EFFECT OF HYDROGEO-CHEMICAL PROCESSES AND SALTWATER INTRUSION ON GROUNDWATER QUALITY IN AQUIFERS OF HYDERABAD, SINDH.

By

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FACULTY OF BIOLOGICAL SCIENCES

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APPROVAL CERTIFICATE

It is to certify that **Mr. Abdul Saboor Akhtar** (Reg. No. 02312111013) conducted the research work presented in this thesis, entitled –***Effect of hydrogeo-chemical processes and saltwater intrusion on groundwater quality in aquifers of Hyderabad, Sindh.***" under the supervision of **Dr Abida Farooqi**. No part of this thesis has been submitted elsewhere for any other degree. This thesis is submitted to the **Department of Environmental Sciences**, in partial fulfilment of the requirements for the degree of **Master of Philosophy in the field of Environmental Science**, Department of Environmental Sciences, Quaid-i-Azam University Islamabad, Pakistan.

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02312111013

DEDICATION

This work is dedicated to my parents, Mr. Muhammad Akram Kamal & Mrs. Naveeda Kamal. They're my first teachers; they have been my source of inspiration, support, and guidance. Whatever I'm today is all because of them. I am truly thankful and honored to have them as my parents.

AUTHOR'S DECLARATION

I, **Abdul Saboor Akhtar**, hereby state that my M.Phil. Thesis titled ***"Effect of hydrogeochemical processes and saltwater intrusion on groundwater quality in aquifers of Hyderabad, Sindh."*** is my own work and has not been submitted previously by me for taking any degree from Quaid-i-Azam University or anywhere else in the country/world.

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Table of Content

LIST OF TABLES

LIST OF FIGURES

ACRONYMS AND ABBREVIATIONS

CAI	Chloro-Alkaline Indices
EC	Electrical Conductivity
EPA	Environmental Protection Agency
FAO	Food and Agriculture Organization
KR	Kelly‘s Ratio
mg/L	milligrams per Liter
MH	Magnesium Hazard
NEQS	National Environmental Quality Standards
PI	Permeability Index
ppm	Parts Per Million
RSC	Residual Sodium Carbonate
SAR	Sodium Adsorption Ratio
SI	Saturation Indices
SSP	Soil Salinity Potential
TDS	Total Dissolved Solids
TH	Total Hardness
WHO	World Health Organization
WQI	Water Quality Index
PCRWR	Pakistan Council of Research in Water Resources
SOPs	Standard Operating Procedures
GPS	Global Positioning System

ABSTRACT

Hyderabad, a city in Pakistan's Sindh Province on the Indus River's banks, often has ground water conditions ranging from neutral to slightly alkaline. More than 69.8 percent of the samples had EC levels above the threshold considered safe for human consumption, and the same percentage of samples had TDS levels above the threshold recommended acceptable by the World Health Organization (WHO). In Sindh, hard groundwater predominates; 52% of the province's aquifers are classified as extremely hard water, making up the bulk of the province's water supply. Groundwater salinity was due to several minerals, including bicarbonate HCO_3^-, calcium Ca^{2+}, magnesium Mg^{2+} and sodium Na^+. There are several factors at play, including the high-water table, the incursion of seawater, the overuse of fertilizers, and the underlying geological structures, that have led to this reduction in water quality.

The hydrogeochemical facies show that the concentrations of Na^+ are larger than those of Ca^{2+} and Mg^{2+}, and those of Cl^- and SO_4^{2-} - are more than those of HCO_3^-. As a result, it is hypothesized that the solutes in Sindh's groundwater originate from the weathering of carbonate deposits. Thirty percent (28.0%) of the groundwater is classified as "drinking quality" by the EC. Thirty percent of the groundwater is drinkable, as determined by the total dissolved solids level of the samples. It was discovered, however, that 57.3% of the groundwater is extremely hard.

According to the SAR, 90% of GW may be irrigated on almost any type of soil with a negligible risk of Na exchange. Inadequate for direct use in agriculture, however, as testing showed that seawater intrusion made it unsuitable for irrigation.

1. INTRODUCTION & LITERATURE REVIEW

1. 1 Increasing Population growth and Water scarcity

Global population growth, accelerating urbanization, industrialization, and irrigation techniques have detrimental impacts on water quality, consumption, and environmental consequences (Vignesh Akshitha, 2021). The world has been significantly impacted by industrialization, particularly in terms of water use and water-related environmental challenges. This has increased dramatically across the world with the rise of industries and commercial enterprises. Throughout the second part of the twentieth century, access to clean water and natural resources became a serious issue for environmental conservation. To maintain a sustainable and clean supply, water is a resource that must be carefully managed (Sneha Santy, 2020). Crop irrigation is a major factor in climate change, notably in arid parts of the world. Crop irrigation could have a significant impact on water pollution. Most irrigation methods have a detrimental impact on the quantity and quality of water, degrading both surface water and groundwater. Additionally, irrigation could have a harmful effect on the environment. Irrigation is frequently seen as a blessing for farmers and the agricultural sector, but if done incorrectly, it may really turn into a curse with damaging consequences felt across the globe. (Abel Chemura, 2014). The process of urbanization involves the migration of millions of people from rural to urban areas, which results in the formation of new cities. This is occurring at an ever-increasing rate all around the planet right now in every region. It is impossible to maintain hygienic and sustainable standards in today's rapidly growing cities, which are also seeing rapid population growth as a result of increased migration. The inhabitants of these cities are facing significant health problems as a direct result of the environmental deterioration brought about by this rapid growth and the rising levels of pollution that have accompanied it. These problems have been brought about as a direct result of the rapid growth that has taken place. As a direct consequence, the human population is massively expanding at a startlingly quick rate. By 2050, it is predicted that there will be 10 billion people on the planet, and perhaps even more. (UN, 2015) (depending on how quickly we can control agricultural output and other variables), which will significantly contribute to an ever-increasing list of adverse effects on the environment. The term "environmental" refers to all the different ways humans interact with the natural world around them, such as through the production of pollution and waste as well as through other anthropogenic processes. (S.Uttara, 2012)

1. 2 Water contamination crisis and Pakistan

The term "water contamination" or "water pollution" refers to the condition in which a particular body of water, becomes degraded for any practical use because of specific chemical, physical, or biological components or sources. These elements or causes can be of any kind. The amount of pollution that must be present in a body of water before it is considered impaired varies substantially based on the kind of body of water, where it is, and the useful purposes it serves. On the other hand, certain naturally occurring catastrophes could poison the water. (Linda Schweitzer, 2018)

Contamination of water supplies is a significant issue in many countries. Consuming contaminated water can severely influence an individual's health; however, pollution also harms the natural environment and can cause glaciers and coastal regions to degrade. In addition to visible pollutants such as oil and foam, other forms of pollution include dissolved chemicals and particles in the water. These can include heavy metals, insecticides, herbicides, and waste products from industrial processes. There is the potential for water pollution to affect all bodies of water, including rivers, streams, lakes, and oceans. The effects of pollution are typically seen to be at their worst in urban areas where many people live close to one another. (Hynds, 2017) (Maimoona Raza, 2017)

When determining whether a water source is polluted, state and local governments can adopt the criteria laid out by the USEPA (Environmental Protection Agency of the United States) or the WHO (World Health Organization). The water source is polluted under the Clean Water Act if it does not meet one or more of the conditions that have been established. According to estimates provided by the United Nations, More than one billion people lack access to safe drinking water, and almost two billion lack proper sanitary facilities. (Azizullah, 2011) Heavy metals, nutrients (phosphates and nitrates), and chemicals from industrial processes, such as those used to make paints, solvents, or plastics, are some of the contaminants found in rivers and streams in nations with inadequate sewage treatment systems. Water pollution also has a damaging effect not just on human health but also on the environment, including fisheries, tourism, recreational activities, and transportation. (Khan S. S., 2013)

1. 3 Available Fresh Water Resources

Surface and groundwater are the two primary categories that comprise a country's water sources. The term "surface water" refers to bodies of water like lakes, reservoirs, ponds, rivers, and streams open to the atmosphere and the underlying terrestrial surfaces. In addition to that, it incorporates water that has fallen as rain, snow, and ice. The term "groundwater" refers to the water held in the ground, which can come from shallow and deep aquifers. (A Balasubramanian, 2015) It is possible for groundwater to be in touch with surface water or to be relatively separated from it. Groundwater is found in porous rock units buried far below the earth's surface. There is a considerable amount of variation in the depth of the groundwater depending on where you are located. Some groundwater may be as shallow as a few feet below the surface, while others may be as deep as several hundred feet. (Naseem S, 2018) The quality of groundwater can differ substantially from one site to another depending on the water's location or its chemical composition. Rocks can filter groundwater, which eliminates many toxins; nevertheless, some compounds are challenging to get rid of. (Winter, 1999)

The increase in the world population, rising living standards, and changing consumption habits, and the expansion of agriculture dependent on irrigation have all contributed to the rising demand for freshwater. (Sanjrani MA, 2019) The most current annual risk report published by the World Economic Forum states that, in terms of the possible effects, water crises rank as the world's biggest concern. There are several regions around the world with a growing scarcity of freshwater resources. It will be more crucial than ever to ensure that people have access to sanitary facilities and safe drinking water as freshwater resources continue to increase in significance (World Economic Forum, 2015). At the same time, the water supply is being stressed by climate change and pollution, causing water scarcity in many locations worldwide. (Kala Vairavamoorthy, 2008) In certain areas, the effects of climate change have already been seen in the form of decreased river flows and increasing drought intensity. The ever-present need for freshwater that the available supply must meet is the root cause of the water crisis that plagues several regions around the globe. This water stress significantly affects the sustainable management of freshwater resources, which has severe ramifications. As a direct consequence of this, the necessity to comprehend and adequately administer water resources is becoming more pressing. (CRED, 2015)

The seas contain around 94 percent of the world's water, and most of that water can only be utilized indirectly if it is purified first. However, a significant amount of water also remains frozen in glaciers and ice caps owing to natural reasons. The remaining Earth's water is where terrestrial life, including humans, must continue to survive. The freshwater (nonsaline) resource that is potentially available for human use is found in rivers, lakes, reservoirs, and groundwater systems all throughout the world. The combined volume of these bodies of water is approximately 475 million km per cube. It is staggering, but focusing just on the planet's freshwater storage capacity is a mistake because a significant portion of the water is unreachable. (Shiklomanov, 1997)

Because of this, it makes more sense to think of the freshwater resources available to humanity as coming from three sources: surface water, accessible groundwater, and rainfall utilized to grow crops. Rainfall is the most critical way that freshwater may be obtained. It is responsible for around 85 percent of the world's freshwater supplies, although only 5 percent of the rain that falls is usable by humans. The remainder is lost as water by evaporation or absorption by the Earth, where it might eventually become groundwater or infiltrate surface water. Rivers, lakes, and other bodies of surface water make up 10% of the global freshwater resources that are surface water. The three percent of the global water supply that comes from groundwater originates in aquifers, which are layers of the Earth's crust that hold water and may be reached through wells or springs. (Isaakovich., 1979)

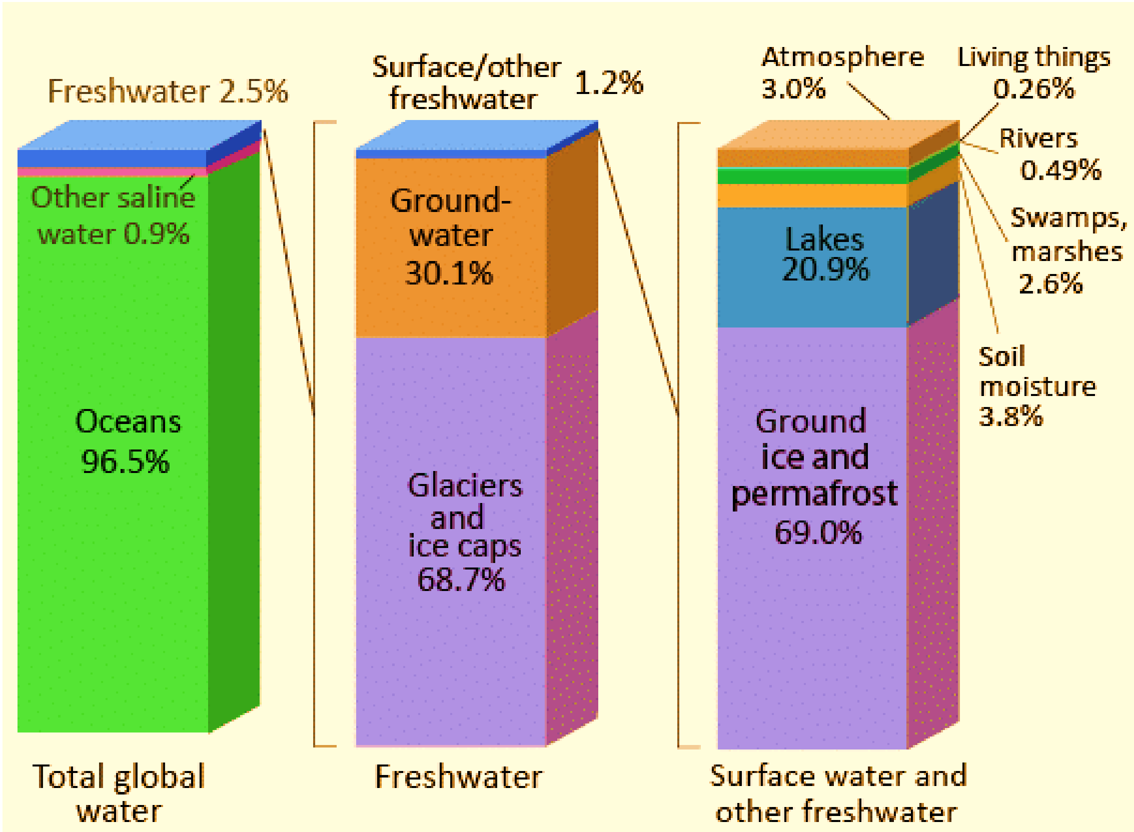


Figure 1. 1: Global total water distribution (Kundzewicz et al., 2007) ["World freshwater resources" in Peter H. Glekk, 1993, water in crises]

1. 4 Groundwater as a main source of freshwater

Groundwater is the main source of water utilized for drinking, industrial usage, and agricultural purposes because of the dry and semi-arid terrain. (Jalali., 2007) In light of dramatic agricultural and commercial activity growth over the past half-century, there has been an unavoidable gap between the amount of groundwater extracted and the amount recharged. This has caused the water level to drop and the water's quality to deteriorate, allowing saltwater to infiltrate the coastal areas. Therefore, the depletion of groundwater supplies has thus become a significant issue all across the world. (Michael N. Fienen, 2016)

For example, a decreased water table level is linked to a variety of issues, such as nutrient leaching and elevated soil salinity, in addition to a diminished water supply for both residential and commercial uses in agriculture and food production. Because of this, groundwater is a valuable resource that has to be managed with extreme care if we want to ensure that future generations will continue to benefit from the environmental resources that groundwater can offer. (Waseem Ishaque, 2017) According to the UNESCO Water Governance Study (2008), "Groundwater management is vitally essential in safeguarding water resources and supporting sustainable development." (UNESCO, 2008)

A significant number of nations already have laws that govern the use of groundwater, and a great number of them have made significant progress in recent years in the process of revising their regulatory frameworks. However, due to the complexity and scope of the issue, a great deal more work must be done to guarantee that groundwater resources are managed appropriately. This emphasizes that there is an immediate need to create more effective tools and approaches that successfully assist states and other stakeholders in managing their groundwater resources. (Rahimi-Feyzabad, 2022) Because of this, the Food and Agricultural Organization (FAO) has suggested a new framework for global action on groundwater governance, this was done so to address these issues. This framework comprises six different policy measures geared toward enhancing the management of groundwater resources and encouraging policies that are both sound and sustainable in this sector. These steps are being taken to ensure that all populations have access to an appropriate quantity of drinking water that is both safe and accessible. This is being done to better future generations' general health and well-being and satisfy all people's demands. (FAO, 2013)

1. 5 Water stress conditions in Pakistan

Pakistan is ranked 130th in the world regarding total water storage capacity, with a reported volume of 191,853 million cubic meters. However, Pakistan has several large reservoirs capable of storing large amounts of water and providing much-needed irrigation to parts of the country where water is scarce. According to Jamshed Iqbal Cheema (Chairman of the Pakistan Agriculture Scientists Association), per capita, water availability at the time of independence was 5,600 cubic meters against the current measure of 1,000 cubic meters, and the shortage is expected to rise to 31% of people‗s needs by 2025. (Naseer, 2013) Consequently, Pakistan faces a growing need for additional storage capacity if it is to keep pace with its growing agricultural sector, It makes up almost one-third of the GDP of the nation. (Hayat, 2016)

Increased water scarcity and falling groundwater levels can severely impact a country‘s economy and development. These environmental problems will potentially cause severe food and water shortages if left unchecked. They could therefore have a potentially devastating effect on the country‘s economic growth and development. Investing in water conservation technologies and building new reservoirs can ensure that we can meet the needs of future generations while promoting sustainable economic growth. (Basharat., 2019)

Approximately 25% to 33% of the nation's population are estimated to currently lack access to clean drinking water. (Azizullah A, 2011) This is primarily due to contaminants such as bacteria and viruses in water sources and poor sanitation and hygiene practices. As a result, thousands of children are killed yearly due to unsafe drinking water and poor sanitation. (Sanjrani, 2019)

Every year, Pakistan loses 13 million cubic seconds of water to the sea, and During times of decreased river flow, saltwater intrusion can ruin up to 100 kilometers of arable land. This is a concerning trend for a nation that depends on agriculture for over 90% of its water supplies and needs it to survive. Only approximately 4 percent of the country's water supply is renewable, and the country's groundwater supplies are being depleted at an alarming rate due to overexploitation and extraction methods that are not sustainable. (Basharat., 2019)

The management of water resources is becoming an increasing problem because of climate change, which includes increased rainfall unpredictability and floods in some areas of the nation, as well as rising water shortages in other parts of the country. Desalination facilities are one example of the sorts of solutions that communities are looking for to fulfill the rising demand for their goods and services. However, these stopgap measures are only effective in the short term and place an additional burden on the country's already stretched-thin resources. (Gaaloul, 2021)

1. 6 Precipitation in Pakistan

Western Depressions typically occur between the months of December and March, and monsoons are Pakistan's primary contributors to the country's annual precipitation totals (July-September). The whole Indus plain receives an average rainfall of 212 millimeters and 53 millimeters, (Asim Rauf Khan, 2000) respectively, Glaciers span over 13,680 square kilometers of Pakistan's entire land, which increases river turn-off during warm weather. (Khoso, 2015) Because Pakistan is situated in a region with solid monsoon activity, the nation receives an amount of rainfall equivalent to two-thirds of its annual average. The monsoon wave sweeps into Pakistan from the Bay of Bengal, which coincides with the southwest monsoon season, which runs from May to September. This is when Pakistan has the highest rainfall. The Indus River, Pakistan's largest river and primary supply of fresh water, receives its water from the Hindu Kush and Karakoram glaciers. It supports about 90% of the country's agricultural production and aids in meeting household and industrial demands. The Indus River is navigable for more than 1,100 kilometers upstream. However, it enters the Arabian Sea via a tributary in the Indian state of Gujarat known as the Rann of Kutch. When the flow volume is lowered or decreased below minimum flow restrictions, the impacts of the canal breach may result in groundwater depletion or lake drying up and, consequently, a reduction in irrigation potential. Additionally, the effects may cause harm to ecosystems. (Khoso, 2015)

1. 7 Surface Water Resources

Due to sedimentation, the initial capacity of the Mangla reservoir, which included the two major dams, was 5.88 million Acre-Feet (MAF). In 2005, this number dropped to 4.674 MAF. The reservoir created by the Tarbela Dam, which was built to keep water for the Indus River, has a surface area of almost 250 square kilometers. The dam is the world's biggest earth-filled dam (97 sq mi). 16 barrages, 3 sizable reservoirs, 2 headworks, 2 siphons across large rivers, and 44 canal systems—23 in Punjab, 14 in Sindh, 5 in KPK, and 2 in Baluchistan—make up the Indus Basin Irrigation System. (Ahmed S. , 2007) Due to growing contamination from improper sewage disposal systems and the disposal of industrial and agricultural waste, the quality of surface water is declining. The dangers of pollution are not exclusive to surface water; it also risks groundwater supplies. Because of salt intrusion and excessive pumping have led to a decline in water tables. (Altaf A, 2002)

