Technical Report

CHARACTERISATION OF GROUNDWATER DYNAMICS IN KRISHNA-GODAVARI DELTA USING GROUNDWATER LEVELS, HYDROCHEMISTRY, ISOTOPES AND EMERGING CONTAMINANTS

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PREFACE

Groundwater situation in different parts of India is diversified because of variation in geological, climatological and topographic set-up. Annual water level fluctuation of premonsoon has shown a fall in water levels for 59 % of the area, predominantly in Rayalaseema region. During post-monsoon about 90% area of the state experienced rise in annual water level fluctuation. Aquifer wise water level analysis shows that during pre-monsoon season shallowest water levels are observed in all the formations except in Intrusives. Deepest water levels are observed alluvium, Limestone and BGC. During post-monsoon season, shallowest water levels are observed in all formations except in Intrusives and Laterites. Deepest water levels are observed in Gneiss, Granite, Limestone, Quartz and Sandstone. Geo-environmental conditions have a marked influence on the groundwater quality. Hydrogeochemical studies relevant to the water quality explain the relationship of water chemistry to aquifer lithology. Such relationship would help not only to explain the origin and distribution of dissolved constituents but also to elucidate the factors controlling the groundwater chemistry.

The term emerging contaminants (ECs) is generally used to refer to compounds previously not considered or known to be significant in groundwater in terms of distribution and/or concentration, which are now being more widely detected and which have the potential to cause known or suspected adverse ecological or human health effects. ECs include perfluorinated compounds (PFCs), nanomaterials, pesticides, pharmaceuticals, industrial compounds, personal care products, fragrances, water treatment by-products, flame retardants and surfactants, UV-filters as well as caffeine and nicotine. Because of their rapidly increasing use in industry, transport, agriculture, and urbanization, these chemicals are entering the environment at increasing levels as hazardous wastes and non-biodegradable substances. ECs may be a significant problem when surface and groundwater are used for drinking water production because the conventional drinking water treatments, like treatment with active carbon, flocculation, and disinfection, are not specifically designed to remove these micro pollutants. Traces of ECs in drinking water are actually measured and reported in only a few studies and the spatial and temporal variability of the majority of ECs in the environment is still poorly understood.

No attempt has been made for assessment of ground water quality in Krishna Godavari Delta with special reference to emerging contamination so far, therefore, a study titled “Characterisation of Groundwater Dynamics in Krishna-Godavari Delta using groundwater levels, Hydrochemistry, Isotopes and Emerging Contaminants” was proposed in collaboration with Deltaic Regional Centre, NIH, Kakinada and Central ground Water Board, Southern Region, Hyderabad and awarded in the Work Program of the year of 2022-23 of Environmental Hydrology Division for a period of 2 years duration. The activities to meet the objectives of the project were started from the month of April 2022 by recruitment of project staff, literature survey, field visit of the study area, collection and analysis of water samples. Support and help provided by Mr. J. Siddhartha Kumar, Scientist E & Head, CGWB, Southern Region, Hyderabad during field investigations are highly appreciated and duly acknowledged. Hydrochemical analysis of the collected groundwater samples was carried out by CGWB. Technical Report titled “Characterisation of Groundwater Dynamics in Krishna-Godavari Delta using groundwater levels, Hydrochemistry, Isotopes and Emerging Contaminants” has been prepared based on the work carried out and findings of this study by Dr. M. K. Sharma, Scientist ‘F’ & Principal Investigator, NIH, Roorkee and Dr. Y. R. S. Rao, Scientist G & Coordinator, DRC, NIH, Kakinada under the work program 2022-23 of Environmental Hydrology Division of the institute. The findings of the study will provide a present status of emerging contaminants in groundwater of KG Delta reign of India

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ABSTRACT

Water Quality is deteriorated due to change in life style. The term emerging contaminants (ECs) is generally used to refer to compounds previously not considered or known to be significant in groundwater in terms of distribution and/or concentration, which are now being more widely detected and which have the potential to cause known or suspected adverse ecological or human health effects. ECs include perfluorinated compounds (PFCs), nanomaterials, pesticides, pharmaceuticals, industrial compounds, personal care products, fragrances, water treatment by-products, flame retardants and surfactants, UV-filters as well as caffeine and nicotine. In view of the above, characterization of groundwater dynamics in Krishna-Godavari Deltas interims had been proposed using geochemical, Isotopes and emerging contamination and their sources and its impacts on human health for sustainable drinking water supply.

One hundred thirty seven ground water samples during pre-monsoon (June 2022) and post-monsoon seasons (December 2022) were collected from the study area and analyzed for physico-chemical parameters, metal concentrations, pesticides, polynuclear aromatic hydrocarbons (PAHs), Polychlorinated biphenyls (PCBs) and volatile organic compounds (VOCs). Hydro-chemical data for pre- and post-monsoon seasons was processed as per BIS and WHO standards to examine the suitability of ground water for drinking purpose. Spatial distribution maps were prepared in the form of contour diagrams to identify degraded water quality zones, possible sources of pollution and specific parameters not conforming to drinking/ & irrigation water quality standards. Very high values of TDS and hardness were observed specially in Krishna delta. The high sodium values in the study area may be attributed to base-exchange phenomena causing sodium hazards. Hydro-chemical data was also processed to understand the geochemical processes controlling the chemical composition of groundwater using Scatter Plots and Gibbs Plot which reveals that hydrochemistry of groundwater of the study area is controlled by evaporation crystallization process and dissolution of rock forming mineral in Godavari delta while dissolution of rock forming minerals in Krishna delta. Carbonate weathering is a major source of dissolved ions in the groundwater of the study area. Cation exchange process and halite dissolution control the chemistry of groundwater of the region. Ground is more saline in Krishna delta than Godavari delta. The sources of groundwater salinity Krishna delta is more due to sea water mixing process. The comparison between LMWL and GWL indicates there is no direct rainfall recharge into shallow groundwater due to alluvial formations. The stable isotopes indicated that there is more evaporation in Krishna delta than in Godavari delta thus supports EC variations. The Tritium values (TU) of groundwater in KG deltas indicated that the Krishna delta groundwater is older than Godavari delta. d-excess vs well depth indicated that there are significant evaporation and mixing processes found in the KG deltas. The presence of heavy metals has been recorded in many samples and the water quality standards have been violated for iron, aluminium, boron, manganese, nickel, lead, mercury and arsenic in few of the samples in Godavari delta during the pre-monsoon period while the concentrations of iron, aluminium, boron, mercury, manganese, lead, uranium and arsenic in few samples have been violated in Krishna delta. Presence of many pesticides were observed in many samples of the study area and BHC-Alfa has exceeded the maximum prescribed limit in more than 90% of the samples of the study area. Polychlorinated Biphenyls have also been detected in the samples of the study area but within the permissible limit of Total PCB. Total PAHs exceeded the maximum prescribed limit in more than 80% of the samples collected from Godavari delta. The presence of volatile organic compounds (Benzene) was also observed in few of the samples of Godavari and Krishna deltas.

1.0 INTRODUCTION

Groundwater situation in different parts of India is diversified because of variation in geological, climatological and topographic set-up. Annual water level fluctuation of premonsoon has shown a fall in water levels for 59 % of the area, predominantly in Rayalaseema region. During post-monsoon about 90% area of the state experienced rise in annual water level fluctuation. Aquifer wise water level analysis shows that during pre-monsoon season shallowest water levels are observed in all the formations except in Intrusives. Deepest water levels are observed alluvium, Limestone and BGC. During post-monsoon season, shallowest water levels are observed in all formations except in Intrusives and Laterites. Deepest water levels are observed in Gneiss, Granite, Limestone, Quartz and Sandstone (CGWB GW Year Book 2019-20 AP).

Geo-environmental conditions have a marked influence on the groundwater quality. Hydrogeochemical studies relevant to the water quality explain the relationship of water chemistry to aquifer lithology. Such relationship would help not only to explain the origin and distribution of dissolved constituents but also to elucidate the factors controlling the groundwater chemistry. Further, groundwater quality in a region is influenced by physical and chemical parameters that are strongly affected by natural processes such as water chemistry in the recharged area, water intermixing, groundwater recharge, aquifer discharge and recharge, water flow path.

The term emerging contaminants (ECs) is generally used to refer to compounds previously not considered or known to be significant in groundwater in terms of distribution and/or concentration, which are now being more widely detected and which have the potential to cause known or suspected adverse ecological or human health effects. ECs include perfluorinated compounds (PFCs), nanomaterials, pesticides, pharmaceuticals, industrial compounds, personal care products, fragrances, water treatment by-products, flame retardants and surfactants, UV-filters as well as caffeine and nicotine. Because of their rapidly increasing use in industry, transport, agriculture, and urbanization, these chemicals are entering the environment at increasing levels as hazardous wastes and non-biodegradable substances.

The pathways through which these pollutants enter surface waters are well known and the main contributions are from effluents of wastewater treatment plants, where some residues are not removed, and from agricultural and industrial activities. Contacts and exchanges between the aquifers, rivers and sewage networks, and leaching from agricultural fields, can cause the contamination of shallow and deep groundwater. ECs may be a significant problem when surface and groundwater are used for drinking water production because the conventional drinking water treatments, like treatment with active carbon, flocculation, and disinfection, are not specifically designed to remove these micropollutants. Traces of ECs in drinking water are actually measured and reported in only a few studies and the spatial and temporal variability of the majority of ECs in the environment is still poorly understood.

The finding of analysis indicates that the scientific literature on the environmental occurrence of emerging contaminants has advanced very quickly during the last 20 years. This is a result of the increased attention that social, political, and legislation authorities are giving to the environment, which has led to the creation of programs for environmental protection and monitoring as well as the emergence of stricter regulations designed to encourage the wiser use of natural resources. From 2002 to 2019, there were 1968 papers about emerging pollutants published in scholarly journals that were indexed in the Scopus database. The top three countries for this type of study were the United State, Spain, and China with Spain taking the top spot in terms of productivity measured as the ratio of publications or citation of GDP. Environmental science, chemistry, and chemical engineering each contributed 41, 18 and 19% of the indexed documents to the global scientific output connected to EC over the past few decades. Absorption and advanced oxidation are the EC treatment methods that have been investigated the most in terms of published studies (Malule et at., 2020).

There are the several studies and research which have been published on the global level for the detection of different types of ECs their impact in the environment and human including Lin et al., 2020; Lei et al., 2015; Riva et al., 2014; Lopez et al., 2015; Krause et al., 2012; Stuart et al., 2012; Sorensen et al., 2014; Rashmeed et al., 2013; Geissen et al., 2015.

There are several challenges in the field of ECs detection and some of them are: -

- The proper lack of knowledge (or) information.
- The advanced treatment including the disinfection process should be proper and upgrade to further dilute the amount of these and undiscovered ECs in different sources in the future.
- The advanced technologies for the sampling and analysis should be adopted.
- Due to constantly expanding the no. of chemicals the accuracy of result will may be fluctuate.
- It must be acknowledged that environmental exposure is not due to the single contaminants(s) infect the mixture consist of ECs plus other chemical substances play a very significant role. Therefore, the potential impact of these mixture in the term of risk needs to be carefully determined.

In recent years, emerging contaminants (ECs) have been found in numerous water bodies around India. According to studies, ECs can pollute water bodies by being present in surface water, groundwater, stormwater, treated wastewater, treated industrial effluent, bottled water, and snow from glaciers along the Indo-Chinese border (Mathew et al., 2019). Pesticides make up 57% of the growing pollutants in India's aquatic environment, followed by medicines (17%), surfactants (15%), personal care products (15%), and phthalates (5%) (Gani and Kazmi, 2016). Active pharmaceutical ingredients (API), personal care products (PCP), pesticides, endocrine disrupting chemicals (EDC) and artificial sweeteners (ASW) were observed in surface water bodies (Gani and Kazmi, 2016).

According to the Delhi-based nonprofit Center for Science and environment (CSE), 78 percent of the sewage produced in India is dumped into rivers, lakes, or groundwater without being treated (CSE, 2016). This might provide an explanation for the elevated API levels found in water matrices. In their investigation of the Ahar River in Udaipur city, William et al. (2019) discovered 19 medicines, including 4 antibiotics. The river starts out as a potable water but becomes polluted as it passes through cities. As the river travelled through highly populated areas, it was seen that the concentration of emerging pollutants rose, potentially indicating the discharge of domestic wastewater into the river. The presence of antibiotics in Delhi's STP influent and effluent as well as the Yamuna River was investigated by Mutiyar and Mittak (2014). The highest reported amounts of API in the world were discovered by similar research by Larsson et al. (2017) in water bodies and wells close to the pharmaceutical manufacturing industrial zone. DEET, a component of insect repellents, has been found in the Ahar River in Udaipur (William et al., 2019). This shows that residential wastewater has contaminated river water.

Similar other research studies were already conducted in previous years for the determination of different concentration of ECs in different water bodies viz; Lapworth et al., 2018, Yeung et al., 2009, Sunantha and Vasudevan, 2016, William et al., 2019, Raj and Muruganandam, 2014, Selvaraj et al., 2014a etc. Numerous studies have identified the presence of phthalates, polychlorinated biphenyls (PCBs), plasticizers, and perchlorate which are EDCs (Endocrine Disrupting Chemicals) (Mathew and Kanmani, 2019). When phthalate content in urine samples from India was analysed, the second-highest quantity (389 ng/ml) was discovered

(Guo et al., 2011). In drinking water from Jawaharlal Nehru University and Okhla industrial region, Das et al. (2014) found 15 phthalates. All phthalates combined were found to have concentrations between 0.39 and 3.804 g/L. the most prevalent phthalates were DEHP, with an estimated consumption level of 70 mg/kg/d. Three wastewater treatment facilities have been documented to include phthalates such as DEP, DBP, BBP, and DEHP. In summer, DEP, DBP, and DEHP had the greatest mean concentrations (7, 14, and 19 g/L, respectively). biotransformation is the primary phthalate elimination method (Gani and Kazmi 2019). In contrast to USA WWTPs (Waste water treatment plants), which accounted for 49.8%, ASWs (Artificial Sweeteners) contributed between 9.7% and 17.1% to the operation of three WWTPs in Chennai, India. ASWs were removed in the WWTP at low rates while Hydraulic Retention Time (HRT) was low, and further removal was seen as HRT increased. Physical adsorption and flocculation processes may have caused the loss (Mathew and Kanmani, 2019).

Toxicology endpoints are necessary in order to assess the risk of ECs. Therefore, considerable toxicological research must be done. There are very few regulatory requirements for the different classes of ECs. Due to a lack of toxicological information, several nations lack adequate laws on ECs. Only a few pesticides regulatory standards are included in India's drinking water standards (Indian Standards) (IS 10500). The presence of ECs is not checked at the WWTPs or water treatment facilities. There is different regulation of ECs as per WHO, USEPA, EU (µg/L) and is mentioned in the Mathew and Kanmani (2019). The United States Environmental Protection Agency (USEPA) under the safe drinking water act regulates the ECs listed on the Contaminated Candidate List (CCL). Every five years, the USEPA regulates at least five contaminants from the CCL. A fresh list of not more than 30 uncontrolled contaminants that must be observed by public water systems every five years and must also be published. The most recent list, CCL4, has 12 microbiological contaminants and 97 chemicals or chemical groupings. The use of effective and affordable treatment technologies for the elimination of ECs makes it possible to control ECs. For the reduction of several key ECs, earlier investigation using adsorption, biological treatment, and advanced oxidation processes (AOPs) are discussed (Mathew and Kanmani 2019).

Changes in pH and Eh have an enormous effect on chemical and biological processes in the soil substrate. Petroleum microseepage in the soil substrate causes several chemical reaction and microbial oxidation of hydrocarbons and also causes decrease in Eh and pH. Mineral stability in any environment is dependent on and is a function of pH and Eh. Hydrocarbons migrating into the near surface soils destablizes many compounds and increases the solubility of the trace and minor elements. Many metal elements are highly soluble in acid solutions but will be precipitated as oxides and hydroxides with increasing pH. Oxidation-reduction potential plays a major role on the mobility of elements. Anomalous amounts of V, Cr, Ni, Co, Mn, Hg, Cu, Mb, U, Zn, Pb & Zr are + indicators of petroleum deposits. Migrating hydrocarbons create a reducing environment in the soil and subsurface, which increases the solubility of many trace and major elements.

Krishna and Godavari rivers are major and large rivers in Peninsula India. Water availability is more in Godavari River. Krishna delta has the water scarcity problem due to unavailability of water in Krishna River. So Andhra Pradesh government took the decision to interlinking the rivers through Polavaram canal. Flood water from the Godavari River could be diverted to the paddy growing region of Rayalaseema, which often suffers from insufficient water. In order to link the two rivers a 174 km-long canal, known as the Polavaram Right Canal, was constructed and supplied with pumps that will remove excess water from the Godavari River and send it to the Krishna River. Paddy farmers in the Krishna Delta are the main beneficiary of the linking of the two rivers. Diverted water will also provide Amaravati, the planned state capital, with drinking water. The project is seen as a means to ensure the future water and food security of Andhra Pradesh.

In view of the above, characterization of groundwater dynamics in Krishna-Godavari Deltas has been proposed using geochemical, Isotopes and emerging contamination and their sources and its impacts on human health for sustainable drinking water supply.

2.0 OBJECTIVES OF THE STUDY

i) To study the groundwater level fluctuations in Krishna-Godavari Deltas
ii) Characterisation of groundwater using Hydro-chemical and Hydrogeochemical investigation
iii) Isotopic Characterisation of groundwater
iv) To study the status of Emerging Contaminants in the groundwater, their sources and its impacts on human health

3.0 STUDY AREA

The Krishna-Godavari Basin is a pericratonic rift margin system with an Archean basement on the east cost of Indian Peninsula (Kotha, 2002). It covers an area of 28,000 km^2 on land and 24,000 km^2 offshore up to 200 m deep (Gupta, 2006). The basin lies between 15°30' to 17° N latitudes and 80° to 82°30' E longitudes (Fig. 1). Geographically, the basin lies between Kakinada in the northeast and Ongole in the southwest. Archean crystalline basement and Upper Cretaceous sedimentary outcrops demarcate the basin margin. The basin extends southeast into the deep water of the Bay of Bengal. A significant part of the onshore basinal area is covered by recent alluvium. Outcrops in the basin margin area includes the Permean Chintalapudi sandstone, Cretaceous to Jurassic Gollapalli sandstone, raghavapuram shale and Tirupati Sandstone exposed around DwarakaTirumala area of the West Godavari district. The Rajahmundry sandstone outcropping near the Rajahmundry and Dowleswaram areas are red, feldspathic, ferruginous and laterised sandstone of Miocene age, which is equivalent to the Ravva formation of the offshore area.

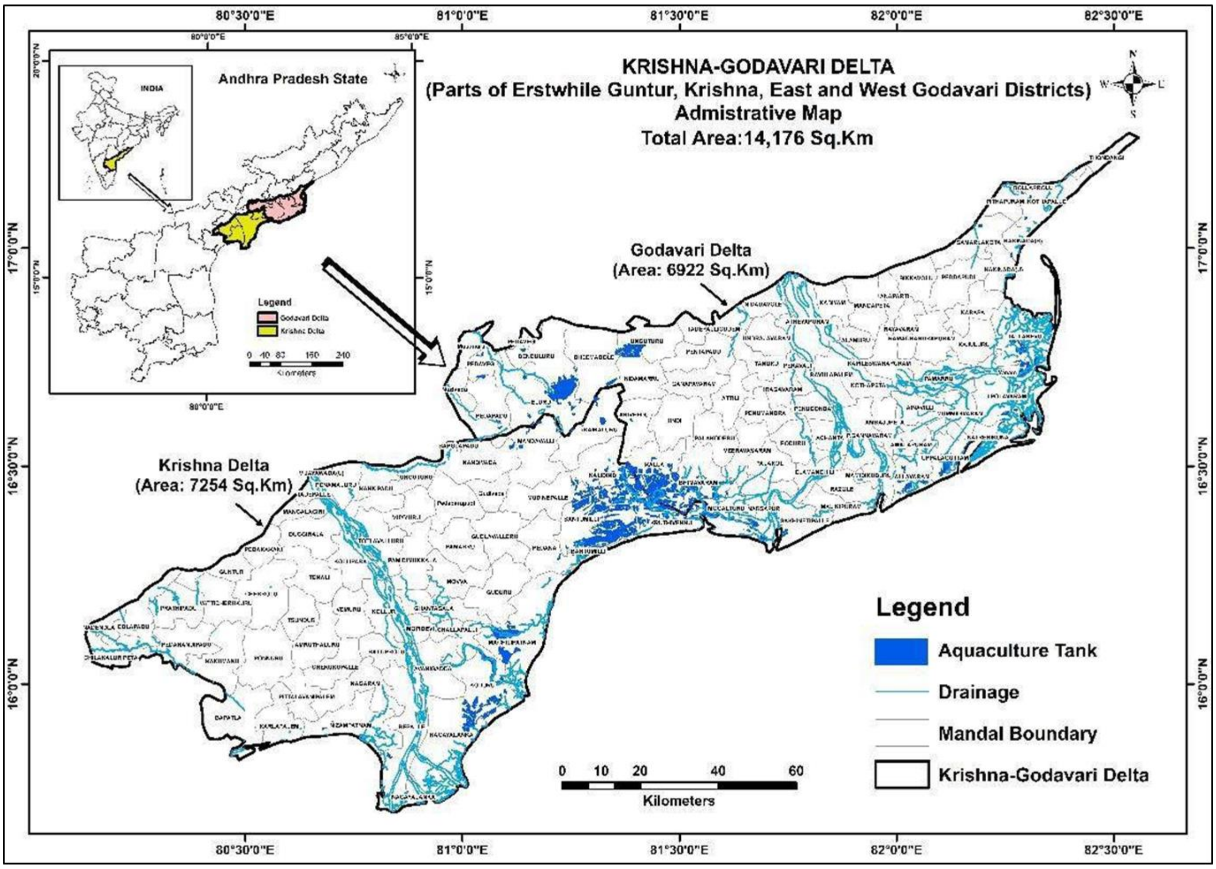


Fig. 1. Location map of Krishna Godavari deltaic region

The basin is divided into the Krishna, East Godavari and West Godavari depressions separated by basement highs at Bapatla and Tanuku horsts, respectively. The East Godavari sub-basin is further divided into the Mandapeta Graben, Narsapur-Razole High and Amalapuram High. The Matsyapuri-Palakollu and Mori faults are the two major NE-SW faults. The West Godavari sub-basin is sub-divided into the Gudivada and Bantumilli graben, separated by the Kaza-Kaikaluru horst (Kumar, 1983). The tertiary alluvium sediments brought by the Godavari delta system attained greater thickness south of the Matsyapuri-Palakollu fault as a result of continuous subsidence and growth fault related tectonics (Sanyal et al, 1998). The depositional environment varies from continental to lagoonal, littoral, infraneritic, deltaic and marine conditions. The sediments yield rich faunal assemblages like arenaceous foraminifera (Ammobaculites sp., Ammodiscoides sp., etc.), Trigonia, Inoceramus, Lima, Pecten, Belemnites, Helicoceras, Cardita, Lamellibranchs and Gastropods (Sastri et al., 1973). The soil map and geological map of the study area are given in Fig. 2 and 3 respectively. Hydrogeological map of Krishna Godavari deltaic region is given in Fig. 4.

