.142	91	0.64	0.022	0.380
28	1.17	0.041	0.696	60	0.65	0.023	0.386	92	0.57	0.020	0.339
29	0.88	0.031	0.523	61	1.32	0.047	0.785	93	0.50	0.017	0.297
30	0.34	0.012	0.202	62	0.76	0.027	0.452	94	1.10	0.039	0.653
31	1.10	0.039	0.654	63	1.61	0.057	0.960	95	0.17	0.006	0.101
32	1.45	0.051	0.863	64	0.28	0.01	0.166	96	0.53	0.018	0.315

97	0.99	0.035	0.589	109	0.66	0.023	0.392	121	0.46	0.016	0.273
98	0.27	0.009	0.160	110	0.41	0.014	0.244	122	0.27	0.009	0.160
99	0.20	0.007	0.119	111	1.20	0.042	0.711	123	0.51	0.018	0.303
100	1.81	0.064	1.077	112	0.72	0.025	0.427	124	0.29	0.010	0.172
101	0.81	0.028	0.482	113	0.13	0.004	0.077	125	0.23	0.008	0.136
102	0.78	0.027	0.464	114	1.29	0.045	0.764	126	0.38	0.013	0.226
103	0.57	0.020	0.339	115	0.05	0.001	0.029	127	0.79	0.028	0.470
104	0.35	0.012	0.208	116	0.28	0.01	0.166	128	0.36	0.012	0.214
105	0.23	0.008	0.136	117	0.88	0.031	0.522	129	0.86	0.030	0.511
106	0.21	0.007	0.125	118	0.15	0.005	0.089	130	0.33	0.011	0.196
107	1.24	0.044	0.739	119	0.16	0.005	0.095	131	0.48	0.017	0.285
108	1.38	0.049	0.820	120	0.56	0.02	0.333	132			

Fluoride analysis of drinking water of Sindh

S.No	F	CDI	HQ	S.No	F	CDI	HQ	S.No	F	CDI	HQ
1	0.39	0.013	0.232	27	0.33	0.011	0.196429	53	0.16	0.005	0.095
2	0.74	0.026	0.440	28	0.24	0.008	0.142857	54	0.16	0.005	0.095
3	0.22	0.007	0.130	29	0.23	0.008	0.136905	55	0.17	0.006	0.101
4	0.31	0.011	0.184	30	0.31	0.011	0.184524	56	0.50	0.017	0.297
5	0.40	0.014	0.238	31	0.36	0.012	0.214286	57	0.25	0.008	0.148
6	0.49	0.017	0.291	32	0.48	0.017	0.285714	58	0.31	0.011	0.184
7	0.51	0.018	0.303	33	1.12	0.04	0.666667	59	0.22	0.007	0.130
8	1.60	0.057	0.952	34	1.41	0.050	0.839286	60	0.33	0.011	0.196
9	0.35	0.012	0.208	35	0.19	0.006	0.113095	61	0.22	0.007	0.130
10	1.67	0.059	0.994	36	0.98	0.035	0.584643	62	0.54	0.019	0.321
11	0.47	0.016	0.279	37	0.76	0.026	0.449821	63	0.12	0.004	0.071
12	0.11	0.003	0.065	38	0.32	0.011	0.190476	64	0.22	0.007	0.130
13	0.38	0.013	0.226	39	50.00	1.785	29.75976	65	0.19	0.006	0.113
14	0.63	0.022	0.375	40	0.46	0.016	0.27381	66	0.07	0.002	0.041
15	1.60	0.057	0.952	41	1.22	0.043	0.729107	67	0.37	0.013	0.220
16	0.76	0.027	0.452	42	1.40	0.050	0.835595	68	0.22	0.007	0.130
17	1.61	0.057	0.956	43	1.22	0.043	0.726131	69	0.33	0.011	0.196
18	2.49	0.088	1.480	44	1.02	0.036	0.609762	70	0.97	0.034	0.577
19	0.19	0.006	0.113	45	0.71	0.025	0.423452	71	0.34	0.012	0.202
20	0.30	0.010	0.178	46	2.00	0.071	1.1875	72	0.40	0.014	0.238
21	1.91	0.068	1.138	47	1.48	0.052	0.880595	73	0.19	0.006	0.113
22	1.35	0.048	0.805	48	1.31	0.046	0.777381	74	0.43	0.015	0.255
23	0.18	0.006	0.107	49	1.60	0.057	0.952083	75	0.31	0.011	0.184
24	1.27	0.045	0.757	50	0.47	0.016	0.279762	76	1.23	0.043	0.732
25	2.15	0.076	1.281	51	1.70	0.060	1.014405	77	0.25	0.008	0.148
26	0.26	0.009	0.154	52	1.77	0.063	1.052679	78	3.68	0.131	2.190

79	1.53	0.054	0.908	**92**	1.15	0.040	0.681	**105**	1.89	0.067	1.12
80	0.62	0.022	0.367	**93**	0.18	0.006	0.107	**106**	0.19	0.006	0.113
81	1.28	0.045	0.759	**94**	1.08	0.038	0.640	**107**	0.04	0.001	0.023
82	0.35	0.012	0.208	**95**	1.29	0.046	0.768	**108**	0.09	0.003	0.053
83	0.32	0.011	0.190	**96**	1.76	0.062	1.046	**109**	0.41	0.014	0.244
84	0.34	0.012	0.202	**97**	1.52	0.054	0.905	**110**	0.47	0.016	0.279
85	1.93	0.068	1.147	**98**	0.05	0.0017	0.029	**111**	1.30	0.046	0.773
86	3.53	0.125	2.099	**99**	0.60	0.021	0.357	**112**	0.28	0.01	0.166
87	1.16	0.041	0.691	**100**	0.45	0.016	0.267	**113**	0.33	0.011	0.196
88	1.14	0.040	0.676	**101**	0.21	0.007	0.125	**114**	0.32	0.011	0.190
89	0.49	0.017	0.291	**102**	0.41	0.014	0.244	**115**	0.39	0.013	0.232
90	0.92	0.032	0.547	**103**	1.70	0.060	1.011	**116**	0.33	0.011	0.196
91	0.17	0.006	0.101	**104**	0.37	0.013	0.220				

This is greater than the 49.3 mg/L concentration observed in Tharparkar (Ahmad *et al.*, 2004). Natural and anthropogenic processes both contribute to the F contamination of groundwater in Pakistan (Siddique *et al.*, 2006), but natural processes have a disproportionate effect on groundwater F contamination (Shah & Danishwar, 2003). F contamination in drinking water is challenging to remediate; the remedy is to manage and track contamination hotspots.