1. 8 Groundwater in Pakistan

Seventy percent of the world's currently available groundwater is taken out of the Earth for agricultural uses (UNESCO, 2003) Pakistan is mostly an agricultural country, so in order to meet the growing demand for food from its people, the country's annual food output needs to be raised by two every 15 years. (Hayat, 2016) For irrigation purposes, the nation possesses an adequate amount of fertile and productive land, as well as freshwater supplies. At the present rate of population growth, which is 2.5% per year, an additional by

2025, 120 million people will require food. Therefore, among many other agricultural processes, agricultural irrigation is a crucial use of groundwater in Pakistan. (Kamal, 2009). In addition, residential and industrial uses, such as the provision of drinking water, are made of groundwater resources. The extraction of groundwater is the human activity that occurs most frequently in connection with the subsurface of the Earth. In 2010, the annual amount of groundwater extracted throughout the world was 982 km^3 (Benejam, 2010). Water scarcity and the amount of water that can be utilized for drinking have been caused by overexploitation of groundwater. Pakistan is one of the nations that is predicted to have fewer renewable water resources by 2030 compared to the established threshold value of 1,500 m^3 per capita annually. This prediction is based on data collected from the World Resources Institute. In addition, Pakistan is included on the list of nations experiencing a scarcity of groundwater (Reig, 2013)

1. 9 Contamination & Degradation of Groundwater

Both chemical (organic and inorganic) and biological pollutants can be found in groundwater. Natural contaminants can be broken down into several categories. Most groundwater's organic pollutants are brought about by anthropogenic activities, whereas geological causes bring about the groundwater's inorganic contaminants. Inorganic pollutants include many different elements, several of which are termed to be active water contaminants. Organic pollutants, including oil and pesticides, comprise most of the environmental hazards today. Anions and cations including phosphate, nitrate, calcium, magnesium, sodium, and potassium, as well as fluoride and chloride, are examples of inorganic pollutants. This group also includes water-soluble radioactive substances and pathogens like bacteria, viruses, and protozoa. (Memon, 2011). Bacterial contamination, Major contaminants detected in Pakistan's groundwater include heavy metals including arsenic (As), cadmium (Cd), lead (Pb), and nickel (Ni), as well as anions such nitrate (NO_3) and fluoride (F). These contaminants potentially threaten the country's groundwater quality. (Khan S. R., 2016)

1. 10 Climate Change and Water

The climate is a dynamic system that is prone to natural fluctuations on a range of timescales, from years to millennia. These changes can have a significant impact on human life. The climate system is like any other system in that if no excitations are forced on it, the average temperature throughout the world will not change. Nevertheless, throughout the course of this century, there has been a significant rise in the concentration of active greenhouse gas emissions. Among these gases are methane (CH_4), nitrous oxide (N_2O), and carbon dioxide (CO_2). Solar energy can pass through the atmosphere and reach the surface of the earth due to greenhouse gasses. but also capture and store infrared heat that is emitted from the earth's surface. This helps keep the earth's surface at a constant temperature (Sherif M. M., 1995). The warming of the planet as a whole and changes in its climate have a myriad of potentially disastrous effects. They alter the nature of the hydrological cycle's constituent parts in the domains of space, time, and frequency, altering both their amount and quality. (Kirshen, 2002)

1. 11 Groundwater Depletion and Human-Caused Climate Change

Many countries around the world, particularly those in arid and semi-arid areas with little surface water, the only source of freshwater supply is groundwater. This is especially the case in landlocked countries. The resources that are associated with groundwater are impacted by global warming in a variety of ways. Excess precipitation or runoff that cannot be stored or put to some other beneficial use eventually makes its way to groundwater basins or the ocean. The changing climate might result in either an increase or a decrease in the amount of rainfall. The pattern of rainfall over the globe could shift significantly, which would affect the rate at which aquifers are recharged. Groundwater resources may be broken down into four distinct categories to assess how climate change would affect them. (Jacoby, 1990)

The first type consists of restricted aquifers with top layers impermeable to water. The only places where the water-bearing rocks outcrop at the surface are where these types of aquifers are refilled. The second kind of aquifer falls into the phreatic, or unconfined, group. These aquifers may be found in rainy locations with high rainfall and low evaporation. Because precipitation throughout the year is more than the amount of water lost to evaporation and evapotranspiration, these aquifers are highly renewable. The anticipated geographical redistribution of rainfall will not influence them. The third kind of aquifer falls under the category of unconfined aquifers. It is found in arid areas of the world where the yearly equilibrium between precipitation and evapotranspiration constantly fluctuates. As a result of the anticipated trend of global warming, such areas could see drier weather. The fourth group consists of coastal aquifers, which are often affected by the incursion of salt water from the ocean.

The land surface, oceans, and seas will all warm up to some degree due to the anticipated rise in the planet's average temperature. The rising temperature will also affect the pressure in the atmosphere. Changes in the barometric pressure will have the opposite effect on the ocean's water level. When there is a one-millibar drop in atmospheric pressure, there is a corresponding ten-millimeter rise in sea level. A string of low-pressure systems in the atmosphere can increase the water levels in ocean basins with shallow depths. (Sherif M. M., 1999)

Furthermore, there are two possible reasons why the sea level might rise. Oceans would grow larger due to two factors: first, they would get warmer, and second, the amount of water in the oceans would increase because of melted ice sheets and glaciers. (Theon, 1993) It is believed that around 25 percent of the rise is due to the thermal expansion of the seas due to climate change. The remaining amount must be the result of atmospheric pressure drops combined with ground-level glacier and ice sheet melting. Within the next fifty to one hundred and fifty years, experts anticipate a rise in sea level between half a meter and one and a half meters (Nicholls, 1999)

1. 12 Sea Level Rise and Seawater Intrusion

According to the Ghyben-Herzberg connection, there will be 40 meters of fresh water below the mean sea level for every one meter, the free water table is elevated above the mean sea level. Similarly, a rise of 50 centimeters in sea level results in a loss of 20 meters in freshwater thickness. Pumping and recharge operations have a greater effect on water tables and piezometric heads than do variations in sea level. (Mohsen, 1990)

The rate of sea level rise because of climate change is sufficiently slow for Instead of staying in their current position, groundwater heads along the coast will rise in parallel. This is because the rising sea level rate is slower than the increase in the average global temperature. But there won't be a comparable rise in groundwater levels on land when the groundwater table near the sea boundary rises. Rather, the water table's gradient and the piezometric head's drop will cause the amount of water sucked in by the land to rise. (Sherif M. M., 1999)

The depth of the freshwater body may become slightly thinner close to the coast because of the rise in the level of the free water table; however, the reduction will be far more pronounced further inland. In the context of climate change and rising sea levels, aquifers deep along the coast and with gentle hydraulic gradients are more susceptible to damage. (Buddemeneir, 1988)

1. 13 Water Quality Standards

Water quality is of extreme importance since it affects both humans and ecosystems. Various techniques are being investigated around the world to address the issue of poor water quality (Marshall, 2013). The concentration of ions and components in water, whether dissolved or suspended, affects its quality (Gorchev, 1993). Human activities have affected the natural components of water, causing it to be polluted/contaminated. TDS (Total dissolved solid), which specifies the quantity of solid present in one litre of water sample, is an important metric of water quality (Fetter, 2014) Quality control standards are established by several organizations such as WHO, USEPA, NEQS Pakistan, and others. Maximum and lowest permitted parameters are established and enforced globally for drinking and irrigation purposes (WHO, 2011)

1. 14 Drinking Water Quality Standards

Around the world, there are several drinking water standards that are acknowledged and adhered to. The guidelines issued by the World Health Organization (WHO, 2011) are widely acknowledged and adhered to. Multiple drinking water components have minimum and maximum limits set by the WHO. Table 1.1 lists the WHO and NEQS Pakistan drinking water quality standards (NEQS, 2010)

Table 1: Drinking water quality standards by NEQS Pak (NEQS, 2010) and WHO (WHO, 2011)

Parameter	Unit	WHO	NEQS
pH		6.5-8.5	6.5-8.5
EC	µS/cm	1500	
TDS	mg/L	1000	<1000
TH		500	
HCO_3^{2-}		500	
Cl^-		250	<250
SO_4^{2-}		250	
K^+		12	
Na^+		200	
Ca^{2+}		200	
Mg^{2+}		150	
Pb		0.01	0.01
Cu		2.0	
Cd		0.003	

1. 15 Irrigation Water Quality Standards

Agriculture productivity is determined by the quality of irrigation water. The intensive use of ground water, combined with human activities, has deteriorated the water quality, rendering it unsuited for agriculture. Different criteria are created and agreed globally to ensure that the water used for irrigation and agriculture is of good quality or not. Table 1.2 contains irrigation water quality parameters that highlight the long-term influence of water quality on cropping, soil requirements, and farm administration.

Table 1.2: Guidelines for the interpretation of irrigation water quality

Parameters	Range	Water Class
EC	<250	Excellent
	250-750	Good
	750-2250	permissible
	>2250	Doubtful
SAR	0-10	Excellent
	10-18	Good
	18-26	Medium
	>26	Bad
RSC	<1.25	Good
	1.25-2.5	Suitable
	>2.5	Doubtful

PI	>75%	Good
	25-75%	Suitable
	<25%	Unsuitable
MH	<50	Suitable
	>50	Unsuitable
Na%	<20%	Excellent
	20-40%	Good
	40-60%	permissible
	60-80%	Doubtful
	>80%	Unsuitable
KR	<1	Suitable
	>1	Unsuitable
SSP	<5	Excellent to Good
	5-10	Good to Injurious
	>10	Injurious to Unsatisfactory

1. 16 Hydro-chemical Factors Controlling Water Quality

The primary indicator of water chemistry is pH. Natural freshwater has a pH range of 6.5 to 8.5, and this fluctuation has varied indirect impacts on human health. It alters the solubility of nutrients and heavy metals in water, hence affecting water quality overall. Surface water has a more basic pH than ground water (Stone et al, 2013); (WHO, 2011).

1. 17 Electrical conductivity and Total Dissolved Solids

An indicator of the number of ions and dissolved particles in water is electrical conductivity (EC). The salinity or salts in water are also described by EC. Anhwange et al. (2012) found that high EC values indicate a high salt concentration in water. Total dissolved solids (TDS) are salts and minerals in water that contribute to an unpleasant taste (Mohsin, 2013). High TDS levels cause a variety of issues, including scaling in water flow pipes, boilers in industries, heaters, and other domestic appliances (Suthar et al., 2010).

1.17. 1 Alkalinity

Water's alkalinity reveals its ability to neutralize certain acids. Total Alkalinity (TA) measures the amount of base in water that raises the pH. This is because water contains HCO_3^-, CO_3^{-2}, OH^- ions (WHO, 2011). Because of the presence of carbonate rocks, these ions are added to water (Dladla, 2010). Groundwater in Hyderabad has alkalinity levels that meet WHO recommendations. The main sources of bicarbonate ions in water are CO_2 from the atmosphere and weathering of carbonate rocks (Khanoranga & Khalid, 2019).

1.17. 2 Total Hardness, Calcium and Magnesium

The concentration of magnesium and calcium salts in water is referred to as total hardness (TH) (Aher & Deshpande, 2011). HCO3-, CO_3^{-2}, Ca^{2+}, Mg^{2+} contribute transitory hardness in drinking water, whereas sulphates and chlorides confer permanent hardness (Uchchariya & Saksena, 2012). Calcium and magnesium are introduced into water by various forms of rock, industrial, and sewage waste

(Suthar et al., 2010). Weathering of magnesium-containing rocks and some carbonate-containing rocks adds Mg to water (Suthar et al., 2010).

1.17. 3 Sodium and Potassium

Sodium is a highly soluble salt that is prevalent on Earth. Increased Na^+ ion concentration in water bodies is caused by industrial and residential activities, as well as rock weathering (M. J. Mohammad et al., 2015). Potassium salts are widely utilized as fertilizers in agriculture and in industry. As a result, these two sources contribute potassium to freshwater deposits (Mustapha & Getso, 2014).

1.17. 4 Chloride

Water contains calcium and sodium chloride salts. Sewage water and municipal waste effluent increase the concentration of chlorine in water. Water with a high chloride concentration has a salty taste (WHO, 2011). NaCl (halite), brines, sea sprays, and hot springs are all common sources of Cl^-. Crops are harmed when the chloride concentration in irrigation water exceeds 350 ppm.

1.17. 5 Sulphates

Sulphates occur naturally in water as sulphate ions (SO_4^{2-}). Sulphate ions are added to water from a variety of sources, including gypsum and anhydrite. An increase in sulphate is associated with an increase in salinity. Plants develop slowly when exposed to high levels of sulphates (1000 ppm).

1. 18 Pakistan's Groundwater Quality

The availability of clean water for consumption is a problem that affects the entire world. In Pakistan, a large portion of the country's potable water comes from groundwater. The pollution of groundwater in Pakistan necessitates allocating considerable resources to studying to protect the public's health. More than 44% of people in Pakistan lack access to safe drinking water, and the situation is much worse in the nation's rural areas. (PCRWR, 2010) In 1951, the annual per capita water availability was 5,800 m^3., but this number had dropped to 1,100 m3 by 2006. It is anticipated that this number will fall to fewer than 1,000 m3 in the coming decade. (Habib, 2006) It is anticipated that there will be an ongoing reduction in the amount of available water over the next few years. A lack of suitable water storage facilities and water resource development projects, drought, climate change, and improper management of water resources are some of the causes responsible for the reduction in water availability in the country. The country does not have enough water treatment plants for wastewater produced; thus, the wastewater is untreated before being released into the environment. This contributes to poor water quality. The inability to dispose of garbage appropriately contributes to higher pollution levels in the body of water. In addition, farmers regularly utilize wastewater that has not been treated for irrigation, leading to an even higher level of pollution in the water bodies. In addition, an excessive amount of groundwater being extracted for use in industry is also one factor leading to the depletion of the existing groundwater resources. (Toqeer Ahmed, 2016)

The result of all the actions and reactions in the water because of its surroundings is the quality of the groundwater. This attribute fluctuates with the depth of the water table and with place to place. Because of human activity, the groundwater quality in several regions of Pakistan is deteriorating. These regions include Because the groundwater passes through soil and rocks on its way to the water table, compared to surface water, it is less likely to be polluted by microorganisms. This is because the soil and rocks function as a filter, removing most of the germs. (Winter, 1999)

On the other hand, bacteria occasionally make their way into the groundwater, and when they do, the quantities of these bacteria may be rather hazardous. Nevertheless, the absence of microorganisms is insufficient evidence that water is safe to consume. A wide variety of dissolved minerals and organic components may be found in groundwater, each of which can be found in its unique concentration. Minerals dissolved in the water, such as fluoride and iron, are to blame for the coloring and taste issues. An unhealthy level of dissolved salts can lead to significant sickness and even death in rare cases. It is possible for harmful bacteria and viruses, such as those that cause dysentery, cholera, and other gastrointestinal disorders, to be present in water polluted with sewage (Cabral, 2010)

Most bacteria are not dangerous, and some may even have some positive effects; some, though uncommon, are potentially hazardous, and a few may even be extremely hazardous. Water that has more than 1000 mg/L of dissolved minerals is generally not deemed suitable for human consumption. Water that contains a few thousand mg/L of dissolved minerals is considered to have a mild salinity. (Van der Aa, 2003) However, it is occasionally utilized in locations where water with a lower mineral content is unavailable. Our land and water resources are coming under growing pressure due to recent developments in areas such as industry, technology, population, and water use. There has been a decline in the local groundwater quality. Inadequately managed urban and industrial waste, together with chemical pesticides, herbicides, and fertilizers that seeped into the soil and into some aquifers, have all contributed to the decline in groundwater quality. (Singh, 2020) Leaks in sewage treatment plants, improperly functioning septic tanks, and leachates from landfills are three more sources of contamination. Because of the extensive pumping of fresh groundwater in certain coastal locations, salt water has begun to seep into the aquifers that contain fresh water. (Tal, 2018)

Only 25.61 percent of people worldwide have access to safe drinking water, even after taking into account international norms (WWF, 2007). Between 2002 and 2006, the Pakistan Council of Research in Water Resources (PCRWR) launched a project to carry out a comprehensive analysis of the water quality in 23 major cities located throughout all the provinces in the country. This project was expanded to include 25 cities beginning in 2015 and will continue moving forward. According to the study's findings, between 84 to 89 % of the water sources across the country have water quality that is not up to the criteria suggested for human consumption. (PCRWR, 2008) It is well acknowledged that the poisoning of groundwater resources poses a significant danger to human health. The World Health Organization (WHO) states that the leading cause of death worldwide is waterborne diseases, accounting for 3.4 million fatalities per year. (Berman, 2009) More specifically, every year in underdeveloped nations, 2.2 million people lose their lives due to the poor quality of drinking water and the absence of sanitary facilities. (WHO & UNICEF, 2000) (UNESCO, 2003)

Since most of the toxins have levels above and beyond what is considered safe by the WHO and the NEQS, the groundwater in Pakistan is considered very contaminated. It should not be used for drinking purposes. (PCRWR, 2012) It is concerning that drinking water is contaminated with high levels of As, Cd, Cr, and Ni. However, the iron deficiency in some regions of Pakistan and the iron excess in other regions are both significant problems. The majority of studies indicate that the concentrations of Na, K, F, and NO_3 are all higher than what is allowed. (Farooqi, 2007) The limited availability of fluoride poses a danger to human health, and at the same time, there is a demand for fluoride supplementation options. However, this results in bone deformation at high concentrations, which necessitates the development of F removal techniques. Most of the factors contributing to the poor quality of groundwater are human activities. These factors include the incorrect disposal of both home and industrial waste. (Ahmad, 2003)

1. 19 Water Quality of Sindh

The Lower Indus Plain of Pakistan is in the Sindh Province. The Indus plain aquifer is one of the most prolific aquifers in terms of total groundwater content. The southern portions of Sindh Province, as well as the city of Karachi, are bordered by the shore of the Arabian Sea. Sindh's water is extremely prone to arsenic contamination, making it unfit for human consumption. One of the four provinces that comprise the Lower Indus Plain is Sindh, which is in southeast Pakistan. It encompasses around 46,569 $miles^2$ and runs from 66°8' East Longitude to 71°, and it is located between 24°4' North and 28°7' North. (Alamgir, 2016) The natural equilibrium of the groundwater in the Indus Basin was upset when a canal irrigation system was installed in the middle of the 19th century. This makes managing the aquifer difficult, as do the environmental issues it raises. Especially in the irrigated portion of Sindh, the region is particularly afflicted with waterlogging as well as salinity. (WCD, 2000)

Sedimentary rocks make up most of the surface of the area. Most of the Cretaceous and Tertiary rocks that make up the geology of the Sindh Plain are limestone, dolomite, marl, chert, marly limestone, and chalky limestone with chert interaction. (Shah, 2009)The Cretaceous and Tertiary epochs saw the deposition of these formations. The geology of Sindh can be divided into three main areas: the Thar Desert, which is to the east of the region, and the mountain ranges of Kirthar and Pab, which contain a chain of lesser hills in the west. The Suleiman and Laki ranges of rocks are in the northern part of Sindh., while the Arabian Sea encompasses the region's southernmost point. The subsurface is made up of roughly 20,000 feet of rocks that date back to the Cretaceous and Pre-Cretaceous epochs. Most of the rocks have sedimentary origins, are clastic or non-clastic, and were deposited in fluvial, semi marine, and marine environments, respectively. An abundant water supply may be found in the lower Indus aquifer. Most of the freshwater is found up to a depth of fifty meters, but farther down, the water turns salty—the extensive irrigation system, which derives most of its water from the Indus River. Because of the extensive irrigation system, the groundwater in Sindh is often rather shallow, and most of the province, including the irrigated parts, may be waterlogged. (Shahab, 2016)

In Pakistan's Sindh Province, the Lower Indus Plain's groundwater typically has properties ranging from neutral to slightly alkaline. In terms of EC, only a portion of the groundwater in the study area is fit for direct consumption. The majority of Sindh is covered with hard groundwater since this type of water falls under the category of extremely hard water. A combination of sulfate, bicarbonate, chlorine, calcium, and magnesium has mostly caused groundwater salinity. Sodium is also a contributor. The region's geological settings, the entry of saline water, the presence of a hard water table, and overuse of fertilizer are the main causes of the deterioration in water quality. In Sindh Province, arsenic is the heavy metal that is most frequently distributed. Several locations whose mobilization was believed to be positively influenced by Fe had a concentration of 250 ppb. According to this, iron most likely mobilized arsenic. (Shahab, 2016)

1. 20 Problem Statement

Urbanization, exponential population growth & industrialization are putting a lot of pressure on available water resources. Increased pollution of surface water is also the cause of degrading groundwater aquifers, excessive pumping, contamination, and seawater intrusion are making it difficult to meet the needs sustainably. Pakistan is a severely water-stressed country heading towards inevitable water scarcity. Regular monitoring and assessment of groundwater aquifers are necessary to ensure water quality parameters meet the National Environmental Quality Standards (NEQS) and are suitable for human consumption.