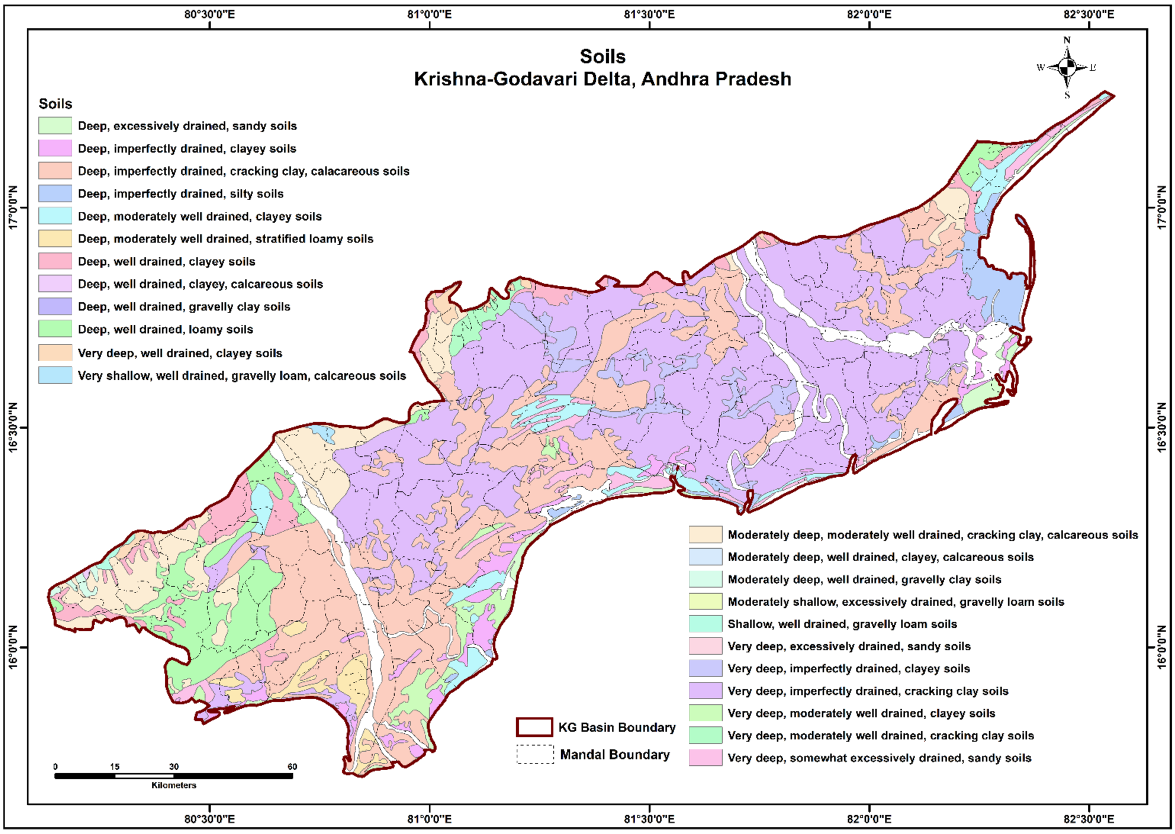


Fig. 2. Soil map of Krishna Godavari deltaic region

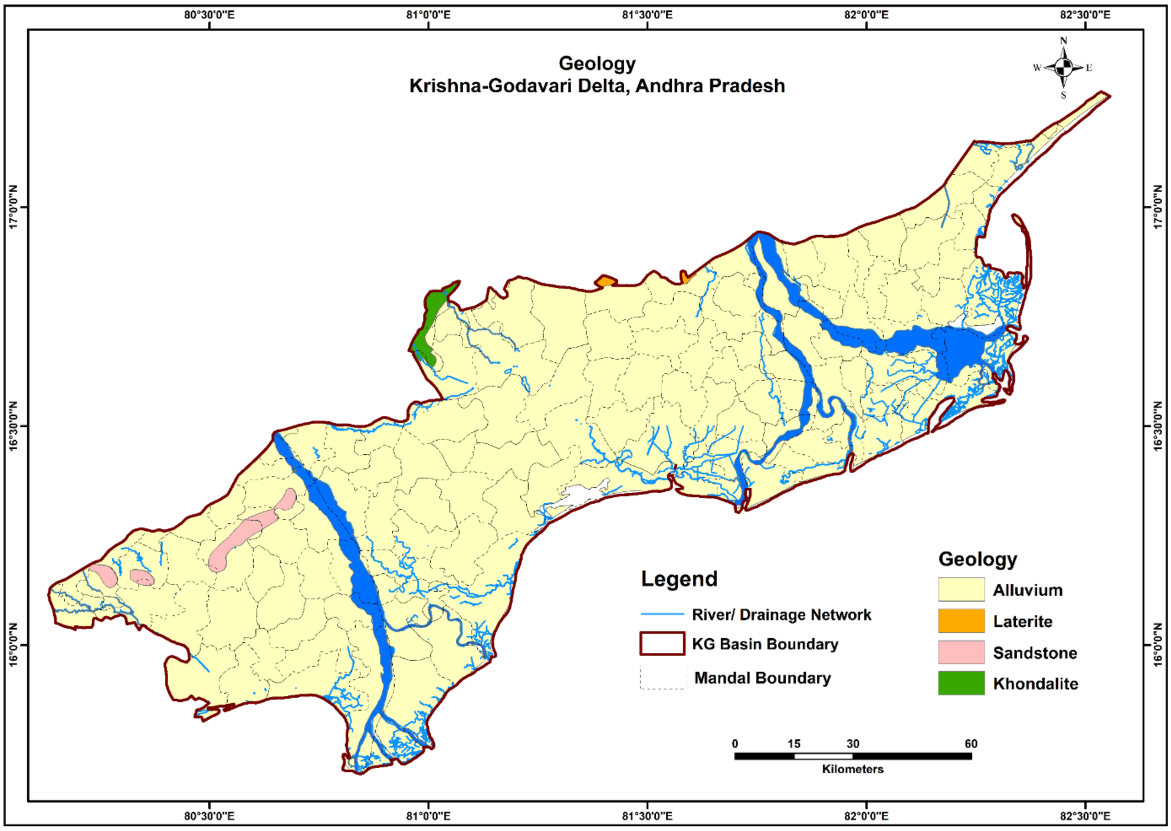


Fig. 3. Geological map of Krishna Godavari deltaic region

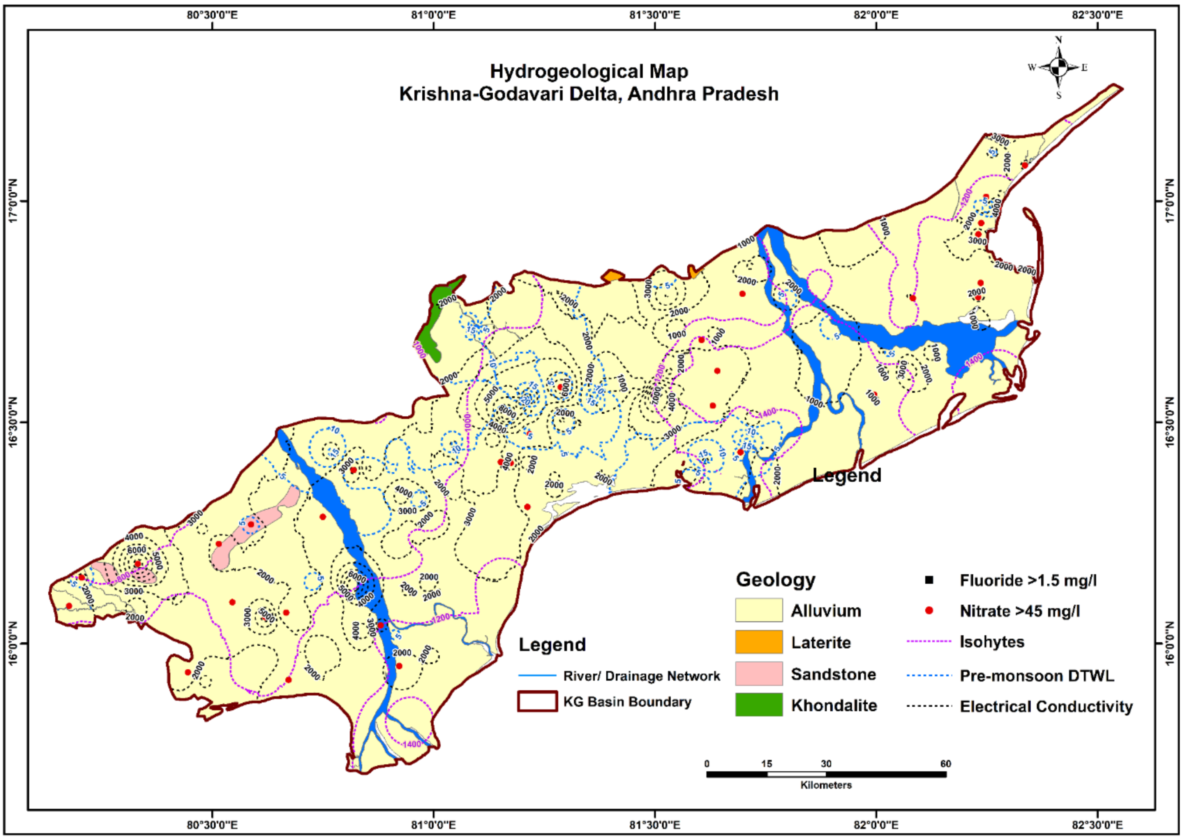


Fig. 4. Hydrogeological map of Krishna Godavari deltaic region

4.0 EXPERIMENTAL METHODOLOGY

A brief methodology of the study is described as below:

i) Collected of groundwater level data, lithological data, water quality data from published report, literature and from various govt. agencies.

ii) Hydrogeological characterization of the study area and establish specific linkages of groundwater quality with hydrogeology.

iii) Collected of groundwater samples from selected sources in pre-monsoon (April-May) and post-monsoon (October-November) season at identified locations.

iv) Analysis on flow and movement of groundwater.

v) Analysis for physico-chemical parameters [pH, EC, TDS, Eh, Alkalinity, Hardness, Major Cations (Na, K, Ca, Mg), Major Anions (Cl, SO_4, NO_3, HCO_3), minor elements (Fluoride, PO_4, NH_4)] metal concentrations (As, Fe, Mn, Cd, Zn, Cu, Cr, Pb, Co, Ni, Ba, Sr, V, Se), and emerging contaminants (Pesticides, PAHs, PCBs, VOCs, BETEX) in the collected water samples.

vi) Analysis of Stable environmental isotopes of Hydrogen and Oxygen in the collected water samples

vii) Processed hydro-chemical data for pre- and post-monsoon seasons as per BIS and WHO standards to examine the suitability of ground water for drinking purpose.

viii) Ionic relationships have been developed and water types identified. Spatial distribution maps have been prepared in the form of contour diagrams to identify degraded water quality zones, possible sources of pollution and specific parameters not conforming to drinking/ & irrigation water quality standards.

ix) Processed of hydro-chemical data to understand the geochemical processes controlling the chemical composition of groundwater using Scatter Plots and Gibbs Plot.

x) Soil quality monitoring for metal concentrations (Zn, Cu, Cr, Co, Ni, Ba, Sr, V, Se) in the petroliferous regions of the study area during pre- and post-monsoon seasons.

xi) Probable impact of emerging contaminants in groundwater on human health.

The study area covers Krishna and Godavari Delta region. Total one hundred thirty seven ground water samples each during pre-monsoon (May-June 2022) and post-monsoon seasons (December 2022) were collected from the study area during the year 2022-23 from various abstraction sources in collaboration of Regional Centre, Kakinada and Central Ground Water Board, Hyderabad. Out of 137 water samples, 73 water samples were collected from Godavari basin delta and 64 water samples from Krishna basin delta. The samples were preserved as per standard procedures and were analyzed for physico chemical parameters by CGWB on Ion Chromatograph and and the analysis correctness was checked by anion-cation balance and the analyses were accepted with the difference of $\pm$10%. The analysis of metals and emerging contaminants (Pesticides, PAHs, PCBs, VOCs, BETEX) was carried out in the NIH Water Quality Laboratory as per APHA (2012).

Metal analysis using Inductively Coupled Plasma – Mass Spectrometry (ICP-MS)

The trace metals (As, Fe, Mn, Cd, Zn, Cu, Cr, Pb, Co, Ni, Ba, Sr, V, Se) were analyzed in the collected samples of the study area by inductively coupled plasma mass spectrometry (ICP-MS) (Agilent 7850 ICP-MS). The ICP-MS were calibrated for the analyte of interest using certified reference materials (CRMs) traceable to NIST (Merck) and the standards/blank were also run after a periodic interval during the analytical run for the continuing calibration verification (CCV). The analysis run was accepted if the percentage recovery in the CCV run was within +10%. The operational conditions were adjusted in accordance with the manufacture's guidelines to yield optimal determination. The calibration curve of mixed trace metal solution of 10, 50, and 100 ppb were prepared and with the help of same the concentration of metals in the samples were quantified. These calibration curves were determined several times during the period of analysis. The samples were filtered through 0.45 micron filter paper before injecting in ICP-MS. All the parameters were analyzed in triplicate for quality control.

Emerging Contaminants analysis using Quadrupole Gas Chromatograph – Mass Spectrometry (GC-MS/MS)

The groundwater samples for the analysis of pesticides were extracted 15% Dichloromethane (DCM) in n-Hexane three times, and the combined extract was concentrated (up to 3 ml) using parallel evaporator (BUCHI SyncorePlus) under reduced vacuum. The moisture from the extracts was removed using anhydrous sodium sulphate. Then, 1 µl of solution was injected with the help of auto-sampler with syringe (PAL RSI 85) in GC oven of GC-MS/MS system of Agilent Technologies Gas Chromatograph (8890 GC) coupled with triple quad mass spectrometer (7010 B MSQQQ) in the EI (Electron Impact) mode with the electron energy set at 100 eV and the mass range at m/z 5–1070. A capillary column HP 5 (30 m (length) x 0.25 mm (ID)) of 0.25 µm film thickness of coated material (5% diphenyl and 95% dimethylpolysiloxane) was used. The injector was set at 280 °C. The detectors used were MS detector. The temperature programmed as follow: 1 min hold at 60 °C with 40 °C/min rise up to 170 °C followed by 10 °C/min rise up to 310 °C. The flow rate of carrier gas (helium) was maintained at 1.0 ml/min. A post-run of 2 min at 310 °C was sufficient for the next injection. Identification of compounds was done by comparing the retention times with those of standard pesticides. The qualitative determination of the pesticides was carried out by comparing the retention time and peak area of the pesticides. Further, PAHs and PCBs were analysed in the extracted, concentrated and dried groundwater samples using selected method for PAHs and PCBs customised by M/s Agilent Technologies.

Before performing the analysis of VOCs, GC-MS/MS was optimized for the operating conditions. Analytes were recovered from the water samples by heating in the Headspace port of Agilent 8890 GC system equipped with a PAL system autosampler coupled to an Agilent 7010 B GC/TQ mass spectrometer. A DB-WAX column was used (30m X 250 µm X 0.25 µm) to separate the VOcs compounds using the oven programme as follows: initial temperature of 35° C (hold for 12 minutes), ramp rate 10° C/min to 140° C, which was held for 11 min. The carrier gas was helium with a constant flow of 1 ml/min. The interface and source temperatures were 150 and 230 °C respectively. Mass spectra were collected under electron ionization (EI) mode at 70 eV and recorded in SIM mode. Compounds were Quantified and confirmed against the calibration curve of each standard. The GC-MS/MS was calibrated using five concentrations viz 20 ppb, 50 ppb, 100 ppb, 200 ppb, and 500 ppb of VOCs (Benzene, Toluene, Ethylbenzene, Butylacetate, Undecane m-Xylene, o-Xylene and p-Xylene, Styrene).

Fig. 5. Photographs showing groundwater sampling from various abstraction sources and groundwater level measurement in the study area

Fig. 6. A view of ICP-MS

Fig. 7. A view of GC-MS/MS

5.0 RESULTS AND DISCUSSIONS

5.1 General Characteristics of Groundwater of Study Area

Total one hundred thirty seven ground water samples each during pre-monsoon (May-June 2022) and post-monsoon seasons (December 2022) were collected from the study area during the year 2022-23 from various abstraction sources in collaboration of Regional Centre, Kakinada and Central Ground Water Board, Hyderabad (Fig. 8). Out of 137 water samples, 73 water samples were collected from Godavari basin delta and 64 water samples from Krishna basin delta. The details of sampling locations and source distribution are given in Table 1 & 2 respectively. The hydro-chemical data for the two sets of samples collected during pre- and post-monsoon seasons for Godavari basin delta and Krishna basin delta are presented in Table 3 & 4 respectively. Variation of groundwater level and different water quality constituents in pre- and post-monsoon seasons are given in Fig. 9 to12. Spatial distribution maps are presented in the form of contour diagrams in Figs. 13 to 22.

Godavari Delta

The pH values in the ground water of the study area mostly fall within the range 6.68 to 8.29 during pre-monsoon season and 6.87 to 8.7 during post-monsoon season. The pH values for most of the samples are well within the limits prescribed by BIS (2012) and WHO (1996) for various uses of water including drinking and other domestic supplies.

The electrical conductivity and dissolved salt concentrations are directly related to the concentration of ionized substance in water and may also be related to problems of excessive hardness and/or other mineral contamination. The conductivity values in the ground water samples of the study area vary widely from 110 to 10000 μS/cm during pre-monsoon season and 360 to 6350 μS/cm during post-monsoon season.

In the study area, the values of total dissolved solids (TDS) in the ground water varies from 52 to 5617 mg/L during pre-monsoon season and 188 to 4123 mg/L during post-monsoon season. About 63% samples were found above the acceptable limit but within the maximum permissible limit of 2000 mg/L in both seasons (pre- and post-monsoon season) (Table 3). The variation of TDS in groundwater of study area for pre- and post-monsoon seasons is shown in Fig. 10. The TDS distribution maps for the pre-monsoon and post-monsoon seasons are shown in Fig. 13. Water containing more than 500 mg/L of TDS is not considered desirable for drinking water supplies, though more highly mineralized water is also used where better water is not available. For this reason, 500 mg/L as the acceptable limit and 2000 mg/L as the maximum permissible limit has been suggested for drinking water (BIS, 2012). In the study area, Water containing TDS more than 500 mg/L causes gastrointestinal irritation (BIS, 2012).

Alkalinity in natural water is mainly due to presence of carbonates, bicarbonates and hydroxides. The alkalinity value in the groundwater of the study area varies from 30 to 880 mg/L during pre-monsoon season and 115 to 1257 mg/L during post-monsoon season. Total 12% of the sample exceeds the maximum permissible limit of 600 mg/L during pre-monsoon season and 14% samples exceed the maximum permissible during post-monsoon season. The variation of alkalinity in groundwater of study area for pre- and post-monsoon seasons is shown in Fig. 10. The alkalinity distribution maps for the pre-monsoon and post-monsoon seasons are shown in Fig. 14.

The presence of calcium and magnesium along with their carbonates, sulphates and chlorides are the main cause of hardness in the water. A limit of 200 mg/L as acceptable limit and 600 mg/L as permissible limit has been recommended for drinking water (BIS, 2012). The total hardness values in the study area range from 20 to 1600 mg/L during pre-monsoon season and 102 to 1031 mg/L during post-monsoon season. About 68% and 75% of all samples of the study area crosses the acceptable limit of 200 mg/L but are well within the permissible limit of 600 mg/L during pre- and post-monsoon season respectively, and 11% and 10% sample crosses the permissible limit of 600 mg/L during pre- and post-monsoon seasons respectively. The variation of hardness in groundwater of study area for pre- and post-monsoon seasons is shown in Fig. 10. The hardness distribution map for the pre- and post-monsoon season is shown in Fig. 15.

In ground water of the study area, the values of calcium range from 6 to 229 mg/L during pre-monsoon season and 18 to 187 mg/L during post-monsoon season. The values of magnesium vary from 1.3 to 280 mg/L during pre-monsoon season and 5.3 to 138 mg/L during post-monsoon season. The acceptable limit for calcium and magnesium for drinking water are 75 and 30 mg/L respectively (BIS, 2012). In ground water, the calcium content generally exceeds the magnesium content in accordance with their relative abundance in rocks. Further, 3% sample exceeds the maximum permissible limit of calcium as 200 mg/L and 8% sample exceeds the maximum permissible limit of magnesium as 100 mg/L in pre-monsoon season. None of sample exceeds the maximum permissible limit of calcium as 200 mg/L and 8% sample exceeds the maximum permissible limit of magnesium as 100 mg/L in post-monsoon season. The variation of calcium and magnesium in groundwater of study area for pre- and post-monsoon seasons is shown in Fig. 11. The calcium and magnesium distribution maps for the pre- and post monsoon seasons are shown in Fig. 16 & 17 respectively.

The concentration of sodium in the study area varies from 9.0 to 1526 mg/L during pre-monsoon season and 9 to 1449 mg/L during post-monsoon season. The high sodium values in the study area may be attributed to base-exchange phenomena causing sodium hazards. The sodium distribution map for the pre- and post-monsoon season is shown in Fig. 18. Ground water with high value of sodium is not suitable for irrigation purpose. The concentration of potassium in ground water of the study area varies from 0.8 to 331 mg/L during pre-monsoon season and 1 to 494 mg/L during post-monsoon season.

The concentration of chloride varies from 6.0 to 3002 mg/L during pre-monsoon season and 6.0 to 2222 mg/L during post-monsoon season. Total 68% samples of the study area fall within the acceptable limit of 250 mg/L during both the seasons (pre-monsoon season and post-monsoon). The variation of chloride in groundwater of study area for pre- and post-monsoon seasons is shown in Fig. 11. The chloride distribution map for the pre- and post-monsoon season is shown in Fig. 19. The sulphate content in ground water generally occurs as soluble salts of calcium, magnesium and sodium. The concentration of sulphate in the study area varies from 0.2 to 256 mg/L during pre-monsoon season and 5.0 to 625 mg/L during post-monsoon season. Bureau of Indian standard has prescribed 200 mg/L as the acceptable limit and 400 mg/L as the permissible limit for sulphate in drinking water. In the study area, 98% of the samples analyzed fall within the acceptable limit of 200 mg/L while 1% of the samples exceed the acceptable limit but are within the permissible limit of 400 mg/L and 1% of the samples exceed the maximum permissible limit of 400 mg/L during pre-monsoon season. In the study area, 96% of the samples analyzed fall within the acceptable limit of 200 mg/L while 3% of the samples exceed the acceptable limit but are within the permissible limit of 400 mg/L and 1% of the samples exceed the maximum permissible limit of 400 mg/L during post-monsoon season. The variation of sulphate in groundwater of study area for pre- and post-monsoon seasons is shown in Fig. 12. The sulphate distribution map for the pre- and post-monsoon season is shown in Fig. 20.

The nitrate content in the study are varies from 0.1 to 234 mg/L during pre-monsoon season and 0.3 to 140 mg/L during post-monsoon season. About 82% of the samples of the study area fall within the permissible limit of 45 mg/L and 18% of samples even cross the permissible limit during both the seasons. In higher concentrations, nitrate may produce a disease known as methaemoglobinaemia (blue babies) which generally affects bottle-fed infants. The variation of nitrate in groundwater of study area for pre- and post-monsoon seasons is shown in Fig. 12. The nitrate distribution map for the pre- and post-monsoon season is shown in Fig. 21.

The fluoride content in the ground water of the study area varies from 0.0 to 6.38 mg/L during pre-monsoon season and 0.03 to 2.28 mg/L during post-monsoon season. Almost, all the samples of the study area fall within the acceptable limit of 1.0 mg/L during pre- as well as post-monsoon season. The variation of fluoride in groundwater of study area for pre- and post-monsoon seasons is shown in Fig. 12. The fluoride distribution map for the pre- and post-monsoon season is shown in Fig. 22.

From the above discussion, it is revealed that in the Godavari basin, the concentration of total dissolved solids exceeds the acceptable limit of 500 mg/L in about 63% samples but falls within permissible limit during both seasons (pre- and post-monsoon season). The alkalinity values also exceed the permissible limit in more than 12% and 14% of the samples in pre- and post-monsoon seasons respectively. From the hardness point of view, about 68% and 75% of all samples of the study area crosses the acceptable limit of 200 mg/L but is well within the permissible limit of 600 mg/L during pre- and post-monsoon seasons respectively. The chloride contents are exceeded for the acceptable limits in 25% and 28% samples over the pre- and post-monsoons respectively. Only 1% and 3% samples exceed the acceptable limit of sulphate but within permissible limit and 1% samples even exceed the permissible limit during pre- and post-monsoon seasons respectively. The nitrate content in about 82% samples is well within the permissible limit during both the seasons. The concentration of fluoride is well within the desirable limit in almost all of the samples in pre-monsoon season. The violation of BIS limit could not be ascertained for sodium and potassium as no permissible limit for these constituents has been prescribed in BIS drinking water specifications.

Krishna Delta

The pH values in the ground water of the study area mostly fall within the range 6.97 to 8.4 during pre-monsoon season and 6.50 to 8.52 during post-monsoon season. The pH values for most of the samples are well within the limits prescribed by BIS (2012) and WHO (1996) for various uses of water including drinking and other domestic supplies.