5.3.4 Exposure and Fluorosis risk assessment

The study area considered a total of 938 samples for the purpose of assessing the health risk posed by F in drinking water, which includes CDI and HQ (Table 5.7). The effects of F ingestion via contaminated water on an individual are best predicted by the F exposure dose (i.e., mg per kg body weight per day), the individual's age, the duration of exposure, and the amount of water consumed (L/day).

According to the USEPA, a HQ value greater than one indicates a high risk of adverse health effects, and the probability of adverse effects increases as the HQ value increases. Thus, a HQ value greater than one indicates a high probability that some of the various manifestations of fluorosis will occur, whereas a HQ value less than one indicates a low probability that significant signs or symptoms of fluorosis will develop. In this analysis, CDI and HQ values were used to assess the health risk related to F-contaminated groundwater intake. In our study area, the highest CDI values observe for F exposure was 1.78 mg/kg/day, from Sindh and 1.47 mg/kg/day, from Punjab, while lowest value 0.00035 mg/kg/day, from both Punjab and KP and 0.001 mg/kg/day, from Gilgit-Baltistan respectively, from the different groundwater sources of Pakistan. Our results elaborate HQ value for F exposure ranged from extremely low level of exposure 0.0007 from Gilgit- Baltistan to extremely high level 29.75, from Sindh which shows that the area is at highest risk of developing fluorosis (Table 5.7).

There is little data on the effects of groundwater contamination on Pakistan's most vulnerable populations, due to Pakistan not yet having adopted fluoridation of drinking water. However, a study done in District Nowshera, KP in 2004 discovered that 66% of the 12-15-year-old children had fluorosis, of which was caused by excessive F intake from F containing tap water (Khan & Khan, 2004). Numerous endemic fluorosis indices were also found to be highly prevalent in various populations in certain areas of Lahore with extremely polluted groundwater with F (Rashid & Rizwan, 2013).

5.4 Conclusions

Contamination of groundwater with As and F has become a serious problem in Pakistan, as it has in many other parts of the world. While geological and geochemical processes are the primary sources of As and F in groundwater, anthropogenic pollution sources such as industrial wastes significantly contribute to the problem. In Pakistan, groundwater is the primary source of drinking water. The concentrations of F and As in groundwater are not constant and vary significantly by source and location due to a variety of factors such as temperature, rock weathering, and ion exchange. Due to As and F contamination, the majority of groundwater sources are unfit for human consumption.

The elevated As and F content of Pakistan's groundwater sources poses a substantial health risk to the population exposed. Because of the high CDI, HQ, and CR values for F and As, immediate action is required to reduce the risk of As and F-induced toxicity in men. It is recommended that comprehensive testing of all water sources be conducted to determine the levels of As and F in Pakistan. It is appropriate that the government take measures to keep As and F at drinking water level, as well as to raise public awareness of the health problems associated with ground water contamination.

5.5. Recommendations

Most of the water supplies on earth are contaminated with As and F. F and As are downed by millions of people. Approximately 200 million people are at risk of fluorosis, in more than 25 countries around the world which includes India, China, Bangladesh and Pakistan as the badly effected regions. Researchers claimed that As is present in at least 70 realms containing more than 140 million individual's majority of whom reside in Asia (Rasool, A. *et al.*, 2017).

- Switch to an alternative source of water free from As and F contamination, like rainwater harvesting, especially in areas where As and F concentration are naturally high in soil and water. China, Bangladesh, and west Bengal are naturally enriched with As and F.

- Elimination of As and F from existing water sources via application of different technologies i.e., Ion Exchange, Electrodialysis and Oxidation/Filtration, Activated Alumina, Lime Softening, Coagulation/Filtration and Reverse Osmosis having removal capacity more than 80%.

- Changing the way, you cook is a good way to reduce F and As exposure.

- Long-lasting effective solutions require concerted government-led action, based on sound local knowledge, involving communities and systemic IM with partners from all sectors involved in water supply (for example, farming) and public health (e.g., nutrition).

- Reduce use of As and F in fertilizers as they are adding up to the content of these toxins in soil and water and hence pollute ground water and aquifers.

- Carefully manage and handle mining activities and industrial processes to avoid any outbreak of these toxins in natural environment.

- Awareness programs should be launched to provide awareness on ground level about lethal impacts of As and F on health. By disseminating knowledge on health risks associated with As and F exposure, a successful public-awareness campaign could change health behaviors.

- Government should conduct studies to indicate the areas which are at high risk, meanwhile they should display sign boards to make public aware about the risk prevailing in their area.

CHAPTER-6

Arsenic and Fluoride mitigation technologies

6.1. Introduction

Multiple natural and anthropogenic activities cause metaled contamination of ground surface and drinking water exposing the humans to toxic health hazards. As and F are the primary contributors to the global water crisis, and these chemicals pose serious health risks when consumed in drinking water. This problem has been exacerbated by many countries' increasing reliance on ground water.

As and F are present (in high quantities) simultaneously in groundwater in many parts of the world. Main cause of the combination of these pollutants in the groundwater can be naturally occurring or anthropogenic. As is a pollutant that takes on a variety of forms depending on the redox potential and pH of the groundwater. Whereas, the high concentration of F in groundwater is due to the presence of calcium (Ca) in poor aquifers and may also increase when a sodium (Na) calcium cation is exchanged.

Numerous technologies and techniques are in use currently to mitigate the two (As & F) contamination from the water which includes Chemical treatments and Physical treatment. Both shall be discussed in detail in the chapter with their possible best outcomes and effectiveness in the process.

6.2. Materials and Methods:

Under laboratory and field conditions, a variety of traditional and advanced treatment methods for removing As from ground water have been suggested. Ozone, Chlorine and other chemical approaches, as well as physical methods like UV treatment and other filtration techniques like membrane filtration, reverse osmosis, adsorption, flocculation and ion-exchange, are all popular methods for removing As from polluted water. The parts that follow will illustrate and review some effective and realistic As mitigation techniques. The success of current techniques, as well as their shortcomings, are further detailed.