1. 21 Objectives

Sea water intrusion is causing havoc in the coastal aquifers of Pakistan. Sea level rise, climate change, and excessive pumping of groundwater are making saline water move upwards in non-coastal aquifers and depleting their quality. To check the possible seawater intrusion in aquifers of Hyderabad, Sindh the purpose of this study was to assess the urban area's groundwater resources. Sea water intrusion and other contaminants are a major concern due to their profound threat to human health. The current study presents its objectives as follows.

- To examine the status of possible seawater intrusion within the study area region of Hyderabad, Sindh
- To examine the water quality of aquifers using hydrogeochemical analysis to evaluate if they are according to the NEQS and are fit for consumption.
- To investigate the water quality of Hyderabad, Sindh by using different water quality evaluation indices, statistical approaches, and hydro facies to characterize water quality.

2. MATERIALS & METHODS

2. 1 Study Area

Hyderabad, which has a total area of 237 square kilometers and an estimated population of 2,201,079 as of the most recent census in 2017, is located on the Indus River's east bank in latitudes 25° 9′ to 25° 33′ north and latitudes 68° 17′ to 68° 38′ east. With an average height of 13 meters, Hyderabad is the fourth-largest city in Pakistan and the second-largest metropolitan in Sindh province. It is located around 150 kilometers from Karachi and the Arabian Sea (43 ft). The main canal in the region, Phuleli, starts on the left side of the Kotri barrage. It passes through the outskirts of Hyderabad and supplies water to the districts of Hyderabad, Tando Muhammad Khan, and Badin for household, industrial, and agricultural uses. Although this canal is not permanent, water is released for home use during dry seasons. (Kazmi, 1997)

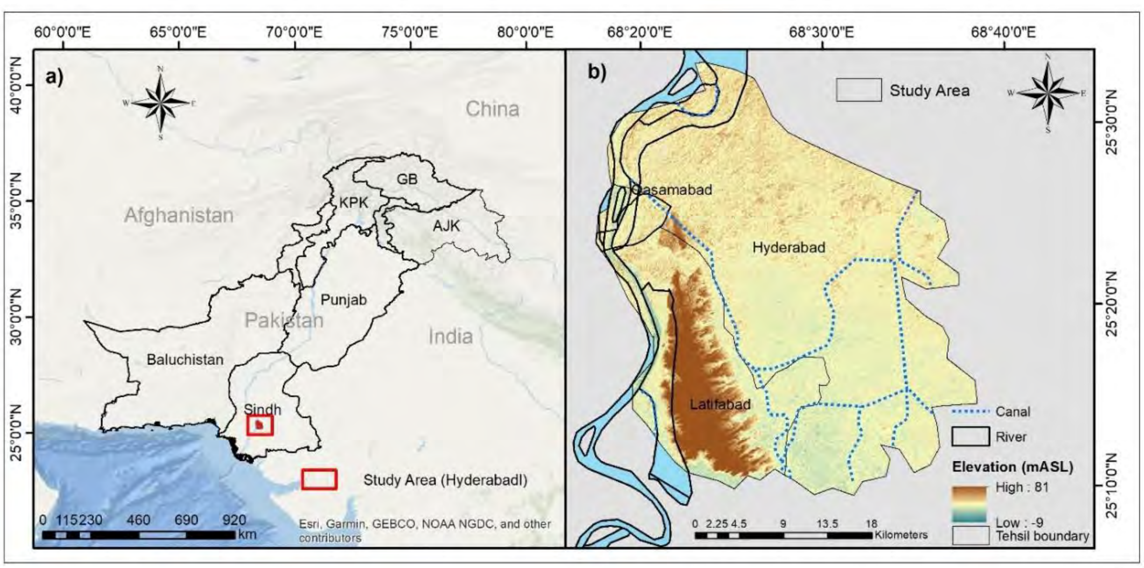


Figure 2. 1: Map of Sampling Area (Hyderabad, Sindh)

2. 2 Climate

Hyderabad, Sindh, experiences a semi-arid, subtropical climate. The city has warm summers and cool winters. April marks the start of the summer season, which lasts through September. Between 25 to 43 degrees Celsius are the typical temperatures throughout these months, with periodic heat waves in June and July. Temperatures during the winter season, which lasts from October to March, range from 7°C to 25°C. About 350 millimeters of rain falls locally on average each year. However, because to its closeness to the Arabian Sea, the city sees monsoon showers during the months of August and July. During this time of year, the city receives more than 40% of its annual rainfall. Due to its location near the Arabian Sea, the city is well renowned for its extreme humidity. The summer months are the wettest, with humidity reaching 95% in July and August. Due to a large population and industrialization, the city has significant levels of air pollution.

2. 3 Geology

Hyderabad is in the Indus Basin, a structural depression of the Indian Plate, according to geology. Sandstones, shales, and conglomerates mostly from the Cretaceous to the modern era make up the sedimentary rocks that make up the Sindh basin. The rifting of the Indian Plate along the Narmadason lineament created an intracratonic basin where these sediments have been deposited. Thick sedimentary layers were deposited because of the basin's creation, and they are currently exposed in the district's southern region. This sedimentary series is covered by the Deccan Traps, a huge igneous province of basaltic lava flows that emerged in the late Cretaceous. Laterite and soil deposited over the Deccan Traps.

2. 4 Hydrogeology

The hydrogeology of Hyderabad (Sindh) is primarily connected with the Indus River, which serves as the principal supply of water for the city. The water table is rather high along the Indus River, making it the principal source of recharge for Hyderabad's aquifers. The city is also distinguished by the presence of a great number of ponds and shallow wells that serve both domestic and agricultural purposes. Shallow aquifers and deep aquifers make up most Hyderabad's aquifers. These two types of aquifers are what make up the city's aquifers. The shallow aquifer is made up of loose deposits of sand and gravel, whereas the deeper aquifer is made up of cemented rock formations of varying depths. Both aquifers serve as potential sources of groundwater. Most of the groundwater is extracted for use in residential, agricultural, and industrial applications. The city is also served by many canals and surface water bodies.

2. 5 Water Sampling

Four districts make up the city of Hyderabad in Sindh; however, only two of the most populous districts, namely Hyderabad city and Qasimabad, were selected. A total of 63 different samples of water were taken from the location under investigation. Because the Water and Sanitation Agency of Hyderabad (WASA) has been supplying water to most of the region through its pumping stations, it was difficult to locate groundwater wells in the area. Most samples were obtained through borehole pumps, whereas only a handful were obtained from hand pumps. June 2022 was the month during which the samples were collected.

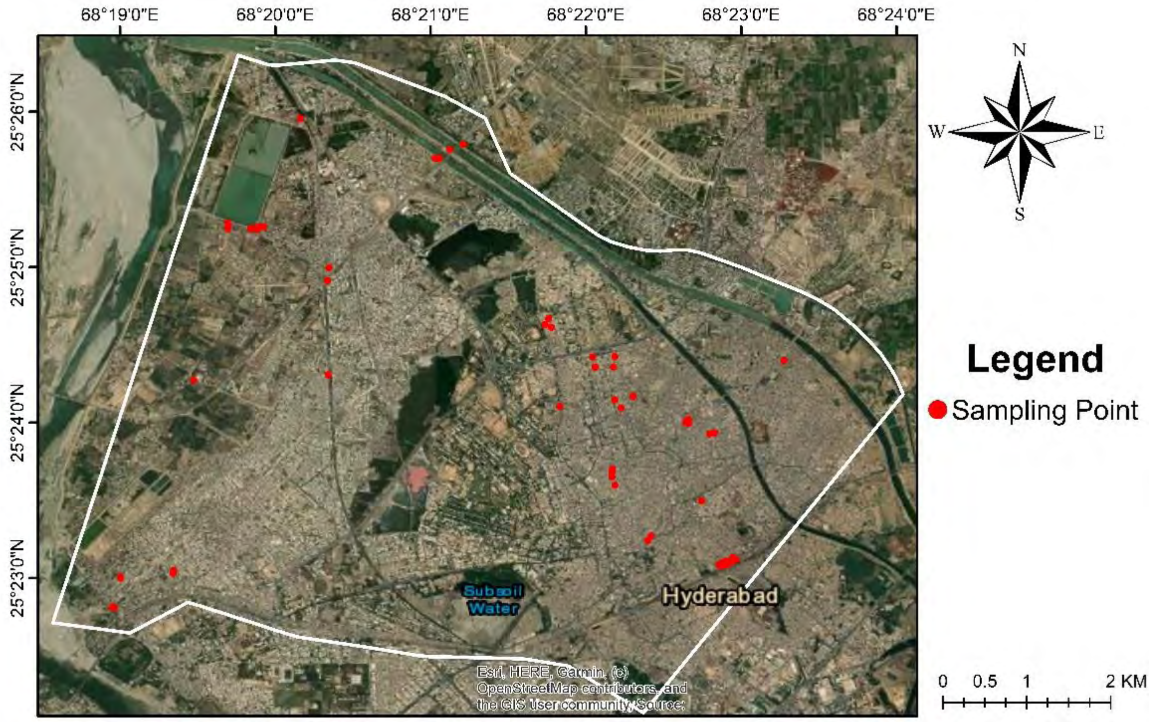


Figure 2. 2: Map of Sampling points of Groundwater Aquifers of Hyderabad, Sindh.

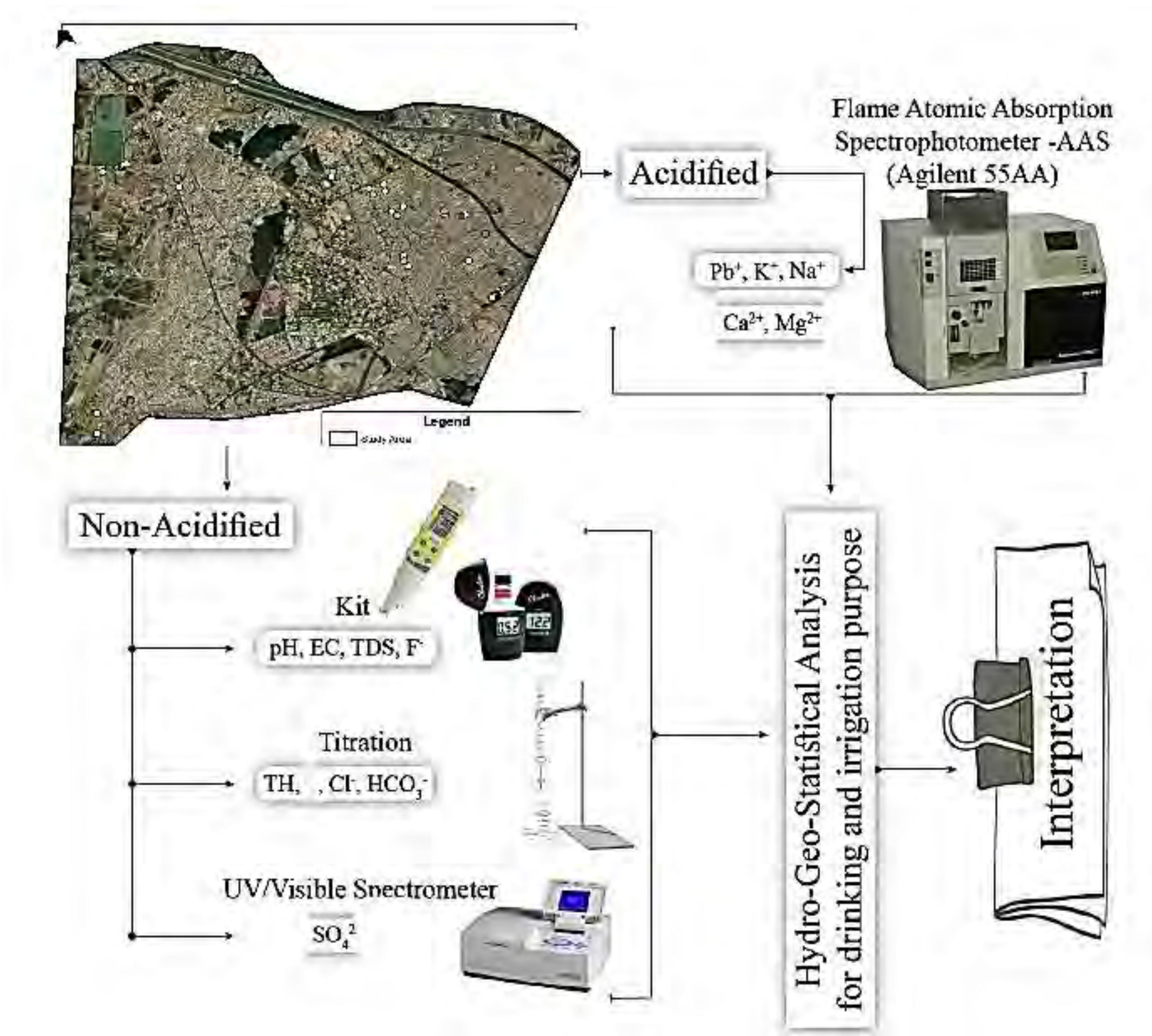


Figure 2. 3: Schematics of study of Ground Water in Hyderabad, Sindh.

2. 6 Sampling Prerequisites

Before any samples were taken, the 250 mL polyethylene (PET) bottles were cleaned with 10% nitric acid to remove any contaminants, washed with distilled water a total of three times, and then labelled appropriately (Rand, 1976). Handpumps and borehole pumps were used to collect the samples for analysis. At each site of sampling, to avoid contamination, each bottle was initially rinsed with the source water, then filled with the sample, and finally sealed. (APHA, 1985) A GPS was used to acquire the sampling coordinates. The samples were collected, packaged, and then delivered to the Quaid-i-Azam University Hydro geochemistry lab in Islamabad.

Every sample was split into two groups for additional examination in order to assess the water quality in the study area. One group was acidified with Nitric Acid (HNO_3) at pH < 2 to minimize chemical alterations, while the other was left unchanged. The acidified samples were used to analyze cations (Na^+, K^+, Ca^+, Mg^+, Lead (Pb), Cadmium (Cd), and Copper (Cu) on AAS, while the other samples were used to analyze other ionic concentrations (HCO_3^-, Cl^-, SO_4^{2-})

2. 7 Quality Control and Quality Assurance

Standard Operating Procedures (SOPs) were followed during the sampling process to ensure the integrity and quality of the samples. All instruments were calibrated before analysis, and sample blanks and field blanks were analyzed at regular intervals to ensure the analysis‘s accuracy. Furthermore, all equipment was soaked in 10% HNO_3 for at least a night prior to their use. Throughout the experimental process, all chemical reagents used for the preparation and analysis of water samples were certified and counter-checked repeatedly and made sure to be of the analytical grade of Sigma Aldrich to minimize the chance of random errors.

2. 8 Physicochemical Analysis

2.8. 1 pH, EC, TDS

Using a "Oakton® Multi-Parameter PCS Tester 35 meter," the pH (potential of hydrogen) and EC (electrical conductivity) were measured in accordance with standard procedure. Prior to analysis, it was calibrated at various points using standard buffer solutions with pH values of 7, 10, and EC values of 84 and 1413 µS/cm, respectively. Using the conversion factor indicated below, which was provided by APHA, the EC values were used to determine the TDS (total dissolved solids).(APHA, 2005)

TDS $(ppm)=EC\ (\mu S\ cm/)\times 0.67$

2. 9 Anions

2.9. 1 Alkalinity

The alkalinity of water samples was determined by acid-base titration, representing the concentration of dissolved carbonates (CO_3^{-2}) and bicarbonate (HCO^{3-}) in water. H_2SO_4 (Strong acid) with 0.02 *N* normality was standardized against a strong base (NaOH), whereas a mixed indicator was used to analyze alkalinity. Due to the addition of sulphuric acid, the color turned from blue to red, marking the endpoint of the titration. This indicated that CO_3^{-2} and HCO^{-3} ions were neutralized. (APHA, 2017)

The alkalinity of water samples was calculated by using the formula:

$$\text{Alkalinity } (mgL/=\frac{\text{V}\times\text{N}\times 50\times 1000}{\text{volume of sample taken (mL)}}$$

Where:

V = Volume of H2SO4 used (*mL*)

N = Normality of H2SO4

2.9. 2 Chlorides

Using potassium chromate (K2CrO4) as an indicator, samples were titrated against a silver nitrate ($AgNO3$) solution of 0.0141 N to determine the chloride concentration in water using the argentometric titration method. The titration's end point was indicated by the red, silver chromate production. (APHA, 2005)

The following formula calculated chlorides in water samples:

$$Cl(mgL/) = \frac{(V-B) \times N \times 35.5 \times 1000}{\text{volume of sample taken (mL)}}$$

Where:

V= Volume of silver nitrate solution titrated for the sample (mL)

B = Blank titration volume (mL)

N = Normality of silver nitrate solution

2.9. 3 Sulphates, Phosphates & Nitrates

A UV visible spectrophotometer (T80+ UV/Visible spectrometer) operating at 420 nm was used to measure sulphates. (APHA, 2005) A 5 ml sample was added in a falcon tube, and to create a milky white precipitate, 0.25 ml of conditional reagent and a little amount of barium chloride were well combined. The precipitate's intensity was then determined using a UV/visible spectrophotometer (T80+ UV/Visible spectrometer) at 420 nm.

A UV/visible spectrophotometer (T80+ UV/Visible spectrometer) operating at a wavelength of 690 nm was used to analyze phosphates. (APHA, 2005). Phosphates were measured by taking 5 *ml* of sample in a falcon tube, 0.2 *ml* of ammonium molybdate solution ($(NH_4)_6Mo_7O_{24}$), and a drop of stannous chloride ($SnCl_2$) reagent was added and mixed thoroughly. The solution was read spectrophotometrically at 690 *nm*. The concentration of phosphates present determined how intense the blue color was. (APHA, 1985)

A UV/visible spectrophotometer (T80+ UV/Visible spectrometer) operating at 410 nm was used to analyze nitrates. (APHA, 2005) To analyze nitrates, 5 *ml* of water sample was taken in the crucible and heated till dried and cooled at room temperature. The remainder was dispersed in 0.2 *ml* of phenol disulphonic acid and 0.6 *ml* liquid ammonia. The solution turned yellow. The solution was analyzed spectrophotometrically at 410 *nm*. (Trivedy, 1987)

2. 10 Cations

2.10. 1 Sodium, Potassium, Calcium & Magnesium

Under standard operating conditions, the Agilent 55AA AAS-Flame Atomic Absorption Spectrophotometer was used to measure the following elements: sodium (Na), potassium (K), calcium (Ca), and magnesium (Mg). (APHA, 2005) at 769.9 *nm* of wavelength in the range of 2-*400 mg/L,* 1-6 *mg/L,* respectively. The calibration curve was generated, and concentrations of Na^+, K^+, Ca^+, and Mg^+ were noted (Cantle, 1986)

Before analysis, each water sample was filtered with Whatman filter paper no. 45, and pH was adjusted with the addition of 5% HNO_3.

2. 11 Heavy metals

Flame Atomic Absorption Spectrophotometer AAS (Agilent 55AA) was used to examine Pb, Cd, and Cu. Pb in the 0.1–30 mg/L range at a wavelength of 217 nm At nm wavelength, Cd is in the range of 0-0 mg/L, while at 0nm wavelength, Cu is in the same range. Whatman filter paper No. 45 was used to filter each sample, and 5% HNO3 was added for adjusting pH.

2. 12 Water Quality Analysis

2.14. 1 Water Quality Index (WQI)

When evaluating the quality of water and whether it is safe to drink, the WQI water quality index is a useful and unique metric. WQI delivers information regarding water quality to authorities, legislators, and the general public, as well as indicating the combined impact of various water quality restrictions. (Kachroud, 2019); (Horton, 1965)
The adequacy of the water quality criteria for human use is investigated in this study and the WHO and EPA Pakistan recommended drinking water quality guidelines. (WHO, 2011). (NEQS, 2010)
The earlier used methods are utilized to calculate the drinking water quality index (WQI). (Ahmed J. W., 2020); (Ponsadailakshmi, 2018) (Şener, 2017). It includes the following steps:

1. Weight (wi) was allocated to each criterion based on its relative significance in the overall quality of drinking water, with a range of one (minimum) to five (maximum). The following formula was used to get the relative weights (Wi) of the chosen water quality parameters:

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

where "n" is the total number of selected parameters, "Wi" is the relative weight, and "wi" is the weight assigned to each parameter.