The electrical conductivity and dissolved salt concentrations are directly related to the concentration of ionized substance in water and may also be related to problems of excessive hardness and/or other mineral contamination. The conductivity values in the ground water samples of the study area vary widely from 770 to 9170 μS/cm during pre-monsoon season and 560 to 66000 μS/cm during post-monsoon season.

In the study area, the values of total dissolved solids (TDS) in the ground water varies from 462 to 5705 mg/L during pre-monsoon season and 308 to 38886 mg/L during post-monsoon season. About 70% and 72% samples were found above the acceptable limit but within the maximum permissible limit of 2000 mg/L during the pre- and post-monsoon seasons respectively (Table 4). The variation of TDS in groundwater of study area for pre- and post-monsoon seasons is shown in Fig. 10. The TDS distribution maps for the pre-monsoon and post-monsoon seasons are shown in Fig. 13. Water containing more than 500 mg/L of TDS is not considered desirable for drinking water supplies, though more highly mineralized water is also used where better water is not available. For this reason, 500 mg/L as the acceptable limit and 2000 mg/L as the maximum permissible limit has been suggested for drinking water (BIS, 2012). In the study area, Water containing TDS more than 500 mg/L causes gastrointestinal irritation (BIS, 2012).

Alkalinity in natural water is mainly due to presence of carbonates, bicarbonates and hydroxides. The alkalinity value in the groundwater of the study area varies from 165 to 900 mg/L during pre-monsoon season and 100 to 760 mg/L during post-monsoon season. Total 13% of the sample exceeds the maximum permissible limit of 600 mg/L during pre-monsoon season and during post-monsoon season. The variation of alkalinity in groundwater of study area for pre- and post-monsoon seasons is shown in Fig. 10. The alkalinity distribution maps for the pre-monsoon and post-monsoon seasons are shown in Fig. 14.

The presence of calcium and magnesium along with their carbonates, sulphates and chlorides are the main cause of hardness in the water. A limit of 200 mg/L as acceptable limit and 600 mg/L as permissible limit has been recommended for drinking water (BIS, 2012). The total hardness values in the study area range from 92 to 2217 mg/L during pre-monsoon season and 107 to 9289 mg/L during post-monsoon season. About 63% and 67% of all samples of the study area crosses the acceptable limit of 200 mg/L but are well within the permissible limit of 600 mg/L during pre- and post-monsoon season respectively, and 21% and 19% sample crosses the permissible limit of 600 mg/L during pre- and post-monsoon seasons respectively. The variation of hardness in groundwater of study area for pre- and post-monsoon seasons is shown in Fig. 10. The hardness distribution map for the pre- and post-monsoon season is shown in Fig. 15.

In ground water of the study area, the values of calcium range from 13 to 367 mg/L during pre-monsoon season and 15 to 739 mg/L during post-monsoon season. The values of magnesium vary from 8 to 382 mg/L during pre-monsoon season and 12 to 1809 mg/L during post-monsoon season. The acceptable limit for calcium and magnesium for drinking water are 75 and 30 mg/L respectively (BIS, 2012). In ground water, the calcium content generally exceeds the magnesium content in accordance with their relative abundance in rocks. Further, 6% sample exceeds the maximum permissible limit of calcium as 200 mg/L and 17% sample exceeds the maximum permissible limit of magnesium as 100 mg/L in pre-monsoon season. About 8% of sample exceeds the maximum permissible limit of calcium as 200 mg/L and 14% sample exceeds the maximum permissible limit of magnesium as 100 mg/L in post-monsoon season. The variation of calcium and magnesium in groundwater of study area for pre- and post-monsoon seasons is shown in Fig. 11. The calcium and magnesium distribution maps for the pre- and post monsoon seasons are shown in Fig. 16 & 17 respectively.

The concentration of sodium in the study area varies from 58 to 1228 mg/L during pre-monsoon season and 36 to 10469 mg/L during post-monsoon season. The high sodium values in the study area may be attributed to base-exchange phenomena causing sodium hazards. The sodium distribution map for the pre- and post-monsoon season is shown in Fig. 18. Ground water with high value of sodium is not suitable for irrigation purpose. The concentration of potassium in ground water of the study area varies from 2.63 to 268 mg/L during pre-monsoon season and 2.97 to 197 mg/L during post-monsoon season.

The concentration of chloride varies from 77 to 2903 mg/L during pre-monsoon season and 33 to 22000 mg/L during post-monsoon season. Total 50% and 56% samples of the study area fall within the acceptable limit of 250 mg/L during pre- and post-monsoon seasons respectively. The variation of chloride in groundwater of study area for pre- and post-monsoon seasons is shown in Fig. 11. The chloride distribution map for the pre- and post-monsoon season is shown in Fig. 19. The sulphate content in ground water generally occurs as soluble salts of calcium, magnesium and sodium. The concentration of sulphate in the study area varies from 3.34 to 1318 mg/L during pre-monsoon season and 2.85 to 3284 mg/L during post-monsoon season. Bureau of Indian standard has prescribed 200 mg/L as the acceptable limit and 400 mg/L as the permissible limit for sulphate in drinking water. In the study area, 78% of the samples analyzed fall within the acceptable limit of 200 mg/L while 13% of the samples exceed the acceptable limit but are within the permissible limit of 400 mg/L and 9% of the samples exceed the maximum permissible limit of 400 mg/L during pre-monsoon season. In the study area, 76% of the samples analyzed fall within the acceptable limit of 200 mg/L while 16% of the samples exceed the acceptable limit but are within the permissible limit of 400 mg/L and 8% of the samples exceed the maximum permissible limit of 400 mg/L during post-monsoon season. The variation of sulphate in groundwater of study area for pre- and post-monsoon seasons is shown in Fig. 12. The sulphate distribution map for the pre- and post-monsoon season is shown in Fig. 20.

The nitrate content in the study area varies from 2 to 575 mg/L during pre-monsoon season and 0 to 856 mg/L during post-monsoon season. About 70% and 61% of all samples of the study area fall within the permissible limit of 45 mg/L while, 30% and 39% of samples even cross the permissible limit during pre- and post-monsoon seasons respectively. In higher concentrations, nitrate may produce a disease known as methaemoglobinaemia (blue babies) which generally affects bottle-fed infants. The variation of nitrate in groundwater of study area for pre- and post-monsoon seasons is shown in Fig. 12. The nitrate distribution map for the pre- and post-monsoon season is shown in Fig. 21.

The fluoride content in the ground water of the study area varies from 0.01 to 1.02 mg/L during pre-monsoon season and 0.04 to 1.72 mg/L during post-monsoon season. Almost, all the samples of the study area fall within the acceptable limit of 1.0 mg/L during pre as well as post-monsoon seasons. The variation of fluoride in groundwater of study area for pre- and post-monsoon seasons is shown in Fig. 12. The fluoride distribution map for the pre- and post-monsoon season is shown in Fig. 22.

From the above discussion, it is revealed that in the Krishna basin, the concentration of total dissolved solids exceeds the acceptable limit of 500 mg/L in about 70% and 72% samples but falls within permissible limit during pre- and post-monsoon seasons respectively. The alkalinity values also exceed the permissible limit in more than 13% of the samples in both pre- and post-monsoon seasons. From the hardness point of view, about 63% and 67% of all samples of the study area crosses the acceptable limit of 200 mg/L but is well within the permissible limit of 600 mg/L during pre- and post-monsoon seasons respectively. The chloride contents are exceeded for the acceptable limits in 41% and 31% samples over the pre- and post-monsoon seasons respectively. About 13% and 16% samples exceed the acceptable limit of sulphate but within permissible limit, and 9% and 8% samples even exceed the permissible limit during pre- and post-monsoon seasons respectively. The nitrate content in about 70% and 61% samples are well within the permissible limit during pre- and post-monsoon seasons respectively. The concentration of fluoride is well within the desirable limit in almost all of the samples in pre- and post-monsoon season. The violation of BIS limit could not be ascertained for sodium and potassium as no permissible limit for these constituents has been prescribed in BIS drinking water specifications.

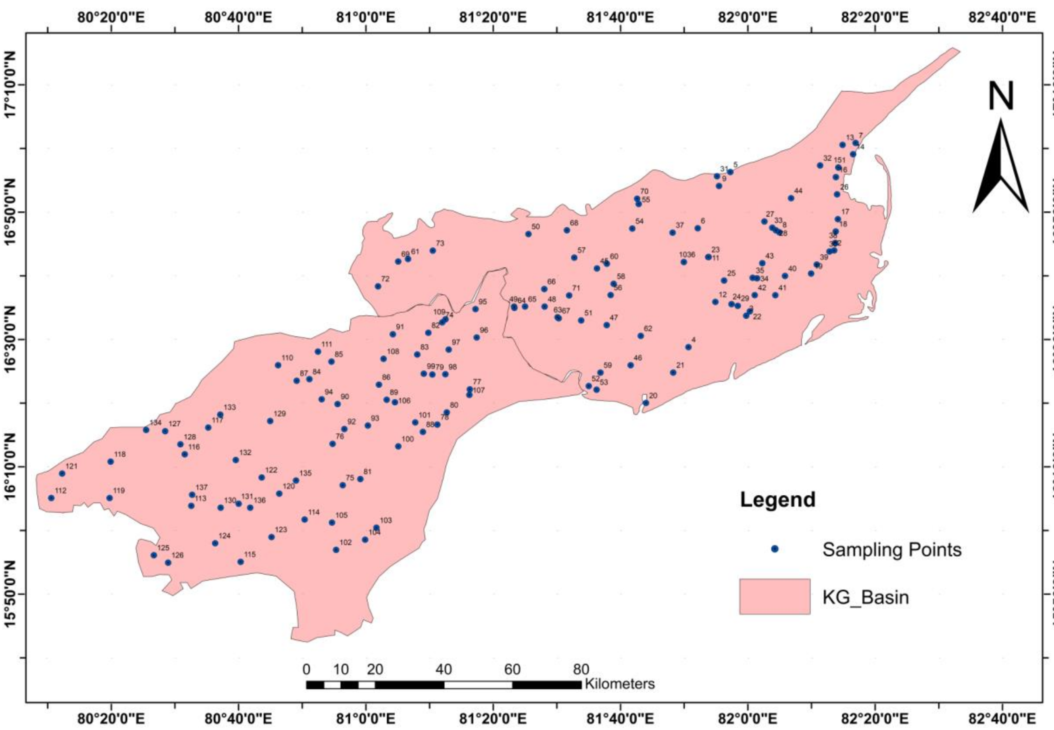


Fig. 8. Map showing Sampling Location in Krishna Godawari delta

Table 1. Details of Sampling in Krishna Godawari delta

S. No.	**District**	**Source**	**Depth range (m)**	**No. of Samples collected**	**Basin**
1	East Godavari	DW & Pz	2.23-22.5	44	Godavari Delta
2	West Godavari	DW & Pz	2.85-28.6	29	
3	Krishna	DW & Pz	2.45-300	38	Krishna Delta
4	Guntur	DW & Pz	3.9-14.4	26	

Table 2. Details of sampling locations in the study area

S. No.	District	Block Name	Site Name	Site Id	Latitude	Longitude	MP (agl)	Well Type	Well Depth
1	East Godavari	Kakinada (Fully Urban)	Kakinada-Ii	C/EG/025	16.95	82.2375	0.7	DW	2.96
2	East Godavari	I.Polavaram	Yanam	C/EG/033	16.7333	82.2261	0.8	DW	6.7
3	East Godavari	Amalapuram	Amalapuram	C/EG/035A	16.5622	81.9957	0.9	DW	5.6
4	East Godavari	Razole	Razole	C/EG/036A	16.4801	81.8446	0.8	DW	5
5	East Godavari	Anaparthy	Anaparthy	C/EG/048	16.9384	81.9542	0.7	DW	10.71
6	East Godavari	Alamuru	Jonnada	C/EG/051	16.7913	81.8689	0.8	DW	2.23
7	East Godavari	Kakinada (Rural)	Vakalpudi	C/EG/052	17.0147	82.2823	1.2	DW	3.28
8	East Godavari	Ramachandrapuram2	Vegayammapeta	C/EG/053	16.7806	82.0827	1.3	DW	4.23
9	East Godavari	Mandapeta	Eppanapadu	C/EG/054A	16.9018	81.9247	0.8	DW	4.8
10	East Godavari	Ravulapalem	Mummidivarampad	C/EG/059	16.7029	81.8325	0.8	DW	6.35
11	East Godavari	Kothapeta	Kothapeta -3	C/EG/075	16.7159	81.8975	0.6	Pz	22.5
12	East Godavari	P.Gannavaram	Munganda Pz	C/EG/079	16.5984	81.9151	0.6	Pz	16
13	East Godavari	Kakinada (Rural)		C/EG/081	17.0095	82.2482	1.1	DW	4.8
14	East Godavari	Kakinada (Rural)	Fishing Horbour	C/EG/083	16.9851	82.2758	0.6	DW	2.9
15	East Godavari	Kakinada (Fully Urban)	Santhacheruvu	C/EG/084	16.9504	82.2371	0.8	DW	4.2
16	East Godavari	Kakinada (Rural)	Kasinadhapuram	C/EG/085	16.925	82.2306	0.8	DW	2.6
17	East Godavari	Thallarevu	Korangi	C/EG/088	16.8151	82.2359	0.8	DW	3
18	East Godavari	Thallarevu	Tallarevu	C/EG/093	16.7829	82.2303	0.8	DW	4.1
19	East Godavari	I. Polavaram	Muramalla	C/EG/094	16.6726	82.1657	0.4	DW	3.9
20	East Godavari	Sakhinetipalle	Antarvedi	C/EG/095	16.3339	81.7334	0.8	DW	3.65
21	East Godavari	Malikipuram	Malikipuram	C/EG/096	16.4135	81.8047	1	DW	4.35
22	East Godavari	Amalapuram	Amalapuram PZ	C/EG/097	16.5738	82.0054	0.6	Pz	20
23	East Godavari	Kothapeta	Kothapeta	C/EG/099	16.7159	81.8965	0.8	DW	8.7
24	East Godavari	Ambajipeta	Ambajipeta	C/EG/101	16.5927	81.9575	0.6	DW	5.7
25	East Godavari	Ambajipeta	Chinalanka	C/EG/102	16.6543	81.938	0.8	DW	7.1
26	East Godavari	Thallarevu	Chollangi	C/EG/104	16.88	82.2338	0.9	DW	6.9
27	East Godavari	Ramachandrapuram2	Tallapolom	C/EG/105	16.809	82.0435	0.7	DW	4.9
28	East Godavari	Ramachandrapuram2	Annaipeta	C/EG/106	16.7858	82.0737	1.2	DW	5.1
29	East Godavari	Amalapuram	Bandurlanka	C/EG/113	16.5882	81.9737	0.9	DW	6.7
30	East Godavari	Pattipuram	Pattipuram	C/EG/114	16.7303	82.2139	0.8	DW	4.1
31	East Godavari	Mandapeta	Dwarapudi	C/EG/115	16.9273	81.9195	0.8	DW	5.8
32	East Godavari	Kakinada (Rural)	Repuru	C/EG/123	16.9556	82.1894	0.8	DW	3.9
33	East Godavari	Ramachandrapuram2	Draksharamam	C/EG/124	16.7926	82.0641	0.9	DW	6.15
34	East Godavari	Ainavilli	Mukteshwaram	C/EG/126	16.6602	82.0244	1	DW	9
35	East Godavari	Ainavilli	Ainavalli	C/EG/127	16.6615	82.0127	0.8	DW	6.9
36	East Godavari	Ravulapalem	Appanapalle	C/EG/128	16.7029	81.8326	0.8	DW	7.97
37	East Godavari	Atreyapuram	Rally	C/EG/129	16.7798	81.8031	0.9	DW	8
38	East Godavari	Thallarevu	Thurpet	C/EG/130	16.7529	82.2289	0.8	DW	3.4
39	East Godavari	I. Polavaram	Komaragiri	C/EG/131	16.6962	82.1805	0.7	DW	5.35
40	East Godavari	Mummidivaram	Thanelankamulli	C/EG/132	16.6664	82.0975	0.8	DW	4.55
41	East Godavari	Mummidivaram	Mobalacherevu	C/EG/133	16.616	82.0722	0.8	DW	4.29
42	East Godavari	Ainavilli	Vilasa	C/EG/134	16.6162	82.0182	0.8	DW	4.15
43	East Godavari	Rajahmundry (Rural)	Kotipalle	C/EG/125	16.6997	82.0381	0.85	DW	6.85
44	East Godavari	Sankhavaram	Velangi	C/EG/136	16.87	82.1134	0.9	DW	7.6
45	West Godavari	Attili	Attili	C/WG/025B	16.6861	81.6051	0.9	DW	3.42
46	West Godavari	Narasapuram	Narsapuram	C/WG/027	16.4327	81.6933	0.9	DW	3.28
47	West Godavari	Veeravasaram	Veeravasaram	C/WG/032	16.5377	81.6306	0.8	DW	4.58
48	West Godavari	Undi	Undi	C/WG/033	16.5861	81.4681	0.9	DW	3.7
49	West Godavari	Akividu	Akiveedu - PZ	C/WG/052	16.5862	81.3882	0.6	Pz	28.6
50	West Godavari	Ungutur	Rachuru	C/WG/056	16.7761	81.4257	0.7	DW	5.75
51	West Godavari	Palacoderu	Vissakoduru	C/WG/057	16.55	81.5639	0.8	DW	3.9
52	West Godavari	Mogalthur	Perupalem	C/WG/058	16.3781	81.5837	0.1	DW	3
53	West Godavari	Mogalthur	Kummarapurugu	C/WG/059	16.3687	81.6042	0.7	DW	4
54	West Godavari	Undrajavaram	Undrajavaram	C/WG/060	16.7904	81.6977	0.9	DW	7.3
55	West Godavari	Nidadavole	Munipalli	C/WG/069	16.8548	81.7143	0.9	DW	15.75
56	West Godavari	Penumantra	Polamuru	C/WG/072	16.6163	81.6409	0.7	DW	4.55
57	West Godavari	Ganapavaram	Pipara	C/WG/075	16.7143	81.5457	0.9	DW	4.85
58	West Godavari	Penumantra	Penumantra	C/WG/076	16.6458	81.6488	0.9	DW	5.47
59	West Godavari	Mogalthur	Mogalturu	C/WG/077	16.4134	81.6142	0.9	DW	4.5
60	West Godavari	Iragavaram	Gowrabalu	C/WG/078	16.6983	81.6311	0.7	DW	4.6
61	West Godavari	Eluru	Eluru	C/WG/079	16.7109	81.1105	0.9	DW	4.3

62	West Godavari	Palacole	Palakolu	C/WG/082	16.5094	81.7198	1	DW	5.69
63	West Godavari	Bhimavaram	Narsimhapuram	C/WG/083	16.5583	81.5019	0.7	DW	4.23
64	West Godavari	Akividu	Akiveedu	C/WG/084	16.5828	81.389	0.7	DW	2.85
65	West Godavari	Undi	Cherukuwada	C/WG/085	16.5863	81.4167	0.8	DW	3.9
66	West Godavari	Undi	Kolamuru (Pamulaparu)	C/WG/086	16.6322	81.4672	0.7	DW	5.3
67	West Godavari	Bhimavaram	Sarepalle	C/WG/087	16.5557	81.5051	0.6	DW	3.3
68	West Godavari	Pentapadu	Pentapadu	C/WG/088	16.7859	81.5264	0.7	DW	4.5
69	West Godavari	Eluru	Eluru (Postal Colony)	C/WG/089	16.7042	81.0847	0.9	DW	5.29
70	West Godavari	Nidadavole	Munipalli	C/WG/095	16.8686	81.7102	0.9	DW	6.7
71	West Godavari	Palakoderu	Garagaparru	C/WG/103	16.6153	81.5322	0.9	DW	6.45
72	West Godavari	Pedapadu	Pedapadu	New Well	16.6392	81.0319	0.5	DW	5.5
73	West Godavari	Denduluru	Kovvali	New Well	16.7326	81.1754	0.7	DW	5
74	Krishna	Mandavalli	Kaikaluru1	C/KR/008A	16.5449	81.2	0.75	DW	4.41
75	Krishna	Challapalle	Challapalli	C/KR/014	16.1186	80.9394	0.78	DW	5.34
76	Krishna	Movva	Movva	C/KR/017	16.2269	80.9129	0.49	DW	5.16
77	Krishna	Bantumilli	Bantumilli1	C/KR/019A	16.3697	81.2722	0.62	DW	3.87
78	Krishna	Pedana	Balliparru	C/KR/021	16.2774	81.1872	0.8	DW	4.39
79	Krishna	Mudinepalle	Upparigudem	C/KR/022	16.4083	81.1741	0.5	DW	4.7
80	Krishna	Bantumilli	Munjuluru	C/KR/023	16.3092	81.212	0.8	DW	5.33
81	Krishna	Ghantasala	Lankapalli	C/KR/050	16.1347	80.9856	0.37	DW	4
82	Krishna	Mandavalli	Mandavalli	C/KR/051	16.5177	81.1637	0.44	DW	3.89
83	Krishna	Mandavalli	Kanukollu	C/KR/052	16.4608	81.1346	0.62	DW	4.6
84	Krishna	Vuyyuru	Kadavakollu	C/KR/055	16.3963	80.8522	0.69	DW	4.7
85	Krishna	Pedaparupudi	Venkatapragada	C/KR/056	16.442	80.9101	0.29	DW	6.53
86	Krishna	Gudlavalleru	Angaluru	C/KR/057	16.3819	81.0343	0.68	DW	4.73
87	Krishna	Vuyyuru	Anukuru	C/KR/058	16.3921	80.8189	0.53	DW	7.69
88	Krishna	Pedana	Pedana_New	C/KR/062	16.2583	81.1494	0.72	DW	5.32
89	Krishna	Gudlavalleru	Gudlavalleru-New	C/KR/064	16.3424	81.0545	0.5	DW	6.3
90	Krishna	Pamarru2	Kurumaddali	C/KR/065	16.3311	80.9261	0.44	DW	5.15
91	Krishna	Mudinepalle	Polukonda	C/KR/066	16.5138	81.0708	0.49	DW	5
92	Krishna	Movva	Ayyanki	C/KR/069	16.2657	80.9438	0.6	DW	5.25
93	Krishna	Pamarru2	Nimmakuru (Ntr Village)	C/KR/071	16.2747	81.0052	0.5	DW	5.45
94	Krishna	Repalle	Tadanki	C/KR/075	16.3435	80.8843	0.73	DW	7.03
95	Krishna	Kaikalur	Palevada	C/KR/076	16.5795	81.287	0.85	DW	3.9
96	Krishna	Kalidindi	Kalidindi	C/KR/081	16.5053	81.2902	0.5	DW	3.38
97	Krishna	Mudinepalle	Bomminampadu	C/KR/082	16.4736	81.217	0.5	DW	4.5
98	Krishna	Bantumilli	Mallapparajgudem	C/KR/083	16.4091	81.2082	1	DW	4.19
99	Krishna	Singarayapalem	Singarayapalem	C/KR/084	16.4106	81.1517	1	DW	2.45
100	Krishna	Guduru	Gudur	C/KR/085	16.2202	81.0849	0.7	DW	4.5
101	Krishna	Pedana	Nadupur	C/KR/086	16.2829	81.1293	0.8	DW	4.44
102	Krishna	Nagayalanka	Marripalem(Nagayalanka)	C/KR/087	15.9494	80.9222	0.8	DW	6.88
103	Krishna	Koduru	Koduru	C/KR/088	16.0073	81.0276	0.5	DW	3.96
104	Krishna	Koduru	Mandapakala	C/KR/089	15.9761	80.9981	0.5	DW	5.47
105	Krishna	Avanigadda	Avanigadda	C/KR/090	16.0208	80.9114	0.3	DW	6.07
106	Krishna	Gudlavalleru	Kautaram	C/KR/092	16.3357	81.0761	0.8	DW	4.9
107	Krishna	Kruthivennu	Malleshwaram	C/KR/095	16.3551	81.2711	0.65	DW	4.1
108	Krishna	Gudivada	Moturu	C/KR/NQM-01	16.4494	81.0464	0.5	Pz	190
109	Krishna	Kaikalur	Kaikalur	C/KR/NQM-02	16.5529	81.2086	0.5	Pz	300
110	Krishna	Kankipadu	Kankipadu	C/KR/NQM-03	16.4328	80.7703	0.5	Pz	207
111	Krishna	Unguturu	Indupalli	C/KR/NQM-04	16.4683	80.8747	0.5	Pz	198
112	Guntur	Chilakaluripet	Chilkaluripet-1	C/GU/027A	16.0851	80.1765	0.6	DW	5.31
113	Guntur	Ponnur	Ponnur(Old)	C/GU/028A	16.0647	80.543	0.86	DW	6.92
114	Guntur	Repalle	Repalle	C/GU/029	16.0288	80.8397	0.53	DW	5.01
115	Guntur	Nizampatnam	Nijampatnam	C/GU/033	15.9181	80.6722	0.54	DW	4.2
116	Guntur	Chebrolu	Chebrolu	C/GU/038	16.1996	80.5258	0.9	DW	8
117	Guntur	Chebrolu	Sekuru	C/GU/041	16.2696	80.5874	1.3	DW	11.14
118	Guntur	Prathipadu2	Prattipadu	C/GU/042	16.1803	80.3318	0.7	DW	8.65
119	Guntur	Pedanandipadu	Varagami	C/GU/049	16.0851	80.3291	0.85	DW	4.58
120	Guntur	Bhattiprolu	Bhattiprollu	C/GU/071	16.0966	80.7733	0.6	DW	3.9
121	Guntur	Edlapadu	Timmapuram	C/GU/081	16.1491	80.2048	0.84	DW	11
122	Guntur	Vemuru	Chavali	C/GU/082	16.1389	80.7274	0.1	DW	10
123	Guntur	Nizampatnam	Pallapatla	C/GU/083	15.9829	80.7531	0.57	DW	4
124	Guntur	Pittalavanipalem	Mannevaripalem	C/GU/084	15.9667	80.6054	0.72	DW	10.5
125	Guntur	Bapatla	Cheruvu Jammulapalem	C/GU/097	15.9354	80.445	0.72	DW	4.6
126	Guntur	Bapatla	Bapatla	C/GU/098	15.9159	80.4824	0.82	DW	5.4
127	Guntur	Guntur	Budampadu	C/GU/099	16.26	80.4746	0.7	DW	8.2
128	Guntur	Chebrolu	Narakoduru	C/GU/103	16.2257	80.5145	0.64	DW	12.1
129	Guntur	Kollipara	Kollipara	C/GU/104	16.2866	80.7496	0.78	DW	9.27
130	Guntur	Amruthalur	Inturu	C/GU/105	16.0597	80.6199	0.47	DW	5.45
131	Guntur	Amruthalur	Govada	C/GU/106	16.0701	80.667	0.33	DW	4.52
132	Guntur	Amruthalur	Kuchipudi	C/GU/107	16.1847	80.6595	0.72	DW	8.4