6.3. Arsenic Mitigation:

6.3.1. Arsenic Mitigation by Oxidation

Since As (III) is the predominate type of As at neutral pH and adsorption of As (V) onto solid surfaces is easier than As (III) (Sharma *et al.,* 2007), oxidation of As (III) to As (V) is a typical pretreatment phase in most As mitigation technologies. As a consequence, adsorption followed by oxidation is deemed effective for reducing levels of As.

$$H_3AsO_4 + 2H+ + 2e- \rightarrow H_3AsO_3 + H_2O$$

Arsenite can be oxidized in the atmosphere by oxygen, ozone, or chemical oxidants. Chlorine, chlorine dioxide, hydrogen peroxide, hypochlorite, potassium permanganate and Fulton's reagent are commonly used in this purpose because of their low cost and ease of accessibility.

H_3AsO_3 + ½ O_2 = H2AsO4- + 2H+ H_3AsO_3 + HClO = $HAsO_4$ $^{-2}$ + Cl $^{-}$ + 3H+

$3H_3AsO_3$ + $2KMnO_4$ = $3HAsO_4$ $^{-2}$ + $2MnO_2$ + 2K+ + 4H+ + H_2O

In dirty water, air and O_2 can oxidize 54-57 percent of As (III) to As (V), but only ozone can complete oxidation (III) (Dodd *et al.,* 2006). However, because of the high energy supply, this process is very costly and mitigation of residual ozone and toxic.

In general, oxidation with atmospheric air is a very slow process compared to chlorine and permanganate under wide range of conditions. However, since the use of chlorine dioxide in surface water is forbidden, American environmental agencies pay close attention to this problem. Permanganate, ammonia, and ozone are all slower than chloramine and hydrogen peroxide. It is widely accepted that while free chlorine or hypochlorite is extremely effective at oxidizing As (II), ozone is extremely effective at oxidizing As (III). However, since the use of chlorine dioxide in surface water is forbidden, American environmental agencies pay close attention to this problem. When manganese dioxide-coated sand is mixed with Iron compounds, it becomes an effective oxidizing agent since the treated materials are simple to handle. However, another treatment phase is required to clear Mn from the water in this process. When it comes to As reduction, using $FeO_4{}^{2-}$ to purify water is recommended. The most critical phase for eliminating As from drinking water around the world appears to be HFO (hydrous ferric oxide). It is well known that high As in the shallow aquifer encountered iron oxides, which may contribute to As mitigation.

As a result, oxidation is a very efficient method for removing As from water. This phase is influenced by interfering particles in the water, such as sulfide (HS and S^{-2}), Fe (II), dissolved organic carbon, Mn (II) and total organic carbon (TOC). The oxidation rate of As (III) by ozone is significantly reduced when S^{2-} and TOC are present (Dodd *et al.,* 2006). Thus, for the appropriate selection of oxidizing agents to accomplish high mitigation efficiency by oxidation it is very important to consider hydrophyte chemistry and water composition.

6.3.2. Solar Oxidation Technique

Several results of research have investigated the photochemical and photocatalytic oxidation of As (III). The oxidation rate of As (III) with oxygen is increased by UV irradiation. This procedure can be catalyzed using sulfite, ferric iron or citrate. In case of solar light hydroxyl radicals generate by the photolysis of Fe (III) species. In the presence of hydroxyl radicals, the rate of oxidation is catalyzed. When As-polluted water in perchlorate and perchloric solutions with a pH of 0.5-2.5 is treated with Fe (III) and then exposed to solar light, the rate of As mitigation increases. If lemon juice is applied after exposure of solar light the mitigation rate of As from water becomes higher, this happens as lemon juice (citrate) reacts with sturdily oxidizing radicals, it releases more radicals. (Miller *et al.,* 2011). several studies have looked into the adsorption of As on TiO_2 after photocatalytic oxidation of As (III) to As (V) and TiO_2. This method will lower

As levels in drinking water to levels below the WHO's recommended cap (Miller et al., 2011). A TiO_2-impregnated chitosan bead (TICB) was made and used to reduce the amount of As in aqueous solution. This research found that when UV light is present, a greater amount of As is adsorbed due to the increased surface area of the TICB, and TiO_2 was able to photo-oxidize more As (III) to As (V). In comparison with a solution which has not been UV-exposed. Nano-crystalline Al_2O_3 and TiO_2 impregnated chitosan was prepared for As mitigation in another sample.

Numerous factors, including initial As concentration, pH, natural organic material (NOM) and anions, affected the rate of "As(V)" adsorption on "TiO_2" (Miller *et al.,* 2011). Due to incomplete oxidation, the TiO_2/UV system has an ineffective As mitigation when there is a very low volume of TiO_2 (Guan et al., 2012). Furthermore, an acidic pH was more successful for As (V) adsorption on the TiO_2 surface. The photocatalytic oxidation of As (III) and the adsorption of As on TiO_2 dependent adsorbent are affected by the existence of silicate, fluoride, and phosphate bicarbonate. Moreover, the treatment required for mitigation of As residues is very complex. Due to several limitations, only oxidation is not considered as a highly effective procedure for mitigation of As.

6.3.3. In-Situ Oxidation

The tube well water is required to oxygenate arsenite to arsenate by the oxygen content of the air, and the ferrous iron in the aquifer is oxidized to ferric iron in the in-situ oxidation phase of As and iron (Nicomel *et al.,* 2016). As a result, the amount of As in tube well water decreases. The oxygenated water which containing As, and iron is flow back into the same tube well. When water is extracted again from the tube well, because of underground precipitation and adsorption on ferric iron, As concentrations will be low. The probable reactions of hydrous iron oxide with arsenate are shown below.

$$Fe(OH)_3\,(s) + H_3AsO_4 \rightarrow FeAsO_4.2H_2O + H_2O$$

$$FeOH^0 + AsO_4^{-3} + 3H^+ \rightarrow FeH_2AsO_4 + H_2O$$

$$FeOH^0 + AsO_4^{-3} + 2\,H+ \rightarrow FeHAsO_4 - + H_2O$$

This process is suitable where the source of water is tube well or deep wells and others. To avoid contamination of the subsurface by introducing microbes from the surface care must also be taken. Some pore spaces may also become clogged with precipitates if dissolved iron levels are high in water. This method has limited potential for As reduction; however, the findings suggest that As levels in the groundwater zone can be reduced prior to water extraction (Sharma *et al.*, 2007).

