# Anthropogenic influences on the quality of groundwater around the Verna Industrial Estate, Goa, India.

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by

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### DECLARATION BY STUDENT

I hereby declare that the data presented in this Dissertation report entitled, "Anthropogenic influences on the quality of groundwater around the Verna Industrial Estate, Goa, India." is based on the results of investigations carried out by me in the M.Sc. Environment Science at the School of Earth, Ocean and Atmospheric Sciences, Goa University under the Supervision of Ms Manjusha Madkaikar and the same has not been submitted elsewhere for the award of a degree or diploma by me. Further, I understand that Goa University or its authorities will not be responsible for the correctness of observations / experimental or other findings given the dissertation.

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#### **PREFACE**

Water is a fundamental resource crucial for sustaining life and supporting various industrial activities. The quality of groundwater holds significant importance, especially in industrial areas like the Verna Industrial Estate in Goa. This preface introduces a comprehensive study conducted to analyse the physical and chemical parameters of groundwater in the Verna Industrial Estate across the pre-monsoon and post-monsoon seasons. The study encompasses an array of parameters including electrical conductivity (EC), total dissolved solids (TDS), turbidity, pH, phosphate, nitrite, fluoride, alkalinity, acidity, calcium, magnesium, total hardness, and heavy metals such as iron, manganese, nickel, copper, and zinc. By examining these parameters, we aim to gain insights into the quality of groundwater and its variations over time. During the pre-monsoon phase, the groundwater exhibited relatively lower levels of EC, TDS, and turbidity compared to the post-monsoon period. However, post-monsoon observations revealed increases in these parameters, likely influenced by factors such as surface runoff, soil erosion, and intensified microbial activity during the monsoon season. One of the notable findings is the consistent acidic nature of the groundwater throughout both seasons, with pH levels falling below permissible limits outlined by regulatory standards. This acidity may be attributed to geochemical reactions involving ferrous iron and manganese oxidation, underscoring the need for further investigation and mitigation measures. Phosphate and nitrite concentrations showed notable increases post-monsoon, possibly due to organic matter leaching, agricultural activities, and microbial processes. Despite these increases, concentrations remained within acceptable limits, suggesting relatively stable water quality concerning these aspects. Fluoride concentrations exhibited a decrease post-monsoon, likely influenced by

groundwater recharge and dilution effects. Conversely, acidity levels increased, possibly linked to organic matter decomposition, and increased microbial activity. Alkalinity levels decreased, potentially influenced by groundwater recharge and ion removal processes. Comparisons with previous research conducted by N. Somasundaram in 2013 revealed significant differences in key parameters over the decade. These discrepancies highlight the evolving dynamics of groundwater quality and emphasize the importance of continuous monitoring and effective management strategies to address emerging water resource challenges in industrial areas like the Verna Industrial Estate. This study contributes to the ongoing efforts in understanding and managing groundwater resources, providing valuable insights for policymakers, industrial stakeholders, and environmental agencies. It underscores the importance of proactive measures to ensure sustainable water management practices and safeguard the health and well-being of communities reliant on groundwater sources.

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Abbreviation	Full form
%0	per mille (parts per thousand)
~	
mg/L	Milligram per Liter
BIS	Bureau of Indian Standard
Ca	Calcium
СРСВ	Central Pollution Control Board
CGWB	Central Ground Water Board
CO <sub>2</sub>	Carbon Dioxide
EBT	Eriochrome Black T
EDTA	Ethylenediamine Tetraacetic Acid
GSPCB	Goa State Pollution Control Board
Mg	Magnesium
NaNO <sub>2</sub>	Sodium Nitrite

## LIST OF ABBREVIATIONS, ACRONYMS, SYMBOLS AND UNITS

#### ABSTRACT

This study provides an in-depth examination of the physical and chemical characteristics of groundwater, coupled with metal analysis, in the villages surrounding the Verna Industrial Estate, Goa, across the pre-monsoon and post-monsoon periods. Parameters analysed include EC, TDS, turbidity, pH, phosphate, nitrite, fluoride, alkalinity, acidity, calcium, magnesium, total hardness, and heavy metals like iron, manganese, nickel, copper, and zinc.

Pre-monsoon groundwater exhibited lower EC, TDS, and turbidity compared to the postmonsoon phase, likely influenced by factors such as surface runoff, soil erosion, and intensified microbial activity. pH remained consistently acidic, falling below permissible limits. Post-monsoon, increased phosphate and nitrite concentrations suggested influences from organic matter leaching, agriculture, and microbial processes, yet within acceptable limits. Fluoride concentrations decreased post-monsoon, possibly due to recharge and dilution effects, while acidity levels increased, linked to organic matter decomposition and microbial activity. Alkalinity decreased, potentially due to groundwater recharge and ion removal. Despite decreasing post-monsoon, calcium and magnesium levels remained within acceptable limits. Total hardness consistently decreased post-monsoon, with most samples categorized as soft water.

Heavy metal concentrations generally complied with regulations, except for elevated iron content in one well. Comparison with Somasundaram's 2013 research highlights significant parameter differences, underscoring evolving groundwater quality dynamics and the imperative for continuous monitoring and effective management strategies to address emerging water resource challenges in industrial areas like the Verna Industrial Estate.

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# CHAPTER 1

# INTRODUCTION

#### **CHAPTER 1: INTRODUCTION**

#### 1.1 Background

The distribution of water across the Earth is mainly characterized by oceans, which contain approximately 97% of the planet's water. The remaining 3% is freshwater, primarily stored in ice caps and glaciers (about 68.7%), followed by groundwater (30.1%), and surface freshwater sources like rivers, lakes, and wetlands (0.3%).

Groundwater serves a crucial role and finds widespread use in domestic, industrial, and agricultural sectors. Groundwater is the water found underground in geological formations of soil, sand, and rocks called aquifers.

Aquifers can be classified into various types based on different criteria such as geological formation, hydrogeological properties, and water quality. Classification of aquifers based on their types include Unconfined Aquifers, also known as a water-table aquifer, an unconfined aquifer is directly connected to the surface and is not confined by impermeable layers above it. Water levels in unconfined aquifers fluctuate with changes in precipitation and surface water levels.

Confined Aquifer, Confined aquifers are sandwiched between impermeable layers of rock or clay, known as aquitards or confining layers. These layers restrict the movement of water into or out of the aquifer, creating pressure that often results in artesian wells. Semi-confined Aquifer, Semi-confined aquifers have a combination of characteristics of both unconfined and confined aquifers. They are partially confined by low-permeability layers but may still interact with surface water or exhibit artesian conditions.

Perched Aquifer, Perched aquifers are localized, shallow aquifers separated from the main groundwater table by an impermeable layer. They often form in areas with alternating layers of permeable and impermeable materials, creating a localized water table above the regional water table.

Fractured Rock Aquifer, Fractured rock aquifers occur in hard, consolidated rocks such as granite, basalt, or shale, where groundwater flows primarily through fractures and fissures in the rock rather than through pore spaces.

Aquifers play a vital role in the storage and transmission of groundwater, serving as indispensable resources for diverse human activities like agriculture, industry, and domestic consumption. Functioning as natural reservoirs beneath the Earth's surface, they hold substantial water volumes, ensuring a reliable source of freshwater. Rocks deemed favorable for aquifer status typically exhibit notable porosity and permeability, facilitating the unhindered movement of water. Porosity denotes the void spaces within a rock, while permeability refers to its capacity to transmit fluids efficiently.

Among the rock types renowned for their efficacy as aquifers, sedimentary formations like sandstone, limestone, and conglomerate stand out due to their extensive porosity and interconnected pore networks, permitting relatively unrestricted water flow. Particularly, sandstone's adeptness at retaining significant water volumes is attributable to its wellinterconnected pore structure. Additionally, fractured igneous and metamorphic rocks can serve as proficient aquifers provided, they harbor extensive fracture networks or fault lines. These structural irregularities act as conduits for groundwater flow, augmenting the rock's permeability and enhancing its aquifer potential.

Groundwater contributes to a significant amount of the earth's drinking water resources, making it a precious natural asset. According to the United States Geological Survey (USGS), groundwater accounts for approximately 30% of the world's freshwater resources.

Groundwater travels beneath the Earth's surface due to the forces of gravity, pressure differences, and geological formations. It moves at a gradual pace through tiny gaps and cracks in rocks or sediment, conforming to the natural tilt of the water table. Groundwater is refilled by a mechanism known as recharge, where water that seeps into the ground percolates through soil and rock layers to replenish the aquifer.

The rate of groundwater recharge varies depending on factors like climatic patterns, geological attributes, and human land usage. Driven by gravity, pressure differentials, and geological formations, groundwater flows gradually beneath the Earth's surface, navigating through minuscule gaps and fractures in rocks or sediment, adhering to the natural inclination of the water table.

Within aquifers, groundwater flow is influenced by several factors, including the

Hydraulic Gradient: The hydraulic gradient, which is the change in hydraulic head (water pressure) over a given distance, dictates the direction and rate of groundwater flow within aquifers. Groundwater flows from areas of higher hydraulic head to lower hydraulic head.

Permeability: Permeability refers to the ability of the aquifer material to transmit water. Highly permeable materials, such as sand and gravel, allow for faster groundwater flow, while less permeable materials, such as clay, impede flow.

Aquifer Thickness: Thicker aquifers generally allow for greater storage and movement of groundwater. In thicker aquifers, groundwater flow may occur over longer distances and at slower velocities compared to thinner aquifers.

Porosity: Porosity refers to the volume of open spaces, or pores, within the aquifer material. Higher porosity allows for greater water storage within the aquifer and influences groundwater flow rates.

Aquifer Connectivity: The connectivity of aquifers, including the presence of fractures, conduits, or other pathways, affects the flow of groundwater within the subsurface. Highly connected aquifers may exhibit faster flow rates and greater lateral movement of groundwater.

Recharge and Discharge Areas: Groundwater recharge areas, where water infiltrates into the aquifer, and discharge areas, where groundwater emerges at the surface or discharges into surface water bodies, influence groundwater flow patterns within aquifers.

Geological Structure: The geological structure of the aquifer, including folding, faulting, and other structural features, can influence groundwater flow pathways and flow velocities within the aquifer.

Human Activities: Human activities such as groundwater extraction, land use changes, and groundwater contamination can alter groundwater flow within aquifers. Groundwater pumping, for example, can create localized cones of depression and change groundwater

flow directions. Understanding these factors is crucial for managing and protecting groundwater resources effectively. It helps in assessing groundwater availability, predicting potential impacts of human activities, and implementing appropriate groundwater management strategies.

Excessive withdrawal of groundwater can lead to depletion of aquifers, reduced groundwater levels, and other adverse environmental impacts. The quality of groundwater can vary depending on factors such as geological conditions, land use practices, and human activities. Human intervention in the hydrological system can significantly compromise groundwater quality.

The presence of undesirable elements in water can cause groundwater pollution. Groundwater can get polluted because of various contaminants being leached into the water along with the rainwater seepage such as infiltration of various pollutants, including fertilizers, pesticides, industrial chemicals, and heavy metals, along with rainwater seepage. Groundwater pollution could be due to various reasons including agricultural practices, and industrial or sewage discharge.

Agricultural practices, particularly the leaching of chemical fertilizers and pesticides, constitute a primary source of groundwater contamination. Livestock farming generates substantial quantities of manure and wastes laden with harmful pathogens, nutrients, and chemicals. Improper management or disposal of these waste products can lead to their seepage into the soil and subsequent contamination of groundwater.

Industrial effluents containing heavy metals, organic compounds, and nutrients pose another threat to groundwater quality. Heavy metals, although essential nutrients in small doses, can pose significant health and environmental risks when present in elevated levels in groundwater.

Soil erosion from agricultural fields can result in the loss of topsoil, which may contain contaminants such as fertilizers, pesticides, and heavy metals. These contaminants can then be transported by runoff and infiltrate into the groundwater. Leaks and spills from underground storage tanks used for storage of petroleum products and chemicals at industrial estates can release harmful substances into the soil which infiltrate into the groundwater. Mining operations, like coal mining, metal mining, and quarrying can release heavy metals, acids, and sediment that can contaminate groundwater. Landfills and waste disposal sites can allow pollutants such as heavy metals, organic chemicals, and household waste to seep into the groundwater.