133	Guntur	Tenali	Kolakaluru	C/GU/108	16.3034	80.6189	0.67	DW	10.4
134	Guntur	Guntur	Etukunu	C/GU/124	16.2632	80.4247	0.77	DW	14.4
135	Guntur	Kollur	Kolluru	C/GU/127	16.1308	80.8171	0.52	DW	7.95
136	Guntur	Cherukupalle	Punnapalle	C/GU/128	16.0598	80.6972	0.47	DW	5.28
137	Guntur	Ponnur	Kattempudi	C/GU/134	16.0936	80.5453	1.04	DW	5.8

Table 3. Hydro-chemical data of groundwater samples collected from Godavari delta during pre- and post-monsoon seasons (2022)

S. No.	Parameters	Minimum	Maximum	Average	Permissible limit
1.	pH	6.68(6.87)	8.29(8.7)	7.67(7.55)	6.5-8.5
2.	EC (µS/cm)	110(360)	10000(6350)	1772(1816)	-
3.	TDS (mg/L)	52(188)	5617(40114123)	1029(1087)	2000
4.	Alkalinity (mg/L)	30(115)	880(1257)	367(421)	600
5.	Hardness (mg/L)	20(102)	1600(1031)	362(377)	600
6.	Na (mg/L)	9.0(9.0)	1526(1449)	201(221)	-
7.	K (mg/L)	0.8(1.0)	331(494)	41(44)	-
8.	Ca (mg/L)	6(18)	229(187)	70(79)	200
9.	Mg (mg/L)	1.3(5.3)	280(138)	45(44)	100
10.	HCO_3 (mg/L)	37(140)	1074(1534)	447(510)	-
11.	Cl (mg/L)	6.0(6.0)	3002(2222)	307(296)	1000
12.	SO_4 (mg/L)	0.2(5.0)	256(625)	56(80)	400
13.	NO_3 (mg/L)	0.1(0.3)	234(140)	25(24)	45
14.	F (mg/L)	0.0(0.03)	6.38(2.28)	0.31(0.29)	1.5

***Values given in parenthesis represent post-monsoon values of different parameters.**

Table 4. Hydro-chemical data of groundwater samples collected from Krishna delta during pre- and post-monsoon seasons (2022)

S. No.	Parameters	Minimum	Maximum	Average	Permissible limit
1.	pH	6.97(6.50)	8.4(8.52)	7.78(7.52)	6.5-8.5
2.	EC (µS/cm)	770(560)	9170(66000)	2756(3595)	-
3.	TDS (mg/L)	462(308)	5705(38886)	1631(2162)	2000
4.	Alkalinity (mg/L)	165(100)	900(760)	447(393)	600
5.	Hardness (mg/L)	92(107)	2217(9289)	535(603)	600
6.	Na (mg/L)	58(36)	1228(10469)	327(506)	-
7.	K (mg/L)	2.63(2.97)	268(197)	63(43)	-
8.	Ca (mg/L)	13(15)	367(739)	96(94)	200
9.	Mg (mg/L)	8(12)	382(1809)	72(90)	100
10.	HCO_3 (mg/L)	201(122)	1098(928)	544(479)	-
11.	Cl (mg/L)	77(33)	2903(22000)	510(827)	1000
12.	SO_4 (mg/L)	3.34(2.85)	1318(3284)	184(225)	400
13.	NO_3 (mg/L)	2.0(0)	575(856)	47(84)	45
14.	F (mg/L)	0.01(0.04)	1.02(1.72)	0.35(0.36)	1.5

***Values given in parenthesis represent post-monsoon values of different parameters.**

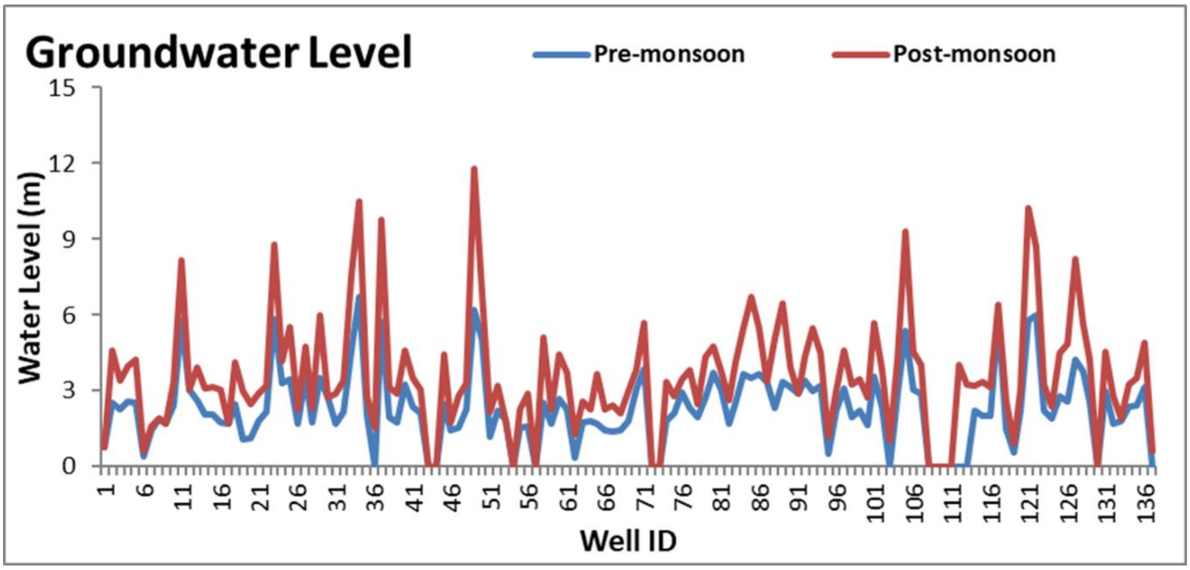


Fig. 9. Map showing groundwater level (msl) in the study area (Pre- & Post-monsoon 2022)

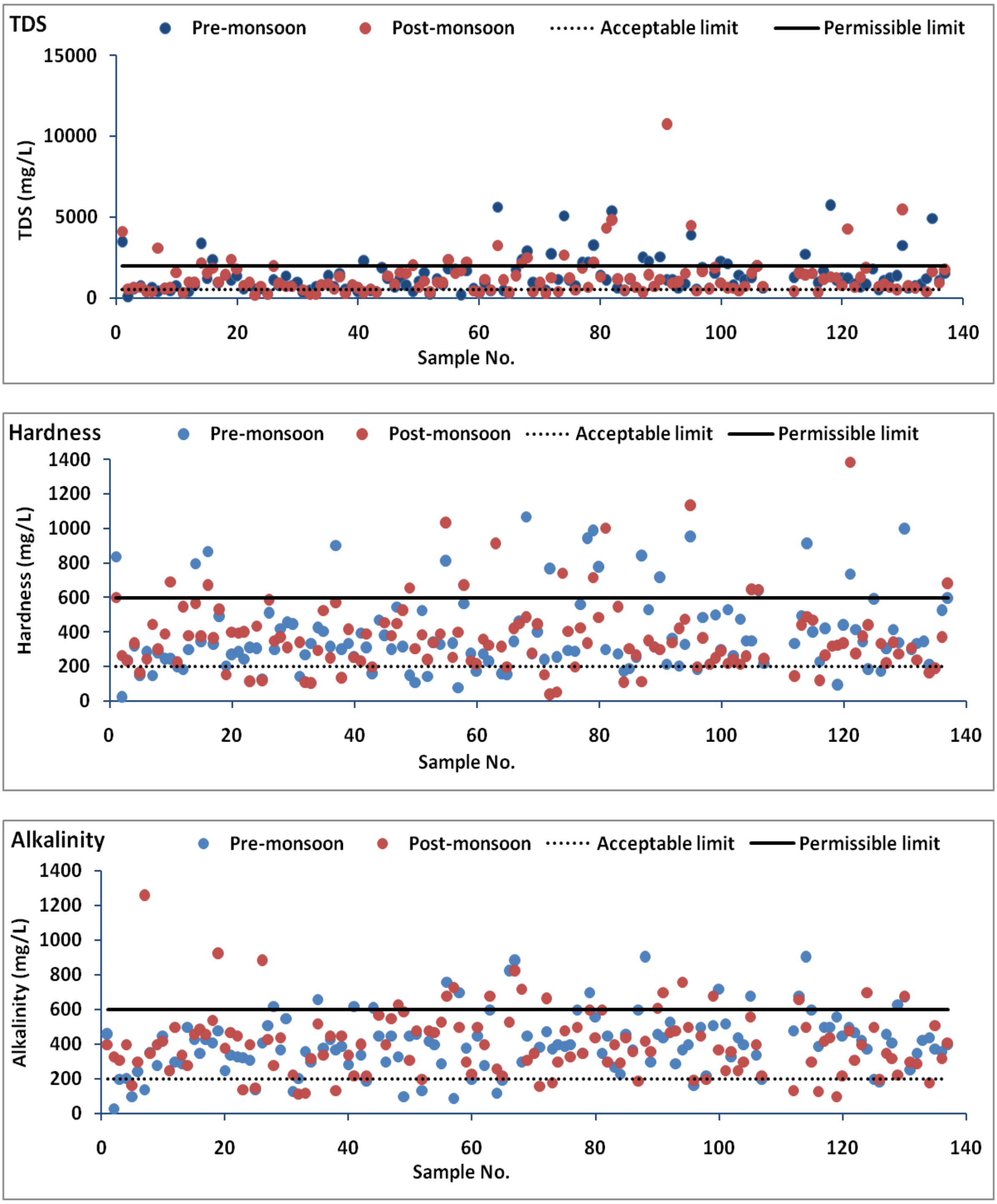


Fig. 10. Variation of TDS, Alkalinity and Hardness in groundwater of the study area

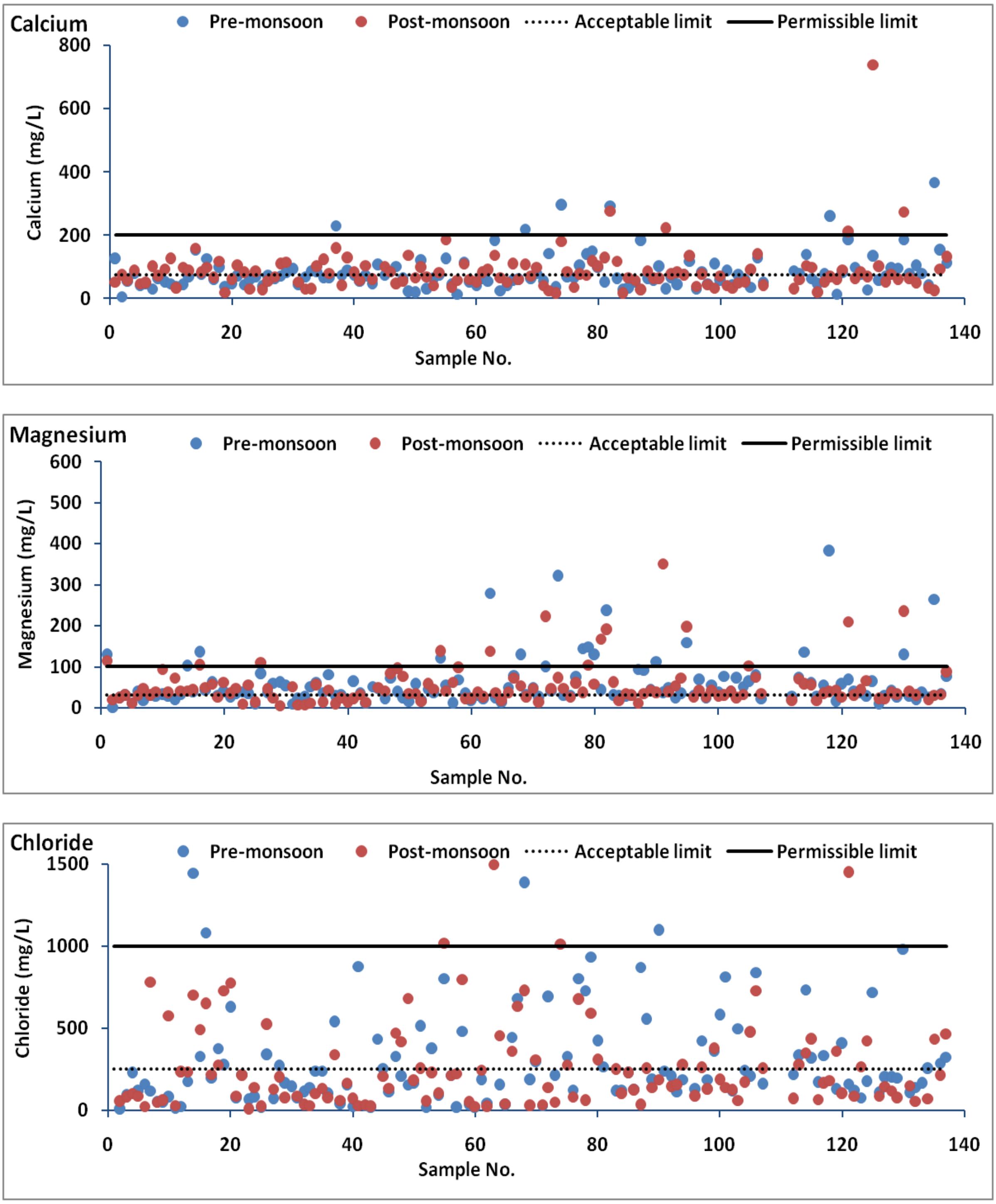


Fig. 11. Variation of Calcium, Magnesium and Chloride in groundwater of the study area

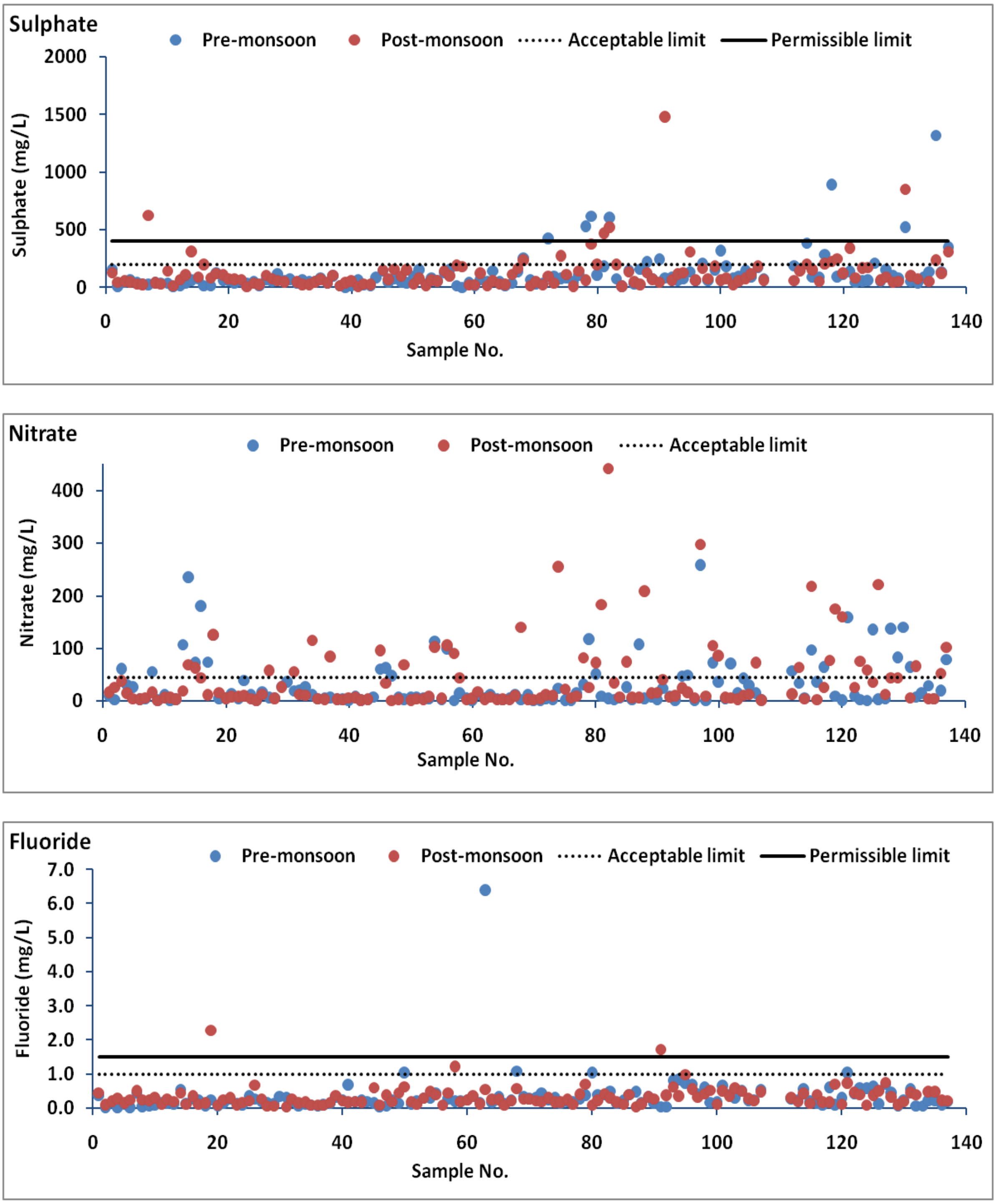


Fig. 12. Variation of Sulphate, Nitrate and Fluoride in groundwater of the study area

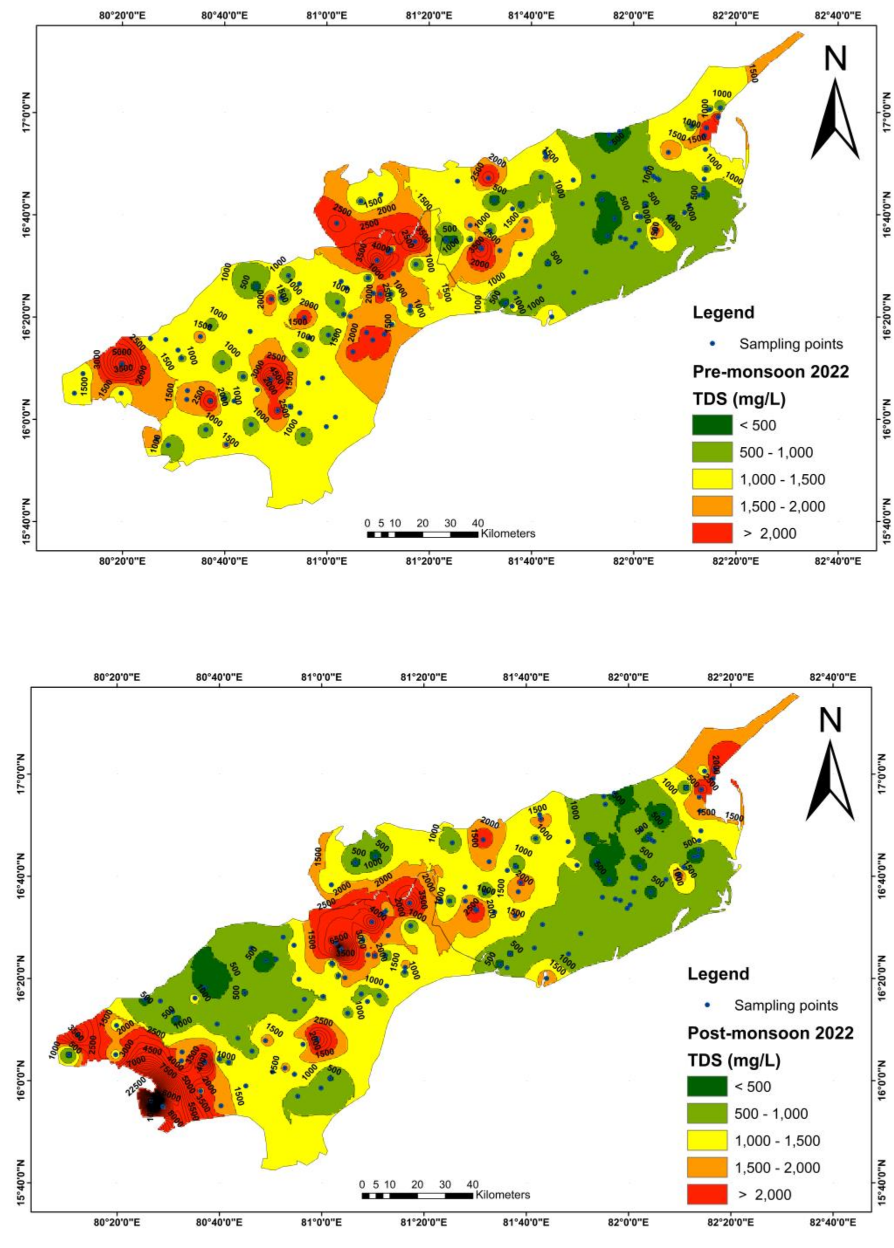


Fig. 13. Spatial distribution of TDS in groundwater of the study area

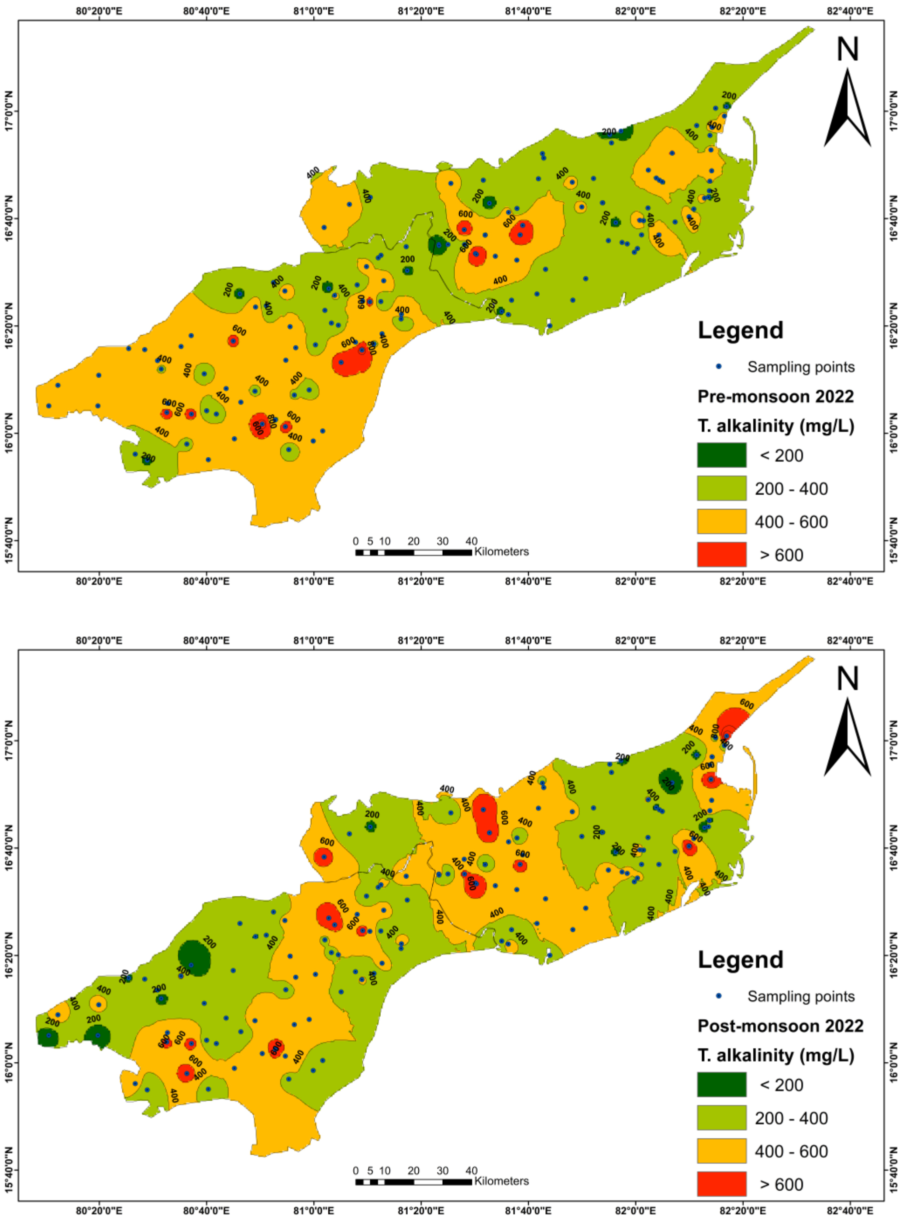


Fig. 14. Spatial distribution of Total Alkalinity in groundwater of the study area