6.3.4. Arsenic Mitigation by Biological Oxidation

Arsenate respiring bacteria (ARD) like Geospirillum barnesi, Geospirillum arsenophilus, Bacillus arsenicselenatis, Desulfutomaculum auripigmentum and Crysiogenes arsenatis can connect anaerobic oxidation of organic substrates to arsenate reduction. (Oremland *et al.*, 2009). Chemicals in drinking water treatment are often prohibited due to the formation of harmful byproducts. To carry out biological oxidation of As, many species of bacteria have been used. Bacterial activity helps to extract As from water by acting as a catalyst. Microorganisms like Gallionella ferruginea and Leptothrix ochracea speed up the biotic iron oxidation process (Ekhlas *et al.*, 2014; Katsoyiannis *et al.*, 2004).

Iron oxides and microbes were deposited in a filter medium with an injectable setting for As adsorption. As (III) is oxidized to As (V), which is adsorbed on Fe by these microorganisms (III). As a result, As levels are reduced by up to 95%. Bacterial oxidation of As (III) assisted by sorption onto biogenic manganese-oxides to mitigate As (V) was also investigated (Sharma *et al.*, 2007). Biological oxidation is a new method for oxidizing iron and manganese as an As mitigation method. These bio treatment methods are natural biological mechanisms, and the removal of metals from soil and groundwater by some plants and microorganisms takes a few days. During recovery, the following chemical reactions occurred in the treatment system:

a) Fe (II) to Fe (III) and Mn (II) to Mn (IV) (oxid.)

b) As (III) to As (V) (oxidation)

c) MnO2 (Precipitation)

d) Abiotic oxidation of As (III) by MnO2

e) As (V) sorption via MnO2

This natural process for treatment can lead to up-to 95% of the mitigation of As (Pallier *et al.,* 2010). The effect on the extraction of As (III) and As(V) from groundwater from biological oxidation was examined by dissolved Fe and Mn in a pipe reactor (PR) following the microfiltration. The new PR-MF method effectively eliminates Fe, Mn, and As without the use of toxic chemicals for oxidation or pH modification, and there is no need for regeneration or backwashing.

6.3.5. Arsenic Mitigation by Coagulation–Flocculation

Another commonly used treatment for eliminating As from ground water is coagulation accompanied by flocculation (Andrianisa *et al.,* 2008; Baskan and Pala *et al.,* 2010; Lakshmanan *et al.,* 2010; Lacasa *et al.,* 2011). It's usually used for larger facilities, and it necessitates the development of a floc to mitigate As in groundwater. This process usually involves Fe and Al based coagulants, such as ferric chloride, ferric sulfate, and aluminum sulfate, among other chemical coagulants. These chemicals must be applied to water and dissolved for 1-10 minutes with vigorous stirring. The negative charge of colloids in this stage should be decreased by cationic coagulants and larger particle aggregation results (Choong *et al.,* 2007). This technique is capable of removing more than 90% of As (V) and 77% of As (III).

Efficient mitigation requires oxidation of As (III) to As (V) with the addition of hypochlorite or potassium permanganate. Aluminum chloride and poly aluminum chloride are also capable of lowering As levels below the MRL (Hu *et al.*, 2012). When kaolinite and $FeCl_3$ are used as coagulants/flocculents, the mitigating performance for As (V) and As (III) is over 90% and 77%, respectively (Pallier *et al.*, 2010). Iron based coagulants have been shown to be more effective than Al-based coagulants in water treatment (Katsoyiannis *et al.*, 2004).

For effective As removal from water, As must be adsorbed on amorphous metal hydroxides formed by coagulant. The consistency and pH of the water before coagulation affect the rate of As mitigation. The presences of organic matter in groundwater also affect the mitigation efficiency of this technique. The optimum mitigation was observed at pH below 8.5. Since coagulation contains significant sludge with a high level of As, this method has a major disadvantage. The control of this sludge is essential to avoid secondary contamination of the atmosphere, and the sludge treatment process is costly (Mondal *et al.*, 2013). Furthermore, in many situations, lowering the As concentration to an appropriate amount using this technique becomes difficult (Shakoor *et al.*, 2017).

6.3.6. Adsorption

Water is flowed through a fixed bed of solid adsorption material filled in a column in the adsorption process (Shakoor *et al.*, 2017). Solutes adsorb on the adsorbent surface and its concentration become reduces in the solvent (Ungureanu *et al.*, 2015; Dong *et al.*, 2009). For treating As contaminated water, activated carbon, Iron-based adsorbents, and low-cost materials such as agricultural wastes and byproducts industrial waste and byproducts, mud, etc. have been used as adsorbents (Khosa *et al.*, 2014; Zongliang *et al.*, 2012; Liu *et al.*, 2012; Ranjan *et al.*, 2009; Chutia *et al.*, 2009; Sasaki *et al.*, 2009; Banerjee *et al.*, 2008; Haque *et al.*, 2007). Nanoparticles and nanomaterial based absorbents have also been investigated for the mitigation of As such as nanoparticles, zero valent iron (ZVI) nanoparticles, iron oxide based nanoparticles, cupric oxide, titanium oxide nanoparticles, zirconium oxide nanoparticles during the flow of water through adsorbent column, As in water are adsorbed onto the surfaces.

Adsorption is the most used method for As reduction because of many benefits, including comparatively high As vindication efficiencies, ease of operation and handling, cost-effectiveness, and no sludge output (Anjum *et al.*, 2011; Jang *et al.*, 2008). The effectiveness of this approach is determined by the particle size, density, adsorbent's surface area, mineralogy, pore characteristics, surface functional group characteristics, zeta potential and other factors, as well as the solution's ionic strength, temperature, As concentration, and pH. (Giménez *et al.*, 2010; Zhu *et al.*, 2014). The formation of other ions such as HCO_3^-, silicate, Ca^{2+}, phosphate, and affects the As adsorption rate and the ability of adsorbents.