2. By dividing each parameter's concentration (Ci), as seen empirically, by the corresponding WHO water quality standards (Si), and then multiplying the result by 100, each parameter was given a quality rating scale (qi). According to the equation:

$$qi = Ci/Si \times 100$$

Where; ‗*Ci*' is the i^{th} parameter observed concentration and *Si* is the i^{th} parameter WHO standard value. (WHO, 2011)

3. The sub-index (SI) for each parameter was calculated by multiplying the relative weight by the quality rating scale. For every parameter, the sub-Index (SIi) was computed as follows:

$$SIi = Wi \times qi$$

Where; ‗*SIi*' is tare sub-Index of i^{th} parameter, *Wi* is the relative weight of i^{th} parameter and *qi* is the i^{th} parameter quality rating.

The overall WQI of a water sample is the sum of these sub-indices, which is calculated as:

$$WQI = \Sigma SIi$$

4. The five WQI categories were used to give water quality classifications.. (Kachroud, 2019)

Table 2. 1: Classification of water quality classes based on WQI.

WQI VALUE	WATER QUALITY CLASS
<50	Excellent Water
50-100	Good Water
100-200	Poor Water
200-300	Very Poor Water
>300	Unsuitable For Drinking

2.14. 2 Irrigation Water Quality Parameters Analysis

Using water quality indices such as sodium adsorption ratio (SAR), residual sodium carbonate (RSC), sodium percentage (Na%), Deneen's permeability index (PI), magnesium hazard (MH), potential salinity (PS), and Keller ratio (KR), all samples were assessed for irrigation water quality to determine its suitability for agricultural purposes.

2.14. 3 Sodium Adsorption Ratio (SAR)

One crucial indicator of salt toxicity is the sodium adsorption ratio (SAR). It calculates the percentage of Na+ ions to Ca^{2+} and Mg^{2+} ions in the water sample. Classified as good if SAR<6, moderate/doubtful if SAR<9, and inappropriate for irrigation usage if SAR>9. The conventional formula that follows is used to compute SAR. (Patterson, 1994); (Allison, 1954)

$$SAR=Na/\sqrt{}\,(Ca+Mg/2$$

Where the ions concentrations are expressed in $meqL^{-1}$.

2.14. 4 Residual Sodium Carbonate (RSC)

Regarding the appropriateness of irrigation water, the residual sodium carbonate (RSC) ratio is especially important. It is the extra CO_3 and HCO_3 that results from the addition of Mg^{2+} and Ca^{2+} to groundwater. Good values were defined as RSC<1.25, dubious values as RSC=1.25-2.5, and inappropriate values for irrigation as RSC>2.5. The following formula was used to calculate the RSC, and all ion concentrations were represented in $meqL^{-1}$ (Allison, 1954) (Murtaza, 2021).

$$RSC=(HCO_3+CO_3)-(Ca+Mg)$$

2.14. 5 Sodium Percent (%)

For irrigation water management, the Na% evaluation is crucial. It is the Na^+ to total cation ratio multiplied by 100 in water. Plant growth is inhibited by the increased salt concentration in soil and water because it reduces soil permeability. Na% <20 in water samples is considered excellent for irrigation usage; Na% <40 in good samples, Na% <80 in dubious samples, and Na% >80 in unstimulating samples. The SAR calculation formula is as: (Wilcox, 1955)

$$Na\% = Na/(Ca+Mg+Na+K) \times 100$$

2.14. 6 Doneen's Permeability Index (PI)

Doneen's permeability index -PI is a measure of the permeability of soil for assessing its usage for irrigation purposes. PI was calculated employing the following standard formula proposed by Doneen (Doneen, 1964), where all ion concentrations are expressed in $meqL^{-1}$. The PI>75 is conceived as good; PI 25-75 is suitable and PI<25 is unsuitable for irrigation use.

$$Permeablity\ Index\ (PI) = Na + \sqrt{HCO_3}/(Ca+Mg+Na) \times 100$$

2.14. 7 Magnesium Hazard (MH)

It was suggested that irrigation water has magnesium hazards by (Szabolcs I. &., 1964) and (Raghunath, 1987) redefined it. It is the excess content of Mg^{2+} over Ca^{2+} + Mg^{2+}. An excess of magnesium has a negative impact on plant development and water quality, which lowers agricultural yields. MH<50 is OK for agricultural usage, while MH>50 is deemed hazardous and undesirable. The concentration of MH was expressed in $meqL^{-1}$ and calculated by the following formula.

$$MH = Mg/(Ca+Mg) \times 100$$

2.14. 8 Soil Salinity Potential (SSP)

Doneen (Doneen, 1964) proposed a measure based on the irrigation water salinity, which is an advancement of USSL -U. S soil salinity. The chloride concentration of half of the sulphate ions gives the soil salinity potential (SSP). SSP is the quantity of salt accumulates gradually in the soil during repeated irrigation. SSP<5 is excellent to good, SSP 5-10 is good to injurious and SSP>10 is injurious to satisfactory. The concentration of soil salinity potential was expressed in $meqL^{-1}$ and calculated by the following formula.

$$Soil\ Salinity\ Potential\ (SSP) = Cl + 1/2\ SO4$$

2.14. 9 Kelly's Ratio

Kelly (Kelly, 1940) suggested a crucial metric based on the level of Na^{+} measured against Ca^{2+} and Mg^{2+} to evaluate irrigation water quality. KR<1 water samples are deemed appropriate for irrigation, however KR>1 water samples are not. The KR concentration was determined using the following formula and expressed in $meqL^{-1}$.

$$Kelley's\ Ratio = Na/\ (Ca+Mg)$$

2. 13 Hydro Geo Statistical Analysis & Visualization

Geographical representation of the study area (Hyderabad, Sindh) andArcGIS (10.7.1) was used to design the sampling sites. MS Excel and XLSTAT (2018) were used to execute statistical procedures (analytical data). For the graphical representation, we used Adobe Illustrator (2017) and Grapher® (16.2.354). Plotting different graphical representations, such as the hydro-geochemical process understanding and appropriateness classification, was used to assess; Piper, Chadha, Stiff, and Gibbs diagrams (Chadha, 1999) (Gibbs, 1970) (Piper, 1944) (Stiff Jr, 1951) for drinking water quality purposes, USSL and Wilcox diagrams (Allison, 1954) (Wilcox, 1955)for irrigation water quality purpose by using Grapher® (version 16.2.354), Microsoft Office 365 and Adobe Illustrator (2017) software.

2. 14 Geo Chemical Modelling

The geochemical modeling program PHREEQC v3.6.2 was used to determine the saturation indices at 25°C with the thermal equilibrium conditions of fluids around the main mineral phases in the aquifer, evaporate (halite, gypsum) and carbonate (dolomite, calcite). (Parkhurst, 2013) Generally, the water's tendency to precipitate or dissolve is expressed by saturation indices (SI).

A mineral's saturation state is represented by the symbol SI, which is computed as follows:

$$SI = Log IAP/K(t)$$

where K(t) is the mineral equilibrium constant, and IAP is the ionic activity product. (When SI>0, the specific mineral is in equilibrium with the solution; when SI=0, undersaturation & dissolution of the specific mineral are conceivable.) Oversaturation and precipitation of the specific mineral are possible.

2. 15 Chloro-Alkaline Indices

Schoeller (Schoeller, 1965) proposed a CAI-I (Chloro-alkaline indices), This is a well-known technique for figuring out how ions are exchanged throughout underground travel and residence times between groundwater and its host environment (the rock-water interaction).

These indices were analyzed through the formula as follows:

$$CAI = Cl - (Na + K)/Cl$$

Where all values are expressed in meq/L^{-1}.

A cation exchange between sodium and potassium in water and calcium and magnesium in rocks is shown by the negative CAI. The positive CAI, on the other hand, suggests that there is no cation exchange.

2. 16 Revelle Index

The research area's groundwater salinization levels were evaluated using the Revelle index. The following equation was used to calculate the Revelle Index.

$$\text{Revelle index (RI)} = Cl^{-} / (HCO_3^{-} + CO_3^{2-})$$

The ions' concentrations in the equation above are given in meq/L. A groundwater body is considered salinized if its RI value is more than 0.5. Ionic ratio plots were created to determine the sources of salinization after the RI technique was used to determine the degree of salinization in the groundwater. (Revelle, 1941)

2. 17 Spatial distribution of Water Quality Parameters

The geographical distributions of the water quality metrics were evaluated using ArcGIS 10.7.1's geostatistical module. The WHO classification system was used to classify the interpolated values after the parameter values were interpolated using the IDW (inverse distance weighted) interpolation approach. (WHO, 2011) drinking water standards.

3. RESULTS & DISCUSSION

In accordance with what was covered in Chapter 2, we collected water samples from two different districts in the city of Hyderabad: the Hyderabad City district and the Qasim Abad district.

The quantitative studies of a variety of physicochemical parameters, these are the main indications of groundwater quality for irrigation and drinking, and they are covered in this chapter. Table 3.1 presents comparative analytical data for both districts based on 13 different parameters. Individual comparisons were made with the suggested standard values provided by the WHO and FAO to ascertain if the water samples that were collected may be used for irrigation or for human consumption.

3. 1 Water Quality for Drinking purposes

The physicochemical characteristics of groundwater are often used to decide whether it can be utilized for residential, agricultural, or commercial purposes. It indicates the existence of several different inorganic and organic components. As was said earlier, the data that are available on the hydro geochemistry of Hyderabad, both in general and specifically, are either nonexistent or very limited. The results of water samples that were taken from the research location in Hyderabad and displayed the general water quality are presented in the table.

A concise explanation of these physicochemical properties is provided in the following. The pH of the groundwater samples taken as a whole range from very close to neutral to only slightly alkaline. The World Health Organization (WHO) recommends setting the permissible range for safe drinking water between 6.5 and 8.5. In addition, all the groundwater samples from the study area had mean values that were within the WHO's safe limits.

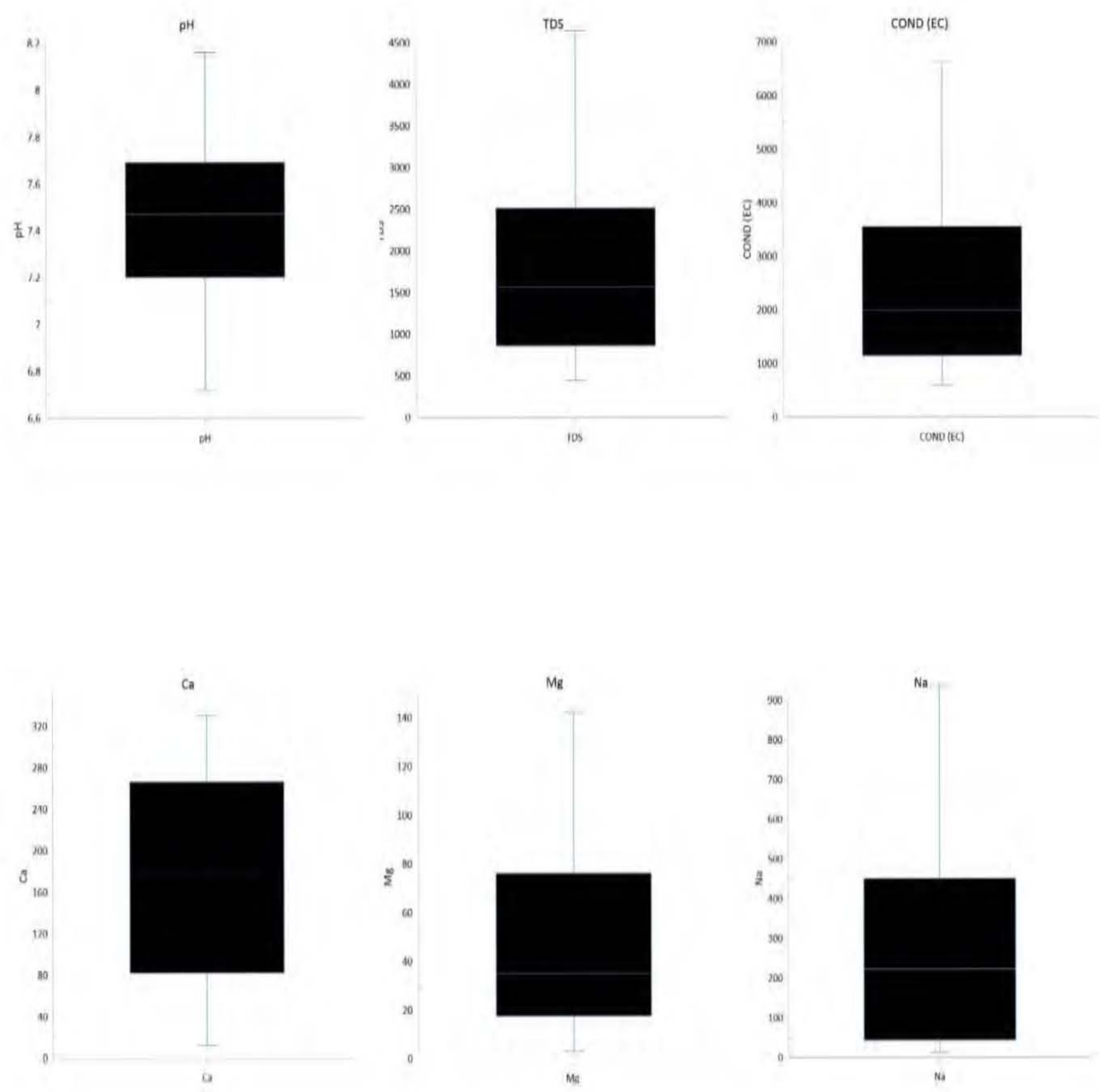


Figure 3. 1:

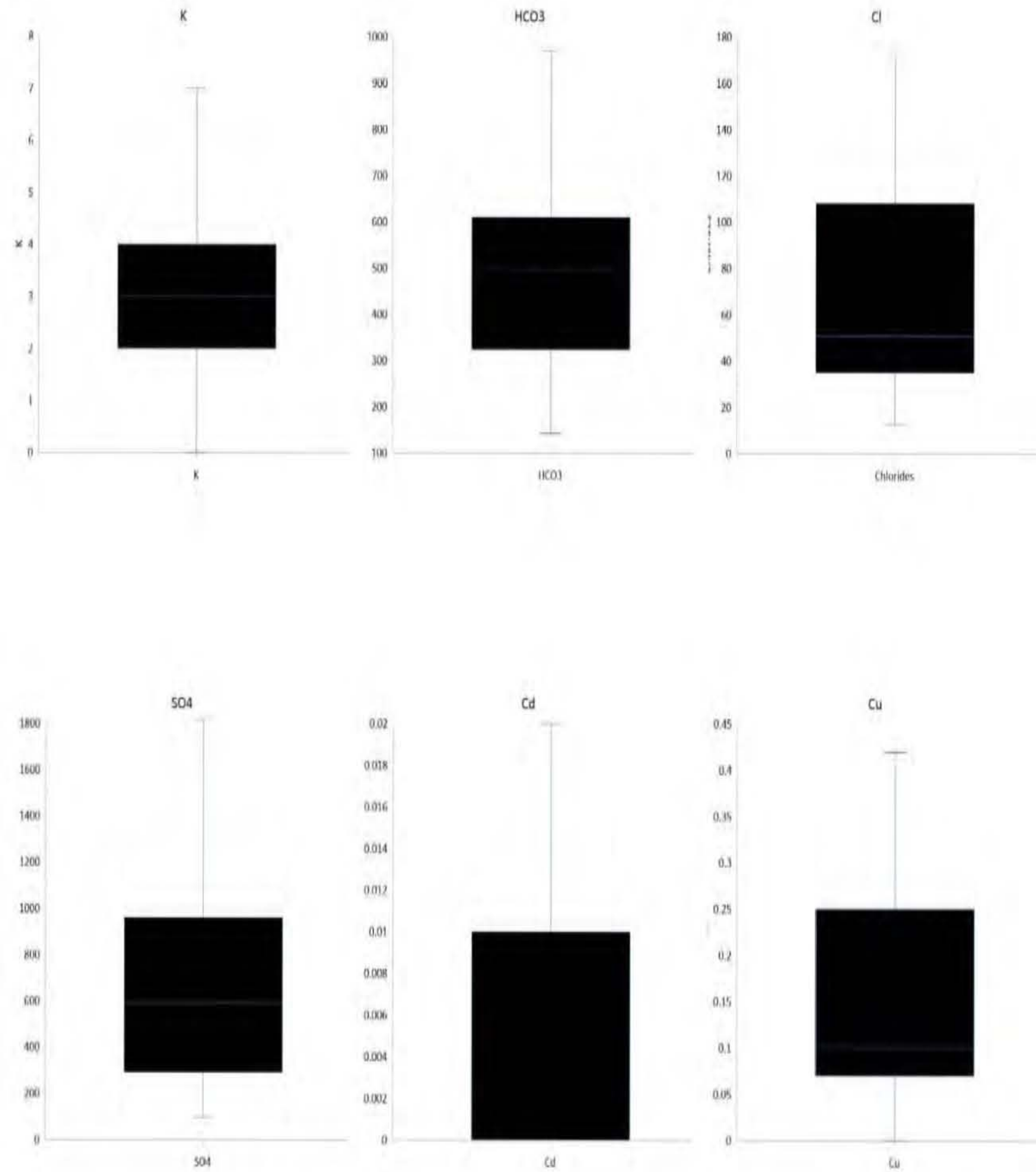


Figure 3. 2: Box and Whisker plot of all the Water Parameters tested in Ground Water of Hyderabad, Sindh.

Table 3. 1: Statistical Summary of drinking water quality parameters in Hyderabad, Sindh.

PARAMETERS	MIN	MAX	MEAN	SD ±
pH	6.7	8.2	7.4	0.3
EC	586	9600	2676.4	2015.7
TDS	441	6650	1946.1	1413.4
TH	97.1	1456.1	648.7	363.8
Alkalinity	182	1116	542	249.7
HCO_3^{2-}	142	1064	495.5	221.5
Cl^-	12.7	1339.1	115.8	193
SO_4^{2-}	94.9	2876	703.3	557.8
K^+	0	14	3.4	2.6
Na^+	12	2200	327.4	374.6
Ca^{2+}	12.5	330	171.4	94.1
Mg^{2+}	3	192	53.6	46.4
Pb	0	0.29	0.05	0.1
Cu	0.02	0.75	0.17	0.1
Cd	0.01	0.06	0.02	0

The salinity of the water is yet another crucial indicator of its quality. Salinity, measured as electrical conductivity (EC), ultimately defines the groundwater conducting capacity. The presence of dissolved ions can influence this capacity. This extremely high value of EC points to the presence of various mechanisms, including water circulation, cation exchanges, surface infiltration, and others (Ahada, 2018). The electrical conductivity (EC) of the bulk of the samples (N = 44) was found to be higher than the permitted range for drinking purposes as determined by WHO (1500 S/cm), which indicates that higher levels of ion concentration were present. Anthropogenic activities and geochemical processes, including ion exchange, weathering, rock-water interaction, evaporation, sulphate reduction, and oxidation processes, can be connected to the significant variability in electrical conductivity (EC). Among these procedures are: (Ramesh, 2012).

In the region under study, the average levels of total dissolved solids (TDS) were 1946.1 mg/L. The TDS readings in 44 samples were higher above the permitted range established by the WHO for the quality of drinking water (i.e., 1000 mg/L). The TDS levels of the water samples that were taken from coastal areas were much higher than average. It is a clear indication that there is a significant concentration of soluble salts in the water, which makes the water unfit for human consumption. The presence of elevated TDS levels in groundwater causes an increase in the salinity of the soil, which in turn influences the fertility and physical features of the soil (Chaudhary, 2018)

Table 3. 2: TDS based Classification of Groundwater Samples

TDS (mg/L)	Water Type	Percent Samples (%)
<500	Desirable for Drinking	8
500-1000	Permissible for Drinking	22
<3000	Useful for Irrigation	56
>3000	Unfit for Drinking & Irrigation	14

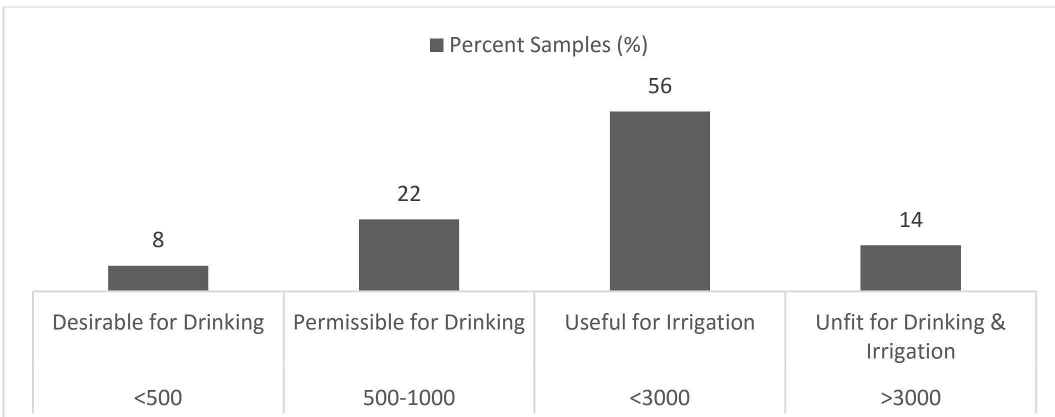


Figure 3. 3: TDS based Classification of Groundwater Samples

The TDS readings of the water samples were utilized by Davis and De Wiest to categorize the samples (Davis, 1966). In the current investigation, most samples were classified as having a TDS that is "Useful for Irrigation," and a total of 18 samples had a TDS that was "permissible for drinking." In dry and semi-arid locations, increased salinity and mineral content are the result of higher evaporation rates, which are reflected in higher levels of total dissolved solids and electrical conductivity.