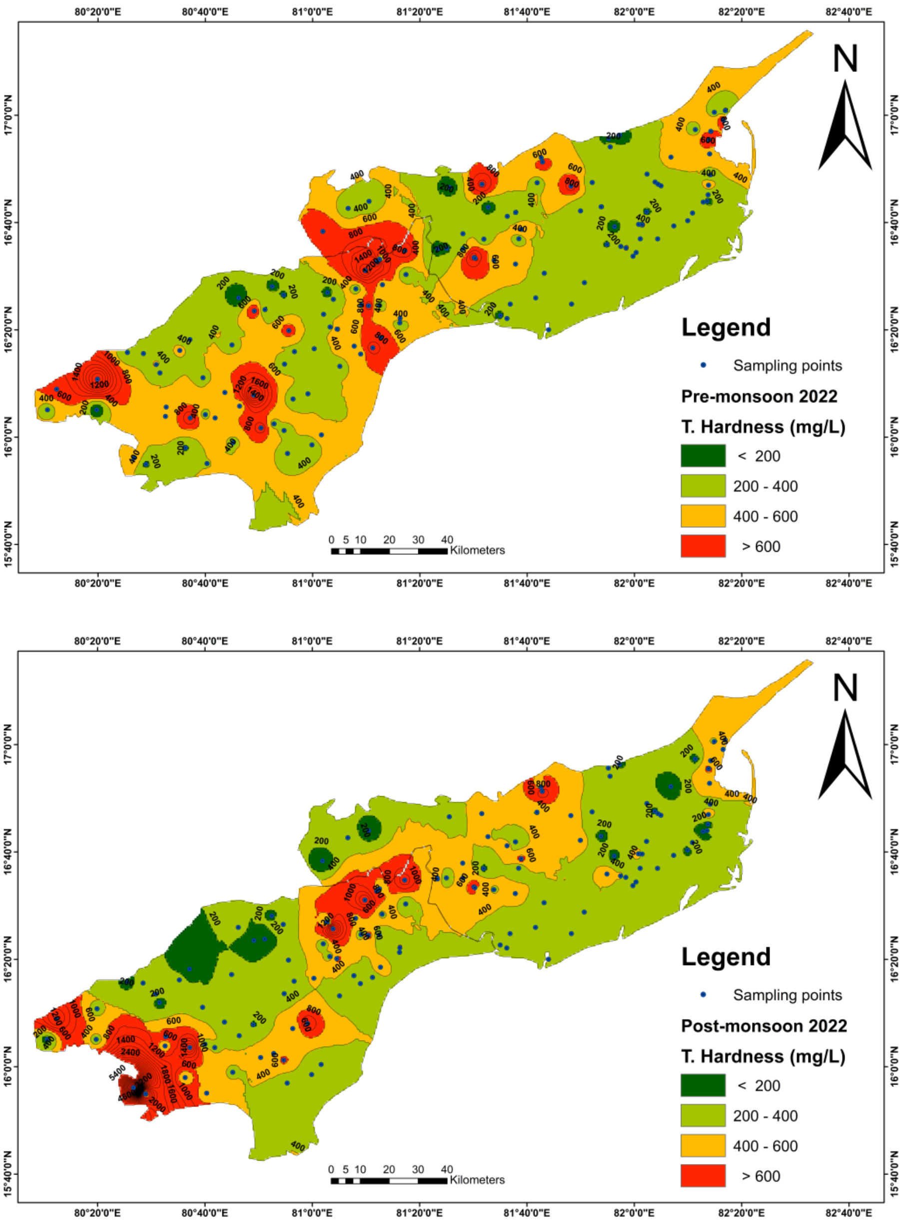


Fig. 15. Spatial distribution of Hardness in groundwater of the study area

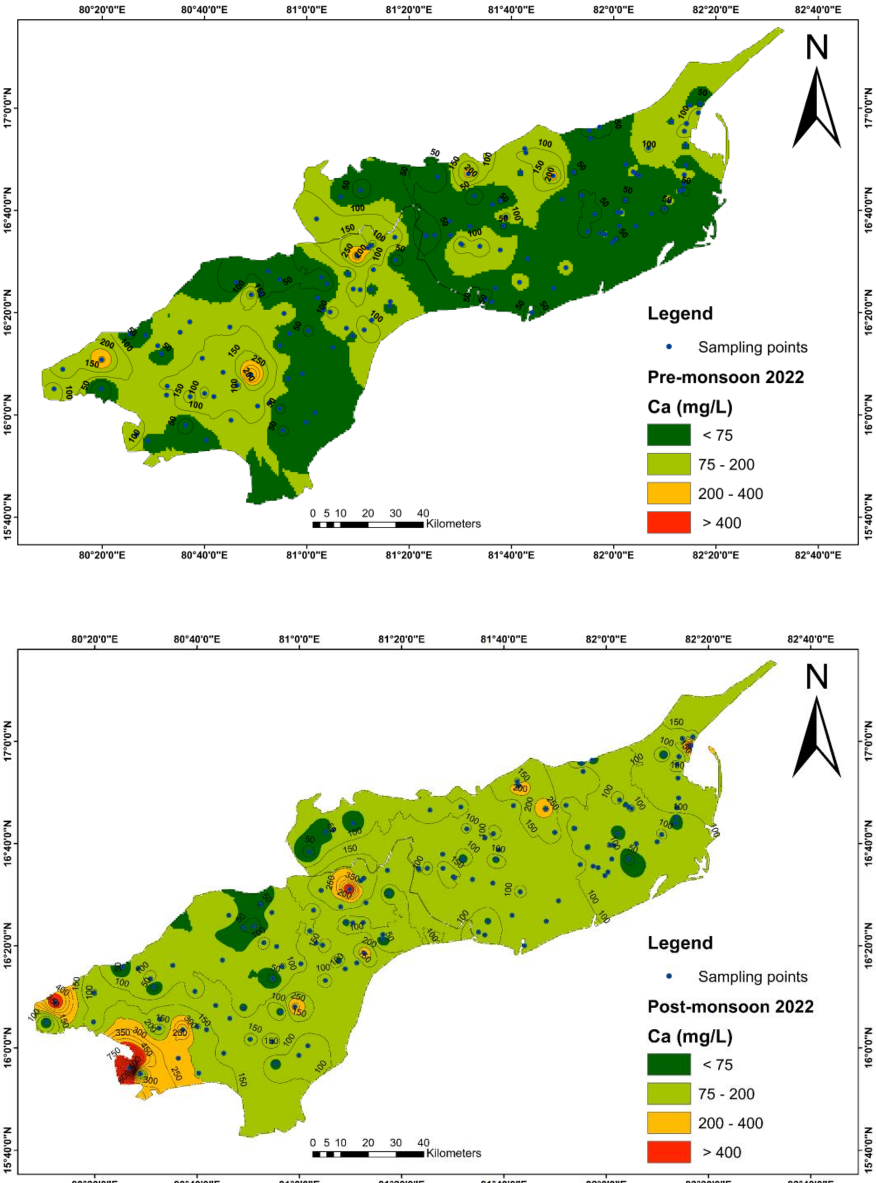
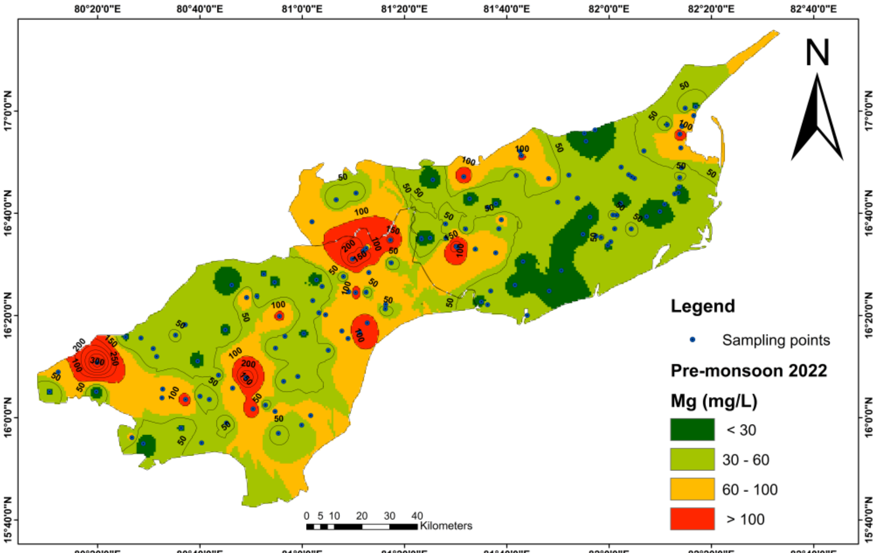


Fig. 16. Spatial distribution of Calcium in groundwater of the study area



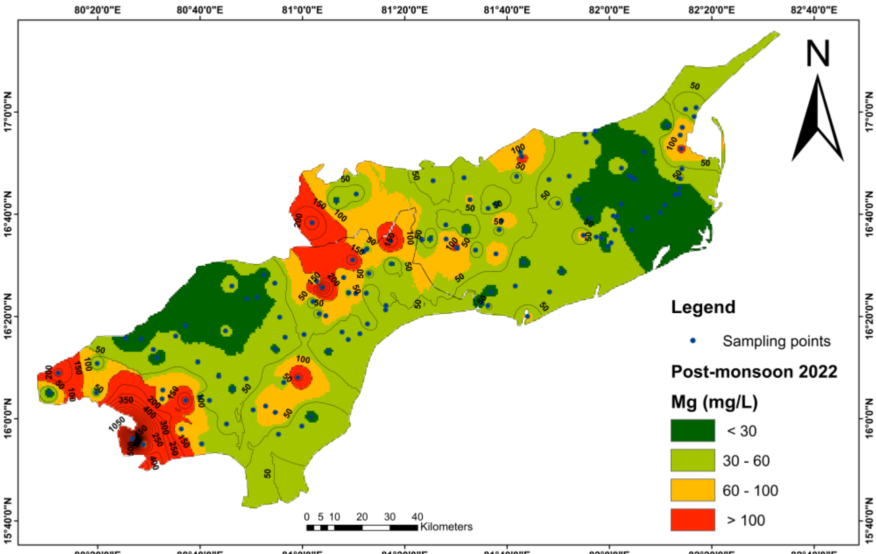


Fig. 17. Spatial distribution of Magnesium in groundwater of the study area

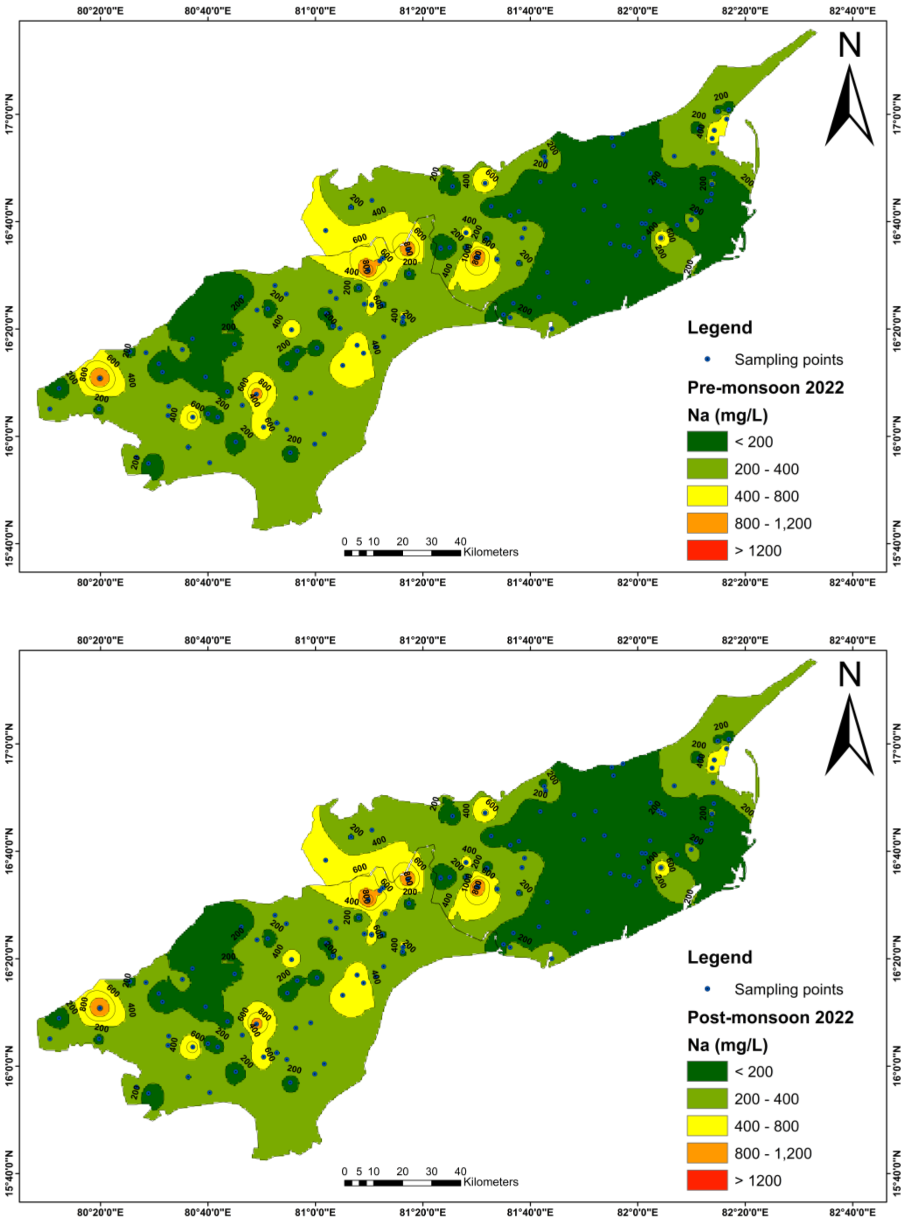


Fig. 18. Spatial distribution of Sodium in groundwater of the study area

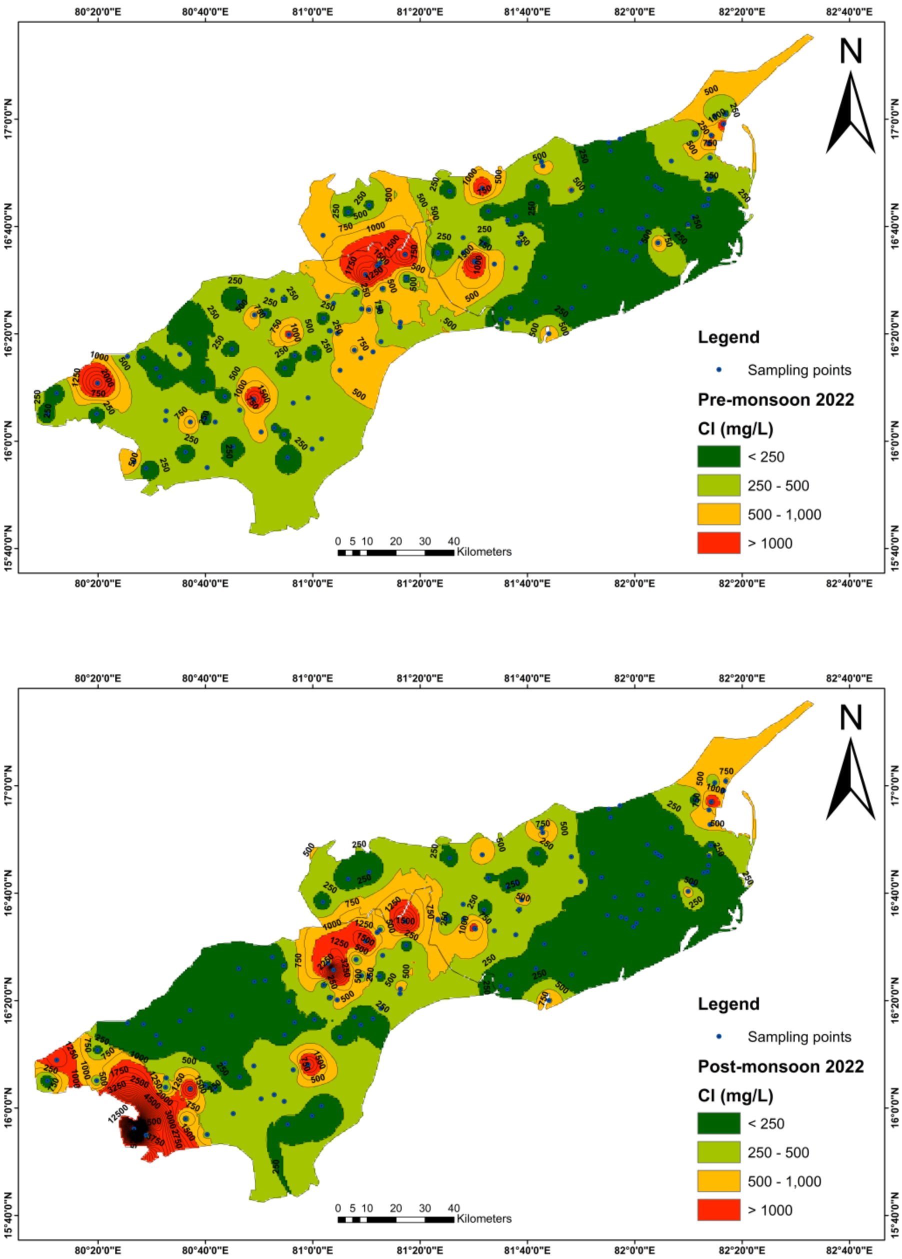
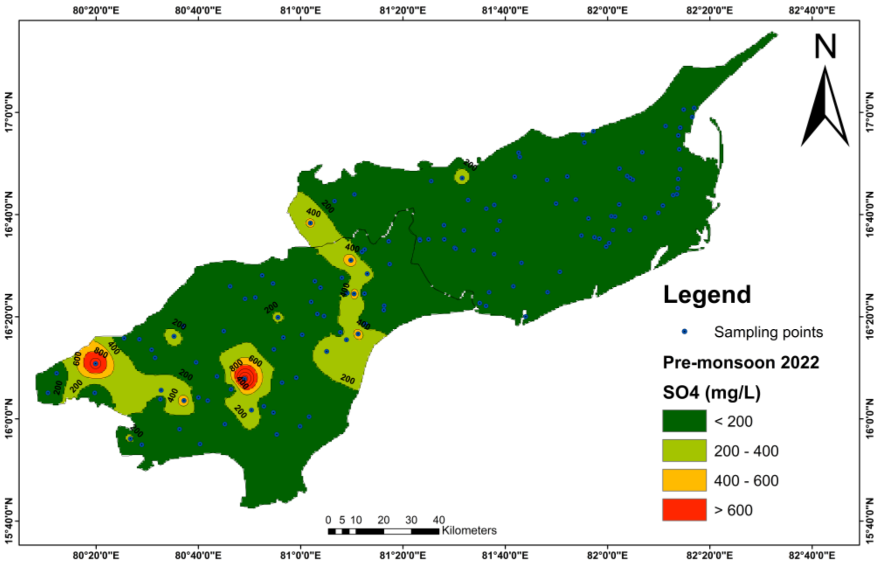