Due to the sluggish movement of groundwater from recharge to discharge areas, pollutants can persist in aquifers for extended periods, posing persistent threats to human health and ecosystems. Hence, a comprehensive understanding of groundwater quality is essential to identify and mitigate groundwater pollution.

Groundwater in India serves as a vital resource for fulfilling the nation's water demands, especially for irrigation, drinking water supply, and industrial uses. Approximately 40% of the country's irrigation needs and 80% of rural drinking water requirements are believed to be fulfilled by groundwater sources. Nevertheless, India has been facing challenges related to groundwater depletion due to excessive extraction and insufficient replenishment efforts over time. This has led to a decline in groundwater levels across various regions of the country, sparking concerns regarding water scarcity, deteriorating water quality from

overuse and contamination, and environmental repercussions such as land subsidence and saltwater intrusion in coastal areas.

The groundwater situation in Goa holds significant importance due to its vital role in fulfilling diverse water needs, encompassing agriculture, domestic consumption, and industrial usage. However, the state confronts numerous challenges regarding the management of groundwater. In recent times, there has been growing concern regarding the diminishing levels of groundwater in specific regions of Goa. Contributing factors to this decline comprise heightened urbanization, industrial expansion, agricultural practices, and escalating demands for domestic water usage. Moreover, inadequate recharge mechanisms, such as reduced precipitation and inadequate water conservation techniques, exacerbate this issue. Additionally, issues like unregulated borewell drilling and unauthorized groundwater extraction have contributed to the depletion of groundwater resources in the state. These activities not only impact water availability but also pose risks of land subsidence and intrusion of saltwater into coastal regions.

Sustainable management of groundwater resources is essential to ensure long-term availability and quality. This includes practices such as groundwater monitoring, aquifer recharge enhancement, water conservation, pollution prevention, and regulation of groundwater abstraction.

### 1.2 Aim and objectives of the study

The dissertation aims to determine the various physio-chemical parameters along with the presence of heavy metals in the groundwater around the Verna industrial estate. The objective of the work include.

- 1. To investigate the quality of well water around the Verna Industrial Estate is in accordance with the prescribed standards (WHO/BIS)
- 2. To study the impacts of Industrial and Agricultural activities on the quality of groundwater.
- 3. To analyze the various physio-chemical parameters of groundwater and compare the results with N. Somasundaram, 2013.
- 4. To study the Spatial distribution of groundwater flow.

1.3 Scope

- 1. This study will help gain insights into the Physio-Chemical parameters of the Groundwater.
- **2.** Help to determine the presence, extent, and sources of contaminants in groundwater, if any.
- **3.** Preparation of a Model of groundwater movement.
- 1.4 Study Area

The state of Goa lies along the western coast of India, positioned between latitudes 14°53'54" and 15°40'00" north and longitudes 73°40'33" and 74°20'13' east. Covering an area of approximately 3702 square kilometres with a coastline that stretches for about 102 km. Goa shares its borders with Maharashtra to the north, Karnataka to the east and south, and to the west lies the Arabian Sea.

Administratively, Goa is divided into two districts: North Goa and South Goa, each comprising 12 talukas. North Goa includes six talukas (Pernem, Bardez, Tiswadi, Bicholim, Ponda, and Sattari), while South Goa comprises six talukas (Mormugao, Salcete,

Quepem, Sanguem, Dharbandora, and Canacona), with district headquarters located in Panaji and Margao, respectively.

The state covers 0.11% of the Indian Territory and is accessible by road via NH17 and NH4A highways, by rail through the Konkan Railway and Southwestern Railway, and by air through Dabolim Airport.

1.4.1 Physiography

The state of Goa can be segmented into three distinct sub-regions, delineated as the Coastal Estuarine Plain in the west, the Midland region in the center, and the Western Ghats in the east, classified according to physiography.

- i. The coastal plains in Goa, span across the talukas of Tiswadi, Bardez, Salcete, and Mormugao, encompassing approximately 22% of the total geographical area. The Coastal Plains feature various low-lying features such as estuarine mudflats, sandy beaches, mangroves, salt pans, fields, khazan lands, and settlements. While the coastal plains are wider and more prominent in North Goa, they are smaller, isolated, and often interrupted by laterite-topped tablelands in the southern part (Mascarenhas & Kalavampara, 2009).
- ii. The intermediate or transitional sub-mountainous region with undulating uplands, covers about 35 per cent of the area. They form the transition between the lower coastal plain and plateau terrain and the steeper, higher terrain of the Western Ghats. The plateaus constitute the central portion of Goa with heights ranging from a hundred meters down to thirty meters from the MSL.

iii. The Western Ghats comprises hills ranging from approximately 100 to 600 meters and valleys that are aligned in NW-SE direction separated by undulate tracts of deeply weathered etch-plain.

1.4.2 Geology

The primary rock formations found in the region range from the Archean to Proterozoic eras. These formations are categorized within the Goa Group of the Dharwar Supergroup of rocks

According to the classification system developed by Gokul et al. (1985), the Goa Group of rocks is made up of four Formations: The Barcem Formation, the Sanvordem Formation, the Bicholim Formation, and the Vageri Formation.

Laterite, with varying thicknesses on residual hills, along with alluvium and sand on the coastal estuarine plains, dominate the geological formations.

### 1.4.3 Drainage



Figure 1.1 Drainage map of Goa

Goa's drainage network is fed by nine major rivers, predominantly flowing from East (Western Ghats) to West (the Arabian Sea), except for the Sal River in south Goa, which follows a northeast-to-southwest course due to the presence of the west coast fault. These major rivers include Terekhol, Mandovi, Zuari, Chapora, Sal, Talpona, Saleri, Canacona, and Galgibagh.

The Sahyadri hill ranges in the east serve as the primary watershed. The Mandovi and Zuari rivers drain a significant portion of the state. Originating in the Western Ghats, these estuarine rivers lose their momentum as they wind through the midlands and estuarine

plains before reaching the sea. The drainage system in the region typically exhibits a dendritic pattern, influenced by the underlying rocks.

While river valleys in the western high hill ranges tend to be V-shaped, they broaden and take on a U-shaped profile in the central midlands and coastal plains. These nine rivers and their 42 tributaries serve as essential sources of potable and irrigation water. All rivers in Goa are subject to tidal influence, often extending inland up to 40 km from their mouths. The salinity levels in the rivers fluctuate significantly between the monsoon and post-monsoon periods, affecting the quality of water in wells along their banks, which tend to become saline as the summer months progress.

#### 1.4.4 Climate and Rainfall

Situated along the western coast of India, Goa has a tropical monsoon climate characterized by distinct orographic influences. Temperature variations range from 20°C to 34°C, creating an equable and humid environment year-round. January and February typically bring dry weather with clear skies, offering pleasant conditions. May emerges as the hottest month, with temperatures ranging between 30°C and 34°C, while January marks the coolest month, with temperatures around 25°C.

Given its proximity to the Arabian Sea, Goa maintains consistently high humidity levels throughout the year, averaging 75.90%. Abundant rainfall is received from the Southwest monsoon, with an annual average of 3483.3 mm based on 30 years of rainfall data.

The minimum rainfall of 2611.7 mm is recorded at the Mormugao station, and the maximum of 5090 mm is observed at Sanguem station indicating an increase in rainfall from west to east. Over 90% of rainfall occurs during the monsoon season while the

remaining 10% is received during the non-monsoon seasons. Rainfall is the main source of groundwater recharge in the State.

The study site lies between Panaji and Margao along National Highway NH 17, approximately 22 km from Panaji and 11 km from Margao city. Which includes the part of the plateau covering the Verna industrial estate and villages located at its foothills.

The geographical boundaries of the area are defined by latitudes  $15^{\circ} 23' 13.2"$  N to  $15^{\circ} 58'$  48" N and longitudes  $73^{\circ} 54' 57.6"$  E to  $73^{\circ} 58' 48"$  E. This region is depicted on the Survey of India topographic sheet No 48 E/15/5, at a scale of 1:25000.

It has an aerial extent of 20.7 sq km which is a 3.3 km buffer zone around the Verna industrial estate, the area encompasses the surrounding villages of Cortalim, Loutolim, Quelossim, Nagoa, and Verna.

The region is bordered to the north and east by the Zuari river, with the Konkan Railway tunnel marking its western boundary, and the plateau gradually blending into the coastal plain to the south. Much of the plateau's runoff flows northward into Zuari Creek, while a portion drains southward into the Sal River basin.



Figure 1.2 Location of groundwater observation well network in the study area

## 1.4.5 Drainage

A significant portion of the plateau channels its runoff northward to the Zuari Creek, while another section directs its flow southward to the Sal River basin. The top of the plateau exhibits a low drainage density, attributed to the presence of a dense, hard laterite covering its surface. Despite this, numerous minor perennial streams originate from the plateau. Surrounding the plateau are several water tanks used for storing water from October onwards, primarily to irrigate second crop paddy. Typically, Kharif paddy cultivation occurs within these reservoir areas.

## 1.4.7 Physiography of study area



Figure 1.3 Physiography map of the study area

The study area consists of the following physiographic units:

A. Plateau: Narrow industrial estate plateau is present in the NW-SE direction. The plateau's topography is predominantly gentle, punctuated by occasional isolated peaks and localized depressions. Overall, the plateau's elevation averages around 60 meters above mean sea level (MSL), with its highest point reaching 156 meters above MSL.

B. Escarpments: - The plateau is bordered by escarpments generally covered with vegetation. There are many valleys originating on the periphery of the plateau along weak zones which are connected with storm water drains which are flowing along local depression on the plateau. (N., Somasundaram 2013)

C. Foot hill region: - Early settlements (villages) are located on the gently sloping foot hill region, elevation of which ranges from 5.0 to 20 m above MSL. The width of the area ranges between 50 and 500 m. (N., Somasundaram 2013)

D. Coastal plains and tidal flats: - Foothill regions are bordered either by coastal plain or tidal flats of the Zuari Creek. It has a flat topography. Coastal plains are predominantly used for paddy cultivation. (N., Somasundaram 2013)

1.4.6 Geology

The primary rock formations found in the region range from the Archean to Proterozoic eras. These formations are categorized within the Goa Group of the Dharwar Supergroup of rocks, as documented by Gokul et al. in 1985. They consist of four distinct stratigraphic sequences: the Barcem Formation, Sanvordem Formation, Bicholim Formation, and Vagheri Formation, alongside intrusive granites and basic rocks. Additionally, a small area in the northeastern part of the state features basalt from the Deccan Trap. Most rock formations are overlaid with laterite. The rocks exposed in the study area belong to the Barcem and Sanvordem formations of Goa group. (N., Somasundaram 2013)

1.4.8 Climate and Rainfall

The area experiences a warm and humid climate. Humidity levels peak during the monsoon season, ranging from 90 to 95 percent, while for the remainder of the year, they typically hover between 80 and 85 percent. Winters see average minimum temperatures of 21.3°C, rising to just 24°C in summer, while average maximum temperatures reach 32.2°C in winter and 36.3°C in summer. The region primarily receives precipitation from the

southwest monsoon between June and September. The average annual rainfall in the area totals approximately 2500 mm.



## 1.4.9 Land Use Pattern

Figure 1.4 Land use Map of the study area

Land use pattern refers to how various types of land are organized or spread across a specific geographic region. The distribution of land use can greatly differ based on factors including geographic location, climate, terrain, population density, economic endeavors, and governmental regulations. The land within the study area is classified according to its primary function, encompassing built-up zones for residential, commercial, and industrial purposes (highlighted in red), vegetated areas (marked in green), agricultural zones (in orange), and the unclassified regions (in white). Understanding these spatial patterns is vital for comprehending the factors contributing to groundwater contamination.

# CHAPTER 2

# LITERATURE REVIEW

## **CHAPTER 2: LITERATURE REVIEW**

**Somasundaram (2013)** conducted his Purpose-driven studies of groundwater hydrology project phase 2 Goa state on the Evaluation of downstream consequences of groundwater development at Verna Industrial Estate and water resources management.