3.1. 1 Anionic Trends

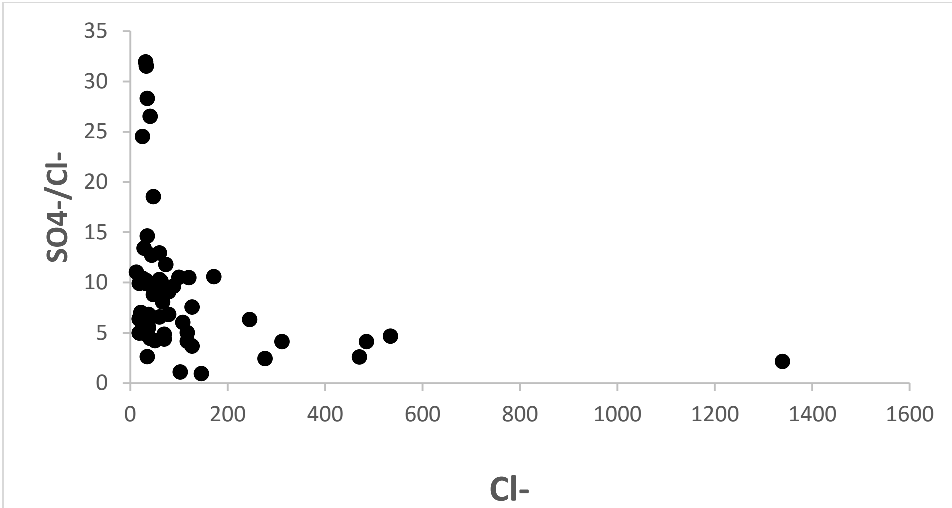
The SO_4^{2-} anion is the predominant anionic contributor in the Hyderabad region. The following is an ascending order of the concentration of anions with respect to the mean value: SO_4^{2-} > HCO_3 > Cl^-. The WHO has established the allowable limit for sulphates at 250 mg/L; however, only 18 of the samples in our research region were found to be within this level.

Table 3. 3: Anionic Trends in Groundwater of Hyderabad

Anions Trend					Percent Sample (%)
SO_4^{2-}	>	HCO_3^{2-}	>	Cl^-	78
HCO_3^{2-}	>	SO_4^{2-}	>	Cl^-	17
SO_4^{2-}	>	Cl^-	>	HCO_3^{2-}	5

Most of the sulphate comes from two different processes: the oxidation of sulfide minerals and the dissolving of sulphate evaporites in groundwater (Alpers, 2000) Groundwater sulphate levels in sandy loam soils can be increased because of surface precipitation that is caused by irrigation. The removal of water causes the subsurface layers of the vadose zone to oxidize, which, according to (Andersen, 2001), leads to the release of SO_4^2 into groundwater as a result of the oxidation of sulfides minerals (Ahada, 2018) In the water of Hyderabad, Cl has been found to have a high positive association with SO_4^2, and it plays an important part in the process of sulphates being leached from the surface into groundwater sources. In this scenario, the ratio of SO_4^{2-} to Cl- might be used as an indicator to determine the number of sulphates that are leaching from surface sources (Suthar, 2009). The chloride comes from a variety of sources on the surface, such as irrigation, precipitation, and evapotranspiration, among other things, and this contributes to an untimely reduction in the ratios of SO_4^2 to Cl in groundwater (Ahada, 2018). The ratio of SO_4^2 to Cl can be found in Hyderabad's groundwater at levels between 0.94 and 31.90. According to the scatter plot of Cl vs SO_4^2/Cl ratio, which shows a decreasing trend with an increase in chloride concentration, surface input was the primary source of sulphates in regions where SO_4^2/Cl ratios were relatively lower. This was the case in areas where SO_4^2/Cl ratios were comparatively lower. Disposal of wastewater, fertilizers, human waste (from pit latrines), animal manure, and other potential sources of dissolved Sulphur dioxide in groundwater could all be major contributors even though human waste and sewage are the most important sources of sulphate (Ahada, 2018) (Suthar, 2009) Both Figure and Figure displayed the results of a statistical study of groundwater that, rather than identifying a single source of sulphate contamination in groundwater across all zones, showed the existence of multiple distinct sources. However, in-depth research is necessary to pinpoint a particular origin of the sulphate found in Hyderabad's groundwater.

Table 3. 4: Distributional trends of Cl− vs SO42−/Cl− ratio within groundwater in Hyderabad, Sindh



3.1. 2 Cationic Trend

It was found that the following is the order in which cations are abundant in Hyderabad: Na^+ > Ca^+ > Mg^+ > K^+. 33 samples fell within the acceptable range when measured against the permitted limit of 200 mg/L, which is the threshold value for Na set by the WHO. The amount of sodium found in natural water directly correlates with the salinity of the groundwater. Sodium is an essential and abundant alkali metal. The most common sodium (Na^+) sources are halite (NaCl), hot springs, sea spray, and brines. Certain silicates and uncommon minerals, such as nahcolite ($NaHCO_3$), are also major contributors. In most cases, sodium is produced because of natural ion exchange, and the rock type of an aquifer is a significant factor in determining the source of the Na^+ concentration in groundwater. (Khan., 2013)

Table 3. 5: Cationic Trends in Groundwater of Hyderabad

Cations Trend							Percent Sample (%)
Na^{+}	>	Ca^{2+}	>	Mg^{2+}	>	K^{+}	43
Ca^{2+}	>	Na^{+}	>	Mg^{2+}	>	K^{+}	24
Ca^{2+}	>	Mg^{2+}	>	Na^{+}	>	K^{+}	21
Na^{+}	>	Mg^{2+}	>	Ca^{2+}	>	K^{+}	11
Mg^{2+}	>	Na^{+}	>	Ca^{2+}	>	K^{+}	2

Ca^{2+} and Mg^{2+} have a permissible limit of 150 mg/L and 200 mg/L, respectively. Of the total of 63 samples for calcium, 38/63 were in the acceptable limit, while for Mg, it was 58/63. The low concentrations of Ca^{2+} and Mg^{2+} in water are caused by the cation exchange of sodium and potassium with calcium and magnesium.

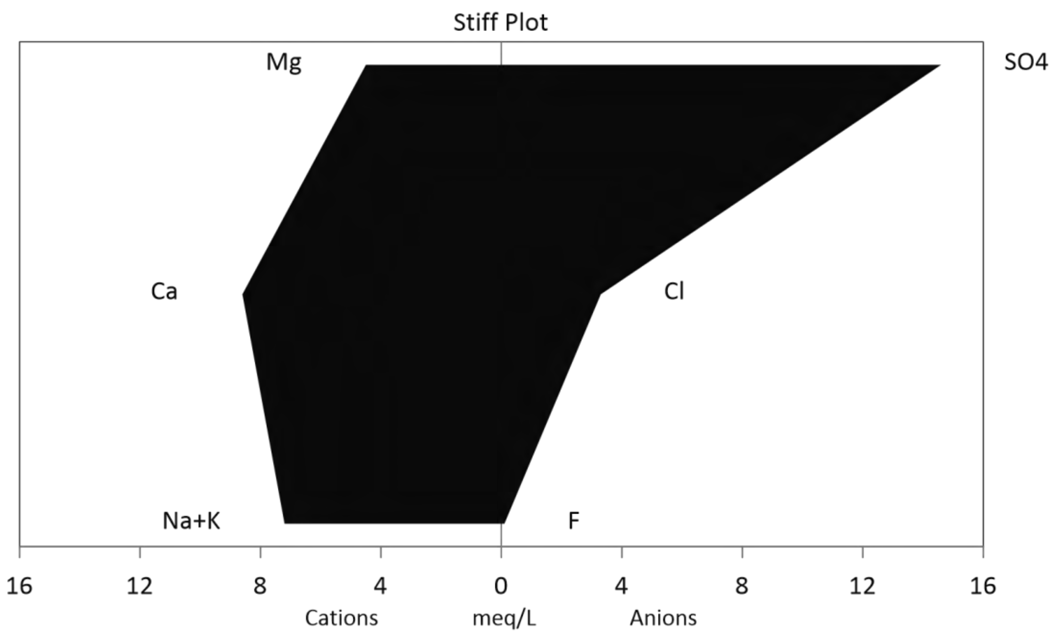


Figure 3. 4: Illustration of Ionic Composition of Groundwater of Hyderabad

Stiff diagrams can also be used to show water quality. A graphical depiction of water quality based on the predominant water ions is called the Stiff diagram. (Stiff, 1951). The stiff diagram represents the average ionic composition analysis of Hyderabad, Sindh which indicates the dominance of SO_4^{2-} and HCO_3^{2-} in anions and in cations the concentrations of Ca^{2+} are greater than that of Mg^{2+} and Na^{+}.

3.1. 3 Spatial Distribution of Groundwater Quality Parameters

To evaluate the spatial distributions of water quality data, the geostatistical module that is included in ArcGIS 10.7.1 was utilized. The parameter values were interpolated utilizing the IDW (inverse distance weighted) interpolation approach, and the values that were interpolated were then categorized utilizing the drinking water standards established by the WHO (WHO, 2011). There was a presentation of maps that showed the spatial distribution of specified measures of water quality.

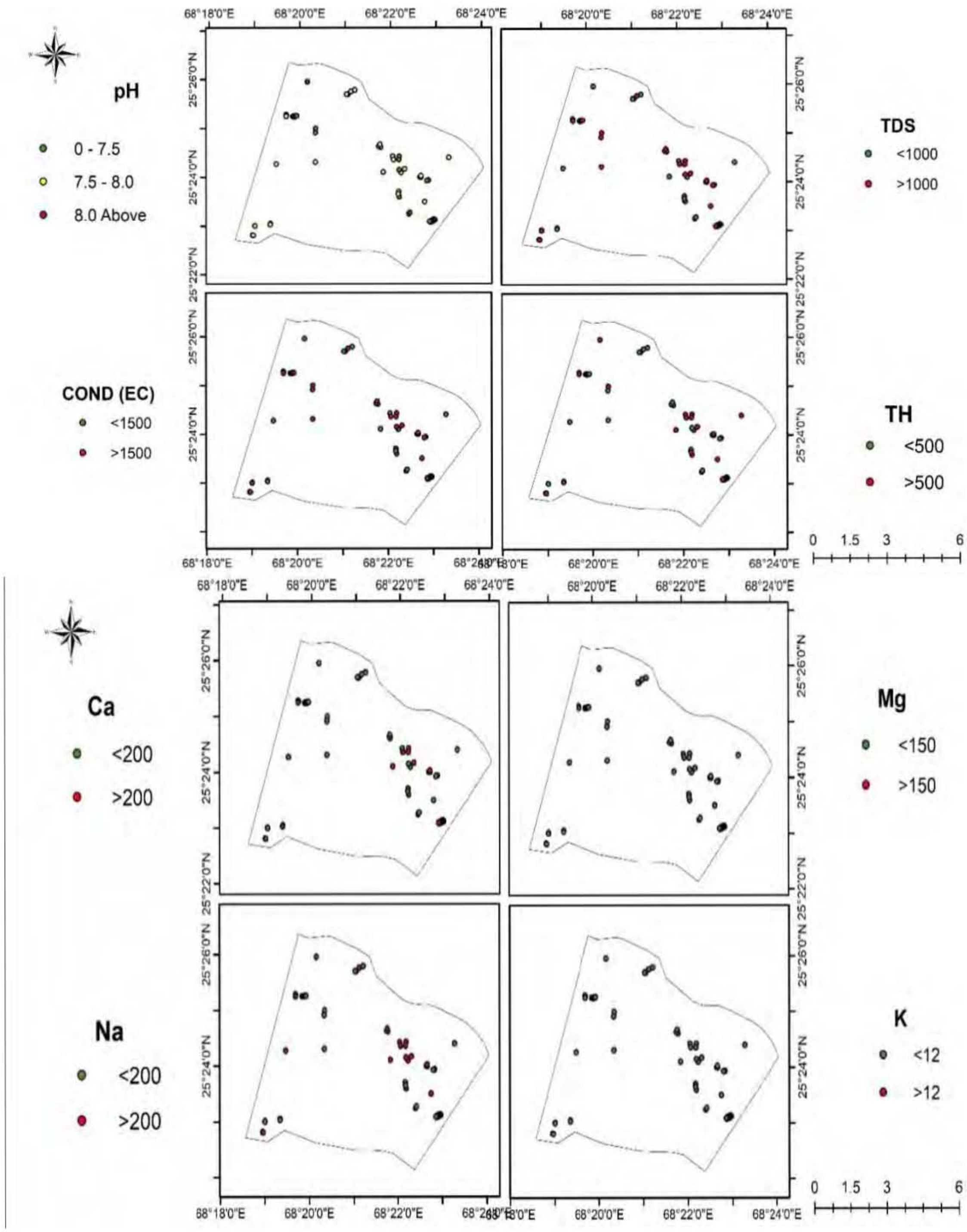


Figure 3. 5: Spatial distribution of pH, EC, TDS, TH, Ca, Mg ,Na & K in Hyderabad

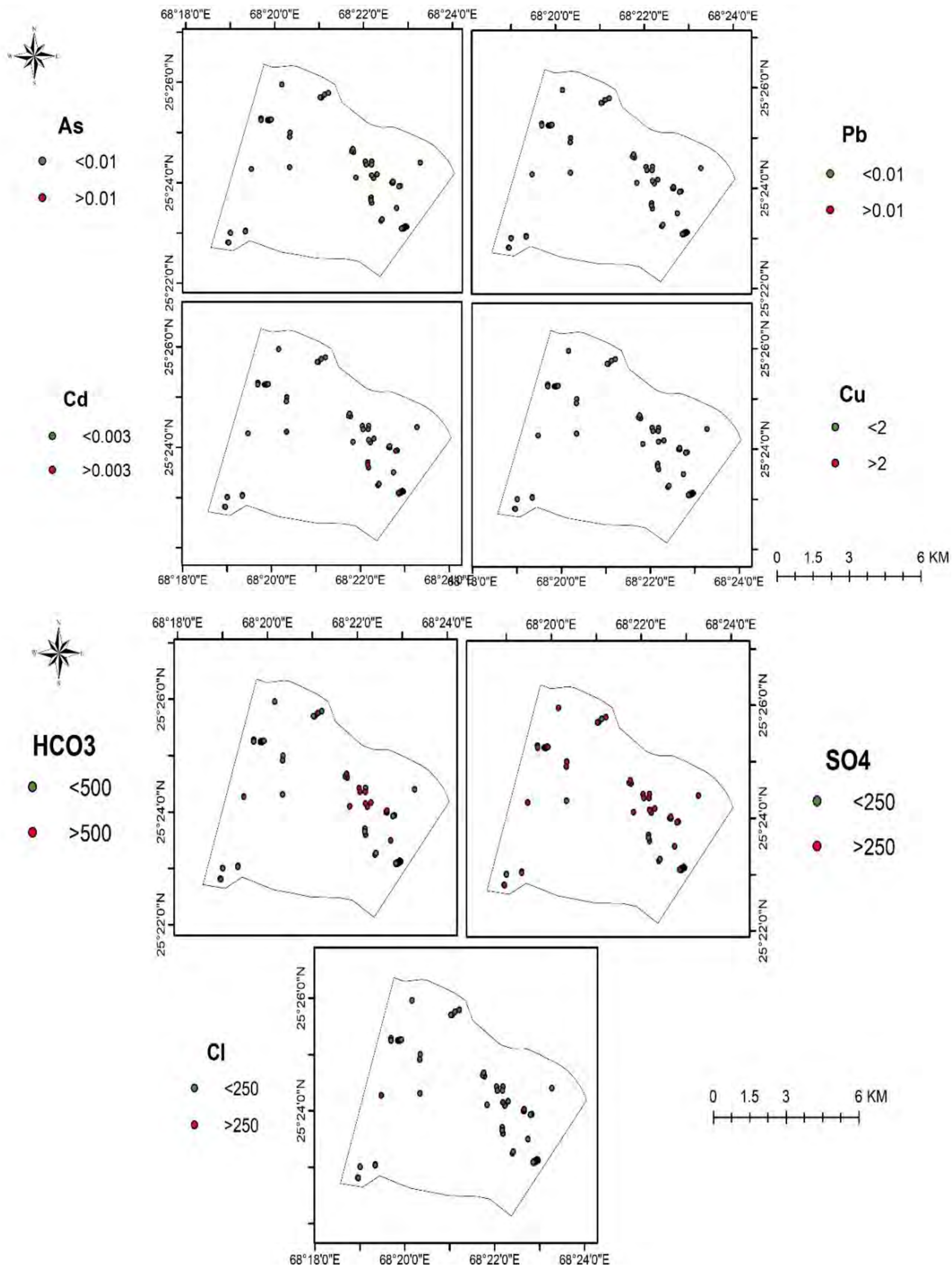


Figure 3. 6: Spatial Distribution of As, Pb, Cd, Cu, HCO3, SO4, Cl in Groundwater Aquifers of Hyderabad

3.1. 4 Hydro-geochemical Facies

The water type of Hyderabad was analyzed by projecting major ionic concentrations on a trilinear Piper diagram in order to gain a better knowledge of hydro-geochemical aspects (Piper, 1944) The Piper diagram is a helpful tool that can be used to illustrate the chemical composition of water as well as the type of hydrogeochemical facies that are present in an area based on the chemistry of the principal ions. The answer was found by plotting values on three fields shaped as triangles, one diamond and another diamond. When projected as a form of water, these two triangles reflect the anions and cations, while the diamond-shaped field reflects the mixture of these two types. The persistent hardness of the water in a region was created by the water samples that were plotted at the top of the diamond. These samples showed that there was a high concentration of Ca^{2+}+Mg^{2+} and SO_4^{2-}+Cl^-. It can be seen in the top left-hand corner that the water has a high concentration of Ca^{2+}+Mg^{2+} and CO_3^{2-} +HCO_3^-, both of which contributed to the temporary hardness of the water in the region. The right side of the diamond might be seen as showing saline water (Na^++K^+ and SO_4^{2-}+Cl^-), depending on your point of view. It is indicated in the lower right-hand corner that the primary components of their make-up are alkali carbonates (Na^++K^+ and CO_3^{2-}+HCO_3^-). The type of water that is mixed is represented in the piper diagram by the diamond in the middle of the diagram (Khan., 2013)

The Chadha diagram (Chadha, 1999) which is another method of expressing hydro-geochemical components of water quality and is also utilized in the current study, is one such method. In this, the groundwater is classified into a total of eight different categories. Ca^{2+}–Mg^{2+}–HCO_3 water-type (temporary-hardness), Ca^{2+}–Mg^{2+}–Cl water-type (permanent-hardness), Na^{+}–Cl water-type (salinity problems both in irrigation and domestic uses), and Na^{+}–HCO_3 water-type (salinity problems both in irrigation and domestic uses). Alkaline earth metals surpass alkali metals. Weak acidic anions surpass (foaming problems in domestic use).