Fig. 19. Spatial distribution of Chloride in groundwater of the study area



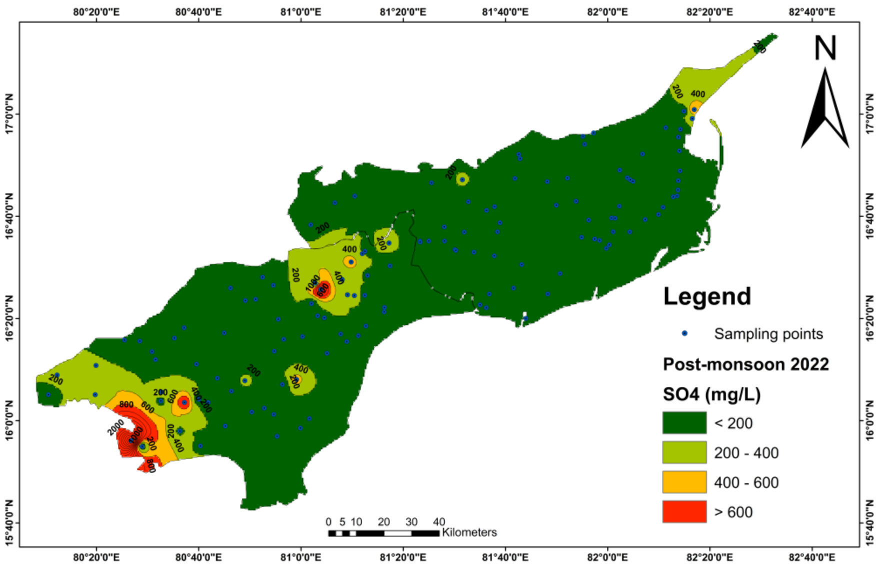


Fig. 20. Spatial distribution of Sulphate in groundwater of the study area

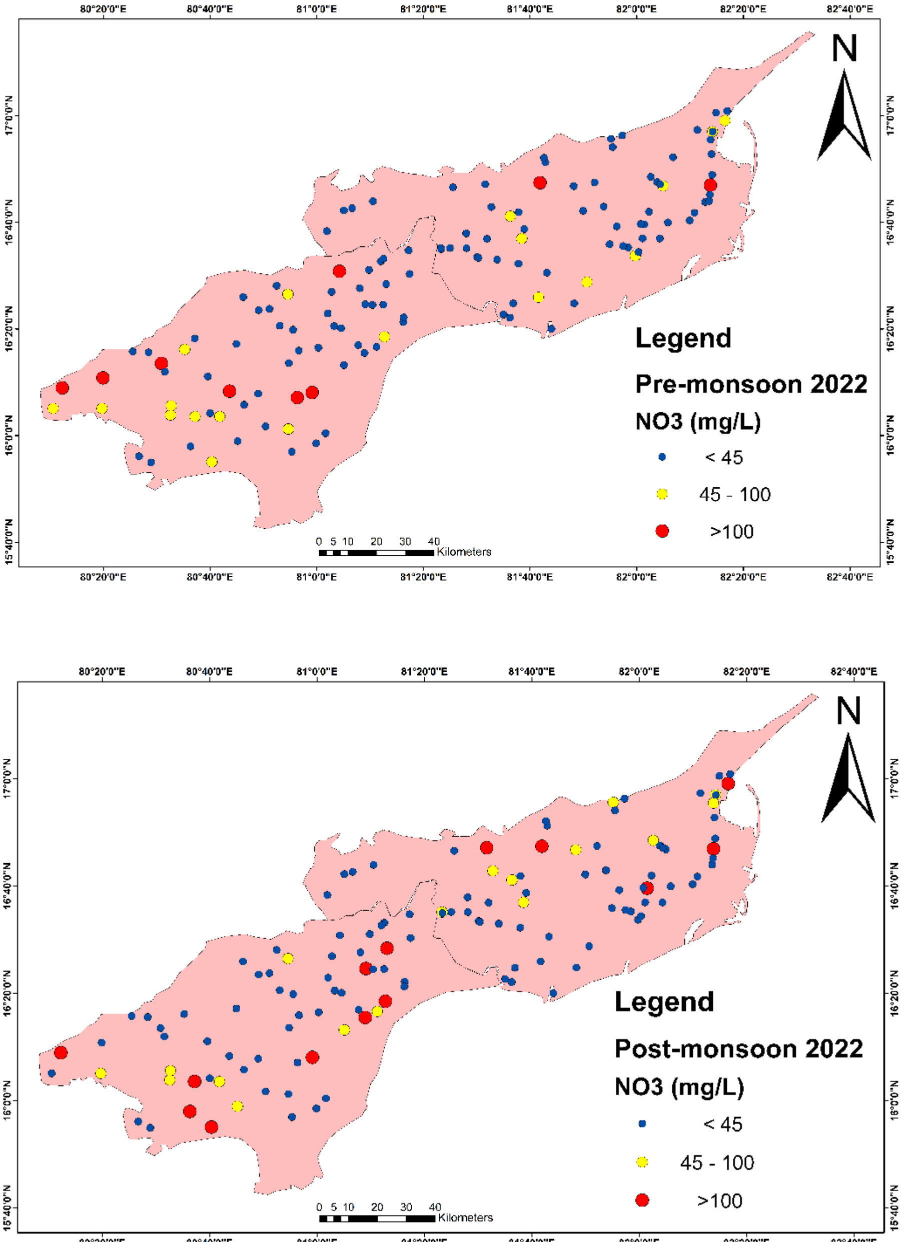
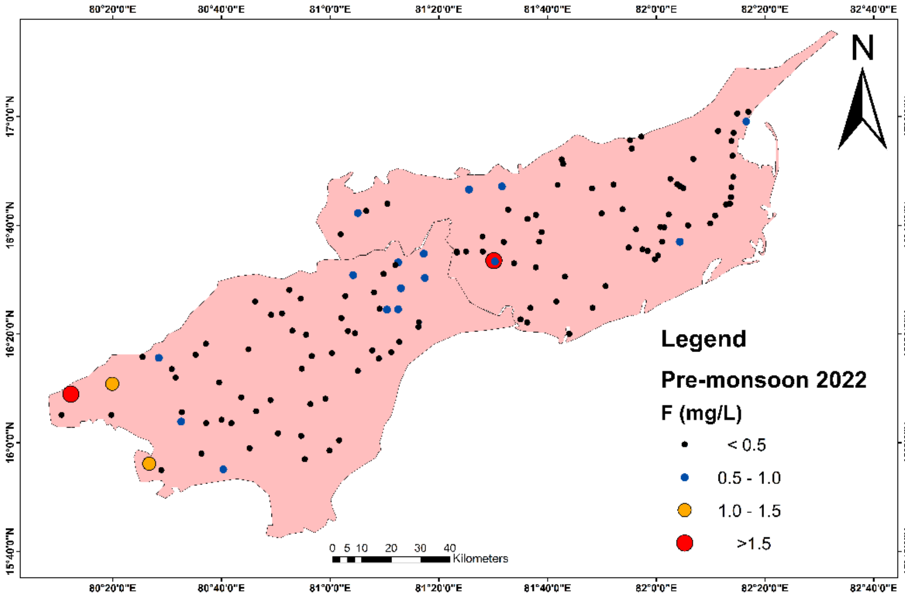


Fig. 21. Point Map of Nitrate in groundwater of the study area



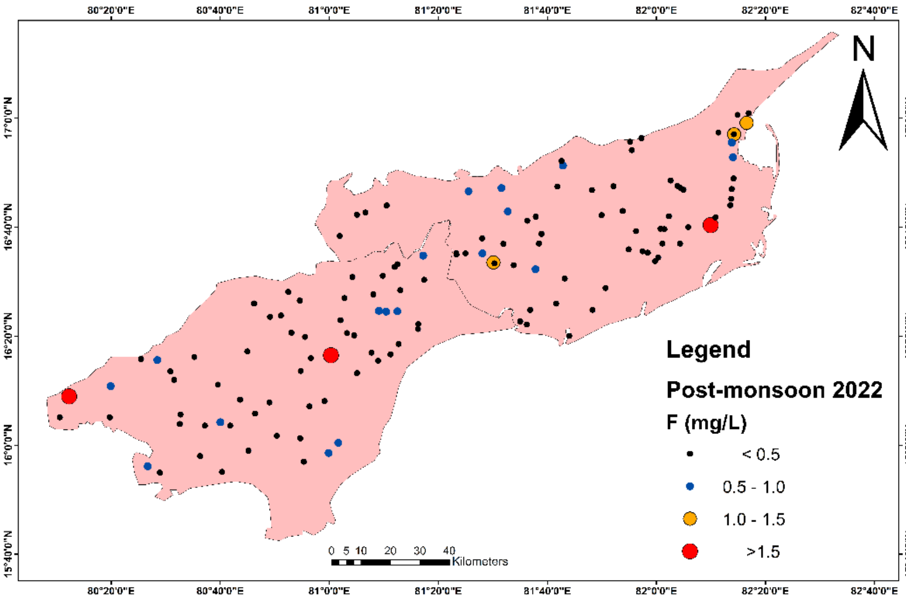


Fig. 22. Point Map of Fluoride in groundwater of the study area

5.2 Metal Concentrations in Groundwater of Study Area

The quality of water is an indispensable concern for mankind since it is directly linked with human welfare. The accumulation of various kinds of pollutants and nutrients through sewage, industrial effluents and agricultural runoff into the water bodies bring about a series of changes in the physicochemical characteristics of water (Raghav and Shrivastava, 2016). The pollutants of living environment are "Hazardous Metals" also termed as "Toxic metals", are of serious concern that the whole world is facing today because they are not readily degradable in nature and often accumulate through tropic level, aggregate in the animal as well as human bodies. Heavy metals are getting importance for causing a deleterious biological effect and create environmental problems (Praveena et al., 2010). These toxic heavy metals entering the environment may lead to bioaccumulation and biomagnifications. After entering to water bodies, metals accumulate in water, sediments, and biota (Pandey and Singh, 2017). Higher concentrations of heavy metals can form harmful complex compounds, which critically affect different biological functions (Rajbanshi, 2009). Because of their high water solubility, heavy metals can be easily absorbed by living organisms and, due to their mobility in natural water ecosystems and their toxicity to living forms, have been ranked as major inorganic contaminants in surface and ground waters (CWC Report, 2019). Some of the heavy metals are extremely essential to humans, for examples cobalt, copper, etc., but large quantities of them may cause physiological disorders. The cadmium, chromium and lead are highly toxic to humans even in low concentrations.

Godavari Delta

Groundwater samples collected from the study area were filtered immediately through 0.45µm membrane filter by hand operated vacuum pump and preserved with conc. HNO_3 for dissolved metals analysis. All the samples are stored in sampling kits maintained at 4°C. The concentrations of trace metals (B, Al, V, Co, Fe, Mn, Cu, Cr, Ni, Zn, Pb, Cd, Se, Sr, Ba, Hg, U and As) were analysed using Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). The metal concentrations of B, Al, V, Co, Fe, Mn, Cu, Cr, Ni, Zn, Pb, Cd, Se, Sr, Ba, Hg, U and As in the groundwater samples of study area collected during pre- and post-monsoon seasons are presented in Table 5 & 6. Variation of different metal concentrations in pre- and post-monsoon seasons during the year 2022-23 are given in Fig. 23 to 27.

Iron, an essential element in human nutrition, is an integral component of cytochromes, porphyrins and metalloenzymes. Iron is an essential constituent in plant metabolism. Deficiency of iron in plants causes chlorosis. The iron values in the ground water of the study area fall within range of 33 to 3545µg/L during the pre-monsoon season and 5.5 to 3190µg/L during post-monsoon season (Table 5). The variation of Iron in groundwater of study area for pre- and post-monsoon seasons is shown in Fig. 23. The Bureau of Indian Standards has recommended 1000 µg/L as the permissible limit for iron in drinking water (BIS 2012). It is evident from the results that 81% samples of the study area below the permissible limit of 1000 µg/L and 19% of the samples exceed the maximum permissible limit in pre-monsoon season while in post-monsoon season, 92% of the samples fall within the permissible limit and 8% of the samples even exceed the maximum permissible limit.The variation of Iron in groundwater of study area for pre- and post-monsoon seasons is shown in Fig. 23. High concentration of iron may be attributed to the dissolution of iron bearing minerals from the soil strata.

It is a known fact that iron in trace amounts is essential for nutrition. High concentrations of iron generally cause inky flavour, bitter and astringent taste to water. Well water containing soluble iron remain clear while pumped out, but exposure to air causes precipitation of iron due to oxidation, with a consequence of rusty colour and turbidity. The objection to iron in the distribution system is not due to health reason but to staining of laundry and plumbing fixtures and appearance. Taste and order problems may be caused by filamentous organism that prey on iron compounds (frenothrix, gallionella and leptothrix are called iron bacteria), originating another consumer's objection (red water).

Manganese (Mn) is one of the important micronutrient that uptakes by aquatic flora and fauna as well as human being for their proper growth. It occurs naturally in surface but human activities are also responsible for Mn pollution in water (Singh and Kumar, 2017). The concentration of manganese ranges from 4.8 to 6831 μg/L during pre-monsoon season and 5.8 to 3372μg/L during post-monsoon season of the year 2022-23 (Table 5). A concentration of 100 μg/L has been recommended as acceptable limit and 300 μg/L as the permissible limit for drinking water (BIS 2012). It is evident from the results that about 37% of the samples of the study area fall within the acceptable limit 100 μg/L and about 47% of the samples exceed the maximum permissible limit 300 μg/L during pre-monsoon season whereas 36% sample crosses the maximum permissible limit of 300 μg/L during post-monsoon season. The variation of Manganese in groundwater of study area for pre- and post-monsoon seasons is shown in Fig. 23. Manganese is an essential trace nutrient for plants and animals, which does not occur naturally as a metal but is found in various salts and minerals frequently in association with iron compounds. Manganese may gain entry into the body by inhalation, consumption of food and through drinking water. In general concentration of manganese in ground water is less than that of iron.

Copper is both essential and toxic to living systems. As an essential metal, copper is required for adequate growth, cardiovascular integrity, lung elasticity, neovascularization, and iron metabolism. Long-term exposure to copper can cause irritation of the nose, mouth and eyes and it causes headaches, stomachaches, vomiting and diarrhea. Intentionally high uptakes of copper may cause liver and kidney damage and even death. There are scientific articles that indicate a link between long-term exposure to high concentrations of copper and a decline in intelligence with young adolescents. The Bureau of Indian Standards has recommended 50 μg/L as the acceptable limit and 1500 μg/L as the permissible limit in the absence of alternate source (BIS 2012). Beyond 50 μg/L the water imparts astringent taste and cause discoloration and corrosion of pipes, fittings and utensils. World Health Organization has recommended 2000 μg/L as the provisional guideline value for drinking purpose (WHO, 2011). The concentration of copper ranges from 0.7 to 45 μg/L during pre-monsoon season and 0.3 to 8.7 μg/L during post-monsoon season (Table 5). It is evident from the results that all (100%) the samples of the study area fall within the acceptable limit of 50 μg/L and none of the samples exceed the maximum permissible limit of 1500 μg/L during pre- and post-monsoon season. The variation of copper in groundwater of study area for pre- and post-monsoon seasons is shown in Fig. 23.

Chromium (Cr) exists in two forms (III) and (VI). Cr (III) is of low toxicity and the hexavalent form is toxic. After breathing in, chromium (VI) can cause nose irritations, nosebleeds, weakened immune systems, respiratory problems, kidney and liver damage, alteration of genetic material and lung cancer. A concentration of 50 μg/L has been recommended as acceptable limit for drinking water (BIS, 2012). WHO has also prescribed 50 μg/L as the guideline value for drinking water (WHO, 2011). The concentration of chromium ranges from 0.1 to 11 μg/L during pre-monsoon season and 0.1 to 7.7 μg/L during post-monsoon season of the year 2022-23 (Table 5). All the samples of the study area have chromium concentration below 50 μg/L for drinking purpose (BIS, 2012) for both the seasons. The variation of Chromium in groundwater of study area for pre- and post-monsoon seasons is shown in Fig. 24.

Nickel is released into the environment from a variety of natural and anthropogenic sources. Wastewater from municipal sewage treatment plants also contributes to environmental metal accumulation. In small quantities nickel is essential, but when the uptake is too high it can be a danger to human health. Humans may be exposed to nickel by breathing air, drinking water, eating food or smoking cigarettes. A concentration of 20 μg/L has been recommended as acceptable limit for drinking water (BIS, 2012). The concentration of Nickel ranges from BDL to 416 μg/L during pre-monsoon season and BDL to 22 μg/L during post-monsoon season (Table 5). The variation of Nickel in groundwater of study area for pre- and post-monsoon seasons is shown in Fig. 24. About 96% of the samples of the study area have Nickel concentration below 20 μg/L for pre-monsoon season and 99% sample fall below acceptable limit over the post-monsoon. Only 4% and 1% samples crosses the permissible limit during the pre- and post-monsoon respectively.

Zinc (Zn) is an essential element for both animals and man which is necessary for the functioning of various enzyme systems. The largest natural emission of zinc to water results from erosion. The main anthropogenic sources of zinc are mining, zinc production facilities, iron and steel production, corrosion of galvanized structures, coal and fuel combustion, waste disposal and incineration, and the use of zinc-containing fertilizers and pesticide. Symptoms of zinc toxicity in humans include vomiting dehydration, electrolyte imbalance, abdominal pain, nausea lethargyness, dizziness and lack of muscular co-ordination The Bureau of Indian Standards has prescribed 5000 μg/L zinc as the acceptable limit and 15000 μg/L as the permissible limit for drinking water (BIS, 2012). The concentration of zinc ranges from 12 to 937 μg/L during pre-monsoon season and 4.6 to 314 μg/L during post-monsoon season (Table 5). All the samples of the study area have zinc concentration well within 5000 μg/L (acceptable limit) for both the seasons except 1% samples exceeds the acceptable limit but not permissible limit during the post-monsoon season. The variation of Zinc in groundwater of study area for pre- and post-monsoon seasons is shown in Fig. 25.

Lead (Pb) is known as one of the systemic poisons because it affects various organs and tissues. Pb poisoning is also manifested by muscle aches and joint pain, lung damage, difficulty in breathing, and diseases such as asthma, bronchitis, and pneumonia. Pb poisoning can also damage the immune system, interfering with cell maturation and skeletal growth. The Bureau of Indian Standards has prescribed 10 μg/L lead as the acceptable limit for drinking water (BIS, 2012). Beyond this limit, the water becomes toxic. WHO has also prescribed 10 μg/L as guideline value for drinking water (WHO, 2011). The concentration of lead ranges from 0.1 to 16 μg/L during pre-monsoon season and BDL to 5.7 μg/L during post-monsoon season (Table 5). The variation of Lead in groundwater of study area for pre- and post-monsoon seasons is shown in Fig. 25. Total 99% of the samples fall within the acceptable limit 10 μg/L and only 1% samples crossed the BIS limit for the pre-monsoon and over the post-monsoon all samples fall within the BIS limit.

Cadmium is an element that occurs naturally in the earth's crust. Cadmium is toxic to humans, animals, micro-organisms and plants, however only a small amount of cadmium intake is absorbed by the body and will be stored mainly in bones, liver and, in case of chronic exposure, in kidneys. BIS has prescribed 3 μg/L cadmium as the acceptable limit for drinking water (BIS, 2012). Beyond this limit, the water becomes toxic. WHO has also prescribed 3 μg/L as the guideline value for Cd for drinking water (WHO, 2011). The concentration of cadmium ranges from BDL to 0.2 μg/L during pre-monsoon season and BDL to 0.9 μg/L during post-monsoon season of the year 2022-23 (Table 5). For the year 2022-23, all samples in the pre- and post-monsoon seasons fall within the acceptable limit 3 μg/L. The variation of Cadmium in groundwater of study area for pre- and post-monsoon seasons is shown in Fig. 24.

Ground water is expected to contain higher arsenic concentrations than surface water. Because of its presence in geological materials, arsenic can be traced in water as originated by natural processes or by industrial activities – industrial waste, arsenical pesticides and smelting operations. Generally, arsenic found in two state – As(+3) and As(+5) in ground water. As(+3) compounds are more toxic than As(+6) compounds. Arsenic compounds are skin and lung carcinogens in humans. The Bureau of Indian Standards has prescribed 10 μg/L arsenic as the permissible limit (BIS, 2012). Beyond this limit, the water becomes toxic. WHO has prescribed 10 μg/L arsenic as the guideline value for drinking water (WHO, 2011).The concentration of arsenic ranges from 0.1 to 27 μg/L during pre-monsoon season and 0.1 to 9.1μg/L during post-monsoon season (Table 5). About 97% samples fall within the permissible limit during the pre-monsoon season but 3% samples were above the permissible limit during the pre-monsoon season and 99% samples fall within the permissible limit during the post-monsoon season but 1% samples were above the permissible limit. The variation of Arsenic in groundwater of study area for pre- and post-monsoon seasons is shown in Fig. 27.

Boron enters the environment from both natural sources such as weathering of rocks and soils and seawater spray, as well as human activities such as fossil fuel combustion and municipal and industrial wastewater discharge. Boron is also found in pesticides, cosmetics, pharmaceuticals and natural health products and is found in many consumer products such as swimming pool and spa products and cleaning products. In water, boron exists primarily as boric acid and borate. Boron is not an essential element, but some studies indicate it may be beneficial to human health. Studies in humans have found possible associations between boron and effects to reproduction and development. The Bureau of Indian Standards has prescribed 500 μg/L boron as the acceptable limit and 2400 μg/L as permissible limit for drinking water (BIS, 2012). Beyond this limit, the water becomes toxic. The concentration of boron ranges from 27 to 1063 μg/L during pre-monsoon season and 28 to 1132 μg/L during post-monsoon season (Table 5). About 97% and 85% samples fall within the acceptable limit during the pre- and post-monsoon season but none of the samples were above the permissible limit, respectively.The variation of Boron in groundwater of study area for pre- and post-monsoon seasons is shown in Fig. 25.

Aluminum is a metal widely distributed in nature. It may be present in water from natural sources or as a result of human activities. The metal is used for many purposes: in the production of construction materials, vehicles, aircraft, electronics, pharmaceuticals and personal care products; as food additives; and as components of food packaging materials. Aluminum salts are commonly added as coagulants during water treatment to remove turbidity, organic matter and microorganisms. Aluminum is also an impurity found in other water treatment chemicals and can leach into drinking water from cement mortar pipes or linings. The Bureau of Indian Standards has prescribed 30 μg/L aluminium as the acceptable limit and 200 μg/L as permissible limit for drinking water (BIS, 2012). The concentration of aluminium ranges from 14 to 554 μg/L during pre-monsoon season and 12 to 822 μg/L during post-monsoon season (Table 5). About 11% samples fall within the acceptable limit during the pre-monsoon season and 32% samples were above the acceptable limit during the post-monsoon season. The variation of Aluminum in groundwater of study area for pre- and post-monsoon seasons is shown in Fig. 27.

Selenium is present in the earth's crust, often in association with sulfur-containing minerals. It can found in various oxidation states (-2, 0, +4, +6) and occurs in many forms, including elemental selenium, selenites and selenates. Selenium is a mineral that gets into water from natural deposits, mining operations, and agricultural runoff. Low levels of selenium are essential to human health, but selenium is known to have serious health effects if found in elevated levels in drinking water. Acute oral doses of selenite and other selenium compounds cause symptoms such as nausea, diarrhoea, abdominal pain, chills, tremor, numbness in limbs, irregular menstrual bleeding, and marked hair loss. The concentration of Selenium ranges from BDL to 3.2 μg/L during pre-monsoon season and BDL to 3.6 μg/L during post-monsoon season (Table 5). The Bureau of Indian Standards has prescribed 700 μg/L selenium as the as acceptable limit for drinking water (BIS, 2012). All (100%) samples fall within the acceptable limit during the pre- and post-monsoon season. The variation of Selenium in groundwater of study area for pre- and post-monsoon seasons is shown in Fig. 26.

Barium is present as a trace element in both igneous and sedimentary rocks. Barium in water comes primarily from natural sources. The acetate, nitrate and halides are soluble in water, but the carbonate, chromate, fluoride, oxalate, phosphate and sulfate are quite insoluble. The solubility of barium compounds increases as the pH level decreases (USEPA, 1985). At high concentrations, barium causes vasoconstriction by its direct stimulation of arterial muscle, peristalsis as a result of the violent stimulation of smooth muscles and convulsions and paralysis following stimulation of the central nervous system (Stockinger, 1981). The concentration of Barium ranges from 7.7 to 369 μg/L during pre-monsoon season and 7.2 to 281 μg/L during post-monsoon season (Table 5). The WHO has prescribed 700 μg/L as the permissible limit for drinking water (WHO, 2011). All (100%) samples fall within the permissible limit during the both the seasons. The variation of Barium in groundwater of study area for pre- and post-monsoon seasons is shown in Fig. 26.

Naturally occurring Mercury has been widely distributed by natural processes such as volcanic activity. The use of mercury in industrial processes significantly increased following the industrial revolution of the 19^{th} century. Mercury is or has been used for the cathode in the electrolytic production of chlorine and caustic soda, in electrical appliances (lamps, arc rectifiers, mercury cells), in industrial and control instruments (switches, thermometers, barometers), in laboratory apparatus and as a raw material for various mercury compounds. The solubility of mercury compounds in water varies: elemental mercury vapour is insoluble, mercury (II) chloride is readily soluble, mercury (I) chloride is much less soluble and mercury sulfide has a very low solubility. Mercury will cause severe disruption of any tissue with which it comes into contact in sufficient concentration, but the two main effects of mercury poisoning are neurological and renal disturbances. Some of the health effects exposure to mercury may cause include: irritation to the eyes, skin, and stomach; cough, chest pain, or difficulty breathing, insomnia, irritability, indecision, headache, weakness or exhaustion, and weight loss. The concentration of Mercury ranges from BDL to 32 μg/L during pre-monsoon season and BDL to 7.8 μg/L during post-monsoon season (Table 5). The Bureau of Indian Standards has prescribed 1 μg/L Mercury as the as acceptable limit for drinking water (BIS, 2012). About 78% samples fall within the permissible limit and 22% samples exceeded the limit during the pre-monsoon season and 75% samples fall within the permissible limit and 25% samples exceeded the limit during the post-monsoon season. The variation of Mercury in groundwater of study area for pre- and post-monsoon seasons is shown in Fig. 26.