This study was undertaken at the Verna industrial estate and the villages around it to study the downstream consequence of borewell pumping at the Verna industrial estate along with the chemical quality of the groundwater. Parameters analyzed in this study were pH, Turbidity, Electrical conductivity (EC), Total dissolved solids (TDS) along with some major cations which include Na, K, Ca, Mg, Fe, and an anion that is F.

Chemical quality of water from all the 35 samples were found to be well within the permissible range for domestic, irrigation and industrial purposes.

However, the pH of open well water was low at the order of 5.0 to 5.8. It is observed that bore well water in the industrial estate is more mineralized than open well water in the village area. The low pH and low mineralization in the water table aquifer is due to heavy leaching during monsoon as the village area is directly recharged during monsoon. Elevation of pumped water level in summers after continuous pumping of water for 1000 minutes in wells, ranges from 16 to 59m. Therefore, the possibility of saltwater intrusion of the aquifer system from the nearby creek is ruled out.

Manjunatha et al. (2016) studied the Hydrochemical facies and assessment of groundwater for drinking purposes in Goa, India

The Physicochemical characteristics of groundwater in the state of Goa have been studied to assess the quality of groundwater and its suitability for domestic and irrigational purposes. Groundwater samples from 38 shallow aquifers and 39 deep aquifers were collected in the year 2014. Parameters analysed include pH, TDS, Calcium, Magnesium, Potassium, Carbonates, Bicarbonates, Chlorides, Nitrates, and Fluoride.

The results of physico-chemical parameters of groundwater samples from dug well (shallow aquifer) and bore well (deeper aquifer) of the study area reveal that pH values of groundwater range from 6.5 - 7.5 (shallow aquifer) and 7.0 - 8.5 (deeper aquifer) respectively. The average pH value of the study area is 7.45, indicating that the groundwater is slightly alkaline in nature and is suitable for drinking purposes according to BIS (1991) and ISI (1983) standards.

Most of the samples have TDS within permissible limits. Around 8% of shallow-water aquifers fell in the hard water category around 13% of the deep-water aquifers fell in the hard to very hard category and hence needed softening for domestic use. Assessment of groundwater samples from various methods indicated that overall groundwater in the State of Goa is chemically suitable for drinking and Irrigation purposes.

**Hejabi et al.** (2011) studied the Heavy metal pollution in water and sediments in the Kabini River, Karnataka, India. Concentrations of heavy metals such as Cr, Cu, Fe, Mn, Pb, Ni, and Zn were analyzed. Sample stations were chosen to provide a good coverage of background and anthropogenic inputs and a total of 17 samples were collected from predefined locations based on GPS. Water samples were determined for Heavy Metals using AAS. Heavy metal inputs in river water may be in particulate or dissolved form, and most of the heavy metals tend to accumulate in sediments.

Their presence in water is usually the result of recent inputs whereas Sediments conserve most of the heavy metals and increasingly are recognized as both carriers and possible sources of contaminants in aquatic ecosystems. The research discovered that the Kabini River in Karnataka, India, carries a mixture of natural and anthropogenic pollutants, with notably high levels of heavy metals such as chromium (Cr), copper (Cu), iron (Fe), manganese (Mn), nickel (Ni), lead (Pb), and zinc (Zn).

These contaminants originate from various sources including industrial discharge, agricultural runoff, and domestic sewage. It was observed that the metal concentrations in affected areas exceeded the background levels. Cr, Zn, and Ni were found in higher concentrations near paper mill influx thus indicating the presence of heavy metals in the vicinity of industrial effluents.

**Gurdeep Singh et al.** (2016) conducted a study focusing on heavy metal contamination and its indexing approach for groundwater in the mining region of Goa, India. The study aimed to investigate seasonal variations in groundwater quality concerning heavy metal contamination. Groundwater samples were collected from 45 different locations in and around Goa's mining areas during the monsoon and post-monsoon seasons to assess the extent of heavy metal contamination. The concentrations of heavy metals, including lead, copper, manganese, zinc, cadmium, iron, and chromium, were analyzed using an atomic absorption spectrophotometer.

The pH of groundwater samples ranged from 4.5 to 7.1 with a mean of 5.9 during the monsoon season, and from 5.5 to 8.2 with a mean of 6.0 during the post-monsoon season, indicating an acidic to slightly alkaline nature in both seasons.
Additionally, approximately 84–87% of groundwater samples in both seasons had pH values below the desirable limit of 6.5 according to Indian drinking water standards. Total dissolved solids (TDS) in water ranged from 452–768 mg/L during the monsoon season and from 542–652 mg/L during the post-monsoon season which is higher than the permissible limit of 300 mg/L (WHO) and 500 mg/L by BIS. Most samples analyzed for heavy metals were within acceptable limits, except for iron content during the monsoon season at two sampling locations, which exceeded the desirable limit of 300  $\mu$ g/L according to Indian drinking water standards.

**Deepika et al. (2020)** studied the Spatial variability of groundwater quality: A case study of Udupi district, Karnataka State, India. The study investigated various parameters including Total Hardness, Fluorides, Chlorides, Iron, Turbidity, Total Dissolved Solids (TDS), and bicarbonates. The pH levels of the groundwater samples ranged from 5 to 7.6, with most samples exhibiting acidic properties, likely influenced by the acidic nature induced by lateritic soil. Chloride content ranged from 11.9 to 361.25 mg/l, surpassing the acceptable limit of 250 mg/l, possibly due to seawater intrusion from nearby seashores.

Iron content varied between 0 and 4.2 mg/l, exceeding the acceptable limit of 0.3 mg/l. Hardness was observed in the range of 16–275.98 mg/l, with a limit of 200 mg/l for acceptability; some samples fell within the hard water category. The groundwater quality was assessed using the Water Quality Index (WQI), resulting in categorization into four types: excellent water, 'good', 'poor', and 'very poor'. The analysis revealed that approximately 14.15% of the study area had excellent-quality groundwater, while around 62.26% contained good-quality groundwater. However, 21.69% of the area exhibited poor-grade groundwater, and about 1.88% suffered from very poor-quality groundwater. Some

samples showed poor and very poor-quality standards, likely due to variations in pH, chlorides, iron, and hardness.

**Malini et al. (2003)** studied the Groundwater Quality Around Mysore, Karnataka, India. Groundwater samples were gathered in the vicinity of Mysore, Karnataka, India, and subjected to analysis for inorganic constituents. These examinations aimed to investigate variations in groundwater quality that may indicate interactions between rocks and water as it transitions from recharge to discharge areas. The study identified four hydrologic flow patterns in the region and analyzed differences in groundwater chemistry across these regimes. Groundwater in the area was categorized as either CaHCO3 or MgHCO3 type, with the anions and cations exhibiting saturation characteristics of CaCO3. Hydrochemical data were modeled using WATEQ4F, revealing oversaturation of groundwater with calcite and, to a lesser extent, with dolomite. Sixty percent of the groundwater samples exceeded the World Health Organization (WHO) limit of 45 mg/L for nitrate concentration, while eighty-six percent had fluoride concentrations below 1.0 mg/L. Trace metal concentrations, excluding iron and zinc, were found to be close to the detection limit at most sampling sites.

**Maurya et al.** (2021) Studied the Evaluation of ground water quality and health risk assessment due to nitrate and fluoride in the Middle Indo-Gangetic plains of India the research focused on evaluating groundwater quality and assessing the non-carcinogenic health risks associated with fluoride and nitrate. Groundwaters exhibited an alkaline pH, with sulfate being the predominant ion, followed by bicarbonate, chloride, nitrate, and fluoride. Approximately 83.8% of the samples demonstrated poor water quality, with 77%

and 93% of them exceeding the permissible limits for nitrate and fluoride concentrations in drinking water, respectively.

Principal component analysis indicated that the alkaline pH of groundwater resulted from high bicarbonate and low calcium concentrations, favoring the release of fluoride due to the precipitation of calcium as calcium carbonate. Cluster analysis revealed a common source for anions and cations (Na, Ca, and Cl) and suggested the influence of anthropogenic activities on groundwater nitrate contamination.

However, a geogenic origin was proposed for fluoride, with alkaline water contributing to the weathering of fluoride-bearing minerals. The hazard quotient for infants, children, and adults due to nitrate was found to be 2.8, 2.19, and 2.0, respectively, while for fluoride, it was 3.39, 2.64, and 2.42, respectively.

Moreover, 99% of the samples exceeded the cumulative hazard index threshold, indicating that the groundwater was unsuitable for drinking purposes.

**Gagandeep et al. (2019)** studied the Evaluation of groundwater quality and human health risks from fluoride and nitrate in semi-arid region of northern India. The study highlights the utilization of integrated hydrogeochemical and chemometric statistical methodologies to assess the geochemical processes and identify the sources of groundwater in the alluvial plains of Jalandhar district, Punjab, India. Additionally, it conducts a human health risk assessment to evaluate the potential non-carcinogenic effects of nitrate and fluoride ingestion from groundwater on human health. In this study, 41 groundwater samples were collected from various groundwater extraction points and analyzed for several parameters including pH, electrical conductivity, total dissolved solids, total hardness, total alkalinity, and major ions (Ca2+, Mg2+, Na+, K+, HCO3-, CO32-, SO42-, NO3-, F-, Cl-, and PO43-) using standardized procedures. The evaluation based on drinking water quality index and Revelle index revealed that the groundwater samples predominantly fall within the poor to unfit water quality category. Particularly, salinization in the southwestern part of the study area exhibited poor water quality.

Furthermore, the hazard index (HIingestion) indicated that 68% of groundwater samples exceeded the threshold value of 1 for children, and 46.34% for adults, suggesting potential health risks. The non-carcinogenic health risk assessment of nitrate (NO3–) and fluoride (F–) indicated that children are more susceptible to adverse health effects through direct ingestion of drinking water compared to adults. Hydrochemical analyses using Piper diagram and saturation index identified the dominant hydrochemical facies as Ca2+– Mg2+–HCO3–, with groundwater being oversaturated with calcite, dolomite, and aragonite minerals.

Further interpretation through Gibbs diagrams, chloro-alkaline indices, and scatter plots suggested that the hydrochemistry of groundwater is primarily influenced by aquifer material interactions such as weathering of silicate and carbonate rocks, halite dissolution, and cation exchange processes. The application of chemometric statistical techniques helped in identifying the sources of various parameters. Parameters like Ca2+, Mg2+, Na+, K+, HCO3-, CO32-, and F- were attributed to geogenic factors, while NO3-, SO42-, Cl-, and PO43- were linked to anthropogenic sources.

Gowd et al (2008) studied the Distribution of heavy metals in surface water of Ranipet industrial area in Tamil Nadu, India.

Research was conducted to investigate the contamination of surface water bodies resulting from industrial effluents. The paper discusses the distribution of metals, their varying concentrations across different locations, and their adverse effects on human health. Findings indicate significant contamination of surface water in the studied area, with notably high concentrations of various heavy and toxic metals including Cadmium (ranging from 0.2 to 401.4 µg/l, with an average of 51.1 µg/l), Chromium (2.4–1,308.6 µg/l, with an average of 247.2 µg/l), Copper (2.1–535.5 µg/l, with an average of 95.5 µg/l), Nickel (1.6– 147.0 µg/l, with an average of 36.7 µg/l), Lead (6.4–2,034.4 µg/l, with an average of 467.8 µg/l), and Zinc (20.8–12,718.0 µg/l, with an average of 3,760.4 µg/l). These concentration levels significantly exceed permissible limits in surface water, posing serious health hazards, particularly for individuals employed in tannery industries. The affected population in the area has been observed to suffer from occupational diseases such as asthma, chromium ulcers, and various skin conditions.

**Savita et al.** (2013) conducted the Assessment and spatial distribution of groundwater quality in industrial areas of Ghaziabad, India. This study aims to assess the groundwater quality in two industrial blocks within Ghaziabad district. Groundwater samples were obtained from shallow wells, deep wells, and hand pumps in the Bulandshahar road industrial area and Meerut road industrial area, both heavily industrialized zones, to evaluate their suitability for various purposes. Sampling was conducted at 30 sites in each block before and after the monsoon season. Analysis encompassed 23 elements, including Ag, Al, As, B, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Na, Ni, P, Pb, Se, U, V, and Zn. Additionally, parameters such as color, odor, turbidity, biological oxygen demand,

chemical oxygen demand (COD), dissolved oxygen, total dissolved solids, and total suspended solids were examined.