Sub techniques under adsorption are:

a) Activated Carbon:

Activated carbon is graphite with amorphous structure with a wide range of pore sizes. Activated carbon is used either in powdered or granular form for As mitigation.

b) Activated Alumina:

Arsenic was successfully extracted from ground water using activated alumina (AA) (Xie *et al.*, 2013). Activated alumina is an aluminum oxide (Al_2O_3) granule with a strong sorptive surface. This is a good way to get rid of As from water with a lot of suspended salts. (Golami *et al.*, 2009).

c) Natural Wastes and Agriculture Wastes:

The use of agricultural waste as an adsorption medium for reducing As in wastewater has been explored as a cost-effective solution. Ketones, Aldehydes, alcohols, carboxylic, phenolic groups and ether were found in lignin and cellulose in agricultural material, which could bind heavy metal ions by complex formation. (Ahluwalia *et al.*, 2005). Because of its simplicity, low cost, high performance, versatility, and recovery, the technique has an advantage over others (Gueye *et al.*, 2016). For the purpose of heavy metal mitigation agro-wastes are used as adsorbents such as, sawdust, orange peel, banana peels, rice straw, seaweed, potato peel, bark and wood, corn cob, tea waste, jatropha oil cake, olive cake, maize, sugarcane bagasse, sugar beet pulp, activated sludge, almond shells, saltbush, rice husk, tamarind hull, olive pomace, marine algal biomass, cactus leaves, wool, sawdust, pine bark and seafood processing waste sludge, charcoal and pine needles.

d) Ion Exchange:

In ion exchange, through dissolved ion the reversible displacement occurs of an ion that will adsorb on the surface of solid materials. Solid base anion exchange resins, in which the oxyanionic compounds of arsenate are actively substituted with the anionic activated functional group of the resin, are widely used for the treatment of As.

e) Membrane Filtration:

Membrane filtration technique is also used for the mitigation of As from groundwater. Man-made membranes contain billions of pores which enable certain dissolved compounds to move, while preventing pollutants from infiltrating. The driving force required for the transportation of water through the membrane is the pressure variance between the feed and permeate sides. There are two distinct forms of pressure-driven membrane filtrations.

(i) Low-pressure membrane processes, for example microfiltration (MF) and ultrafiltration (UF)

(ii) (ii) High-pressure membrane processes, for example reverse osmosis (RO) and Nano filtration (NF) (Shih, 2005).

f) Reverse Osmosis:

A high-pressure procedure that can effectively strip dissolved As from water is known as Reverse Osmosis. Water RO membranes can effectively strip both As

(V) and As (III) (up to 99 percent) (BAMWSP, 2001). The separation is regulated by size exclusion rather than charge interaction in this case. Charged membranes normally reject charged solutes more effectively than non-charged solutes (Seidel *et al.*, 2001). The pore size in the membrane has no impact on As rejection; rather, charge exclusion predominates over the size exclusion method.

g) Nano-Filtration:

NF is effective at removing dissolved compounds with molecular weights greater than 300 g/mol from water. NF membranes are normally negatively charged in acidic and alkaline solutions. Electrostatic repulsion between the anionic As species and the charge of the membrane causes As separation in this case. When it comes to pH and ionic strength of the solution, NF is more susceptible than RO. As (V) had stronger rejection than As (III), and As (III) cannot be converted to MCL (Uddin *et al.*, 2007). As a result, pretreatment with As (III) to As (V) is necessary.

Table 6.1 summarizes the comparison of some effective available techniques based on expense, suitability and percentage of As mitigation.

Table 6.1: summarizes the comparison of some effective available techniques based on expense, suitability and percentage of arsenic mitigation.

PERFORMANCE AND EFFECTIVENESS OF ARSENIC CONTAMINCATION REMOVAL TECHNIQUES					
S.No.	**Techniques**	**Removal Efficiency of As (III)**	**Removal Efficiency of As (V)**	**Relative Cost**	**Operating Skill**
1	Oxidation	Less than 30%	60% to 90%	Low	Low
2	Solar Oxidation	Less than 30%	60% to 90%	Low	Low
3	In-Situ Oxidation	60% to 90%	Greater than 90%	Medium	Medium
4	Biological Oxidation	Less than 30%	60% to 90%	Low	Low
5	Coagulation Flocculation (Iron/Alum)	Less than 30% / 60% to 90%	Greater than 90%	High	High
6	Adsorption-Activated Carbon	Less than 30%	Greater than 90%	Low	Low
7	Adsorption-Activated Alumina	60% to 90%	Greater than 90%	Medium	Low
8	Adsoprtion-Natural Waste and Agriculture Wastes	60% to 90%	22.8% to 82%	Low	Low
9	Adsorption-Ion Exchangers	Less than 30%	Greater than 90%	High	High
10	Adsorption-Membrane Filtration	60% to 90%	60% to 90%	High	Medium
11	Adsorption-Reverse Osmosis	60% to 90%	60% to 90%	High	High
12	Adsorption-Nano Filtration	60% to 90%	60% to 90%	High	High

6.4 Fluoride Mitigation

Fluoride is crucial for the body's normal growth and development. F is abundant in the atmosphere, and the F level in drinkable water is the primary contributor of regular F intake. The activity of F ions in the human body can be defined as a "double-edged sword." In small doses, F is safe, but in large doses, it is harmful. Fluorosis develops as a result of excessive F intake in different ways. Fluorosis is a significant public health problem in 24 countries, including India, which lies within the F belt. F is being removed from water using a variety of methods, but the issue has yet to be solved. The methods most widely used to minimize F excess pollution from ground water are listed below. The following categories can be used to categorize defluoridation methods.