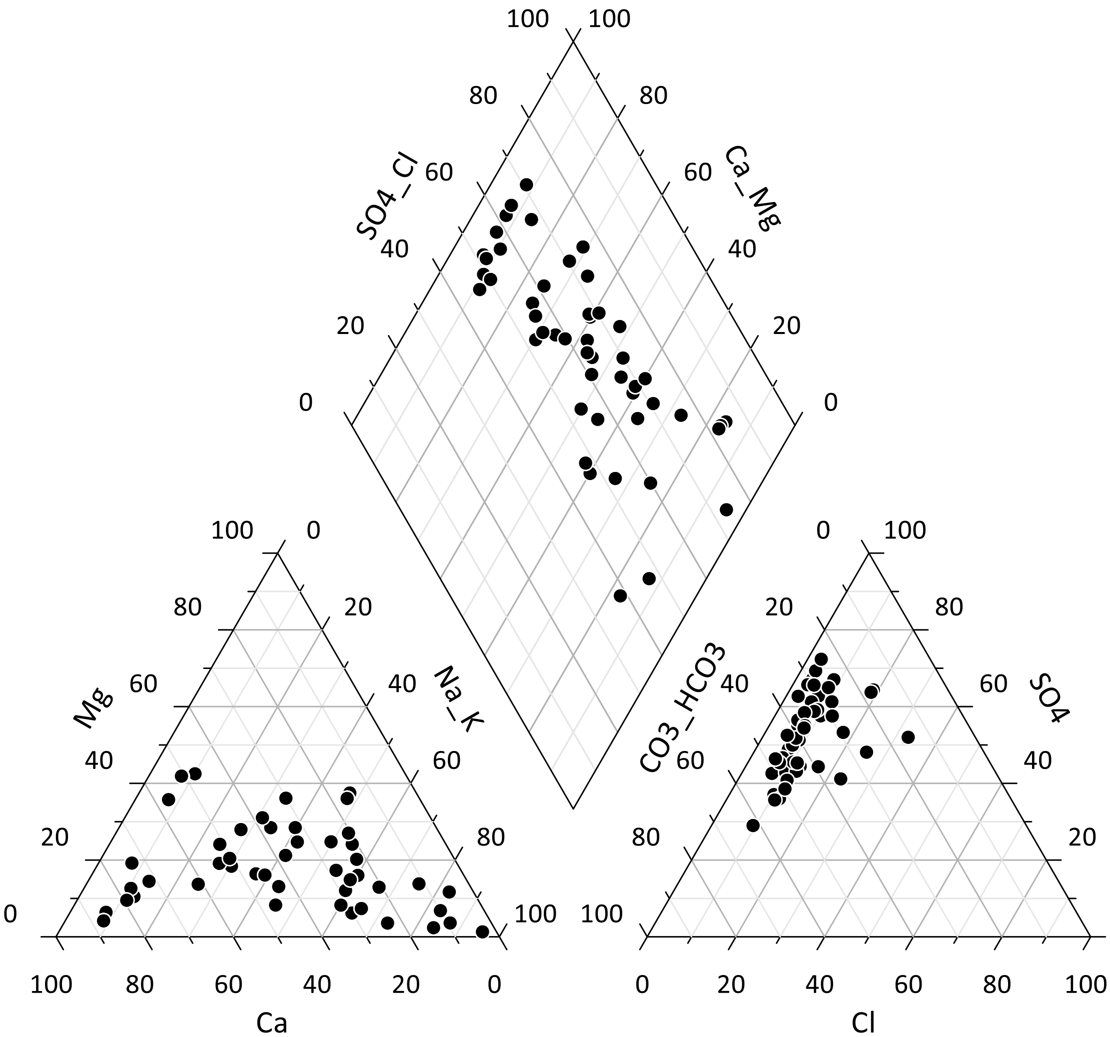


Figure 3. 7: Piper diagram representation of water types in Hyderabad

Both figures showed that most of the groundwater samples in Hyderabad suggest that the amount of alkaline earth metals exceeded the amount of alkali metals, and that the amount of strong acidic anions exceeded the amount of weak acidic anions. The Ca-Mg-SO_4 water type dominates in Hyderabad, accounting for 65% of the clustered samples that demonstrate the city's predominant hydrogeological facies. This is followed by the Na-Cl water type, which accounts for 20%, and the Na-HCO_3 water type, which accounts for 10%. The presence of Ca–Mg–Cl in the water strongly supports the dissolution of carbonate-containing minerals. These findings are consistent with what was seen in the study. The bulk of the water samples in Hyderabad were of the Ca-Mg-SO_4 type, which presented difficulties in terms of both its hardness and its salinity when it came to irrigation and the use of water in homes. 20% sodium chloride water type, which demonstrates the process of seawater intrusion and evaporation.

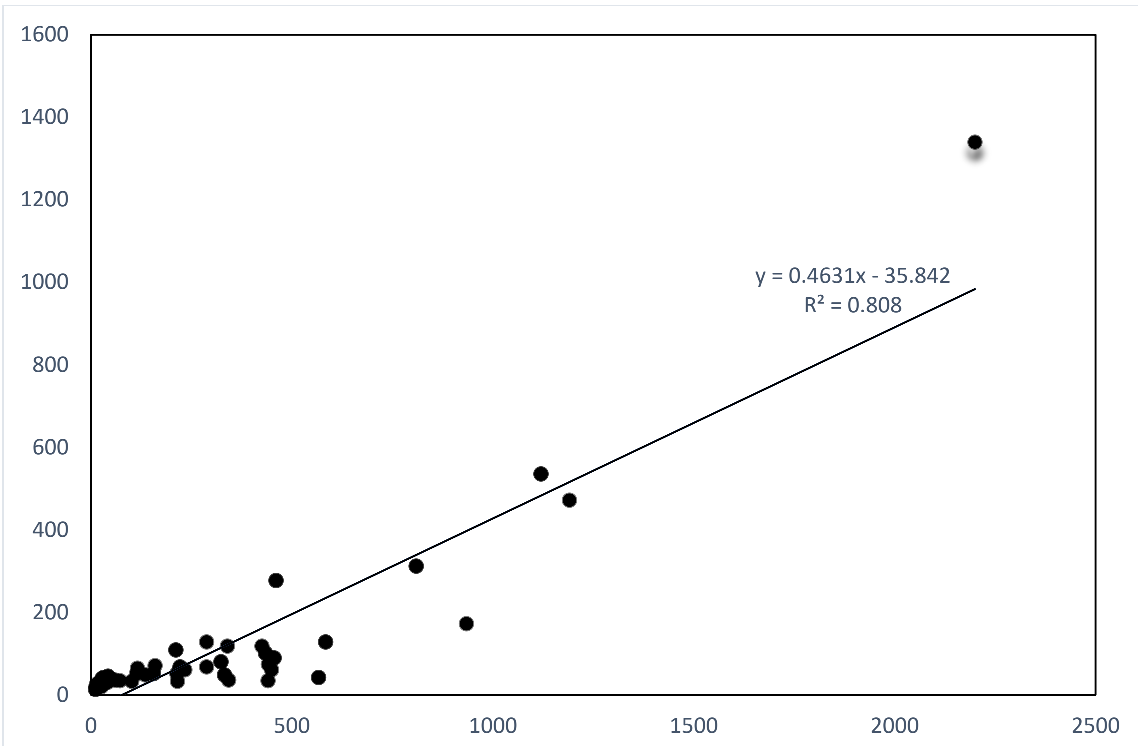


Figure 3. 8: Correlation of Na^+ Vs Cl^- (Na^+ is on x-axis and Cl^- is on y-axis)

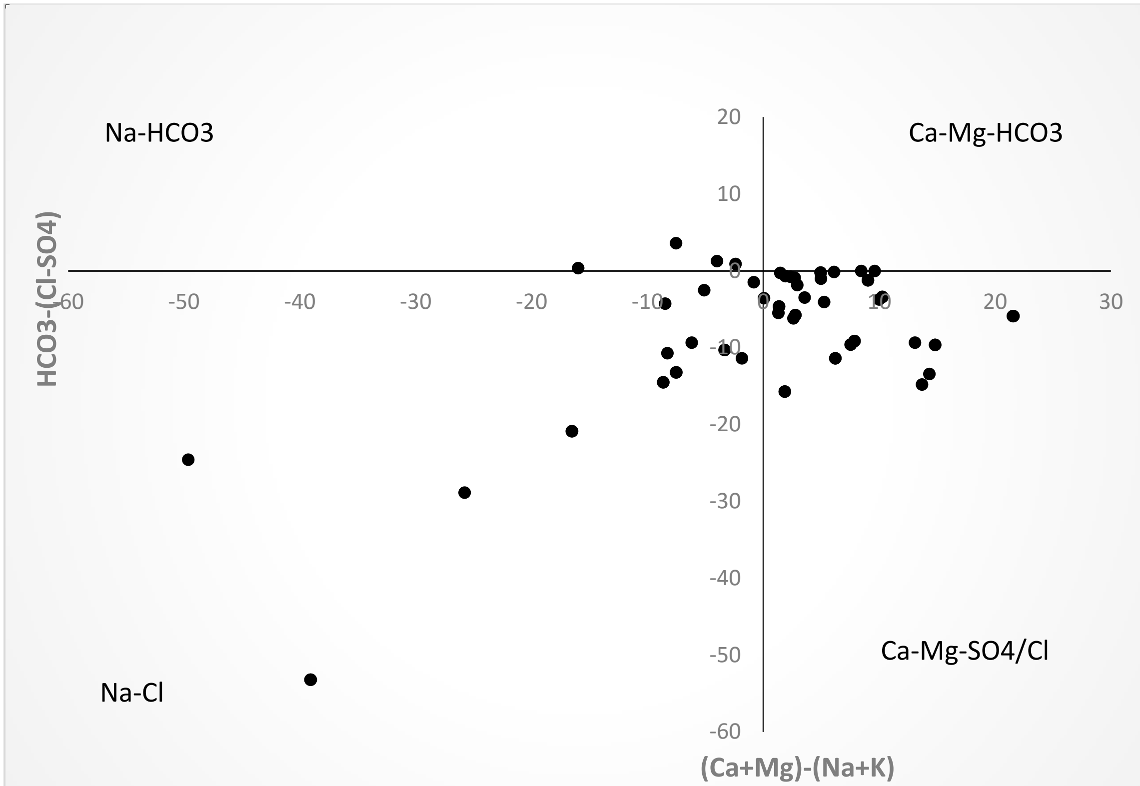


Figure 3. 9: Chadha Diagram of water Samples of Hyderabad, Sindh.

Calcium and magnesium are the anion species that make up most water types. However, in cationic species, sulphates were found to be the most common type of cation, whereas bicarbonate was only shown to be the common type in a few cases. Sodium and chloride were also found in 20% of the samples.

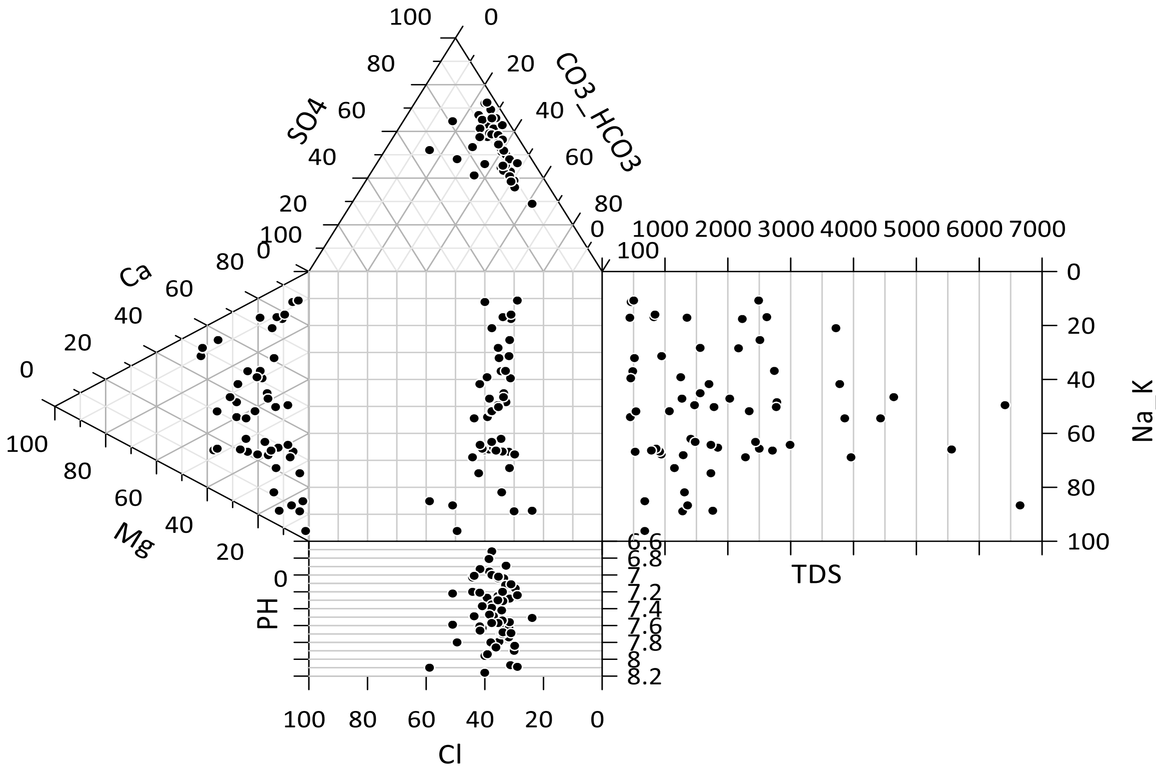


Figure 3. 10: Durov Plot Diagram of Groundwater of Hyderabad

The Durov diagram is a composite plot made up of two ternary diagrams with the cations displayed against the anions; the expanded version adds TDS and pH data to the sides for further comparisons. The side plots the total cations against the total anions concentrations. The primary goals of the Durov diagram are to reveal correlations and characteristics for a sizable sample group and to cluster data points that reflect samples with comparable chemical makeup. This method was used to provide the total or absolute concentrations of two specified parameters, such as pH, TDS, or total cation or ion concentration, as well as to evaluate the water types based on the geochemical processes that could have changed the groundwater type. Groundwater can be changed by geochemical processes, as demonstrated by the Durov diagram in the above figure. In the anion part, most samples are of the Intermediate type in the Cations section, followed by the Na type of water and the Mg^{2+} type. Most of the samples are of HCO_3^{2-}type and some samples lie in intermixing section. In the binary section most, samples show simple dissolution or mixing while a no number of samples were plotted in Na^+ and K^+ ion exchange or reverse ion exchange zone.

3.1. 5 Mechanisms controlling Groundwater Chemistry

After determining the kind of water and the hydro-geochemistry of the water, the next stage in characterizing water quality is to determine the various mechanisms that define the different types of water or the quality of the water. A scatter diagram model was proposed by Gibbs (Gibbs, 1970) to look deeper into hydrogeochemical processes. This model demonstrated three fundamental natural mechanisms that regulate the principal ion chemistry of groundwater. These mechanisms consist of evaporation, weathering of rocks, and atmospheric precipitation. To evaluate the concentrations of total dissolved solids (TDS), the ratios of $Cl/(Cl+HCO^3)$ for anions and $(Na^++K^+)/(Na^++K^++Ca^{2+})$ for cations were utilized.

It shows that the water samples fall into evaporation dominance and rock weathering interaction has an impact on groundwater. The Gibbs diagram for the research area showed how crucial rock-weathering is as the main source of dissolved ions that control the chemical composition (Liu et al., 2015). Water samples shifted from the rock domination field to the evaporation field because of the high evaporation rates, which raised TDS concentrations. This illustrates how evaporation affects the chemistry of shallow groundwater and elevation above sea level. Conversely, the degree of rock-water contact was determined by elements such as aquifer water residence duration, topographic condition, mining, and human (agricultural and sewage wastes) activities. Because Hyderabad has a semi-arid environment, groundwater evaporation is a typical occurrence. Evaporation increases salinity by increasing sodium and chloride content in proportion to TDS value; these ions are produced by the weathering of Mg^{2+}, Na^{+}, and SO_4^{2} minerals (dolomite, anglesite, anhydrite, halite, gypsum).

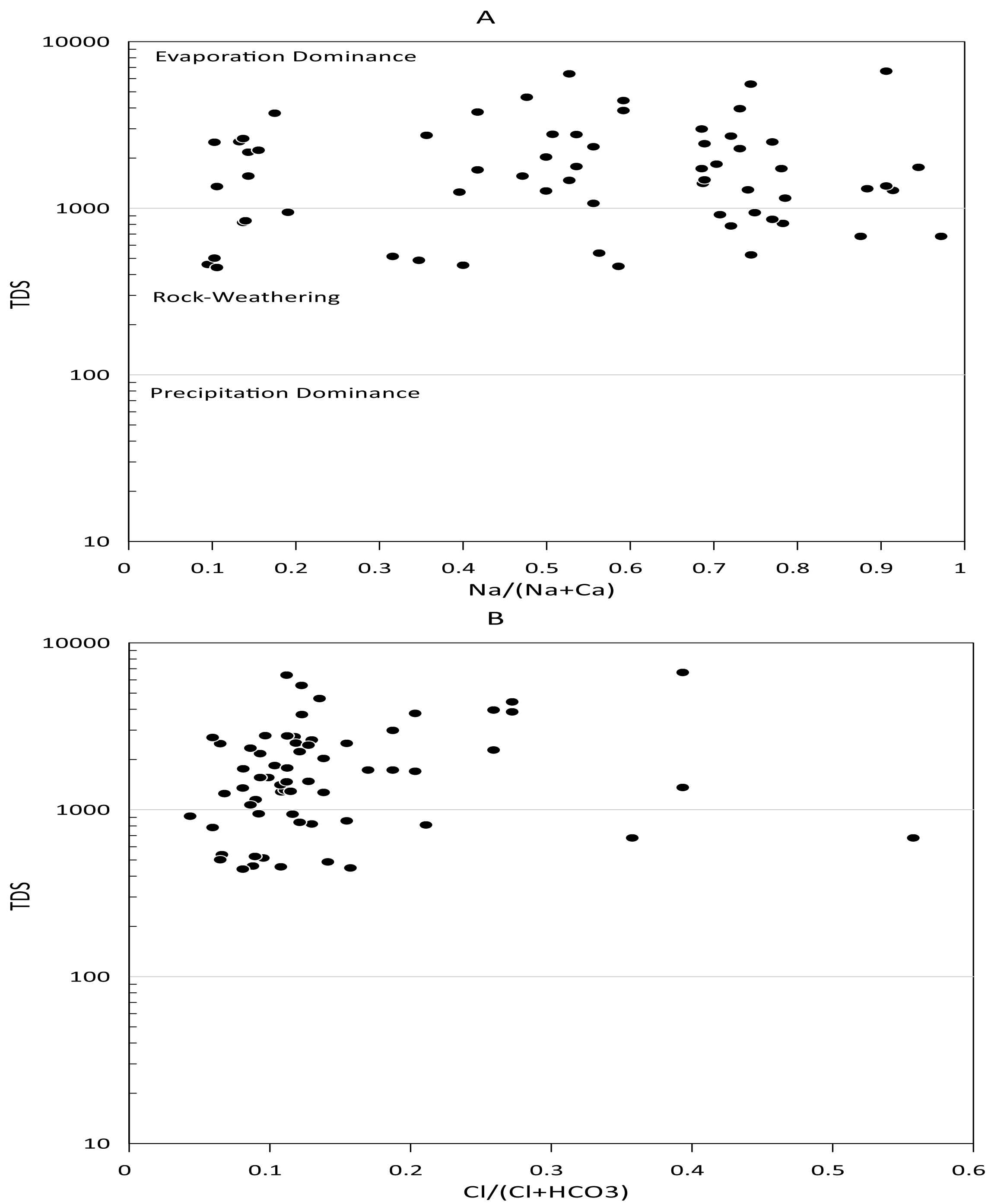


Figure 3. 11: Gibbs diagram representing the water chemistry of Hyderabad [A] Cations [B] Anions.

3.1. 6 Cation Exchange

During its travel or residence underground, groundwater may exchange ions with its host environment (rock-water interaction), and one established method for doing so is the CAI-I (Chloro-alkaline indices) introduced by Schoeller (Schoeller, 1965) The CAIs were computed. Numerous researchers have utilized CAI to calculate ion exchange in different regions globally (Adimalla, 2018); (Koffi, 2017)

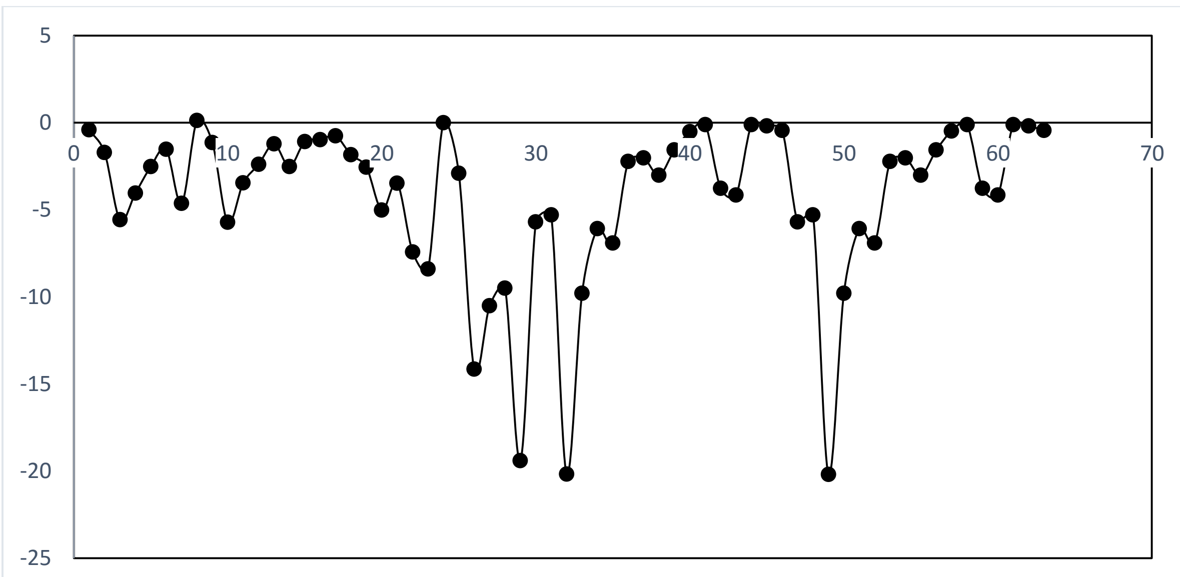


Figure 3. 12: Chloro-Alkaline Indices of Hyderabad, Sindh.