A water quality index was computed based on selected parameters. Mean values of 12 elements (Al, As, Ca, Cd, Cr, Mg, Mn, Na, Ni, Pb, Se, and U) exceeded prescribed standard limits. Concentrations (in milligrams per liter) of highly toxic metals—Al, As, Cd, Cr, Ni, Pb, Se, and U—ranged from 1.33 to 6.30, 0.04 to 0.54, 0.005 to 0.013, 4.51 to 7.09, 0.14 to 0.27, 0.13 to 0.32, 0.16 to 2.11, and 0.10 to 1.21, respectively, across all groundwater samples.

These levels exceeded WHO/BIS standards for drinking water. Electrical conductivity (EC), pH, and COD ranged from 0.74 to 4.21, 6.05 to 7.72, and 4.5 to 20.0, respectively, in all samples, surpassing permissible limits of 0.7 dS m–1, 6.5–8.5, and 10 mg L–1. Water quality index values ranged from 101 to 491 and 871 to 2904 based on physico-chemical and metal contamination criteria, respectively. The mean values were 265 and 1,174, respectively, while the safe limit for drinking water is below 50. The findings indicate that groundwater in the two blocks is unsuitable for drinking according to WHO/BIS guidelines, with the presence of elements like As, Se, and U in toxic amounts raising serious concerns.

# CHAPTER 3

# MATERIALS AND METHODS

# **CHAPTER 3: METHODOLOGY**

#### 3.1 Introduction

The study site includes the part of the plateau covering the Verna industrial estate and villages located at its foothills the study area is defined by latitudes  $15^{\circ} 23' 13.2"$  N to  $15^{\circ} 58' 48"$  N and longitudes  $73^{\circ} 54' 57.6"$  E to  $73^{\circ} 58' 48"$  E and is depicted on the Survey of India topographic sheet No 48 E/15/5, at a scale of 1:25000.

The study area has an aerial extent of 20.7 sq km which is a 3.3 km buffer zone around the Verna industrial estate.

#### 3.1.1 Pre Field-Preparations

- i. Literature Review: To gain insights into the hydrogeological characteristics of the study area and to understand existing groundwater data, a thorough review of existing literature was conducted.
- Data Collection Planning: The planning phase involved determining the specific data to be gathered, including groundwater levels and various water quality parameters such as pH, electrical conductivity, and chemical composition. Additionally, the quantity of water samples to be collected and the identification of suitable sampling locations were addressed.
- iii. Field Equipment Preparation: Prior to fieldwork, attention was given to ensuring that all necessary equipment, including pH meters and electrical conductivity meters, were properly calibrated, tested, and prepared for use.
- iv. Field Reconnaissance: A preliminary field survey was conducted to become acquainted with the study area, identify potential sampling sites, assess their

accessibility, and develop a comprehensive sampling plan specifying the locations, depths, and frequencies of groundwater sampling.

- v. Site Location and Mapping: Google Earth Pro was used to define the study area boundaries and locate sampling sites. A base map was created using QGIS. Using the base map number 48E/15, the study area and wells were located on the toposheet.
- vi. Water Sampling Equipment: To facilitate the collection of water samples and subsequent chemical analysis in the laboratory according to standardized procedures, a total of 20 high-density polyethylene bottles, comprising 500 ml and 1000 ml capacities, were procured, and organized. The sampling was conducted on a 3.3 km buffer zone around the Verna Industrial Estate, During the Pre-Monsoon season in the month of May and during the Post Monsoon season in the month of January.

#### 3.1.2 Field work

Monitoring of dug wells or drilled wells is one of the most widely used methods for investigating groundwater. Ground water levels from 20 wells were collected to analyze it for the impacts of anthropogenic activities on the quality of ground water in the year 2023 during the pre-monsoon and post monsoon season in the villages of Cortalim, Loutolim, Quelossim, Nagoa, and Verna.

The pH and EC of groundwater for all 20 wells were tested in field using portable instruments. For laboratory analysis, each water samples were collected in 1000 ml and

500 ml High-density polyethylene (HDPE) bottles to analyze physicochemical parameters and for metal analysis respectively. Samples were sourced from the selected study area, treated beforehand, and then analyzed for numerous parameters. The analysis is executed following standardized procedures to maximize result accuracy.



Figure 3.1 Location of groundwater observation well network in the study area

Sr. No	Sample No.	Latitude	Longitude
1	W1	15°21′31.65″N	73°55′45.80″E
2	W2	15°21′31.72″N	73°55′46.83″E
3	W3	15°21′33.19″N	73°55′52.19″E
4	W4	15°21′50.48″N	73°56′16.49″E
5	W5	15°21′4.20″N	73°56′18.97″E
6	W6	15°21′41.10″N	73°56′31.63″E
7	W7	15°21′42.48″N	73°56′42.59″E
8	W8	15°21′44.07″N	73°56′39.95″E
9	W9	15°21′39.16″N	73°56′41.39″E
10	W10	15°21′39.33″N	73°56′43.98″E
11	W11	15°21′16.19″N	73°55′37.86″E
12	W12	15°21′53.08″N	73°55′51.47″E
13	W13	15°21′53.08″N	73°58′4.49″E
14	W14	15°22′0.82″N	73°57′55.29″E
15	W15	15°23′11.73″N	73°56′49.92″E
16	W16	15°20′31.40″N	73°55′54.06″E
17	W17	15°20′31.57″N	73°56′10.73″E
18	W18	15°21′24″N	73°55′34″E
19	W19	15°23′14″N	73°55′02″E
20	W20	15°23′2.44″N	73°55′2.01″E

Table 3.1: Location of sampling sites around the Verna Industrial Estate

#### 3.2 Physical Parameters:

#### 3.2.1 Electrical Conductivity

The conductivity of water refers to its capacity to conduct electrical current, which is indicative of the presence of dissolved ions, primarily salts, minerals, and other substances that ionize when dissolved in water.

Pure water, devoid of dissolved ions, exhibits very minimal electrical conductivity. However, as the concentration of dissolved ions rises, so does the water's conductivity. Higher conductivity readings signify a greater abundance of dissolved ions, indicating a higher level of impurities such as dissolved substances, chemicals, and minerals.

EC is typically measured in Siemens per meter (S/m) or microsiemens per centimeter ( $\mu$ S/cm), electrical conductivity serves as a crucial parameter in water quality assessment.

In field assessments, the electrical conductivity of water samples from all 20 wells was determined using a Solinst TLC EC meter. The procedure employed to obtain the EC values for each sample involved measuring them in millisiemens ( $\mu$ S).

To begin the procedure, position the digital EC meter securely on a stable surface. Proceed by releasing the knob located on the rear side of the device, and with caution, detach the electrode.

Next, press and hold the black button adjacent to the digital bar. Unwind the wire carefully, and gradually lower the electrode into the well, ensuring it remains clear of contact with the well's lining.

Once the probe has been rinsed with distilled water, activate the unit by pressing the on/off button. Upon activation, the display should indicate the value 000. Submerge the probe gently into the well until it emits a beep upon reaching the water's surface as shown in Figure 3.2.

Take note of the numbers displayed on the screen, as they represent the EC (Electrical Conductivity Value) at the surface of the well.



Figure 3.2 Measuring Electrical Conductivity at well no 8

#### 3.2.2 Total Dissolved Solids

TDS stands for Total Dissolved Solids. It refers to the combined concentration of all inorganic and organic substances dissolved in water. These substances encompass minerals, salts, metals, ions, and various other dissolved particles. TDS measurements are typically expressed in milligrams per liter (mg/L) or parts per million (ppm).

Elevated TDS levels indicate a higher concentration of dissolved solids within the water, whereas lower levels suggest a lesser presence of dissolved solids. Elevated TDS levels may impart a salty or brackish taste, while excessively low levels may indicate a deficiency in essential minerals. TDS serves as a crucial metric in evaluating water quality, as it can influence the taste, smell, and overall suitability of water for diverse applications.

The TDS of water samples from all 20 wells was determined using,

TDS (mg/L) = k x Electrical Conductivity( $\mu$ S/cm) Where value of k is 0.64.

3.2.3 Turbidity:

Turbidity is the measure of relative clarity of a liquid. It is an optical characteristic of water and is a measurement of the amount of light that is scattered by material in the water when a light is shined through the water sample. Increased intensity of scattered light correlates with higher turbidity levels.

Turbidity, quantified in nephelometric turbidity units (NTU), is assessed with a device known as a turbidimeter.

To maintain optimal drinking water quality, turbidity levels should ideally fall within the range of 1 to 5 NTU, as stipulated by the Bureau of Indian Standards.

The Turbidity of water samples from all 20 wells were measured in the lab using the Eutech TN-100 Turbidimeter. The following approach was used to acquire the Turbidity values for each sample, and the values were reported in NTU.

To initiate the procedure, procure a clean and dry sample vial, ensuring it is handled only by the top. Proceed to thoroughly rinse the vial with approximately 10 ml of the sample water. Cap the vial with the provided black screw cap and gently invert it several times. Discard the used sample and repeat this rinsing procedure two more times.

Once the rinsing is complete, fill the vial with the remaining portion (approximately 10 ml) of the grab sample up to the marked indication on the vial, securely capping it afterward. Utilize the soft, lint-free cloth provided to wipe the vial clean, ensuring the exterior is free from any smudges and completely dry.

Apply a thin layer of the supplied silicone oil onto the surface of the sample vial, evenly distributing it using a soft cloth. Position the turbidimeter on a flat and level surface, then place the sample vial inside the designated sample well, aligning the vial's index mark with the meter's index mark.

Press the vial firmly until it snaps securely in place, then cover the vial with the light shield cap. Proceed to switch on the meter by pressing the ON/OFF key. After the power-up sequence, the meter will enter measurement mode, indicated by the display blinking "Read." The measured reading will then be displayed on the screen for observation as shown in Figure 3.3



Figure 3.3 Measuring Turbidity of sample no 10

3.3.1 pH

pH, or "potential of Hydrogen," is a measure of the acidity or alkalinity of a solution. It is expressed on a scale ranging from 0 to 14, where 7 is considered neutral.

A pH value below 7 indicates acidity, while a pH above 7 indicates alkalinity. pH is determined by the concentration of hydrogen ions (H+) in the solution; higher concentrations of H+ ions result in lower pH values (more acidic), while lower concentrations lead to higher pH values (more alkaline). The permissible limits of pH in drinking water typically fall within a range of 6.5 to 8.5, as recommended by World Health Organization (WHO).

The pH of water samples from all 20 wells were determined in the field with the help of a Mettler Toledo portable pH meter. The pH meter was calibrated prior to field operations using standard solutions of pH 4, pH 7, and pH 10. The pH readings for each sample were acquired and recorded using the following procedure.

To commence the procedure, draw water from the well. Subsequently, remove the pH meter probe from the KCl solution and rinse it thoroughly with distilled water before powering it on. Upon activation, the display should illuminate, showing a reading of 7.00. Insert the probe's tip into the freshly drawn well water, positioning it approximately half an inch inside, and await the signal. Record the reading displayed on the monitor, as it indicates the pH level of the water as shown in figure 3.4.

Following this, cleanse the probe with distilled water and submerge it in a 3M KCl solution. It's important to note that the electrode should be immersed in the KCl solution when the pH meter is not in use.



Figure 3.4 Measuring pH at well no 6

#### 3.3.2 Phosphate

Phosphates can infiltrate water sources through a variety of natural and human-induced activities, including agricultural runoff, discharge of wastewater, and erosion.

According to the World Health Organization (WHO) in 1999, the permissible limit for phosphate in drinking water is set at 1 mg/l.

For phosphate analysis, the Murphy and Riley's Molybdenum blue method was used.

This method involves the reaction of orthophosphate with ammonium molybdate under specific conditions, resulting in the formation of 12-molybdophosphate, a yellow-colored complex. Subsequently, this complex undergoes reduction by either ascorbic acid or stannous chloride in the presence of antimony, yielding a blue-colored complex known as molybdenum blue.