1. Adsorption technique

2. Ion-exchange technique

3. Precipitation technique

4. Other techniques, which include Reverse Osmosis and electro chemical defluoridation.

6.4.1 Fluoride Mitigation by Adsorption:

This procedure is based on the adsorption of F ions onto the surface of an active agent. In the adsorption process, raw water is passed through a bed containing defluoridating material. F is retained in the content through physical, chemical, or ion exchange processes. After a period of use, the adsorbent becomes saturated and must be replenished.

a. *Activated Alumina:*

Activated alumina (Al_2O_3), which has been used for defluoridation since 1934, is made by dehydrating aluminum hydroxides at low temperatures (300-600°C). The F removal process is considered to be a ligand exchange response at the surface of activated alumina.

b. *Bone Char:*

Bone char is made from ground animal bones that have been burned at a high temperature (5000°C) to extract organic matter. The F removal procedure requires the F ion replacing the carbonate of bone char. Caustic soda is used to restore depleted bone char. In the 1950s and 1960s, bone char was used to defluoridate drinking water in the United States. On the other hand, the Intercountry Centre for Oral Health (ICOH) established the first domestic water defluoridation unit, primarily using bone char.

c. *Calcined Clay:*

The aluminum oxide (Al_2O_3) in the brick soil is stimulated during the burning process and adsorbs excess F from the fresh drinking water. If the F concentration of raw water is 2.5 ppm, filter media should be changed after three months (WHO, 1985). In Sri Lanka, fresh-fired brick parts were used to remove F from domestic defluoridation systems.

d. Mud Pots:

Collection and storing of water in mud pots is an ancient method. Red soil and clay are used to prepare the mud pots. The raw pots are subjected to heat treatment as in the case of brick production. Hence, the mud pots also act as an adsorbent media. The major advantages of mud pots are they are economic and readily acceptable for the rural communities.

e. Natural Adsorbents:

A relatively unknown technique with potential utility, particularly in third world rural communities, has piqued researchers' interest in recent years i.e. plant-based (natural) defluoridation. Plants can be grown locally as needed, and production and transportation costs can be kept to a minimum. Additionally, the use of plants for defluoridation may gain widespread acceptance and application by local communities. Numerous natural adsorbents derived from a variety of trees and animals have been investigated as defluoridation agents.

6.4.2 Fluoride Mitigation by Ion Exchange:

Various ion exchange materials have been investigated, including bone, bone char, and anion and cation exchange resins such as carbon, defluoron-1, and defluoron-2. F in drinking water can be removed using a strongly basic anion-exchange resin containing quaternary ammonium functional groups. The removal takes place according to the following reaction:

$$\text{Matrix-NR}_3\text{+Cl}^- + \text{F}^- \rightarrow \text{Matrix-NR}_3\text{+F}^- + \text{Cl}^-$$

The ions of F substitute the ions of resin chloride. This process goes on until all the resin sites are occupied. The water is then used to re-wash the resin using salt containing dissolved sodium chloride. New chloride ions replace then the F ions which cause the resin to recover and restart the process. The powerful electronegativity of the Fs is the driving force for the substitution of chloride ions from the resin.

6.4.3 Fluoride Mitigation by Precipitation

Chemicals applied to raw water allow the F salt to precipitate as insoluble fluorapatite, which is then extracted from the water. Commonly used materials in precipitation technique are Aluminum Chloride, Aluminum salts (e.g. Alum), Poly Poly Aluminum Hydroxy sulphate, lime and Brushite.

a. Nalgonda Technique:

Nalgonda Technique involves the addition, following the quick blending, flocculation, sedimentation, filtration and disinfection of aluminum salts and lime and bleaching powder. Aluminum salt may be added to or combined with aluminum sulfate (alum) or aluminum chloride. The F is removed from the water. For large communities, the technique for filling and drawing is highly versatile and includes small communities, defluoridation plant for rural water provision, domestic defluoridation unit, etc.

b. Contact Precipitation:

Calcium and phosphate compounds, leading to F precipitation is recently reported as the technique by which F is removed from water. The water is then filtered by the bone char pre-saturated with F. The presence of saturated bone carbon dioxide is a catalyst for F precipitation either as CaF2 or as fluorapatite. The process uses spools, column filters or both (developed by WHO; 2006).

c. IISc Method:

Magnesium oxide, calcium hydroxide and sodium bisulfate are used in this method. By precipitating F as insoluble magnesium, magnesium Oxide is used to remove dissolved F ion from water samples.

$$MgO + H_2O \rightarrow Mg\ (OH)_2\ 2NaF + Mg(OH)_2 \rightarrow MgF_2 + 2NaOH$$

At Kolar, Karnataka, an easy to use household defluoridation device based on the IISc Method was designed to treat 15 liters of F polluted water.

6.4.4 Membrane process

Many conventional water purification methods have been employed to solve the present groundwater pollution issues, but none is readily used by the general public and has no or a lengthy payback period. Over the last decade, RO process has been chosen for safe drinking water with no other issues. The RO process relies on applying pressure to the feed water to the membrane to get the contaminants out. As a result of the applied pressure to the concentrated side of the membrane, which overcomes the natural osmotic pressure, the process is the inverse of natural osmosis. The RO membrane rejects ions based on their size and charge. Cost, recovery, rejection, raw water characteristics, and pretreatment all influence membrane selection. The efficiency of the process is determined by a variety of factors, including the characteristics of the raw water, the pressure and temperature of the water, and the frequency of monitoring and maintenance.

Two types of membranes are available for removing F from water: NF and RO. In comparison to RO, NF is a relatively low-pressure process that concentrates on the removal of larger dissolved solids. On the other hand, RO operates at higher pressures and rejects all dissolved solids. Numerous researchers have documented F removal efficiencies of up to 98 percent using membrane processes. Previously, the use of membrane technology for water treatment, particularly for drinking water production, was considered uneconomical in comparison to conventional methods, but increased demand and contamination of water, increased water quality standards, and the problems associated with conventional methods have prompted a reconsideration of membrane technology for water purification. The progressive advancements in the design and material composition of membranes have made the water treatment process economically viable and extremely reliable. Additionally, the capital and operating costs of RO plants continue to decrease as plant capacity increases. Thus, with improved management, this novel method of producing drinking water may be the best option. Additionally, membrane processes have a number of advantages over other methods of treatment.

6.4.5 Other techniques of defluoridation of water:

Water is defluoridated using physical methods such as reverse osmosis, electrolysis & electro dialysis, and distillation (Ngoc and Suzana, 2016). While they are effective at removing F salts from water, certain procedural limitations prevent their widespread use.

The comparison of some effective available techniques based on expense, suitability and percentage of F mitigation techniques summarized in Table 6.2.