Uranium occurs naturally in the +2, +3, +4, +5 and +6 valence states, but it is most commonly found in the hexavalent form. Uranium is used mainly as fuel in nuclear power stations, although some uranium compounds are also used as catalysts and staining pigments (Berlin & Rudell, 1986). Uranium is present in the environment as a result of leaching from natural deposits, release in mill tailings, emissions from the nuclear industry, the combustion of coal and other fuels and the use of phosphate fertilizers that contain uranium. Nephritis is the primary chemically induced effect of uranium in humans (Hursh & Spoor, 1973). Little information is available on the chronic health effects of exposure to environmental uranium in humans. The concentration of Uranium ranges from 0.1 to 15 μg/L during pre-monsoon season and 0.1 to 15 μg/L during post-monsoon season (Table 5). The WHO has prescribed 30 μg/L Uranium as the permissible limit for drinking water (WHO, 2011). Total 100% samples fall within the permissible limit during both the seasons. The variation of Uranium in groundwater of study area for pre- and post-monsoon seasons is shown in Fig. 27.

Vanadium is a metal that naturally occurs in many different minerals and in fossil fuel deposits. The primary industrial use of vanadium is in the strengthening of steel. The oxidation states +3, +4, and +5 being the most common. Oxidation state +4 is the most stable. Vanadium pentoxide (V_2O_5) is the most common commercial form of vanadium. It dissolves in water and acids and forms vanadates with bases. Vanadium in the +3 oxidation state (e.g., V_2O_3) is basic and dissolves in acid forming a green hexa-aquo ion. From the point of view of environmental pollution, power and heat-producing plants using fossil fuels (petroleum, coal, oil) cause the most widespread discharge of vanadium into the environment. Exposure to the levels of vanadium that are naturally present in food and water are not considered to be harmful. The concentration of Vanadium ranges from 0.4 to 125 μg/L during pre-monsoon season and 0.5 to 133 μg/L during post-monsoon season (Table 5).

Cobalt is a naturally-occurring element that has properties similar to those of iron and nickel. Small amounts of cobalt are naturally found in most rocks, soil, water, plants, and animals, typically in small amounts. Cobalt is also found in meteorites. Elemental cobalt is a hard, silvery grey metal. However, cobalt is usually found in the environment combined with other elements such as oxygen, sulfur, and arsenic. It may enter air and water, and settle on land from windblown dust, seawater spray, volcanic eruptions, and forest fires and may additionally get into surface water from runoff and leaching when rainwater washes through soil and rock containing cobalt. Cobalt has both beneficial and harmful effects on human health. Cobalt is beneficial for humans because it is part of vitamin B12, which is essential to maintain human health. When too much cobalt is taken into your body, however, harmful health effects can occur. Serious effects on the lungs, including asthma, pneumonia, and wheezing, have been found in people exposed to 0.005 mg cobalt/m3 while working with hard metal, a cobalttungsten carbide alloy. The concentration of Cobalt ranges from 0.1 to 4.6 μg/L during pre-monsoon season and 0.1 to 3.2 μg/L during post-monsoon season (Table 5).

Strontium is widely distributed in nature and has been identified in many different minerals. It may be present in water in the environment from natural sources (rock and soil weathering) or as a result of human activities. Strontium can be released to the environment as a by-product of other mining operations or from its usage in many industries. Strontium is used in electrical applications and paint, to remove lead from zinc electrolytic solutions, in pyrotechnics and signalling devices, as well as in the manufacture of various other products (e.g., glass, ceramic permanent magnets and glazes, aluminum alloys). Strontium can replace calcium in bones and cause rickets. Rickets is a bone disorder that may weaken or soften the bones, stunt growth and cause bone deformities. Drinking water that contains high levels of strontium may pose a risk to infants because their bones are actively developing. The concentration of Strontium ranges from 102 to 2436 μg/L during pre-monsoon season and 103 to 2142 μg/L during post-monsoon season (Table 5).

It is inferred from the discussion that the presence of heavy metals has been recorded in many samples and the water quality standards have been violated for iron in 19% & 8% samples, aluminium in 11% & 4% samples, manganese in 47% & 36% samples, nickel in 4% & 1% samples, lead in 1% & 0% samples, mercury in 22% & 25% samples and arsenic in 3% & 1% samples during the pre- & post-monsoon period respectively.

Krishna Delta

Groundwater samples collected from the study area were filtered immediately through 0.45μm membrane filter by hand operated vacuum pump and preserved with conc. HNO_3 for dissolved metals analysis. All the samples are stored in sampling kits maintained at 4^oC. The concentrations of trace metals (B, Al, V, Co, Fe, Mn, Cu, Cr, Ni, Zn, Pb, Cd, Se, Sr, Ba, Hg, U and As) were analysed using inductively coupled plasma-mass spectrometry (ICPMS). The metal concentrations of B, Al, V, Co, Fe, Mn, Cu, Cr, Ni, Zn, Pb, Cd, Se, Sr, Ba, Hg, U and As in groundwater of study area for the samples collected during pre- and post-monsoon seasons are presented in Table 5 & 6. Variation of different metal concentrations in pre- and post-monsoon seasons during the year 2022-23 are given in Fig. 23 to 27.

The iron values in the ground water of the study area fall within range of 23 to 4852μg/L during the pre-monsoon season and 20 to 3661 μg/L during post-monsoon season (Table 6). The Bureau of Indian Standards has recommended 1000 μg/L as the permissible limit for iron in drinking water (BIS 2012). It is evident from the results that 86% samples of the study area below the permissible limit of 1000 μg/L and 14% of the samples exceed the maximum permissible limit in pre-monsoon season while in post-monsoon season, 84% of the samples fall within the permissible limit and 16% of the samples even exceed the maximum permissible limit.The variation of Iron in groundwater of study area for pre- and post-monsoon seasons is shown in Fig. 23. High concentration of iron may be attributed to the dissolution of iron bearing minerals from the soil strata.

The concentration of manganese ranges from 6.7 to 2916 μg/L during pre-monsoon season and 4.6 to 4256μg/L during post-monsoon season of the year 2022-23 (Table 6). A concentration of 100 μg/L has been recommended as acceptable limit and 300 μg/L as the permissible limit for drinking water (BIS 2012). It is evident from the results that about 25% of the samples of the study area fall within the acceptable limit 100 μg/L and about 47% of the samples exceed the maximum permissible limit 300 μg/L during pre-monsoon season while in post-monsoon season, 30% of the samples fall within the acceptable limit and 44% of the samples even exceed the maximum acceptable limit. The variation of Manganese in groundwater of study area for pre- and post-monsoon seasons is shown in Fig. 23. In general concentration of manganese in ground water is less than that of iron.

The Bureau of Indian Standards has recommended 50 μg/L as the acceptable limit and 1500 μg/L as the permissible limit of Copper in the absence of alternate source (BIS 2012). Beyond 50 μg/L the water imparts astringent taste and cause discoloration and corrosion of pipes, fittings and utensils. World Health Organization has recommended 2000 μg/L as the provisional guideline value for drinking purpose (WHO, 2011). The concentration of copper ranges from 0.1 to 7.0 μg/L during pre-monsoon season and 0.5 to 78 μg/L during post-monsoon season (Table 6). The variation of copper in groundwater of study area for pre- and post-monsoon seasons is shown in Fig. 23. It is evident from the results that 100% and 97% of the samples of the study area fall within the acceptable limit of 50 μg/L and none of the samples exceed the maximum permissible limit of 1500 μg/L during pre- and post-monsoon season, respectively.

A concentration of Chromium of 50 μg/L has been recommended as acceptable limit for drinking water (BIS, 2012). WHO has also prescribed 50 μg/L as the guideline value for drinking water (WHO, 2011). The concentration of chromium ranges from 0.1 to 45 μg/L during pre-monsoon season and 0.1 to 6.7 μg/L during post-monsoon season of the year 2022-23 (Table 6). The variation of Chromium in groundwater of study area for pre- and post-monsoon seasons is shown in Fig. 24. All the samples of the study area have chromium concentration below 50 μg/L for drinking purposes (BIS, 2012) for both the seasons.

A concentration of Nickel of 20 μg/L has been recommended as acceptable limit for drinking water (BIS, 2012). The concentration of Nickel ranges from BDL to 3.9 μg/L during pre-monsoon season and BDL to 2.9 μg/L during post-monsoon season (Table 6). The variation of Nickel in groundwater of study area for pre- and post-monsoon seasons is shown in Fig. 24. All samples (100%) of the study area have Nickel concentration below 20 μg/L for pre- and post-monsoon season.

The Bureau of Indian Standards has prescribed 5000 μg/L zinc as the acceptable limit and 15000 μg/L as the permissible limit for drinking water (BIS, 2012). The concentration of zinc ranges from 3.7 to 1462 μg/L during pre-monsoon season and 4.5 to 5475 μg/L during post-monsoon season (Table 6). The variation of Zinc in groundwater of study area for pre- and post-monsoon seasons is shown in Fig. 25. All the samples of the study area have zinc concentration well within 5000 μg/L (acceptable limit) for pre-monsoon seasons and 97% of the samples were fall within the BIS limit i.e 5000 µg/L during the post-monsoon.

The Bureau of Indian Standards has prescribed 10 µg/L lead as the acceptable limit for drinking water (BIS, 2012). Beyond this limit, the water becomes toxic. WHO has also prescribed 10 µg/L as guideline value for drinking water (WHO, 2011). The concentration of lead ranges from BDL to 12 µg/L during pre-monsoon season and 0.2 to 50 µg/L during post-monsoon season (Table 6). The variation of Lead in groundwater of study area for pre- and post-monsoon seasons is shown in Fig. 25. Total 98% and 97% of the samples fall within the acceptable limit 10 µg/L, and only 2% and 3% samples crossed the BIS limit over the pre-monsoon and post-monsoon, respectively.

BIS has prescribed 3 µg/L cadmium as the acceptable limit for drinking water (BIS, 2012). Beyond this limit, the water becomes toxic. WHO has also prescribed 3 µg/L as the guideline value for Cd for drinking water (WHO, 2011). The concentration of cadmium ranges from BDL to 0.2 µg/L during pre-monsoon season and 0.0 to 0.3 µg/L during post-monsoon season of the year 2022-23 (Table 6). The variation of Cadmium in groundwater of study area for pre- and post-monsoon seasons is shown in Fig. 24. For the year 2022-23, all samples in both seasons fall within the acceptable limit 3 µg/L.

The Bureau of Indian Standards has prescribed 10 µg/L arsenic as the permissible limit (BIS, 2012). Beyond this limit, the water becomes toxic. WHO has also prescribed 10 µg/L arsenic as the guideline value for drinking water (WHO, 2011). The concentration of arsenic ranges from 0.2 to 21 µg/L during pre-monsoon season and 0.2 to 23 µg/L during post-monsoon season (Table 6). The variation of Arsenic in groundwater of study area for pre- and post-monsoon seasons is shown in Fig. 27. About 97% samples fall within the permissible limit but 3% samples were above the permissible limit during the pre- and post-monsoon season.

The Bureau of Indian Standards has prescribed 500 µg/L boron as the acceptable limit and 2400 µg/L as permissible limit for drinking water (BIS, 2012). Beyond this limit, the water becomes toxic. The concentration of boron ranges from 87 to 3599 µg/L during pre-monsoon season and 74 to 1652 µg/L during post-monsoon season (Table 6). The variation of Boron in groundwater of study area for pre- and post-monsoon seasons is shown in Fig. 25. About 74% and 90% samples fall within the acceptable limit during the pre- and post-monsoon season but 0% and 2% samples were above the permissible limit over the pre- and post-monsoon, respectively.

The Bureau of Indian Standards has prescribed 30 µg/L Aluminium as the acceptable limit and 200 µg/L as permissible limit for drinking water (BIS, 2012). The concentration of aluminium ranges from 8.1 to 1532 µg/L during pre-monsoon season and 6.8 to 371 µg/L during post-monsoon season (Table 6). The variation of Aluminium in groundwater of study area for pre- and post-monsoon seasons is shown in Fig. 27. About 24% samples fall within the acceptable limit and 41% samples were above the permissible limit during the pre-monsoon season and over the post-monsoon season, 6% samples were above the permissible limit.

The concentration of Selenium ranges from BDL to 3.3 µg/L during pre-monsoon season and BDL to 3.0 µg/L during post-monsoon season (Table 6). The Bureau of Indian Standards has prescribed 10 µg/L selenium as the as acceptable limit for drinking water (BIS, 2012). The variation of Selenium in groundwater of study area for pre- and post-monsoon seasons is shown in Fig. 26. All (100%) samples fall within the acceptable limit during the pre- and post-monsoon season.

The concentration of Barium ranges from 5.0 to 244 µg/L during pre-monsoon season and 4.9 to 250 µg/L during post-monsoon season (Table 6). The Bureau of Indian Standards has prescribed 700 µg/L Barium as the as permissible limit for drinking water (BIS, 2012). The variation of Barium in groundwater of study area for pre- and post-monsoon seasons is shown in Fig. 26. All (100%) samples fall within the permissible limit during the pre- and post-monsoon seasons.

The concentration of Mercury ranges from BDL to 13 μg/L during pre-monsoon season and 0.1 to 4.2 μg/L during post-monsoon season (Table 6). The Bureau of Indian Standards has prescribed 1 μg/L Mercury as the as acceptable limit for drinking water (BIS, 2012). The variation of Mercury in groundwater of study area for pre- and post-monsoon seasons is shown in Fig. 26. About 83% samples fall within the acceptable limit and 17% samples exceeded the limit during the pre-monsoon season while 19% samples exceeded the acceptable limit during the post-monsoon season.

The concentration of Uranium ranges from 0.1 to 86 μg/L during pre-monsoon season and 0.1 to 21 μg/L during post-monsoon season (Table 6). The WHO has prescribed 30 μg/L Uranium as the as permissible limit for drinking water (WHO, 2011). The variation of Uranium in groundwater of study area for pre- and post-monsoon seasons is shown in Fig. 27. Total 99% samples fall within the permissible limit and only 1% samples found above the limit during the pre-monsoon season while over the post-monsoon, all samples were found within the permissible limit.

The concentration of Vanadium ranges from 0.4 to 210 μg/L during pre-monsoon season and 0.5 to 128 μg/L during post-monsoon season (Table 6).

The concentration of Cobalt ranges from BDL to 2.4 μg/L during pre-monsoon season and 0.1 to 4.1 μg/L during post-monsoon season (Table 6).

Drinking water that contains high levels of strontium may pose a risk to infants because their bones are actively developing. The concentration of Strontium ranges from 107 to 5013 μg/L during pre-monsoon season and 163 to 10639 μg/L during post-monsoon season (Table 6).

It is inferred from the discussion that the presence of heavy metals has been recorded in many samples and the water quality standards have been violated for iron in 37% & 42% samples, aluminium in 47% & 6% samples, boron in 6% & 5% samples, manganese in 47% & 44% samples, lead in 2% & 0% samples, mercury in 17% & 19% samples and arsenic in 3% & 3% samples during the pre- & post-monsoon period respectively.

Table 5 Metal Concentrations in Groundwater of Godavari delta (Pre- & Post-monsoon 2022)

S.No.	Metal (µg/L)	Minimum	Maximum	Mean	Permissible Limit
1	B	27(28)	1063(1132)	765(245)	2400
2	Al	14(12)	554(822)	62(164)	200
3	V	0.4(0.5)	125(133)	9.0(22)	-
4	Cr	0.1(0.1)	11(7.7)	0.7(1.0)	50
5	Mn	4.8(5.8)	6831(3372)	20(452)	300
6	Fe	33(5.5)	3545(3190)	141(408)	1000
7	Co	0.1(0.1)	4.6(3.2)	0.3(0.8)	-
8	Ni	BDL(BDL)	416(22)	1.1(2.3)	20
9	Cu	0.7(0.3)	45(8.7)	5.5(2.8)	1500
10	Zn	12(4.6)	937(314)	162(30)	15000
11	As	0.1(0.1)	27(9.1)	1.1(2.1)	10
12	Se	BDL(BDL)	3.2(3.6)	1.1(0.5)	10
13	Sr	102(103)	2436(2142)	884(517)	-
14	Cd	BDFL(BDL)	0.2(0.9)	0.1(0.1)	3
15	Ba	7.7(7.2)	369(281)	43(88)	700
16	Hg	BDL(BDL)	32(7.8)	2.7(0.9)	1
17	Pb	0.1(BDL)	16(5.7)	1.6(0.9)	10
18	U	0.1(0.1)	15(15)	6.3(2.2)	30

Table 6 Metal Concentrations in Groundwater of Krishna delta (Pre- & Post-monsoon 2022)

S.No.	Metal (µg/L)	Minimum	Maximum	Mean	Permissible Limit
1	B	84(74)	3599(1652)	244(304)	2400
2	Al	8.1(6.8)	1532(371)	214(69)	200
3	V	0.4(0.5)	210(128)	15(23)	-
4	Cr	0.1(0.1)	45(6.7)	3.4(1.2)	50
5	Mn	6.7(4.6)	2916(4256)	843(445)	300
6	Fe	23(20)	4852(3661)	461(511)	1000
7	Co	BDL(0.1)	2.4(4.1)	0.3(0.7)	-
8	Ni	BDL(BDL)	3.9(2.9)	1.3(1.1)	20
9	Cu	0.1(0.5)	7.0(78)	1.8(4.0)	1500
10	Zn	3.7(4.5)	1462(5475)	107(181.5)	15000
11	As	0.2(0.2)	21(23)	1.4(2.9)	10
12	Se	BDL(BDL)	3.3(3.0)	1.1(0.7)	10
13	Sr	107(163)	5013(10639)	1330(870.7)	-
14	Cd	BDL(0.0)	0.2(0.3)	0.03(0.04)	3
15	Ba	5.0(4.9)	244(250)	81(55.0)	700
16	Hg	BDL(0.1)	13(4.2)	13(0.7)	1
17	Pb	BDL(0.2)	12(50)	2.8(2.3)	10
18	U	0.1(0.066)	21(86.32)	2.9(3.68)	30