The light absorption of this complex is measured using a spectrophotometer at a wavelength of 880 nm.

The procedure begins by dispensing blank volumes (0 ml) and volumes ranging from 2 to 12 ml of the working solution (Potassium dihydrogen phosphate) into separate 50 ml graduated tubes. These volumes are then diluted to the marked lines using distilled water. Additionally, 50 ml of the water sample is added to other graduated tubes.

Following this, 1 ml of the mixed reagent and 1 ml of ascorbic acid are introduced into each tube and thoroughly mixed. As shown in Figure 3.5 the graduated tubes were kept aside for a 30-minute incubation period, the absorbance is measured at a wavelength of 880 nm. Subsequently, a calibration curve is constructed by plotting the known concentrations of phosphate against their corresponding absorbance values, with the concentration of phosphate ( $\mu$  mol / L) calculated using the formula:

Concentration of phosphate = Average Factor × Optical Density.



Figure 3.5 Measuring Phosphate using UV Visible spectrophotometer.

Levels of nitrite in water sources can be impacted by a range of factors, including agricultural runoff, wastewater discharges, and industrial activities.

The World Health Organization (WHO) has established a guideline value for nitrite in drinking water, set at 0.1 milligrams per liter (mg/L) or 0.1 parts per million (ppm).

This guideline is established considering the potential health risks linked to nitrite ingestion, notably the risk of methemoglobinemia, particularly among infants.

The determination of nitrite is conducted following the methodology outlined by Strickland and Parsons (1968). Nitrite undergoes a reaction with sulfanilamide in an acidic solution, producing a diazonium compound.

Subsequently, this compound couples with N-(1-Naphthyl)-ethylenediamine dihydrochloride to generate a colored azo dye, the absorbance of which can be assessed spectrophotometrically at a wavelength of 540 nm.

The procedure for the analysis is conducted as follows: Volumes of 0 (Blank), 1, 2, 3, 4, and 5 ml of the working solution (NaNO2) are dispensed into 50 ml graduated tubes and then diluted to the marked lines using distilled water. Additionally, 50 ml of the water sample is added to separate graduated tubes.

Subsequently, 1 ml of sulfanilamide and 1 ml of diamine are introduced into each tube, and the contents are thoroughly mixed and kept for a 20-minute incubation period as seen in Figure 3.6. The absorbance of the resulting solution is measured using a spectrophotometer set to a wavelength of 540 nm.

It is crucial to ensure that the dye is shielded from sunlight during the analysis process to prevent any potential interference.



Concentration of Nitrite ( $\mu$  mol / L) = Average Factor × Optical Density

Figure 3.6 Measuring Nitrite using UV Visible spectrophotometer.

Fluoride, a naturally transpiring mineral, is present in different concentrations across water sources globally.

The levels of fluoride in drinking water can fluctuate based on factors like geological attributes, water treatment methodologies, and the introduction of fluoride for dental care objectives.

The World Health Organization (WHO) suggests a guideline value of 1.5 mg/L (milligrams per liter) or 1.5 ppm (parts per million) for fluoride in drinking water. This guideline aims to strike a balance between the advantages of fluoride in averting dental cavities and the probable risks linked to excessive fluoride consumption.

To determine the fluoride concentration in water, a spectrophotometer is employed at a wavelength of 622 nm. Initially, various volumes of sodium fluoride working solution, including blank (0 ml), 0.5, 1, 1.5, 2, 2.5, and 3 ml, are dispensed into 50 ml graduated tubes. These volumes are then diluted to 15 ml with distilled water, followed by the addition of 8 ml of lanthanum alizarin complex and 0.4 ml of acetic acid. Subsequently, this solution is further diluted to 25 ml with distilled water, ensuring that the pH falls within the range of 4.5 to 0.02. Furthermore, 15 ml of the water sample is taken into a graduated tube, and 8 ml of lanthanum alizarin complex along with 0.4 ml of acetic acid are added before dilution to 25 ml with distilled water.

A calibration curve is established by correlating the optical density with the concentration. The fluoride concentration (mg / L) is determined using the formula:

Concentration of fluoride = Average Factor  $\times$  Optical Density  $\times$  1.667.

#### 3.3.5 Alkalinity

Alkalinity in water refers to its capacity to neutralize acids. It's a measure of the water's buffering capacity against changes in pH.

Alkalinity is primarily due to the presence of carbonate (CO3<sup>2</sup>-) and bicarbonate (HCO3<sup>-</sup>-) ions, although hydroxide (OH<sup>-</sup>-) ions can also contribute. Alkalinity in water can come from various natural and anthropogenic sources.

Natural sources include the weathering of rocks and minerals containing carbonates and bicarbonates, as well as the decomposition of organic matter. Human activities such as agriculture, industrial processes, and wastewater discharge can also contribute to alkalinity levels in water bodies.

Permissible limits for alkalinity in drinking water is 200 mg/L.

The procedure for determining the alkalinity of water involves titration with sulfuric acid and subsequent calculations based on stoichiometry. Initially, a 100 ml water sample is obtained, to which 2 drops of phenolphthalein indicator are added to facilitate titration.

The sample is then titrated with 0.02 N sulfuric acid until it becomes colorless, indicating the endpoint of the first titration. Following this, a few drops of methyl orange indicator are introduced, and titration continues until the solution changes from yellow to orange, marking the endpoint of the second titration.

The volumes of sulfuric acid used in each titration are recorded for further analysis. By considering the stoichiometry of the reaction and the volumes of sulfuric acid required to reach the endpoints, the concentration of alkalinity in the water can be calculated.

Alkalinity (mg / L as CaCO<sub>3</sub>) = Volume of  $H_2SO_4 \times Normality$  of  $H_2SO_4 \times 50 \times 1000$ 

### Volume of water sample

#### 3.3.6 Acidity

The presence of acidity in water can originate from natural phenomena such as organic decomposition and geological influences, along with human activities including industrial emissions, agricultural practices, and mining operations. The procedure for determining the acidity of wastewater and natural water involves the use of methyl orange acidity (pH 3.7) and phenolphthalein acidity (pH 8.3). Initially, the volumes of standard alkali required to induce color changes at pH 8.3 and pH 3.7 are measured.

In the process, 50 mL of the sample is pipetted into a flask, and 2 to 3 drops of methyl orange indicator are added. The mixture is then titrated against 0.02 N NaOH, and the endpoint is recorded when the color shifts from orange-red to yellow, indicating the Methyl orange acidity (V1). Subsequently, two drops of phenolphthalein indicator are added, and titration continues until a pink color just emerges. The volumes of the titrant used are recorded, providing the total acidity (V2).

Phenolphthalein acidity is calculated by subtracting the Methyl orange acidity from the total acidity. (V3 = V2 - V1)

Methyl orange acidity (mg / L as CaCO<sub>3</sub>) = V1 × Normality of NaOH × 50 × 1000

Volume of water sample

Total acidity (mg / L as CaCO<sub>3</sub>) = V2 × Normality of NaOH × 50 × 1000

Volume of water sample

Phenolphthalein acidity (mg / L as  $CaCO_3$ ) = Total acidity - Methyl orange acidity

#### 3.3.7 Hardness

Water hardness can be measured using a procedure known as complexometric titration by adding a known concentration of the chelating agent EDTA (Ethylenediamine tetraacetic acid) through a burette to a sample containing an unknown amount of calcium and magnesium ions.

The procedure for determining Calcium and Magnesium involves titration with EDTA. Initially, a water sample, along with NaOH buffer and Patton and Reeder's indicator, is titrated against 0.01 M EDTA.

At the endpoint, indicated by the disappearance of the last pinkish tinge and the appearance of a pure blue color, the amount of EDTA added is measured. Similarly, for determining Calcium and Magnesium, NH3 buffer and Eriochrome Black T (EBT) indicator are utilized.

The volume of EDTA consumed for Magnesium is calculated by subtracting the volume of EDTA consumed by Calcium from the total volume of EDTA consumed by both Calcium and Magnesium.

## To determine Calcium

1 M of EDTA is equivalent to 1 M of Ca

The atomic weight of Ca is 40.008 g

Therefore 1 M of EDTA is equivalent to 40.008 g of Ca

Concentration of Ca (g/l) = Volume of EDTA  $\times$  Normality of EDTA  $\times$  40.008

Volume of water sample

To determine Magnesium

1 M of EDTA is equivalent to 1 M of Mg

The atomic weight of Mg is 24.31 g

Therefore 1 M of EDTA is equivalent to 24.31 g of Mg

Concentration of Mg (g/l) = Volume of EDTA  $\times$  Normality of EDTA  $\times$  24.31

Volume of water sample

Total Hardness = Concentration of Ca and Concentration of Mg

3.3.8 Trace Metals

Preconcentration of trace metals from well water

A 500 ml sample of acidified filtered and was utilized to concentrate trace metals (Fe, Mn, Zn, Cu and Ni) using the ammonium pyrrolidine dithiocarbamate (APDC) and methyl isobutyl ketone (MIBK) extraction method (Brooks et al., 1967). Prior to extraction, the pH of the sample was adjusted to a range of 4-5 using ammonia. Subsequently, the sample was transferred to a 1000 ml separating funnel, followed by the sequential addition of 10 ml APDC and 15 ml MIBK. The mixture was vigorously shaken for 2 minutes to ensure thorough extraction.

After allowing the layers to separate, the organic fraction was transferred to a 100 ml separating funnel. This process was repeated with the addition of 5 ml APDC and 10 ml MIBK, and the collection of organic fractions. To the combined organic layer obtained from the two extractions, 15 ml of 1N HNO3 was added and vigorously shaken for 2 minutes. After allowing the layers to separate for 10 minutes, the metals were back-extracted (Tsukaijan and Young, 1978).

The aqueous layer containing HNO3 was separated, and the back-extraction procedure was repeated with the addition of 10 ml of 1N HNO3.

The two aqueous layers were combined and collected in a polyethylene bottle for subsequent analysis via AAS. The concentration of metals in the sample were determined using flame AAS Thermo Fischer iCE 3000 series.

The concentration of trace metals in water was computed using the below equation:

$$C = A \times V$$

Where,

C = Concentration of trace metal

V = Final volume after preconcentration

A= AAS response

The concentration of trace metals in seaweeds were calculated using the below formula

$$C = \frac{(A \times V \times d)}{W}$$

Where,

C= concentration of trace metal

A=AAS response

V= final volume

d= dilution factor (if any)

W= weight of the seaweed sample (g)

The dilution factor 'd' was calculated using the equation

$$d = \frac{V1 + V2}{V1}$$

Where,

V1- digested sample taken in ml.

V2- deionized water added for dilution in ml.

3.4 Preparation of Maps

3.4.1 To prepare Groundwater level map and to determine the flow direction in the study area using in Surfer Software

To generate an equipotential map, begin by creating a CSV file in Microsoft Excel. Enter the coordinates of the wells in degree decimal format, placing Longitude coordinates first, followed by Latitude coordinates, and Depth values of the water table for each well. Next, open Surfer and choose "New Plot" from the dialogue box. Then, select the "Grid data" option from the top toolbar and set the Gridding Method as Kriging. Browse and select the desired CSV file, then click Ok.

A new dialogue box will appear showing X for Longitude, Y for Latitude, and Z for Depth. Choose the "Skip to End" option, set Nodes to 150 and 100, and click Finish. Save the Grid File in a designated folder.

Equipotential lines will be automatically generated on the Plot after clicking the finish button. To include the study area, create a vector shape file of the study area in QGIS. Select contours from the contents box and choose the "Layer" option from the top toolbar.

Select "Base" and locate the saved shape file of the study area in .shp format. Click Ok to add the shape file to the equipotential map. Follow the mentioned steps to add well locations and determine flow direction.

Finally, go to the File option and select print to export the file in PDF format.

3.4.2 Preparation of study area map in Qgis

Open QGIS and follow the steps mentioned. Select Layer from the top toolbar and choose Add Layer, then Add Raster Layer. Locate and add the georeferenced file. Next, select Layer again, then Create Layer, and choose New Shape File Layer.