Water samples from all over Hyderabad have the maximum negative CAI value in the rock-dominant arid and semi-arid region, indicating a clear cation exchange (Na^{+} and K^{+} from water are exchanged with Ca^{2+} and Mg^{2+} in host rocks during the period of residence and movement). This suggests that potassium and sodium are released into the water and calcium and magnesium are taken out (Liu, 2015). The primary mechanism regulating the chemical composition of Hyderabad's groundwater, as per the CAI investigation, is cation exchange.

3.1. 7 Drinking Water Quality Index

A method for consistently providing data on water quality that the general public can easily comprehend and report on is the water quality index (WQI). The water quality index enhances the evaluation of inland water quality since it is connected to personal health. (Ponsadailakshmi et al., 2018; ener et al., 2017). The goal of the water quality index is to provide sophisticated data on water quality to a variety of management and policymaking organizations and translate it into figures that the public can use and comprehend. (A. D. Mohammad & Rind, 2020). An index called the Water Quality Index (WQI) assesses the overall impact of multiple water quality issues. (ener et al., 2017).

Based on WQI values, water quality is classified into five categories: excellent water, good water, bad water, very poor water, and water unfit for drinking [50, 51-100, 101-200, 201-300, & >300] (J. Ahmed et al., 2020; ener et al., 2017). These values were classified according to their WHO standard limits. Based on recent research (J. Ahmed et al., 2020; Ponsadailakshmi et al., 2018; ener et al., 2017), Based on the relative importance of each of the fifteen drinking water quality indicators to health and portability in the total drinking water quality, each parameter was given a weight (wi). Following that, relative weights were calculated using the weights.

Table 3. 6: Classification of Samples into different water classes of the basis of their WQI

WQI VALUE	WATER CLASS	No of Samples	Percent Sample (%)
<50	Excellent Water	40	63.5
50-100	Good Water	0	0.0
100-200	Poor Water	8	12.7
200-300	Very Poor Water	6	9.5
>300	Unsuitable for Drinking	9	14.3

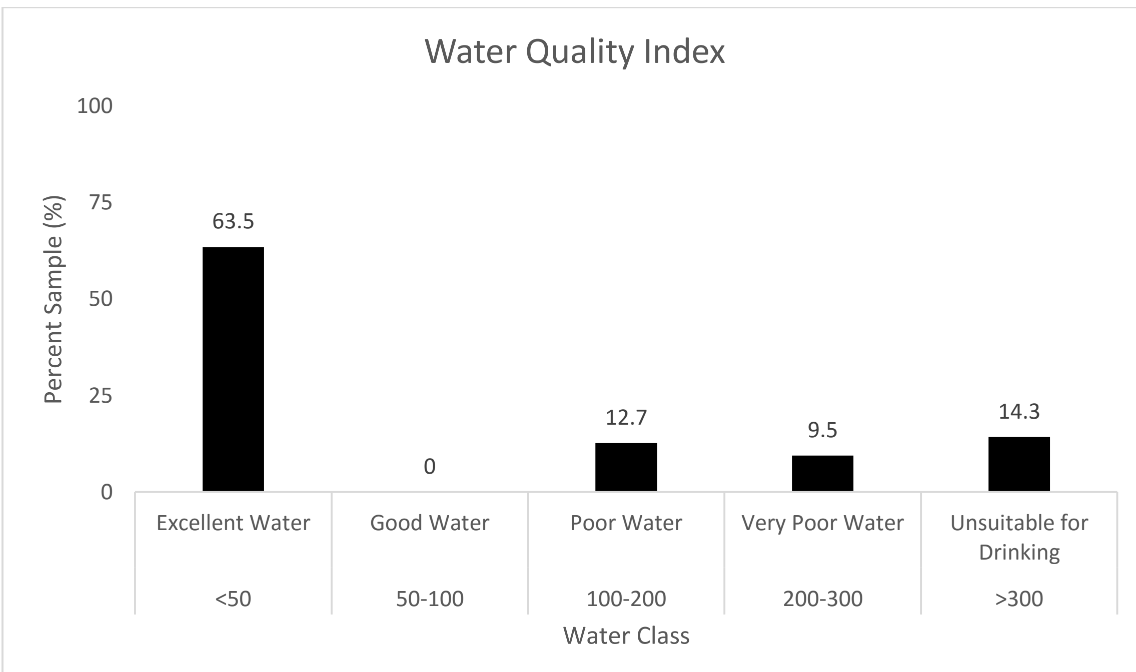


Figure 3. 13: Bar Graph representation of Percent Samples (%) in each class of WQI

As per the WQI 63.5% samples are in Excellent water category, while 12.7% are of Poor quality water and 9.5% percent samples are in very poor water class the remaining 14.3% samples are unsuitable for drinking. From these results it is shown that the water of groundwater aquifers of Hyderabad, Sindh are not very much detrioted and only a few samples were above the limit and are suitable for human consumption

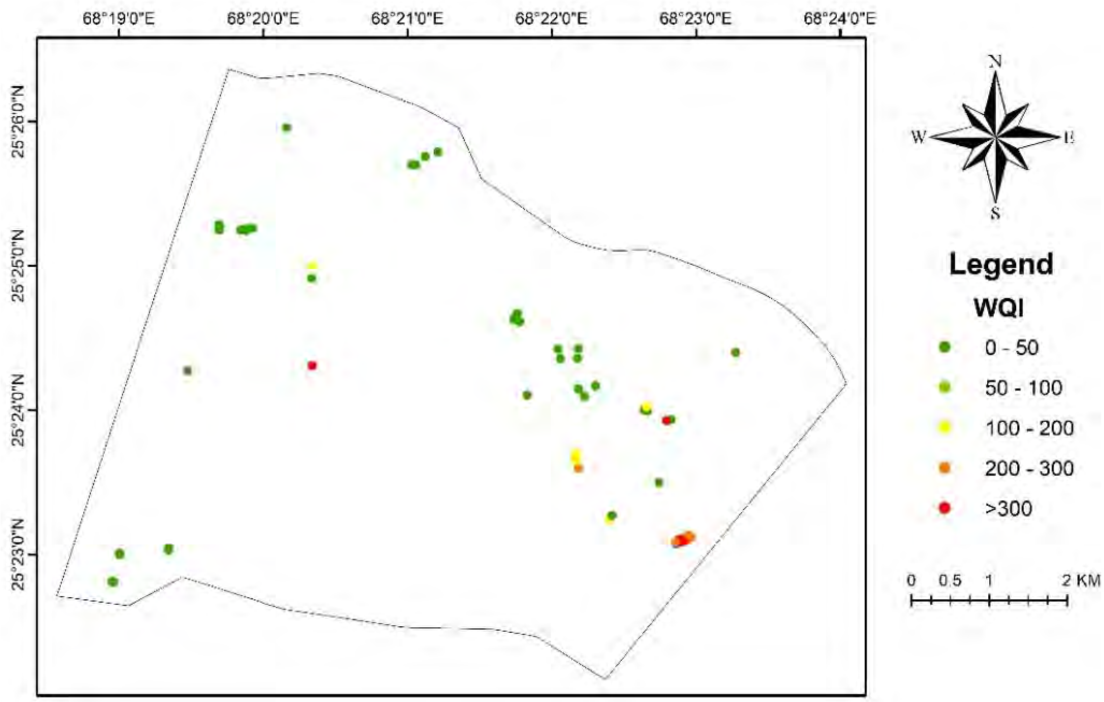


Figure 3. 14: Spatial Distribution of Water Quality Index in Groundwater Aquifers of Hyderabad

3. 2 Irrigation Water Quality

Pakistan is primarily based on agriculture. Crop productivity is directly impacted by the water quality used in irrigation systems. The effects of groundwater's mineral components on plants and soil determine whether it is suitable for agriculture. Plant metabolic disturbance is one impact of the chemicals. Water is physically blocked from reaching the plant's stems and leaves due to reduced soil permeability and decreased osmotic pressure within the plant's cells (Ghalib H. B., 2017). As a result, it's crucial to understand how water quality affects your home.

Hyderabad's groundwater aquifers were assessed for irrigation water quality using a few critical hydro-chemical criteria. Among them were the following: permeability index (PI), percent sodium (%Na), residual sodium carbonate (RSC), sodium adsorption ratio (SAR), magnesium hazard (MH), electrical conductivity (EC), soil salinity potential (SSP), and Kelley ratio (KR).

3.2. 1 Irrigation Water Quality Parameters

The quality of the water used for irrigation was investigated and evaluated to establish whether Hyderabad's groundwater is appropriate for use in irrigation. The statistical information is included in the table together with the calculated values of the water samples. The indicators of irrigation water quality include the minimum, maximum, mean, and standard deviation. The groundwater quality data interpretation for irrigation has been completed in accordance with the FAO's criteria (Ayers, 1977) (Christiansen, 1977)

Table 3. 7: Statistical Summary of irrigation water quality parameters

PARAMETERS		MIN	MAX	MEAN	SD ±
	EC	586	9600	2676.4	2015.7
	SAR	0.3	47	6	7.8
	RSC	-21.2	14.7	-4.7	7.3
	Na%	7.4	95.1	42	-23.6
	MH%	4.5	71.4	32.9	16.2
	PI	17.9	109.9	57.4	22.1
	SSP	1.53	67.7	10.59	10.7
	KR	0.08	21.35	1.48	2.9

3.2. 2 Electrical Conductance (EC)

Another important factor to consider when assessing the quality of water for irrigation is electrical conductivity (EC). Salinity is commonly expressed as electrical conductance (EC), which is a factor that impacts the amount of water that is available to crops. The measured EC of the area ranged from 586 microS/cm to 9600 microS/cm. As seen in the table, there were four different categories of salinity: excellent, good, permissible, and doubtful (Richards, 1954) In the area where our research was conducted, there was not a single sample that belonged to the excellent water class. 13% of samples were rated as good, 41% fell within the acceptable range, and 46% were not suitable for irrigation in any way. According to the findings, a significant proportion of the samples are unsuitable for irrigation and should not be used.

3.2. 3 Sodium Adsorption Ratio

Another factor to consider when assessing irrigation water quality is the sodium absorption ratio (SAR). The harm posed by salt and alkali to irrigation water is assessed using the relative and absolute concentrations of cations in the water. It was brought to our attention by the USSL, and it is expressed as the sodium absorption ratio (SAR). (Richards, 1954). The term "salinity" refers to an extremely high sodium concentration. It is possible for salinity to be harmful to fruit trees and to influence crop output as well as the physical features of the soil (soil degradation). If a certain water quality or type is going to be the only source of irrigation for a lengthy period of time, it is recommended that you discontinue the use of water with a SAR value that is more than 10 milligrams per liter (mg/L) (Zaman, 2018). The computed SAR values were in the range of 0.2 and 70.7. A high SAR value indicates that the soil's calcium and magnesium ions may be replaced by the salt content of irrigation water, which could eventually cause the soil's structure to deteriorate. (Khan., 2013). Only six of the samples were found to have SAR levels that were higher than the permissible limit, meaning that most of the samples have SAR levels that place them in the excellent to good water class. These waters are suitable for use in irrigation.

3.2. 4 Residual Sodium Carbonate

In the form of residual sodium carbonate is yet another method that has been extensively applied for the purpose of evaluating the risks posed by increased sodium (RSC). This phenomenon is linked to the precipitation of CaCO3 and MgCO3 (Zaman, 2018). The classifications of irrigation water according to the RSC (Wilcox, 1955) values were shown in a table. This table reveals that most of the research region samples were suitable for use in agriculture. According to the findings of the research, the mean values of RSC are -3.5, and the concentrations range anywhere from -35.6 to 13.1. The presence of negative RSC values indicates that the water is of a high enough quality to be used for irrigation. 43% of the samples had a positive RSC and were not fit to be used for irrigation.

3.2. 5 Permeability Index

The Permeability Index of the soil is a comparable metric that can be used to gauge the quality of irrigation water (Doneen, 1964) It is affected by prolonged usage of irrigation water that is high in sodium carbonate (HCO_3), total dissolved solids (TDS), and soil type. (Kouadra, 2020); (Naseem S. A., 2012)The permeability index can range from 17.1 to 109.9 at different times. 33% of the samples were rated as great, 59% of the samples were rated as good, and just 5 samples were rated as unsuitable. (Naseem S. A., 2012)

3.2. 6 Magnesium Hazard

Magnesium Hazard, also known as MH, is another significant component of irrigation water. Its high concentrations indicate that there has been an increase in the soil's alkalinity, which in turn has a negative impact on crop productivity (Naseem S. A., 2012). The magnesium hazard (MH) was calculated to be anywhere from 4.5 to 91.7 about the mean values of 39.7. According to the guidelines established for the classification of water in terms of magnesium hazard, water is considered dangerous and unsuitable for use in irrigation if its magnesium hazard level exceeds 50. (Szabolcs I. &., 1964). The findings indicate that the water in Hyderabad is suitable because unsuitable conditions were discovered in only 33 percent of the samples tested. A high MH content may lead to an increase in the soil's alkalinity, which has a negative impact on crop output (Naseem S. A., 2012)

3.2. 7 Sodium Percentage

One of the most important factors to consider when determining whether natural water is suitable for agricultural use is the sodium concentration expressed as a percentage (Na%) (Wilcox, 1955). Plant growth is inhibited when there is a high concentration of sodium in the water and soil because this reduces the permeability of the soil (Khanoranga, 2018). In Hyderabad, the range of possible percentages of sodium was from 5.5 to 97%, with a value of 44.4 accounting as the city's average. Irrigation water with a sodium concentration of more than 60 percent has the potential to cause sodium accumulation as well as possible degradation of the soil's structure, infiltration, and aeration (Naseem S. R., 2010). In Hyderabad, 27 percent of samples had levels that were unsafely high.

3.2. 8 Kelley's Ratio

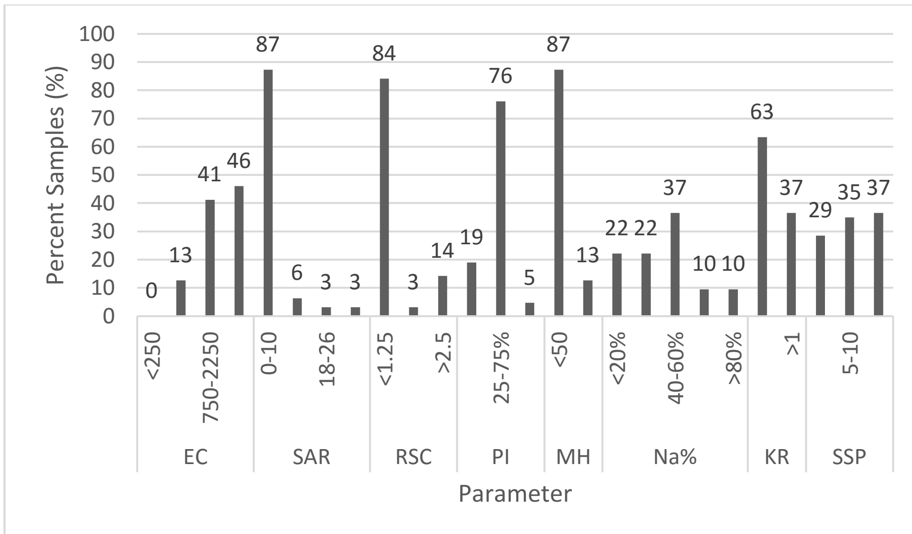
Kelley (Kelly, 1940) suggested using a key factor called Kelley's ratio (KR) to assess irrigation water quality based on the ratio of observed salt to calcium and magnesium levels. It is commonly accepted that irrigation should not be conducted with water that has a Kelley's ratio greater than one. In Hyderabad, the range of KR values is 0.1 to 32,1, with an average of 1.7; 36% of the samples above the permissible threshold.

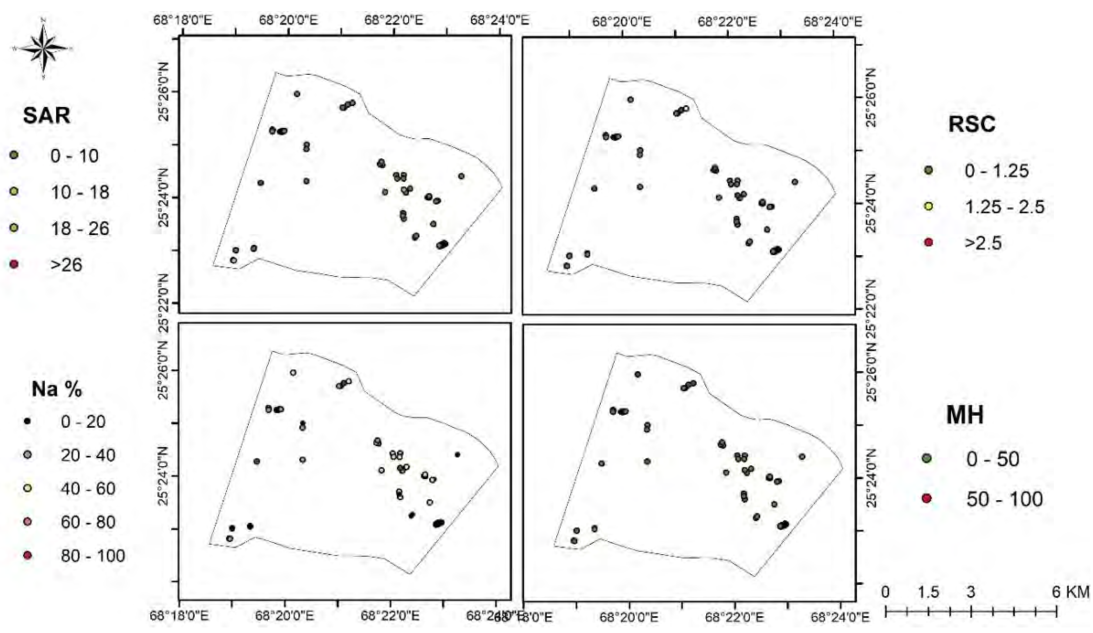
3.2. 9 Soil Salinity Potential

Doneen (Doneen, 1964) studied the salinity potential of irrigation water. He began his discussion by stating that the suitability of water for irrigation is not solely dependent on the quantities of soluble salts present in the water. According to the findings of several studies, when salts have a low solubility, they first precipitate and then accumulate in the soil for several successive irrigations. On the other hand, an increase in the amount of highly soluble salts leads to a rise in the salinity of the soil (Ogunfowokan, 2013). In Hyderabad, the results for SSP vary from 1.5 to 67.8, and the mean value was found to be 9.7. Twenty-eight percent of the samples were found to be higher than the acceptable level.

Generally, according to the above interpretation of various irrigation parameters, most of the water samples studied were suitable for irrigation in terms of SAR, RSC and PI, EC, KR, Na% and SSP.