Table 6.2: summarizes the comparison of some effective available techniques based on expense, suitability and percentage of Fluoride mitigation techniques

PERFORMANCE AND EFFECTIVENESS OF FLUORIDE CONTAMINCATION REMOVAL TECHNIQUES				
S.No.	**Techniques**	**Removal Efficiency of F**	**Relative Cost**	**Operating Skill**
1	Adsorption-Activated Alumina	90%	Medium	Medium
2	Adsorption-Bone Char	90%	High	High
3	Adsorption-Calcined Clay	90%	Medium	Medium
4	Adsorption-Mud Pots	90%	Low	High
5	Adsorption-Natural Adsorbents	90%	Low	Medium
6	Ion Exchange Method	90% to 95%	High	High
7	Precipitation-Nalgonda Technique	40%	High	High
8	Precipitation-contact Precipitation	50%	High	Medium
9	Precipitation-IISc Method	50%	High	Low
10	Membrane Process- Reverse Osmosis	98%	Medium	Low
11	Physical-Electrolysis	90%	High	High
12	Physical-Electro Dialysis	80%	High	High
13	Physical-Distillation	80%	High	High

6.5 Conclusion

Arsenic and fluoride-polluted water must be dealt immediately in Pakistan. While As and F contamination is a significant problem, a variety of approaches, drawn from fields as disparate as chemistry, bacteriology, and geochemistry, are required to overcome it. To remove As and F from water, soil, and sediment, phytoremediation techniques can be used e.g. As-tolerant dissect plants can be used. Phytoremediation is a potential cost-effective option for removing As and F from water. Water hyacinth can be used as an alternative adsorbent for aqueous F immobilization when water hyacinth is doped with hydrous metal oxide. Activated carbon made from citrus limetta peel waste could effectively remove F from water. Also, it has been shown that the cement-paste mud pot is an effective F-remover. When it comes to removing As and F, combining biological and chemical treatment is a frequently successful approach. The absorbent granular activated carbon (GAC) or ferrous sulfate (FeS) are excellent for removing aqueous As (80–96% efficiency). Additional options include rainwater harvesting, use of As and F-safe aquifers, and surface water. Inadequate monitoring is dangerous. In order to meet the sustainable development goals (SDGs) and safe drinking water framework, government and non-government organizations must work with researchers to ensure proper As and F mitigation in the high risk areas of Pakistan. Sustainable Development Programs (SDPs) for safe drinking water should be maintained by all governments and non-government agencies, like PCRWR and UNDP etc.

CHAPTER-7

Conclusions and Recommendations

Political will is hard to come by and charities work in. There are two ways to reduce water contamination: create new policies and shift power to lower levels. Additional attempts are under way, on grass root level include providing underground plumbing and filter water to drought-afflicted areas. The next measures include the prohibition on industrial use of groundwater, agricultural pesticides, control of groundwater, planned cities, and industrial waste policies.

7.1. Policies and laws

As opposed to surface water, which is usually contaminated, groundwater is the major source of water for household, commercial, and agricultural use in Pakistan. Groundwater is still used by a significant portion of the population. There is a scarcity of explicit rules for underground water and regulations tend to be lacking in detail. In order to be able to tackle potential problems with water contamination, it is important to be aware of both the long-term and short-term issues.

Pakistan's water policy was developed at the federal level and drinking water was declared a fundamental human right in 2009. Prior to the coming into effect of power of the repeal of the 18th amendment, the policies of the provinces have been adopted (Jabeen *et al.,* 2015). Industries particularly waste disposal and cement factories use subterranean water, as well as hydrothermal power plants. As a result, the water table drops dramatically, and the water's consistency deteriorates.

The laws and policies governing the monitoring and protection of water resources fall into two groups. Government agencies responsible for policy making and resource distribution, as well as Non-Governmental Organizations (NGOs) that provide policy guidance and enter areas where bureaucracy is unable to reach and respond in a timely manner. Collaboration between the two is crucial for enacting environmental regulations and maintaining secure water supply. They act as a check on one another, ensuring transparency and prompt action. Concerning As and F contamination, government organizations operating in rural Sindh and Punjab have produced useful data that has served as a policy guide for environmental policy changes and clean water provision projects.

7.2. On-the-ground efforts

Apart from creating laws and regulations that govern industries that produce As and F contamination, work on minimizing exposure is also to be done. The following steps fall into two categories i.e. the things we must do to mitigate the effects of the disaster, namely: preparedness and mitigation. Typically, water conservation and water quality strategies employ filtration plants, rain catching facilities, and deep wells. While community engagement is critical in the implementation of management policies for protecting the environment, location assessment is needed for monitoring and treating water pollution as well.

i. Measures aimed at mitigating risks

As previously noted, one of the top priorities for As and F pollution management is mitigation measures, which include swift action in impacted areas to minimize population exposure.

a. Plants for Filtration

The filtration techniques are an effective and fast way to resolve the As and F contamination. They may meet the needs of a substantial population and an extended period of time. It is focused on the population density and the state of the groundwater in the area (Hashmi & Pearce, 2011). On a daily basis, the filtration plant should be maintained. As recommended by the WHO, it decreases the As and F content in the water.

However, this approach does have some obvious disadvantages. Since Pakistan is a developing country with regular power outages, filtration plants cannot operate without a reliable and continuous supply of electricity. Second, filtration plant maintenance is often complicated and costly, requiring expensive filters and technical support. Additionally, the filter's sludge is difficult to treat safely away from the community. However, water filtration plants are commonly used in Pakistan (Hashmi & Pearce, 2011).

b. Rainwater harvesting

The rainwater catchment (or harvesting system) consists of simple trenches (or "burrows") where water collects in individual trenches (or "saps"). Another way to ensure enough and drinkable water supply is by means of rainwater harvesting. This also benefits reducing the maintenance because the rain catchments can be installed on the roofs of the facilities. As an added drawback, however, it is not in use in the industry because of obvious shortcomings. Both the microbiological pollution of stored water, the unanticipated frequency of rain, and water that takes on new qualities and new properties with changing rainfall. Where should we build water catchments? It depends on how small the city is. It is used in Baluchistan and the Indus Valley area where water supply is hard to come by and go.

c. Tube-wells

As and F pollution are also mitigated using this process. Very often, deep wells are implemented for quality control purposes. Additionally, maintenance is very cheap. where large populations have access to a single source of fresh water, no waterborne pathogens or pollutants enter the groundwater.

d. The electrocoagulation technique

The use of electricity to extract As and F is another approach that scientists have tested and has shown encouraging results. The procedure has been shown to remove not only As and F, but also other heavy elements and ions. However, the disadvantages of such strategies outweigh the advantages. The key disadvantage is the use of electrical energy; however, this process produces potable water at a slower rate and only for a small population, rendering it unsuitable for field use.