Save the file in the dialogue box that appears, selecting polygon as the geometry type, and Text Data or Whole Number in New Field. After saving, a new layer will open; toggle edit this layer and begin tracing the boundary of the village. To plot the well locations, create a Delimiter File/CSV. Ensure the coordinates are in decimal degree format. Enter the coordinates, assigned well numbers, and create three columns in Microsoft Excel: Longitudes, Latitudes, and well numbers.

Save the file as a CSV (Comma Delimited) format. Back in QGIS, go to the prepared map of the study area, select Layer, Add Layer, then Delimited Text Layer. Navigate to the saved CSV file, choose x field as longitude and y field as latitude, and select EPSG:4326 WGS 84 as the Geometry CRS.

To customize symbols, colors, numbers, size, and text, select the layer and go to properties. Proceed to print layout option in the toolbar and press ok. Adjust symbols and labels as preferred. To save the map, select Layer, then export as an image.

Utilizing QGIS, contour map, Geological map, Drainage map, Land use land cover map, and location map were prepared.

# CHAPTER 4 ANALYSIS AND CONCLUSIONS

#### 4.1 Physical parameters



# 4.1.1 Electrical Conductivity

Figure 4.1: Seasonal Variations in Electrical Conductivity

The electrical conductivity (EC) of water samples was assessed both during the Premonsoon and the post-monsoon season. In the pre-monsoon period, well number 20 exhibited the highest EC at 268  $\mu$ S/cm, while the lowest readings of 33  $\mu$ S/cm were noted in wells 4 and 14. Conversely, during the post-monsoon phase, the highest EC of 309  $\mu$ S/cm was observed in well 20, while the lowest was 43  $\mu$ S/cm in well 10. On average, the EC during the pre-monsoon period stood at 98.3  $\mu$ S/cm, slightly below the 113  $\mu$ S/cm recorded during the post-monsoon phase.

Data analysis reveals that 85% of the samples exhibit higher electrical conductivity (EC) levels during the post-monsoon period compared to the pre-monsoon phase.

The rise in electrical conductivity post-monsoon may be attributed to various factors. Heavy rainfall during the monsoon season can cause increased surface runoff, carrying dissolved solids such as salts, minerals, and organic matter into nearby wells. Additionally, since laterite rock is porous in nature, it can facilitate the percolation of these solid salts in the ground water along with water. Consequently, this runoff can introduce elevated levels of dissolved solids into groundwater, resulting in higher electrical conductivity levels postmonsoon.



Figure 4.2: Spatial distribution of Electrical Conductivity (Pre-monsoon)



Figure 4.3: Spatial distribution of Electrical Conductivity (Post-monsoon)



4.1.2 Total Dissolved Solids

Figure 4.4: Seasonal Variations in Total Dissolved Solids

The Total Dissolved Solids of water samples was assessed both during the Pre-monsoon and the Post-Monsoon season. In the pre-monsoon period, well number 20 exhibited the highest TDS at 171.5 mg/L, while the lowest readings of 21.12 mg/L were noted in wells 4 and 14.

Conversely, during the post-monsoon phase, the highest TDS of 197.8 mg/L was observed in well 20, while the lowest was 27.52 mg/L in well 10. On average, the TDS during the pre-monsoon period stood at 62.91 mg/L slightly below the 72.4 mg/L recorded during the post-monsoon season.

Analysis of the data indicates that 85% of the samples show elevated Total Dissolved Solids (TDS) levels during the post-monsoon period compared to the pre-monsoon. This phenomenon is likely to be attributed to rainfall facilitating the leaching of organic matter, minerals, and salts from the soil into groundwater. As rainwater infiltrates through the soil, it has the potential to dissolve minerals and salts along the way, consequently increasing the concentration of Total Dissolved Solids in the groundwater. The TDS readings in all the samples both in the Pre monsoon and Post Monsoon season were found to be well within the acceptable limits of 300 mg/L given by BIS (IS 10500) in 2012


Figure 4.5: Spatial distribution of TDS (Pre-monsoon)



Figure 4.6: Spatial distribution of TDS (Post-monsoon)

### 4.1.3 Turbidity



Figure 4.7: Seasonal Variations in Turbidity

Turbidity of water samples was assessed both during the Pre-monsoon and the Post-Monsoon season. In the pre-monsoon period, well number 20 exhibited the highest Turbidity of 7.78 NTU, while the lowest readings of 0.26 NTU were noted in well number 12.

During the post-monsoon phase, the highest Turbidity of 6.21 NTU was again observed in well 20, while the lowest was 0.39 NTU in well 12. On average, the Turbidity during the pre-monsoon period stood at 1.63 NTU slightly below the 1.92 NTU recorded during the post-monsoon phase.

Analysis of the data indicates that 80% of the samples show elevated Turbidity levels during the post-monsoon period compared to the pre-monsoon phase. This could occur due to heavy rainfall during the monsoon season introducing suspended solids into groundwater, consequently elevating turbidity levels in wells post-monsoon. Moreover, the increased soil moisture post-monsoon could facilitate the leaching of organic matter from the soil into groundwater. These dissolved organic compounds could interact with suspended particles, leading to the formation of colloidal aggregates that further increase the turbidity.

In the pre-monsoon season, 50% of the samples and in the post-monsoon season, 45% of the samples exhibited turbidity levels well within the acceptable limits of 1 NTU. The remaining 45% of pre-monsoon samples and 40% of post-monsoon samples were slightly above the acceptable limits but still within the permissible limits of 5 NTU, as specified by BIS (IS 10500) in 2012. Notably, well number 20 was the only sample that exceeded the permissible limits for turbidity in both seasons.



Figure 4.8: Spatial distribution of Turbidity (Pre-monsoon)



Figure 4.9: Spatial distribution of Turbidity (Post-monsoon)

Sample No	EC (µS/cm)	TDS(Mg/L)	Turbidity (NTU)	Temperature(°C)
1	159	101.76	0.68	27.9
2	145	92.8	1.43	27.8
3	59	37.76	2.59	28
4	33	21.12	3.44	27.2
5	54	34.56	1.01	27.9
6	77	49.28	1.18	28.2
7	68	43.52	0.41	27.4
8	195	124.8	0.89	27.8
9	121	77.44	1.36	27.8
10	37	23.68	0.6	27.7
11	99	63.36	1.9	29.8
12	96	61.44	0.26	28.5
13	93	59.52	3.18	27.1
14	33	21.12	0.5	27.6
15	110	70.4	0.59	27.6
16	91	58.24	0.75	25.8
17	76	48.64	2.21	27.7
18	102	65.28	1.13	27.8
19	50	32	0.7	27.6
20	268	171.52	7.78	27.4

Table 4.1 Measured Physical parameters of groundwater samples during Pre-monsoon Season.

Sample No	Sample No EC (uS/cm)		Turbidity (NTU)	Temperature (°C)	
1	171	109.44	0.83	27.2	
2	163	104.32	1.49	27.6	
3	70	101.32	2.88	28.3	
4	40	21.26	4.20	20.5	
5	49 50	27.76	4.59	28.1	
5	100	37.70	1.55	28.1	
6	126	80.64	1.69	27.5	
7	98	62.72	0.73	27.4	
8	212	135.68	0.78	27.4	
9	117	74.88	1.99	28	
10	43	27.52	0.68	27.9	
11	134	85.76	2.1	28.7	
12	105	67.2	0.39	28.8	
13	81	51.84	4.32	27.5	
14	58	37.12	0.88	28.1	
15	133		0.48	27.4	
16	86	55.04	0.98	26.2	
17	89	56.96	3.78	27.4	
18	105	67.2	1.55	27.8	
19	56	35.84	0.72	27.1	
20	309	197.76	6.21	26.5	

Table 4.2 Physical parameters of groundwater samples during post monsoon.

#### 4.2 Chemical parameters

### 4.2.1 pH



Figure 4.10: Seasonal Variations in pH

pH of water samples was assessed both during the Pre-monsoon and the Post-Monsoon season. In the pre-monsoon period, well number 8 exhibited the highest pH of 6.37 while the lowest readings of 5.23 were noted in well number 18.

During the post-monsoon phase, again the highest pH of 5.98 was observed in well 8 and the lowest was in well 18 i.e. 5.09. On average, the pH values during the pre-monsoon period stood at 5.90 which is above the 5.60 recorded value during the post-monsoon phase.

The data analysis reveals a consistent trend across all samples, indicating a decrease in pH levels during the post-monsoon period in contrast to the pre-monsoon. The groundwater in

the study area exhibits acidic properties during both, the pre-monsoon and post-monsoon seasons.

Moreover, all wells in the study area were found to have pH levels below the permissible limits outlined by the Bureau of Indian Standards (BIS) in 2012, which stipulate a range of 6.5 to 8.5. Interestingly, the absence of an alternative source doesn't warrant any relaxation in adhering to these standards.

The possible geochemical reactions for low pH of groundwater in Goa have been explained by Mandrekar and Chachadi. (Modassir, Ibrampurkar, Virginkar, & Jyai, 2015).

1. When ferrous iron combines with water in the presence of oxygen to precipitate iron oxide hydroxide (goethite), the reaction releases hydrogen ion resulting in lowering of pH of water.  $4Fe^{+2}$ +  $O_2$  + 6 H<sub>2</sub>O  $\rightarrow$  4FeO (OH) + 8H<sup>+</sup>

2. Manganese oxidation also releases hydrogen ion.

 $2Mn^{\scriptscriptstyle +2} + O_2 + 2H_2O \rightarrow 2MnO_2 + 4H^{\scriptscriptstyle +}$ 



Figure 4.11: Spatial distribution of pH (Pre-monsoon)



Figure 4.12: Spatial distribution of pH (post-monsoon)

### 4.2.2 Phosphate



Figure 4.13: Seasonal Variations in Phosphate

The concentration of phosphate in ground water samples was assessed both during the Premonsoon and the Post-Monsoon season. In the pre-monsoon period, well number 4 exhibited the highest concentration of phosphate of 0.0352 mg/L while the lowest readings of 0.01 mg/L were noted in well number 11 and 14.

During the post-monsoon phase, the highest concentration of phosphate was observed in well 6 at 0.06 mg/L and the lowest was in well 9 i.e. 0.008. On average, the Phosphate concentration during the pre-monsoon period stood at 0.02 mg/L which is lower than 0.032 mg/L recorded value during the post-monsoon phase.

Analysis of the data indicates that 85% of the samples show elevated phosphate levels during the post-monsoon period compared to the pre-monsoon phase. Phosphates can infiltrate water sources through a variety of natural and human-induced activities. Heavy rainfall during the monsoon season could cause soil erosion, potentially washing sediment and organic matter into the ground water. Additionally, increased soil moisture postmonsoon could foster microbial activity, potentially releasing phosphate through organic matter decomposition. Agricultural activities could intensify during the monsoon, potentially leading to increased use of phosphate-based fertilizers, which could potentially wash into water bodies, further raising phosphate levels in well water in the post monsoon season.

Although there is an increase in phosphate content in the post monsoon season, Phosphate levels in both, the Pre-monsoon and the Post-Monsoon season were found to be well within the Permissible limits of 1mg/L by WHO 1999



Figure 4.14: Spatial distribution of Phosphate (Pre-monsoon)



Figure 4.15: Spatial distribution of Phosphate (Post-monsoon)

### 4.2.3 Nitrite



Figure 4.16: Seasonal Variations in Nitrite

The concentration of Nitrite in ground water samples was assessed both during the Premonsoon and the Post-Monsoon season. In the pre-monsoon period, well number 18 exhibited the highest concentration of Nitrite of 0.0156 mg/L while the lowest readings of 0.0007 mg/L were noted in well number 3.

During the post-monsoon phase, the highest concentration of Nitrite was observed in well 6 at 0.1625 mg/L and the lowest was in well 3,4,9,12 i.e. 0.0056 mg/L. On average, the Nitrite concentration during the pre-monsoon period stood at 0.005 mg/L which is lower than 0.028 mg/L recorded value during the post-monsoon phase.

Analysis of the data indicates that all the samples show elevated nitrite levels during the post-monsoon period compared to pre-monsoon. Post-monsoon, nitrite levels in well water could increase due to natural and anthropogenic factors. The heightened soil moisture might foster microbial activity, potentially leading certain bacteria to reduce nitrate to nitrite through denitrification processes, raising nitrite levels. Additionally, agricultural activities could also increase the nitrite content in wells post-monsoon, due to the use of nitrogen-based fertilizers.