Table 3. 8: Graphical Representation of Irrigation water classes based on %





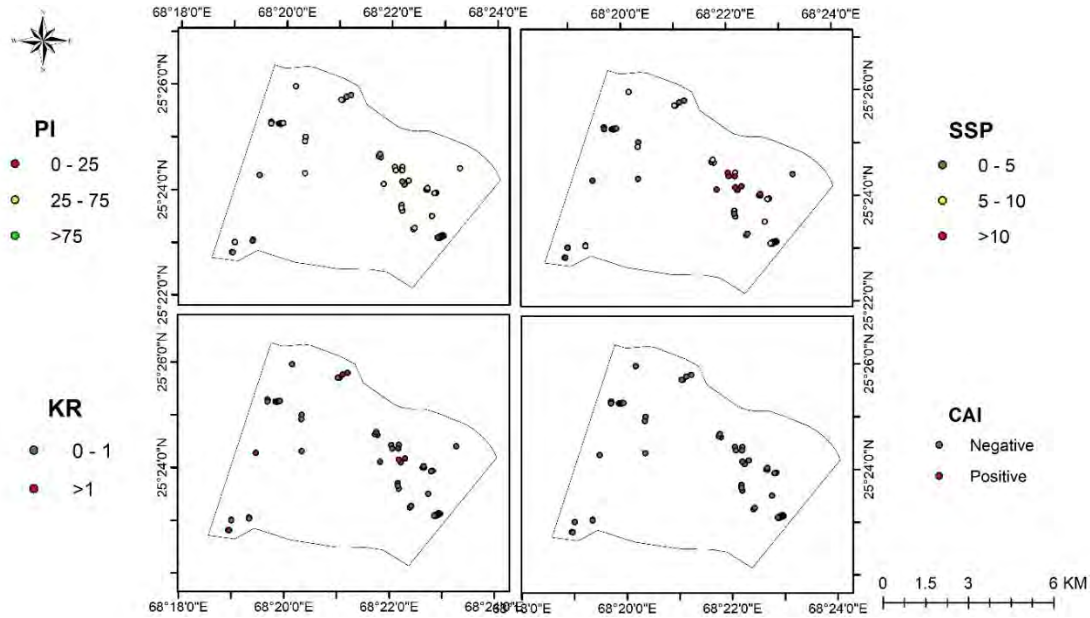


Figure 3. 15: Spatial Distribution of Irrigation Water Quality Parameters in Hyderabad, Sindh.

Table 3. 9: Classification of irrigation water based on different parameters in percent

Parameters	Range	Water Class	Percent Samples (%)
EC	<250	Excellent	0
	250-750	Good	13
	750-2250	permissible	41
	>2250	Doubtful	46
SAR	0-10	Excellent	87
	10-18	Good	6
	18-26	Medium	3
	>26	Bad	3
RSC	<1.25	Good	84
	1.25-2.5	Suitable	3
	>2.5	Doubtful	14
PI	>75%	Good	19
	25-75%	Suitable	76
	<25%	Unsuitable	5
MH	<50	Suitable	87
	>50	Unsuitable	13
Na%	<20%	Excellent	22
	20-40%	Good	22
	40-60%	permissible	37
	60-80%	Doubtful	10

	>80%	Unsuitable	10
KR	<1	Suitable	63
	>1	Unsuitable	37
SSP	<5	Excellent to Good	29
	5-10	Good to Injurious	35
	>10	Injurious to Unsatisfactory	37

3.2. 10 Hydro-chemical Analysis of Ground Water

The U.S. Salinity Laboratory diagram (Richards, 1954) is used to comprehend the hydro-chemical examination of water samples for irrigation applications by showing the association between SAR and EC (on a log scale). The integrated impact of EC and SAR—which stand for salinity and alkalinity hazards, respectively—is depicted in the graphic.

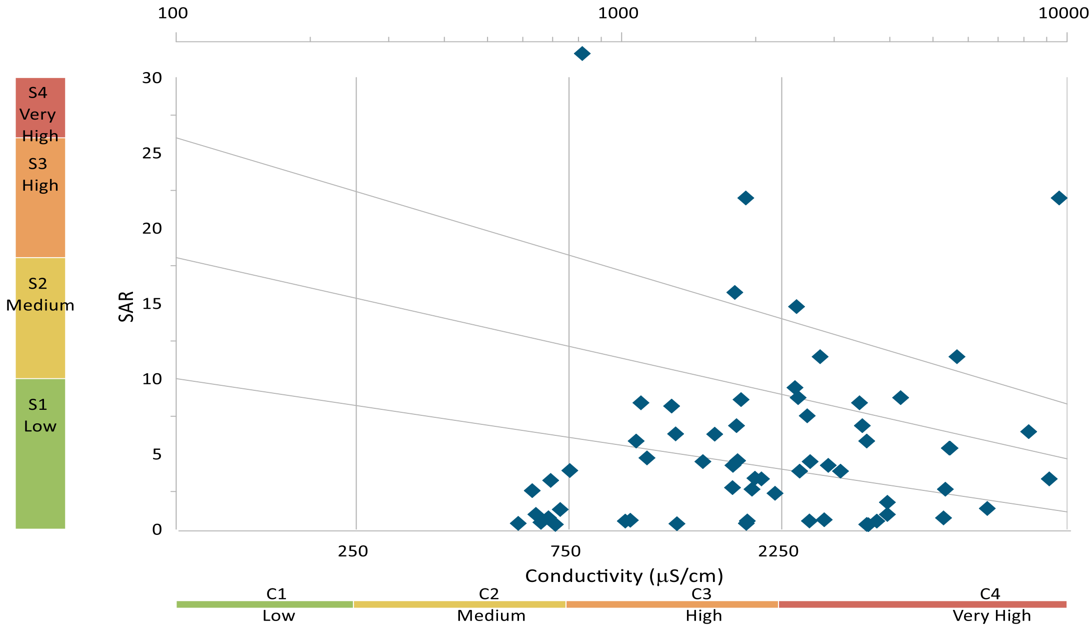


Figure 3. 16: USSL (U.S. Salinity Laboratory diagram) water classification of Hyderabad, Sindh.

The samples fell in C4S1, C3S1, C2S1, C4S2, C3S2, C4S3, C4S4 and C3S4 sections of the USSL diagram, most of the samples were between C4 and C3 zones that indicates high level of salinity while sodium hazard is lower. Only 7 samples were in high salinity and high sodium hazard zone.

Wilcox (Lv. Wilcox, 1955) used a Wilcox diagram and separated irrigated water into five classes based on Na^{+}% and electrical conductivity (EC).

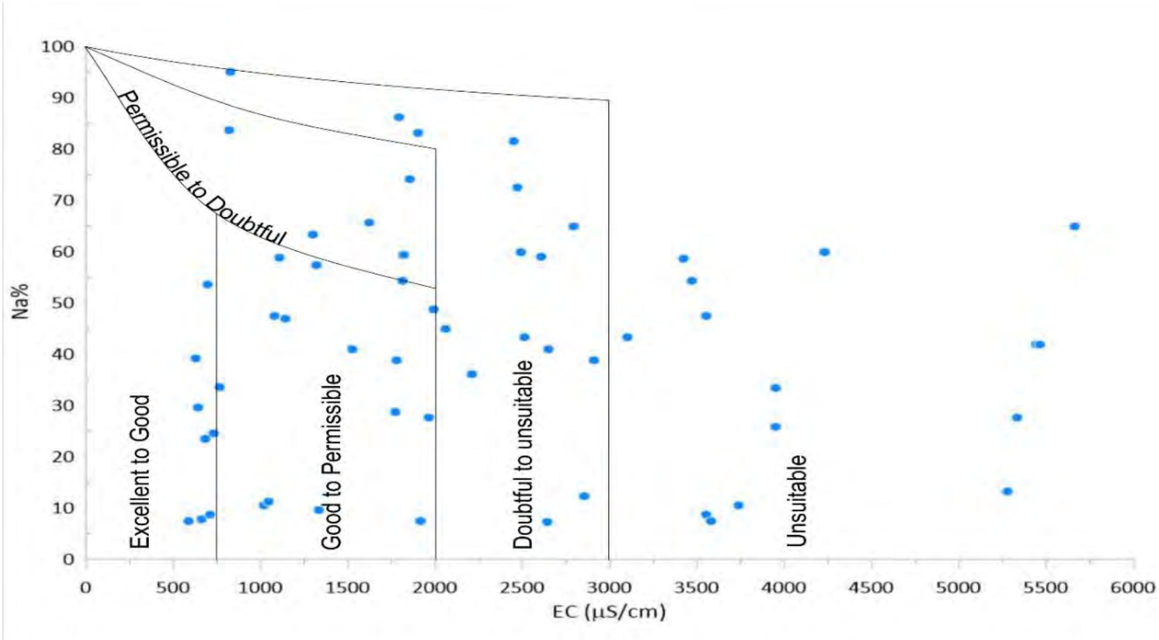


Figure 3. 17: Wilcox diagram for irrigation water of Hyderabad, Sindh.

Samples from groundwater of Hyderabad, Sindh were plotted, and 8 samples were in ―Excellent to Good" class while 15 were in ―Good to permissible" range, 5 samples were in ―Permissible to Doubtful" class while 15 samples were ―Doubtful to unsuitable" and 15 samples were Unsuitable for usage due to high values of EC and Na%. Overall, the groundwater of Hyderabad can be utilized for irrigation practices while the adverse consequences are caused by high Na levels in irrigation water. It absorbs clay particles and disperses calcium and magnesium ions. Such dispersion affects soil permeability, which is further associated with reduced infiltration, hydraulic condition, and surface crusting (Chaudhary & Satheeshkumar, 2018).

3. 3 Statistical Analysis of Ground Water

3.3. 1 Pearson's Correlation

A multivariate analysis of the groundwater quality data set was conducted using principal components analysis, cluster analysis (CA), and Pearson's correlation. Based on the data displayed in the table, EC, and the ions Na^{+}, SO_4^{2-}, HCO_3^{-}, and Cl^{-} have a significant relationship. EC and Ca^{2+} are more strongly correlated than Mg^{2+} is. The correlation between SO_4^{2-} and Cl^{-} reveals anthropogenic causes to be the cause of the correlation.

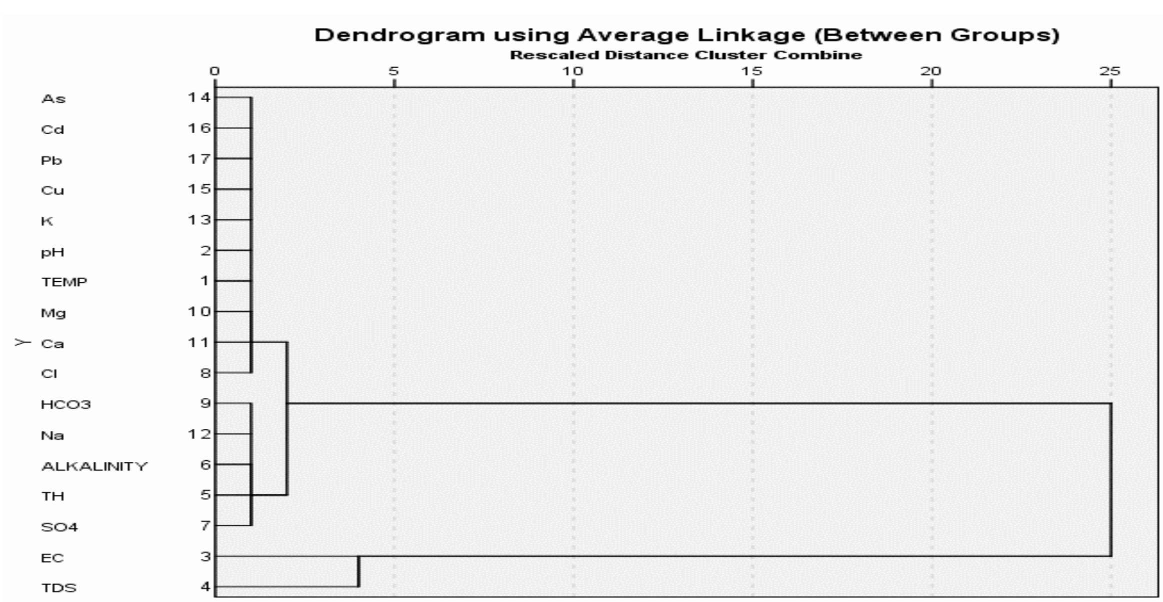
Table 3. 10: Correlation coefficient matrix for physicochemical parameters in ground water of Hyderabad, Sindh.

	TEMP	pH	COND (EC)	TDS	TH	M Alkalinity	SO42-	Cl-	HCO32-	Mg2+	Ca2+	Na+	K+	As	Cu	Cd	Pb
TEMP	1																
pH	0.049813	1															
COND (EC)	0.190137	-0.51354	1														
TDS	0.182004	-0.52232	0.994721	1													
TH	0.134282	-0.19645	0.139441	0.175359	1												
M Alkalinity	0.050952	-0.52066	0.677701	0.680723	0.003638	1											
SO42-	0.208479	0.066152	0.136962	0.139546	0.364132	0.0545756	1										
Cl-	0.250212	0.18043	0.085209	0.092586	0.150209	0.076963	0.789122	1									
HCO32-	0.209475	0.065476	0.09427	0.109904	0.303367	0.0951378	0.754982	0.644204	1								
Mg2+	0.166069	-0.08855	0.125332	0.150501	0.817885	0.038828	0.228924	0.025803	0.227096	1							
Ca2+	0.072927	-0.23228	0.114052	0.149216	0.883742	-0.025944	0.377833	0.21168	0.285197	0.453534	1						
Na+	0.328409	0.134957	0.09708	0.101248	0.240909	0.0556423	0.917963	0.898868	0.819694	0.11505	0.279583	1					
K+	0.340915	0.123723	0.139407	0.132953	0.021706	0.1626574	0.665193	0.710876	0.771108	0.015386	0.021107	0.814934	1				
As	0.066843	0.099921	0.045435	0.02025	-0.05655	0.1515734	0.120011	0.141712	0.138237	0.001029	-0.08843	0.142708	0.350208	1			
Cu	0.060102	-0.20086	0.144124	0.153168	0.068642	0.1196845	-0.01567	0.014134	0.07465	-0.0193	0.122024	0.062865	0.031508	-0.05913	1		
Cd	0.180678	-0.37977	0.790176	0.772532	0.16906	0.4130427	0.208857	0.096082	0.10276	0.168794	0.124581	0.141721	0.121605	-0.00998	0.034718	1	
Pb	0.339566	-0.26484	0.431233	0.419212	0.222446	0.2687297	0.034655	-0.01118	0.032279	0.286499	0.11154	0.034628	0.184017	0.188843	-0.01954	0.510515	1

3.3. 2 Cluster Analysis

CA was carried out to differentiate between geographic similarities for the purpose of grouping sampling sites (spatial variability). In the output dendrogram, three groups were clustered together, with the first group displaying strong connections between Cl^-, Ca^{2+}, and Mg^{2+}, and pH. This may be the result of non-point sources, such as fertilizer and big dumping sites, as well as leakage from sewage water and, to some extent, contact between rock and water. Cl^- and SO_4^{2-} did not have a significant association, which is most likely because their origins are different. Seawater intrusion is where Cl^- comes from, but anthropogenic sources such as dumping sites, industrial waste, and domestic waste are where SO_4^2 comes from. EC is mostly associated with ions with the charge states SO_4^{2-}, HCO_3^-, and Na^+. These ions have a relatively high level of solubility in water and can easily pass through ion exchange membranes.

Table 3. 11: Dendrogram of Groundwater Samples



3.3. 3 Principal Component Analysis

The first component has the highest strongly positive loadings for TDS, EC, and Cd. These variables' loadings for components one and two plot closely together, indicating that the processes influencing these variables' concentrations and variability in groundwater are likely similar. The first component benefits greatly from the EC's contribution. In terms of physical makeup, it shows the contributions of each component in the groundwater samples, with the result that the first component is seen to be suggestive of a salinity issue. This salinity component is heavily impacted by Cl^- and Na^+ quantities found in our tests of groundwater. Because of their greater solubility, these components become more soluble in groundwater, where their concentrations are regulated by the interaction of water and rock. Interestingly K^+, SO_4^{2-} and HCO_3^{2-} reveals negative loadings in PCA2 and positive loadings in PCA1. Oxidation-reduction processes like pyrite oxidation can raise SO_4^{2-} concentrations in groundwater. As a result, this component is regarded as redox because of its substantial contribution to PC2, which affects groundwater quality through water-rock interactions. The groundwater pH, which in our analysis shows groundwater acidity that may be impacted by CO2, mostly explains the third component. Because Ca^{2+} and Mg^{2+} have positive loadings in both PCA1 and PCA2, total hardness in Hyderabad's groundwater is closely correlated with these elements. The strongest Pearson correlation between Pb and pH is found in Cu.

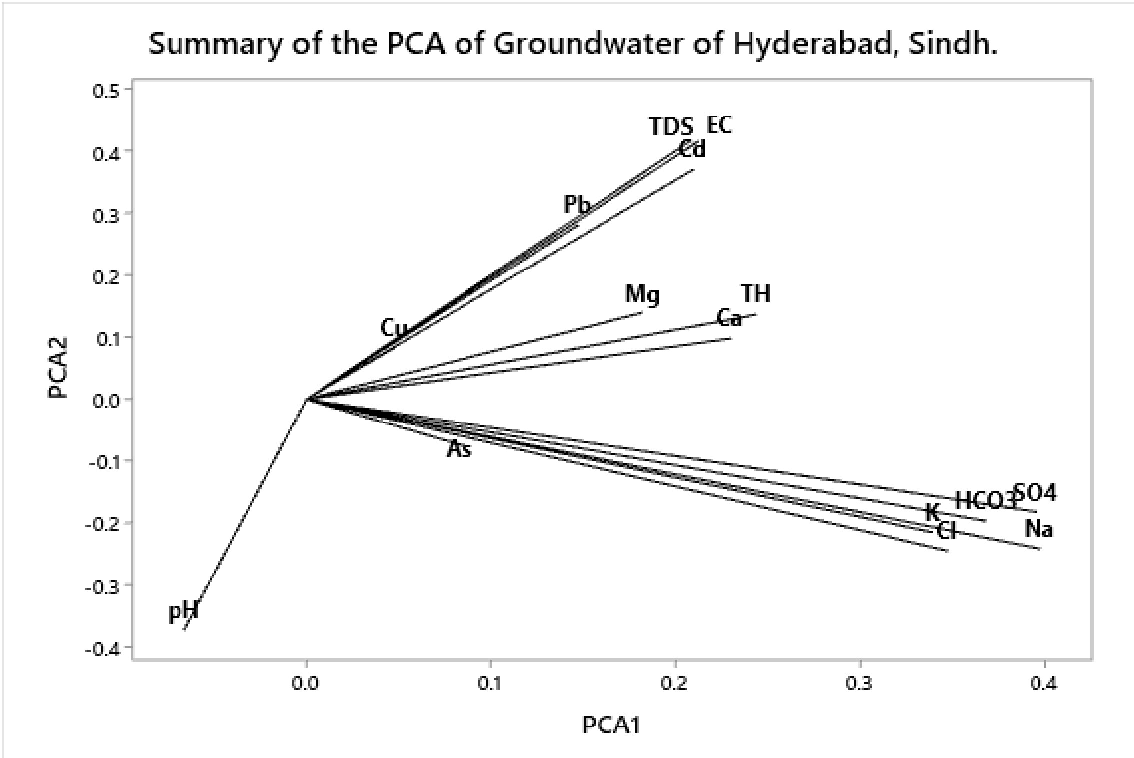

Summary of the PCA of Groundwater of Hyderabad, Sindh.
PCA2
PCA1
0.5
0.4
0.3
0.2
0.1
0.0
-0.1
-0.2
-0.3
-0.4
0.0
0.1
0.2
0.3
0.4
TDS
EC
Cd
Pb
Mg
TH
Ca
Cu
As
SO4
HCO3
K
Cl
Na
pH

Figure 3. 18:

CONCLUSION

The typical ground water condition in the city of Hyderabad, which is in the Sindh Province of Pakistan and is situated on the bank of the river Indus, ranges from neutral to slightly alkaline in its composition. More than 69.8 percent of the samples exceeded the maximum amount of EC that is considered safe for human consumption, Additionally, the same proportion of samples went beyond the World Health Organization's (WHO) maximum allowable level for total dissolved solids. The majority of Sindh is covered in groundwater that is hard, as 52% of the province's groundwater falls into the category of very hard water. The salinity of the groundwater was mostly caused by a combination of sulphate, bicarbonate, calcium, and magnesium, as well as sodium. The primary contributors to the decline in water quality include the presence of a high-water table, the intrusion of seawater, an excessive application of fertilizers, and the geological settings of the region.

According to the hydrogeochemical facies, the levels of alkali (Na^{+}) are higher than those of alkaline earth metals (Ca^{2+} and Mg^{2+}), and the levels of Cl^{-} and SO_4^{2-} - are higher than HCO^{3-}. This points to the presence of salty groundwater and proposes that the weathering of carbonate deposits may be the source of solutes found in Sindh's groundwater. Thirty-two percent of the groundwater is good for drinking, based on the EC classification. According to the samples' total dissolved solids level, 30.2% of the groundwater is likewise fit for human consumption. However, 57.3% of the groundwater was found to be in the very hard category.

90% of GW was estimated by the SAR to be appropriate for irrigation in nearly all soil types with a negligible risk of Na exchange. However, samples were determined to have seawater intrusion, making them unsuitable for irrigation and limiting their direct application to agriculture.

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