7.3. Administrative policies

Usage of water policy has a longer-term effect on As and F pollution. Such regulations have been in place for several years to reduce the As or F content in the subsurface aquifers. These long-term policies include continuity, the assistance of non-governmental organizations, and constant monitoring and data generation.

i. Management of floodplains

Flooding basins help to reduce the amount of As and F in sub-ground aquifers. If the floodwaters rise, subsurface water supplies also rise. River infrastructure and management during the monsoon season would be severely undermined. Historically, there have been 0.013 billion cases of As-related illness on the bank of the Indus river (Khan *et. al,* 2017). More than 2.7% of the resources in the river Indus river are polluted with 50ug/l As due to the combination of polluted river water with groundwater (Ahmad *et al.,* 2004). This means policies that are concerned with river flow and water-level regulation monitoring and locating critical hot spots must be a long-term undertaking (i.e. integrated partnership between governmental and non-governmental organizations).

ii. Predictive mapping and ground truthing

The predictive mapping approach is extremely affordable and offers long-term data. Several models are being used by different researchers throughout the world. Collecting this data would aid in policy development of mitigation strategies. This system tracks the tube wells in the affected areas and collects and tests samples on a daily and predetermined schedule (Van Geen *et al.,* 2002). According to the data, tube wells are judged to be critically polluted, of low risk, and "extremely contaminated". If the As and F level continue to rise, the water supply is withdrawn and replaced with another before an alternative source of water is established (Hassan, 2005).

iii. Participation of community

Another thing to consider when preparing a mitigation strategy is participation of the local communities. The importance of participation of the people in the process of creating the result means that something important is a matter of public concern, and, thus, should be addressed by the public (George *et al.*, 2012). A million people determine each day which behaviors are better for their wellbeing based on what they think is good for others, such knowledge needs to be disseminated. New initiatives and technical innovations are required in order to enable the group to participate in on the decision-making process; we must give our consumers all the knowledge necessary to allow them to become active participants (Rammelt & Boes, 2004).

iv. Policies in industry and mining

Industries and mining are two of the country's biggest financial contributors. It creates jobs and generates income and investment. Industries are the center for jobs and have a special status in countries such as Pakistan. They earn subsidies and no environmental sanctions are enforced. This is primarily to maintain high and low production costs (Hameed & Raemaekers, 1999).

But the untreated effluents are discharged into the potable water supply. Industrial effluents are the primary cause of heavy metal pollution in Pakistan's major cities (Rehman *et al.*, 2008). Industry-specific legislation is required to regulate the use of water and wastewater treatment prior to their inclusion in the public water supply. This will help to reduce the cost of health-related expenses associated with As and F pollution (Farooqi *et al.*, 2009).

v. Governmental and nongovernmental collaborations

Before beginning a blanket and specific initiative, it is usually required to have a substantial GIS effort in place. National and international organizations are involved in this reaching the groundwater pollution hotspot. Government organizations working with NGOs offers several advantages: one of which is more personnel and expert support from an outside source (Ahmad *et al.*, 2004). Volunteers may provide significant hands-on experience and such data allows for sound decision-making on water policy choices and for the location of known pollution zones (Alaerts & Khouri, 2004). Moreover, governments save money because NGOs also receive funding from local and foreign donors.

7.4. Future Prospects

Water is essential for life, economic activity, and agricultural production. Large populations would be difficult to provide with potable water in the future, as the availability of potable water to the masses has recently emerged as a major issue for governments worldwide. Southeast Asia is one of the most dynamic and far-reaching parts of the global trade in art and culture. It is among the most threatened by water scarcity and contamination as well. As and F pollution poses a significant problem in regions where 0.06 billion people are exposed to an elevated level of As in their drinking water like Pakistan. This may cause significant problems for the country's economy and health care system. These criteria will guide all of the policies, studies, and the construction of infrastructure for years to come.

a. Research studies

There is an urgent need for additional data on As and F pollution in Pakistan's subsurface aquifers. While a lot of information about the causes of As and F pollution is already available, country-specific information is not available. There is a dearth of concrete evidence based on countrywide sampling in the available data. Although considerable research has been conducted on As and F poisoning through water, little is known about the effect of As and F contaminated dietary products such as rice and fish. Similarly, little is known about As and F toxicity from sources other than drinking water, such as soil and air.

Research on those pathways ensures that the possible health dangers from sources other than water can be better understood. The research also aimed to establish economically efficient and easy techniques for reducing the amount of As and F in groundwater, thereby reducing the burden of disease. At present, the technology available for water processing methods is costly, complex and cannot support a large population (Luong *et al.*, 2018).

b. Policy level

Future action often depends on quality research that establishes a sound basis for policies. The direction of the policy is determined by the quality of the study; in the absence of research, policies are either poorly formulated or completely miss the mark. Pakistan would need to establish a framework of action if the population is projected to double by 2025. Though WHO says the safe limit is 10 µg/l, the current amount permitted limit for As in drinking water in Pakistan is at 50 µg/l. We must update our government policies to help the future generations who will benefit from emerging technologies.

Policies must prioritize the regularization of industries and the mining industry in order to reduce the use and degradation of subsurface aquifers. As and F poisoning are mostly caused by anthropogenic as well as geogenic activities. Including industry in policy formulation and management of industrial effluents is a critical step toward achieving the target of sustainable development. Incentive-based programs that penalize and subsidize businesses that contribute to As and F poisoning.

Arsenic pollution in the Indus river delta is mostly due to poor flood management. Additional policy dimensions include the construction of dams to replenish the diminishing supply of underground water supplies. A significant move will be the formation of intergovernmental committees to review and update existing water policies and to determine a course of action for the future. This type of consensus eliminates conflict of interest and allows for the stalling of policies. The financing of research and development of technologies for reducing As and F levels in drinking water must be

simplified. This would also contribute to the generation of critical data for the development of mitigation policies in highly polluted areas.

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