Although there is increase in nitrite content in the post monsoon season, Nitrite levels in both, the Pre-monsoon and the Post-Monsoon season were found to be well within the Permissible limits of 3 mg/L by WHO.



Figure 4.17: Spatial distribution of Nitrite (Pre-monsoon)



Figure 4.18: Spatial distribution of Nitrite (Post-monsoon)

### 4.2.4 Fluoride



Figure 4.19: Seasonal Variations in Fluoride

The concentration of Fluoride in ground water samples was assessed both during the Premonsoon and the Post-Monsoon season. In the pre-monsoon period, well number 13 exhibited the highest concentration of fluoride of 0.0053 mg/L while the lowest readings of 0.0001 mg/L were noted in well number.

During the post-monsoon phase, the highest concentration of Fluoride was observed in well 16 at 0.0012 mg/L and the lowest was in well no 18 i.e. 0.00 mg/L. On average, the Fluoride concentration during the pre-monsoon period stood at 0.0017 mg/L which is higher than 0.0003 mg/L recorded value during the post-monsoon phase.

Analysis of the data indicates that 95 the samples show higher Fluoride levels during the post-monsoon period compared to pre-monsoon. During heavy monsoon rainfall, there is a possibility of increased groundwater recharge, which could elevate water levels in wells. This influx of water could potentially dilute the concentration of fluoride in groundwater,

resulting in decreased fluoride levels post-monsoon. Additionally, if the rock type in the study area does not contain fluoride, there might not be a natural source for fluoride to infiltrate and raise its levels after the monsoon. The fluoride content in both, the Pre-monsoon and the Post-Monsoon season were found to be well within the Permissible limits of 1 mg/L given by the World Health Organization (WHO) and Bureau of Indian Standards (BIS) in 2012



Figure 4.20: Spatial distribution of Fluoride (Pre-monsoon)



Figure 4.21: Spatial distribution of Fluoride (Post-monsoon)



# 4.2.5 Alkalinity

Figure 4.22: Seasonal Variations in Alkalinity

Alkalinity in ground water samples was assessed both during the Pre-monsoon and the Post-Monsoon season. In the pre-monsoon period, well number 8 exhibited the highest Alkalinity of 32.1 mg/L while the lowest readings of 3.7 mg/L were noted in well number 18.

During the post-monsoon phase, the highest Alkalinity was observed in well 8 at 24.1 mg/L and the lowest was in well 14 i.e. 1.5 mg/L. On average, the Alkalinity during the premonsoon period stood at 13.27 mg/L which is slightly higher than 9.05 mg/L recorded value during the post-monsoon phase.

Analysis of the data indicates that all the samples show lower Alkalinity levels during the post-monsoon period compared to pre-monsoon season. During the monsoon season, heavy rainfall could increase groundwater recharge, raising water levels in wells. This influx of water might dilute the alkalinity of groundwater, potentially leading to reduced alkalinity levels post-monsoon. Additionally, the intense rainfall could flush dissolved ions and minerals from the soil and aquifer into nearby water bodies. This flushing effect may remove alkaline substances from groundwater, possibly contributing to decreased alkalinity levels in wells afterward.

The Alkalinity in both, the Pre-monsoon and the Post-Monsoon season were found to be well within the acceptable limits of 200 mg/L given by the Bureau of Indian Standards (BIS) in 2012.



Figure 4.23: Spatial distribution of Alkalinity (Pre-monsoon)



Figure 4.24: Spatial distribution of Alkalinity (Post-monsoon)

### 4.2.5 Acidity



Figure 4.25: Seasonal Variations in Acidity

Acidity in ground water samples was assessed both during the Pre-monsoon and the Post-Monsoon season. In the pre-monsoon period, well number 18 exhibited the highest Acidity of 30.3 mg/L while the lowest readings of 7.8 mg/L were noted in well number 11.

During the post-monsoon phase, the highest Acidity was observed in well 18 at 32.9 mg/L and the lowest was in well i.e. 9.8 mg/L. On average, the Acidity values during the premonsoon period stood at 17.84 mg/L which is lower than 21.31 mg/L recorded value during the post-monsoon phase.

Analysis of the data indicates that all the samples show higher Acidity levels during the post-monsoon period compared to pre-monsoon season. Following the monsoon, the wet conditions in soil might facilitate organic matter decomposition, potentially increasing microbial activity and the release of acidic byproducts into groundwater. This scenario, combined with decreased alkalinity levels, could potentially reduce the natural buffering

capacity against acidity, leading to a possible elevation in acidity levels in wells after the monsoon.

The Acidity in both, the Pre-monsoon and the Post-Monsoon season were found to be well within the acceptable limits of 200 mg/L given by the Bureau of Indian Standards (BIS) in 2012.



Figure 4.26: Spatial distribution of Acidity (Pre-monsoon)



Figure 4.27: Spatial distribution of Acidity (Post-monsoon)

## 4.2.6 Calcium



Figure 4.28: Seasonal Variations in Calcium

Calcium in ground water samples was assessed both during the Pre-monsoon and the postmonsoon season. In the pre-monsoon period, well number 6 exhibited the highest concentration of Calcium of 38.6 mg/L while the lowest readings of 0 mg/L were noted in well number 4,5,19,20.

During the post-monsoon phase, the highest Calcium was observed in well 15 at 24 mg/L and the lowest was in well no 4,5,19,20 i.e. 0.0mg/L. On average, the Calcium concentration during the pre-monsoon period stood at 13.7 mg/L which is higher than 9.62mg/L recorded value during the post-monsoon phase.

Analysis of the data indicates that 80% of the samples show lower calcium levels during the post-monsoon period compared to pre-monsoon season. During heavy monsoon rainfall, it's possible that groundwater recharge could increase, potentially raising water levels in wells. This influx of water might dilute the concentration of calcium in groundwater, leading to a reduction in calcium levels post-monsoon. Additionally, a flushing effect from the intense rainfall may remove calcium-rich minerals from the groundwater, further contributing to decreased calcium levels in wells afterward. Furthermore, if the rock type in the study area lacks calcium content, there may be no natural source for calcium to infiltrate and raise its levels post-monsoon.

The calcium content in both, the Pre-monsoon and the Post-Monsoon season were found to be well within the Acceptable limits of 75 mg/L as CaCo<sub>3</sub> given by the Bureau of Indian Standards (BIS) in 2012.



Figure 4.29: Spatial distribution of Calcium (Pre-monsoon)



Figure 4.30: Spatial distribution of Calcium (Post-monsoon)

### 4.2.7 Magnesium



Figure 4.31: Seasonal Variations in Magnesium

Magnesium in ground water samples was assessed both during the Pre-monsoon and the Post-Monsoon season. In the pre-monsoon period, well number 15 exhibited the highest concentration of Magnesium I.e. 40.8 mg/L while the lowest readings of 9.71 mg/L were noted in well number 7.

During the post-monsoon phase, the highest Magnesium was observed in well 15 at 34.9 mg/L and the lowest was in well 18 i.e. 5.2 mg/L. On average, the Magnesium concentration during the pre-monsoon period stood at 24.03 mg/L which is higher than 18.94 mg/L recorded value during the post-monsoon phase.

Analysis of the data indicates that all the samples show lower magnesium levels during the post-monsoon period compared to pre-monsoon season. During intense monsoon rains, there is a likelihood of the increased groundwater recharge, could result in elevated water levels within wells. This increased water influx may dilute the magnesium concentration

in groundwater, causing a subsequent decrease in magnesium levels following the monsoon season. Moreover, the heavy rainfall may facilitate a flushing effect, potentially removing minerals rich in magnesium from the groundwater, thereby exacerbating the decline in magnesium levels post-monsoon. Additionally, if the geological composition of the study area is deficient in magnesium-bearing minerals, there may be insufficient natural sources for calcium infiltration, leading to lower magnesium levels after the monsoon period.

The magnesium content in 75% of the water samples during the Pre-monsoon season were within the acceptable limits of 30 mg/L as CaCo<sub>3</sub>, The remaining 25% of the samples were found to be above the Acceptable limits but within the Permissible limits of 100mg/L as CaCo<sub>3</sub>. During the Post-Monsoon season 95% of the samples were found to be well within the Acceptable limits of 30 mg/L as CaCo<sub>3</sub>, only 5% of the samples had values above the acceptable limits but within the permissible limits given by the Bureau of Indian Standards (BIS) in 2012.



Figure 4.32: Spatial distribution of Magnesium (Pre-monsoon)



Figure 4.33: Spatial distribution of Magnesium (Post-monsoon)

### 4.2.8 Total Hardness



Figure 4.34: Seasonal Variations in Total Hardness

Total Hardness in ground water samples was assessed both during the Pre-monsoon and the Post-Monsoon season. In the pre-monsoon period, well number 15 exhibited the highest concentration of Hardness of 72.9 mg/L while the lowest readings of 20.8 mg/L were noted in well number 9.

During the post-monsoon phase, the highest Hardness was observed in well 15 at 58.9 mg/L and the lowest was in well 9 i.e. 14.02 mg/L. On average, the Hardness concentration during the pre-monsoon period stood at 37.72 mg/L which is higher than 28.56 mg/L recorded value during the post-monsoon phase.

Analysis of the data indicates that all the samples show lower Hardness levels during the post-monsoon period compared to pre-monsoon season. During intense monsoon rains, it's possible that there could be increased groundwater recharge, potentially leading to higher

water levels within wells. This influx of water might result in reduced hardness in groundwater due to the dilution effect.

According to the range provided by the United States Geological Survey, 95% of the samples during the pre-monsoon season and 100% during the post-monsoon season were categorized as soft water. However, 5% of the water samples from the pre-monsoon season were classified as moderately hard.

The Hardness in both, the Pre-monsoon and the Post-Monsoon season were found to be well within the Acceptable limits of 200 mg/L as CaCo<sub>3</sub> given by the Bureau of Indian Standards (BIS) in 2012.



Figure 4.35: Spatial distribution of Total Hardness (Pre-monsoon)



Figure 4.36: Spatial distribution of Total Hardness (Post-monsoon)

# 4.2 Chemical parameters

Table 4.3 Measured chemical parameters of groundwater samples during Pre-monsoon Season.

Sample									Total
No	pН	PO <sub>4</sub> <sup>3-</sup>	$NO_2^-$	F-	Alkalinity	Acidity	Ca	Mg	Hardness
1	5.98	0.028	0.0092	0.0016	19.8	21.6	16.2	29.72	45.924
2	5.93	0.033	0.0139	0.0019	15.6	21.2	8.8	37.86	46.662
3	5.91	0.023	0.0007	0.0013	14.2	23.8	8.6	16.86	25.462
4	5.87	0.035	0.0008	0.0024	7.7	23.3	0	31.45	31.448
5	5.89	0.013	0.0029	0.0018	8.9	21.5	0	35.48	35.48
6	5.78	0.029	0.0148	0.0018	15.9	18.7	38.6	19.72	58.324
7	5.73	0.012	0.0013	0.0009	7.9	21.6	20.2	9.71	29.91
8	6.37	0.011	0.0027	0.0008	32.1	10.8	7.8	26.45	34.248
9	5.92	0.013	0.0009	0.0001	22.1	11.3	8.3	12.5	20.8
10	6.1	0.015	0.0019	0.0001	19.6	15.3	8.2	37.24	45.44
11	6.33	0.01	0.0018	0.0021	20.1	7.8	16.8	24.86	41.662
12	5.87	0.027	0.0008	0.0015	18.5	11.1	17.2	19.86	37.062
13	5.92	0.015	0.0061	0.0053	6.1	9.6	18.3	15.72	34.024
14	5.87	0.01	0.0013	0.0021	4.3	17.7	12.2	18.62	30.82
15	5.63	0.022	0.001	0.0012	4.8	24.8	32.1	40.8	72.9
16	5.84	0.017	0.0012	0.0031	12	13.7	19.2	14.86	34.062
17	5.59	0.024	0.002	0.0018	8.2	19.8	17.6	24.86	42.462
18	5.23	0.032	0.0156	0.0017	3.7	30.3	23.7	9.86	33.562
19	6.29	0.015	0.0064	0.0019	12.1	11.7	0	29.72	29.724
20	5.92	0.014	0.0073	0.0018	11.7	21.2	0	24.5	24.5

Sample									Total
No	pН	PO4 <sup>3-</sup>	$NO_2^-$	F-	Alkalinity	Acidity	Ca	Mg	Hardness
1	5.55	0.038	0.0291	0.0001	12.98	24.2	8.4	22.4	30.8
2	5.57	0.036	0.0478	0.0002	9.29	25.3	3	29.2	32.2
3	5.62	0.038	0.0056	0.0001	9.03	25.1	5.3	15.8	21.1
4	5.47	0.054	0.0056	0.0001	3.03	29.5	0	25.0	25.0
5	5.56	0.027	0.0103	0.0002	6.11	24.2	0	29.3	29.3
6	5.74	0.059	0.1625	0.0009	9.85	21.7	21.4	18.4	39.8
7	5.59	0.023	0.0103	0.0002	6.59	27.3	17	8.2	25.2
8	5.98	0.028	0.0244	0.0001	24.11	14.9	6.1	23.2	29.3
9	5.6	0.008	0.0056	0.0001	16.16	15.6	5.3	8.7	14.0
10	5.77	0.018	0.0150	0.0001	10.98	16.9	8	29.2	37.2
11	5.97	0.033	0.0150	0.0008	15.11	9.8	12.6	17.4	30.0
12	5.65	0.052	0.0056	0.0003	12.68	14.2	12	14.6	26.6
13	5.69	0.027	0.0713	0.0004	3.70	15.4	13	15.9	28.9
14	5.36	0.022	0.0094	0.0002	1.46	20.6	8.5	12.6	21.1
15	5.15	0.017	0.0150	0.0005	4.07	26.5	24	34.9	58.9
16	5.68	0.012	0.0103	0.0012	9.25	18.8	16	12.6	28.6
17	5.52	0.032	0.0244	0.0008	7.72	24.7	15.6	19.4	35.0
18	5.09	0.038	0.0331	0.0000	2.20	32.9	16.2	5.2	21.4
19	5.79	0.039	0.0244	0.0002	8.25	14.3	0	21.17	21.17
20	5.69	0.027	0.0291	0.0001	8.43	24.3	0	15.59	15.59

Table 4.4 Measured chemical parameters of groundwater samples during Post-monsoon Season.

#### 4.3 Heavy Metals

### 4.3.1 Iron



Figure 4.37: Graphical representation of Iron in various samples

Iron in ground water samples was assessed during the Post-Monsoon season. Well number 20 exhibited the highest concentration of Iron of 0.91 mg/L while the lowest readings of 0.059 mg/L were noted in well number 3. The average Iron concentration in water stood at 0.1432 mg/L. The iron concentration in almost all the water samples was within the permissible limit of 0.3 mg/L set by the Bureau of Indian Standards (BIS) in 2012. However, sample number 20 exhibited an iron concentration three times higher than the permissible limit.

The high iron levels in well no. 20 may be due to two factors: the chemical weathering of laterite rocks, releasing soluble iron compounds into groundwater, and anaerobic conditions in the groundwater, promoting the conversion of iron to its more soluble form (Fe^2+). These processes together increase iron solubility, leading to heightened concentrations in the well.



Figure 4.38: Spatial distribution of Iron

## 4.3.2 Manganese



Figure 4.39: Graphical representation of Manganese in various samples

Manganese in ground water samples was assessed during the Post-Monsoon season. Well number 14 exhibited the highest concentration of Mn of 0.008 mg/L while the lowest readings of 0 mg/L were noted in well number 1,2,11,12,19. The average Manganese concentration in water stood at 0.0017 mg/L.

The Manganese concentration in all the water samples were well within the permissible limit of 0.1 mg/L set by the Bureau of Indian Standards (BIS) in 2012.



Figure 4.40: Spatial distribution of Manganese

### 4.3.3 Nickle



Figure 4.41: Graphical representation of Nickle in various samples

Nickle in ground water samples was assessed during the Post-Monsoon season. Well number 16 exhibited the highest concentration of Ni of 0.008 mg/L while the lowest readings of 0.002 mg/L were noted in well number 1,2,3. The average Nickle concentration in water stood at 0.0041mg/L.

In all water samples, the nickel concentration remained within the permissible limit of 0.02 mg/L set by BIS 2012.


Figure 4.42: Spatial distribution of Nickle



## 4.3.4 Copper

Figure 4.43: Graphical representation of Copper in various samples

Copper in ground water samples was assessed during the Post-Monsoon season. Well number 15 exhibited the highest concentration of Copper of 0.046 mg/L while the lowest readings of 0 mg/L were noted in well number 3,4,9,16,17. The average CU concentration in water stood at 0.0041mg/L.

In all water samples, the copper concentration remained within the acceptable limit of 0.05 mg/L set by BIS 2012.



Figure 4.44: Spatial distribution of Copper





Figure 4.45: Graphical representation of Zinc in various samples

Zinc in ground water samples was assessed during the Post-Monsoon season. Well number 8 exhibited the highest concentration of Zn of 0.093 mg/L while the lowest readings of 0.007 mg/L were noted in well number 17. The average Zinc concentration in water stood at 0.029 mg/L.

In all water samples, the Zinc concentration remained within the acceptable limit of 5 mg/L set by BIS 2012.



Figure 4.6: Spatial distribution of Zinc

Sample No	Fe	Mn	Ni	Cu	Zn
1	0.076	0	0.002	0.001	0.04
2	0.074	0	0.002	0.002	0.014
3	0.059	0.003	0.002	0	0.013
4	0.100	0.003	0.002	0	0.01
5	0.007	0.001	0.004	0	0.02
5	0.067	0.001	0.003	0.001	0.02
6	0.114	0.001	0.004	0.01	0.039
7	0.062	0.002	0.003	0.001	0.02
8	0.084	0.001	0.005	0.004	0.093
9	0.083	0.001	0.003	0	0.024
10	0.25	0.002	0.004	0.003	0.047
11	0.086	0	0.003	0.002	0.014
12	0.063	0	0.003	0	0.016
13	0.225	0.001	0.006	0.002	0.023
14	0.069	0.008	0.004	0	0.012
15	0.227	0.002	0.006	0.046	0.068
16	0.068	0.001	0.008	0	0.024
17	0.085	0.002	0.003	0	0.007
18	0.062	0.004	0.007	0.003	0.021
19	0.091	0	0.005	0.004	0.066
20	0.91	0.002	0.005	0.004	0.014

Table 4.5 Measured Heavy Metals in groundwater samples.

## 4.7 Groundwater flow-net analysis



Figure 4.47 Groundwater flow-net analysis

This flow-net sketch illustrates groundwater movement underground. In an unconfined aquifer, flow direction depends on hydraulic head, representing the total energy for water movement. At the water table, hydraulic head equals water-table elevation. Groundwater flows from high to low hydraulic head areas.

In our study, groundwater generally flows from the Industrial Estate plateau, acting as a water divide, towards the Zuari river in the Northeast, and lower fields in the south and southeast. The plateau's elevated region shows closely spaced equi-potential lines, indicating steep hydraulic gradients. Conversely, low-lying areas northeast and southeast have equi-potential lines spaced further apart, indicating gentler hydraulic conductivity.

## Conclusion

The comprehensive analysis of physical and chemical parameters of groundwater in the study area across pre-monsoon and post-monsoon seasons reveals significant variations and trends. The assessment encompassed parameters such as electrical conductivity (EC), total dissolved solids (TDS), turbidity, pH, phosphate, nitrite, fluoride, alkalinity, acidity, calcium, magnesium, and total hardness, along with heavy metals including iron, manganese, nickel, copper, and zinc.

During the pre-monsoon phase, the groundwater exhibited relatively lower electrical conductivity, total dissolved solids, and turbidity compared to the post-monsoon period. However, post-monsoon observations revealed increase in the levels of these parameters, which can be linked to factors like surface runoff, soil erosion, intensified microbial activity, and the leaching of organic matter, minerals, and salts from the soil into groundwater during the monsoon season. The pH of groundwater showed a consistent acidic trend throughout both seasons, with all samples falling below the permissible limits outlined by The Bureau of Indian Standards and the World Health Organization. This acidity may result from geochemical reactions involving ferrous iron and manganese oxidation, impacting water quality and necessitating mitigation measures.

Phosphate and nitrite concentrations increased notably post-monsoon, potentially due to organic matter leaching, agricultural activities, and microbial processes facilitated by enhanced soil moisture. Despite these increases, both parameters remained within permissible limits, highlighting relatively stable water quality concerning these aspects.

Fluoride concentrations exhibited a decrease post-monsoon, likely influenced by groundwater recharge and dilution effects during heavy rainfall. Following the monsoon season, acidity levels were noted to increase compared to the pre-monsoon period. This rise may be linked to the moist soil conditions, fostering organic matter decomposition, and heightened microbial activity, consequently releasing acidic byproducts into groundwater. Conversely, alkalinity levels decreased, possibly due to groundwater recharge and the removal of dissolved ions and minerals. Despite these fluctuations, both parameters remained within permissible limits.

Post-monsoon, calcium and magnesium levels experienced a decrease, likely influenced by increased groundwater recharge and flushing effects, compounded by the limited presence of calcium and magnesium content in the rocks. Nevertheless, both parameters remained within acceptable limits, suggesting a minimal impact on water quality. Total hardness exhibited a consistent decrease post-monsoon, possibly due to increased groundwater recharge and dilution effects, with most samples categorized as soft water according to USGS standards.

The heavy metal concentrations, including iron, manganese, nickel, copper, and zinc, were generally within acceptable limits across all samples, except for one well that displayed iron levels exceeding permissible thresholds by threefold. The elevated iron levels in well no. 20 are likely attributed to two factors: the chemical weathering of laterite rocks, which releases soluble iron compounds into groundwater, and the anaerobic conditions in the groundwater, facilitating the conversion of iron to its more soluble form (Fe^2+). These combined processes increase iron solubility, leading to heightened concentrations in the well. Despite this, the overall water quality remains satisfactory regarding heavy metal

contamination. Despite fluctuations in water quality between the pre-monsoon and postmonsoon periods, the groundwater quality in the study area generally complies with acceptable limits set by regulatory standards for most parameters. However, the consistently low pH observed in all 20 samples collected raises concerns regarding potential health implications.

N. Somasundaram's 2013 research focused on evaluating the downstream effects of groundwater development at the Verna Industrial Estate and water resource management. As compared to Somasundaram's findings with the current study, conducted a decade later, significant divergences in crucial parameters have been found. Somasundaram noted a pH range of 5.0 to 5.8 in open well water, whereas in my investigation, pH levels ranged from 5.09 to 6.37, marginally higher but still below the permissible thresholds set by both the BIS and WHO. In terms of total dissolved solids (TDS), Somasundaram reported values ranging from 36 to 128 mg/L, while in m study, they spanned 21.12 to 197.8 mg/L, indicating a slight decrease at the lower end but an increase at the upper limit. Calcium concentrations were notably higher in the current study, ranging from 0 to 38.6 mg/L, compared to Somasundaram's findings of 2.4 to 10 mg/L. Similarly, magnesium levels exhibited an increase, ranging from 5.2 to 40.8 mg/L in my research, compared to Somasundaram's reported range of 0.24 to 4.1 mg/L. The total hardness also displayed an upward trend over the years, rising from 7 to 43 mg/L in Somasundaram's study to 14 to 72.9 mg/L in mine. Conversely, alkalinity levels decreased from 8 to 40 mg/L in Somasundaram's findings to 1.5 to 32.1 mg/L in this study over the same period. Furthermore, iron content demonstrated an increase in this study, ranging from 0.06 to 0.91 mg/L, compared to Somasundaram's findings of 0.002 to 0.05 mg/L, with one sample

surpassing permissible limits in this study. These comparisons underscore the evolving dynamics of groundwater quality and emphasize the critical need for continuous monitoring and effective management strategies to tackle emerging water resource challenges.

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