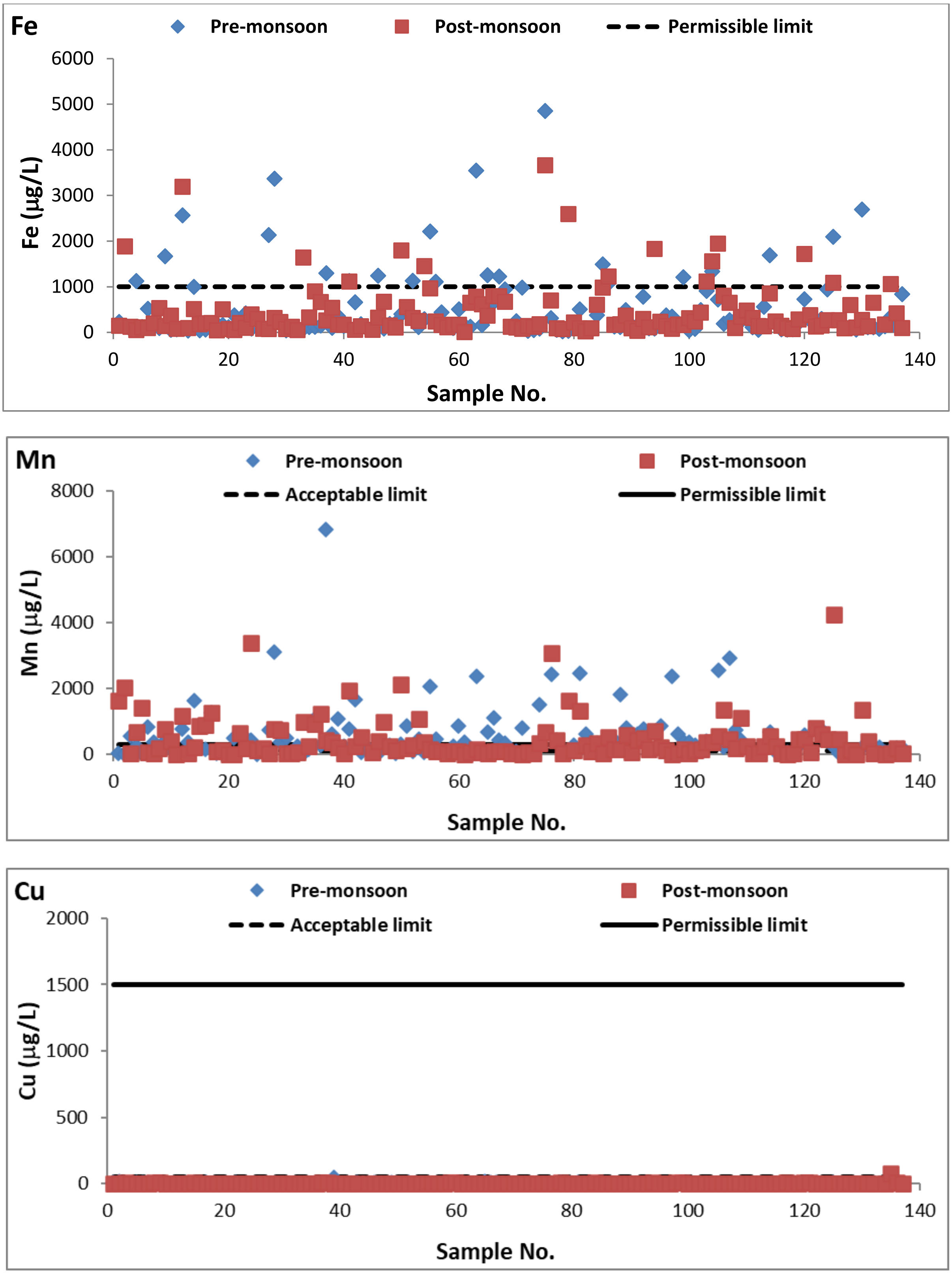


Fig. 23. Metal concentrations (Fe, Mn, Cu) in the groundwater of the study area

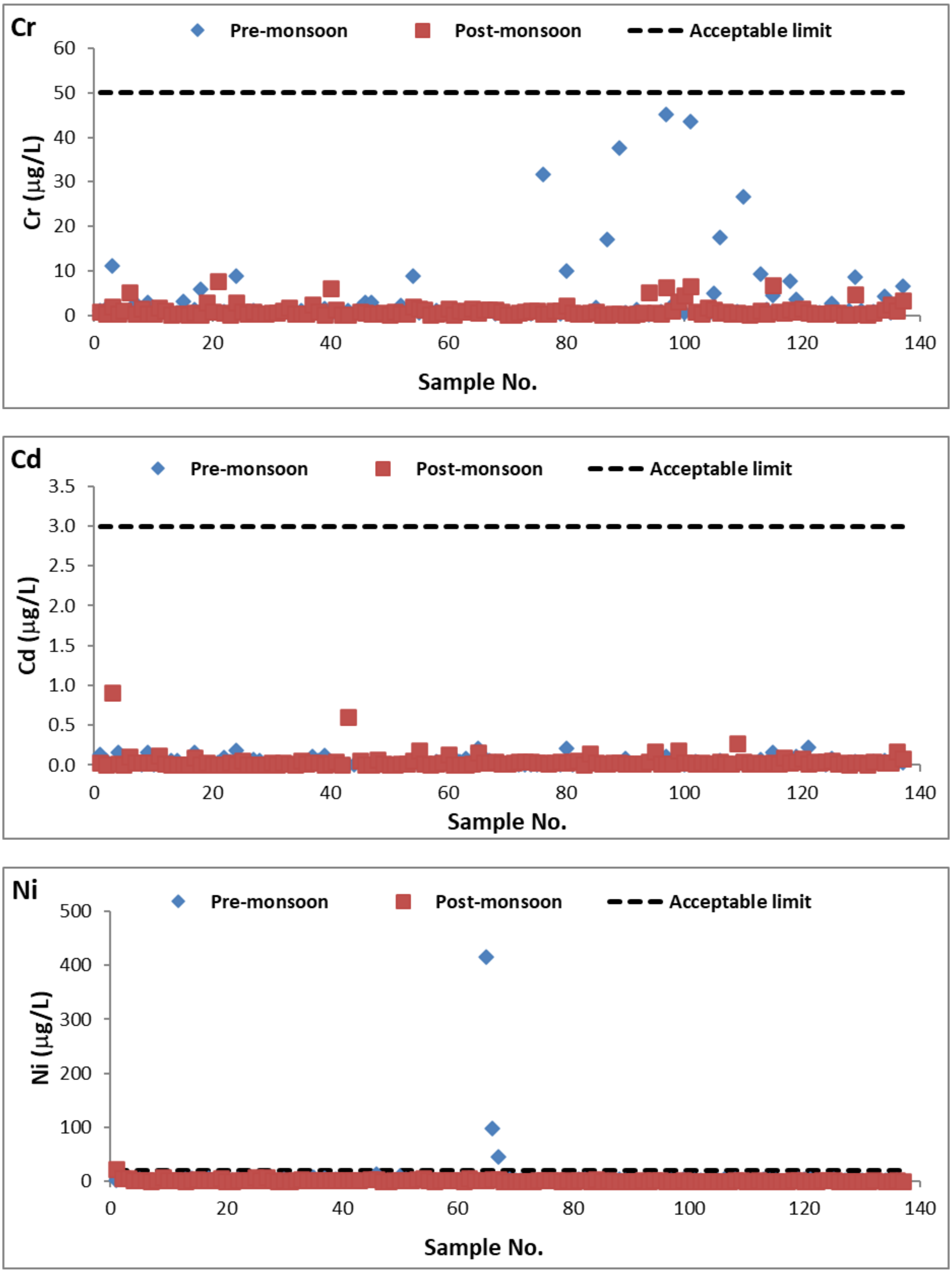


Fig. 24. Metal concentrations (Cr, Cd, Ni) in the groundwater of the study area

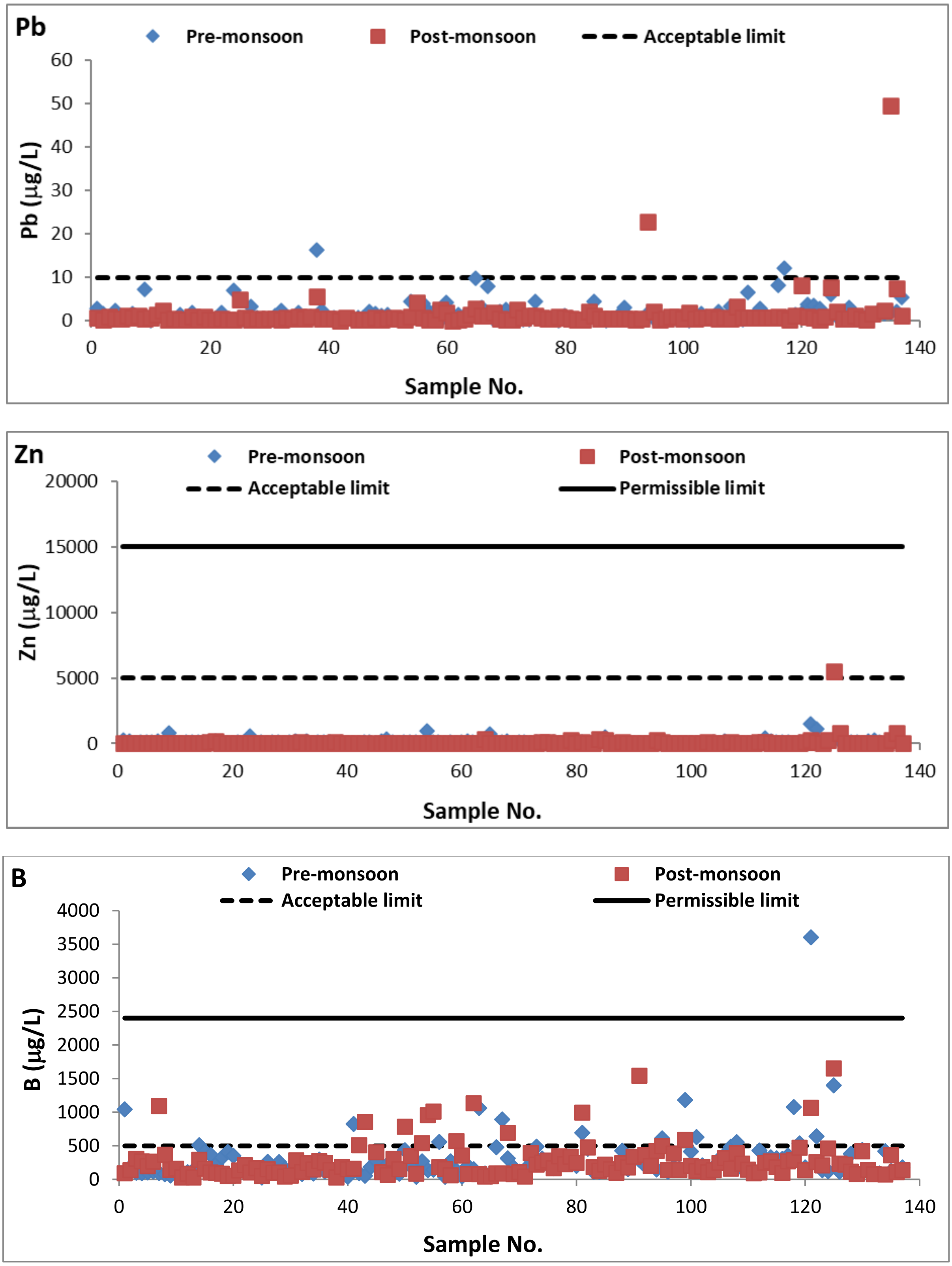


Fig. 25. Metal concentrations (Pb, Zn, B) in the groundwater of the study area

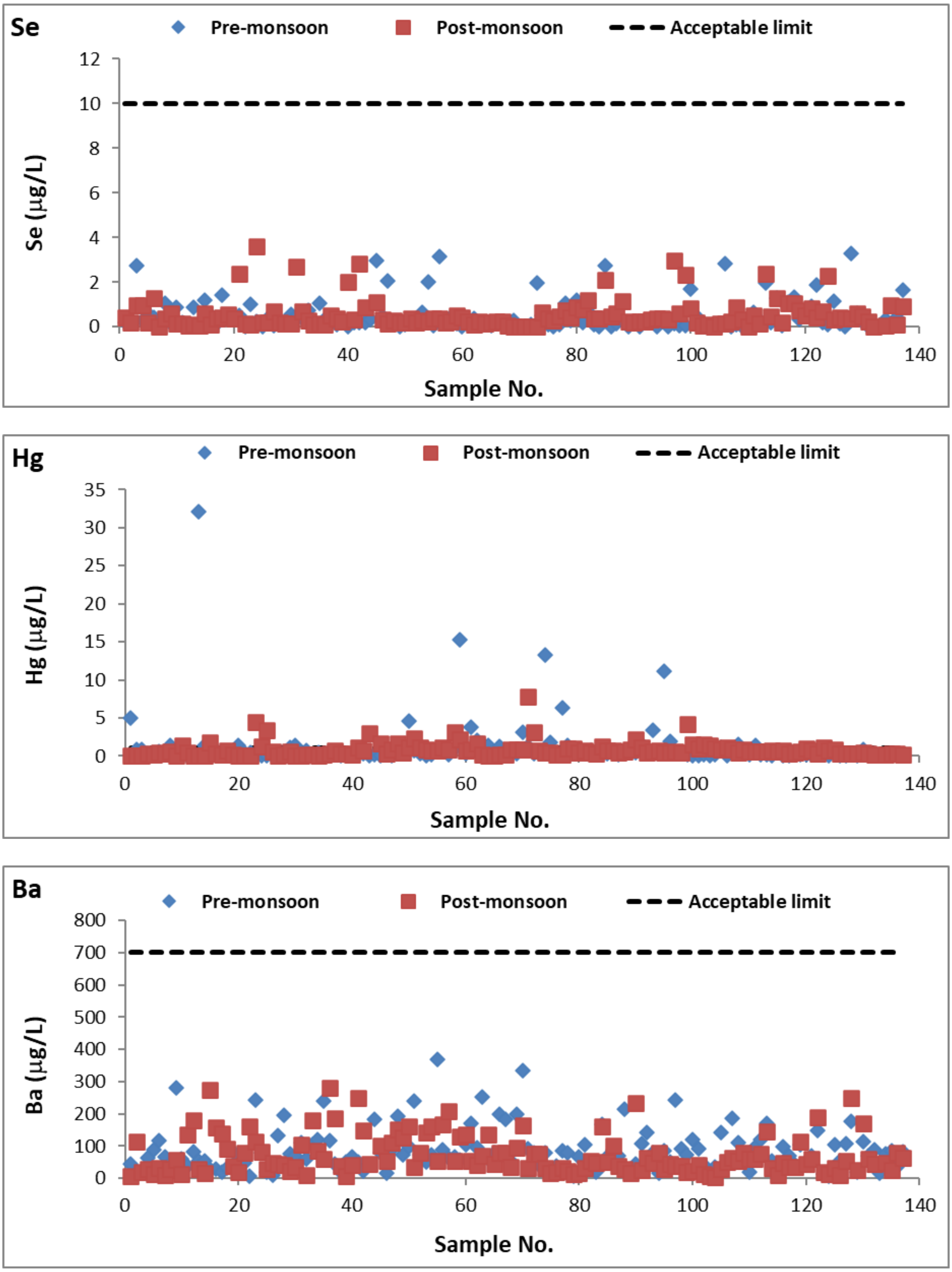


Fig. 26. Metal concentrations (Se, Hg, Ba) in the groundwater of the study area

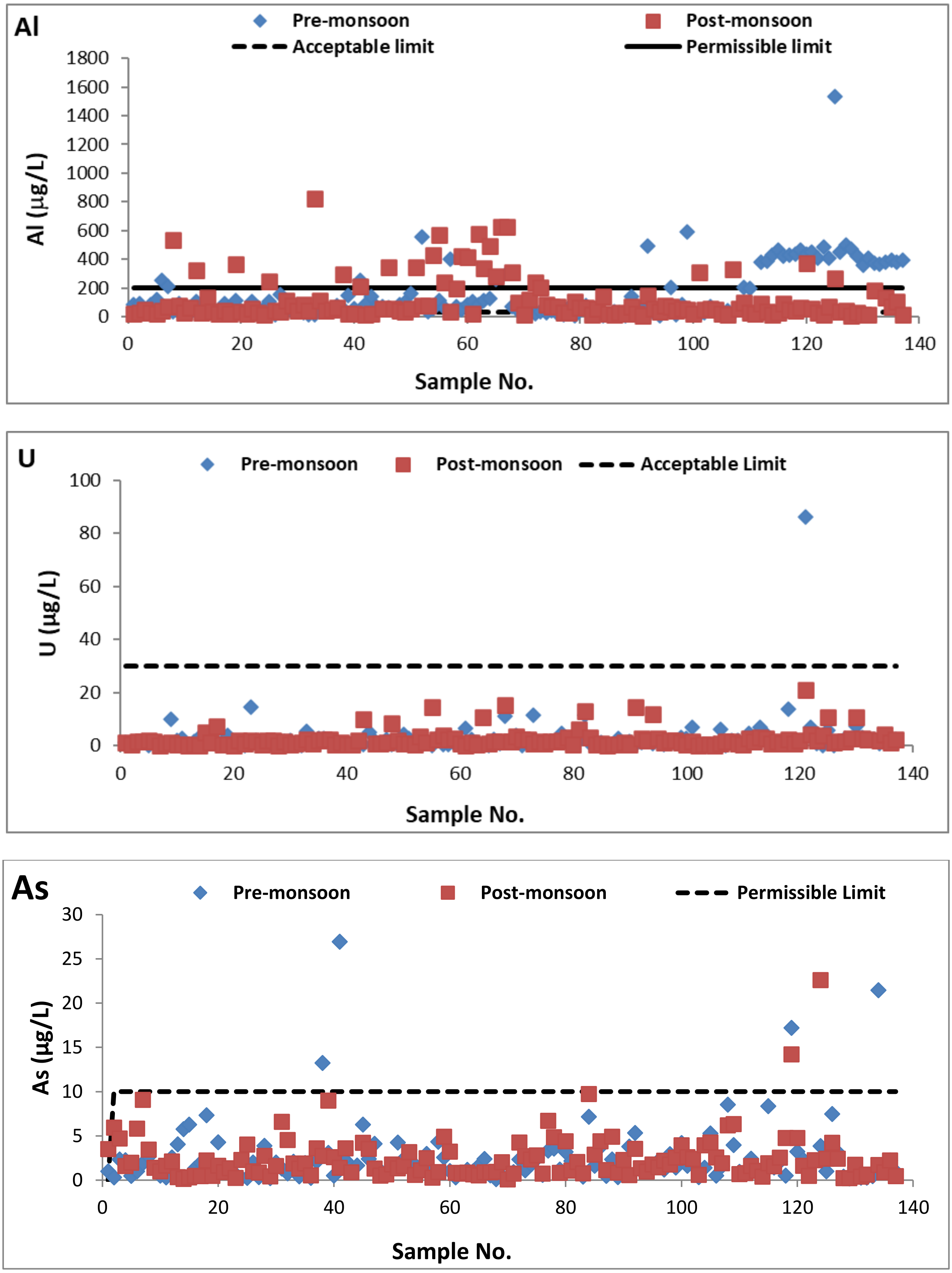
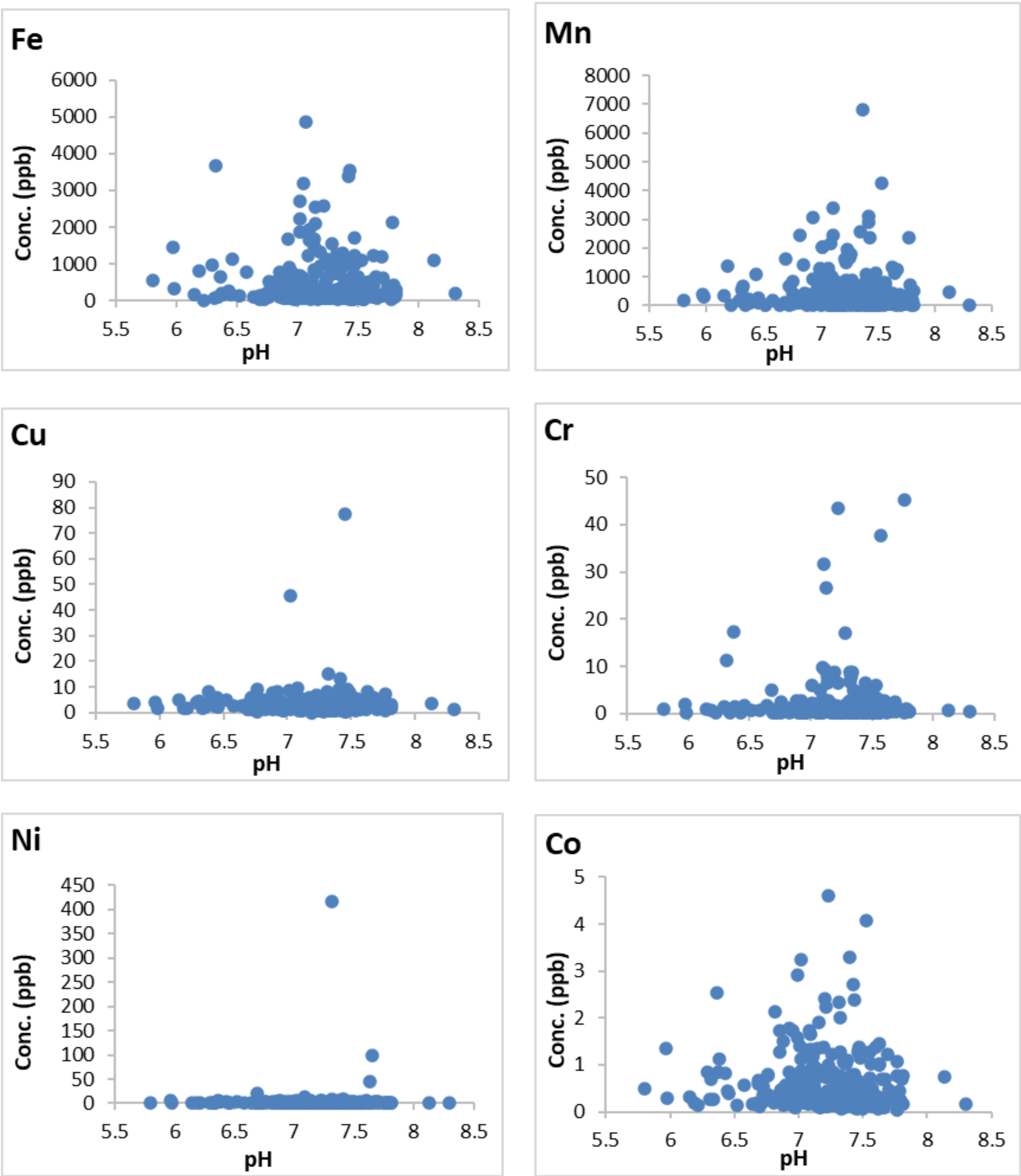
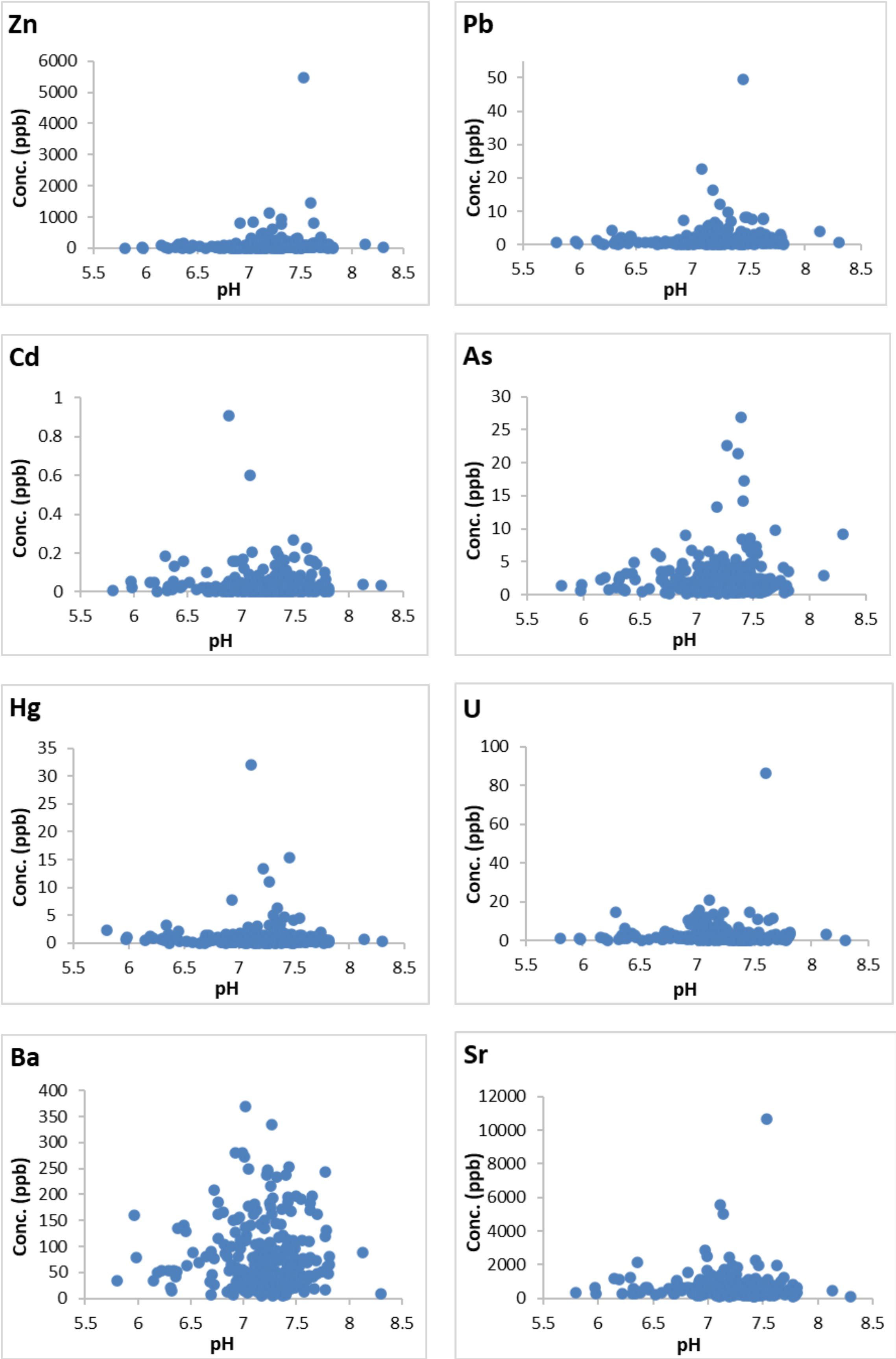


Fig. 27. Metal concentrations (Al, U, As) in the groundwater of the study area

5.2.1 Relationship of metal concentration in Groundwater with pH & ORP

Mineral stability in any environment is dependent on and is a function of pH and Eh. Hydrocarbons migrating into the near surface soils destabilizes many compounds and increases the solubility of the trace and minor elements. Many metal elements are highly soluble in acid solutions but will be precipitated as oxides and hydroxides with increasing pH. Oxidation-reduction potential plays a major role on the mobility of elements. Anomalous amounts of V, Cr, Ni, Co, Mn, Hg, Cu, Mb, U, Zn, Pb & Zr are + indicators of petroleum deposits. Migrating hydrocarbons create a reducing environment in the soil and subsurface, which increases the solubility of many trace and major elements. In the present study, an attempt has been made to study the behaviour of metal concentrations with pH and Oxidation Reduction Potential (ORP). The maximum concentration of almost all metal was observed between pH 7.0 and 7.5 and ORP between 400 and 450 mv. The variation of analyzed trace metals with pH and ORP are shown in Fig. 28 and Fig. 29, respectively.




Zn
Pb
Cd
As
Hg
U
Ba
Sr
Conc. (ppb)
pH
5.5
6
6.5
7
7.5
8
8.5

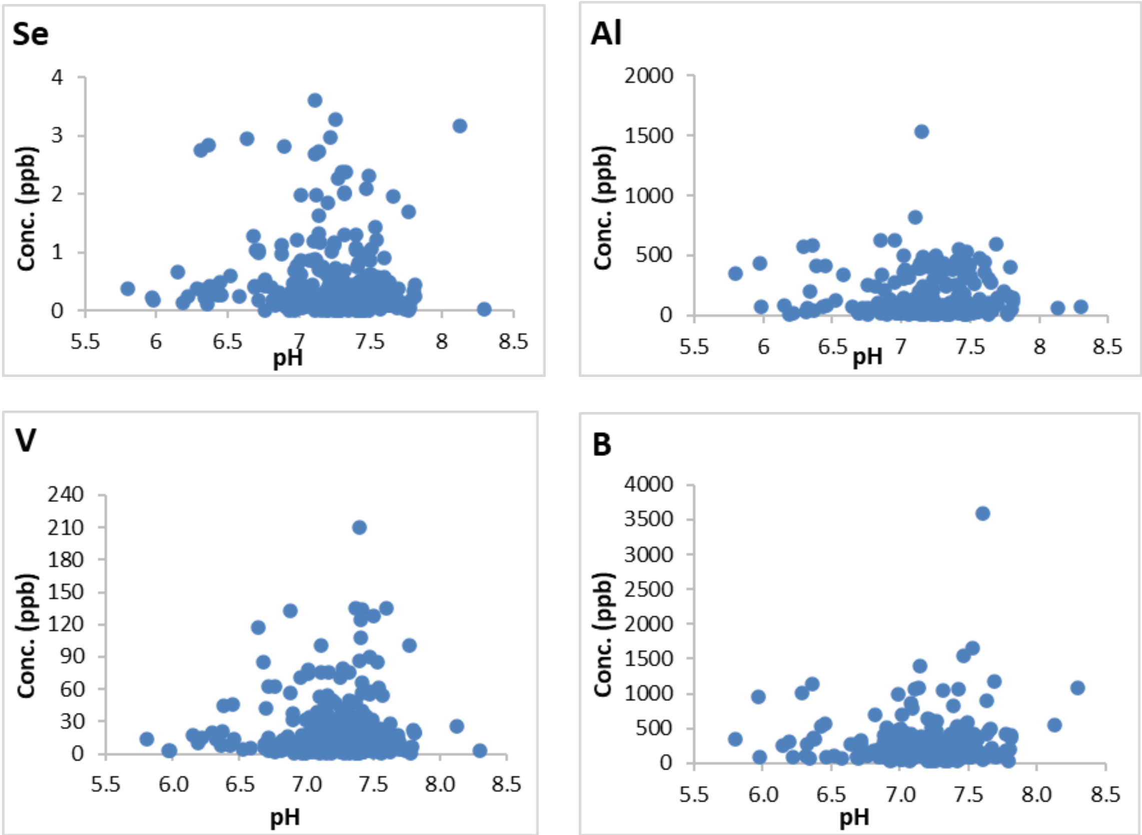
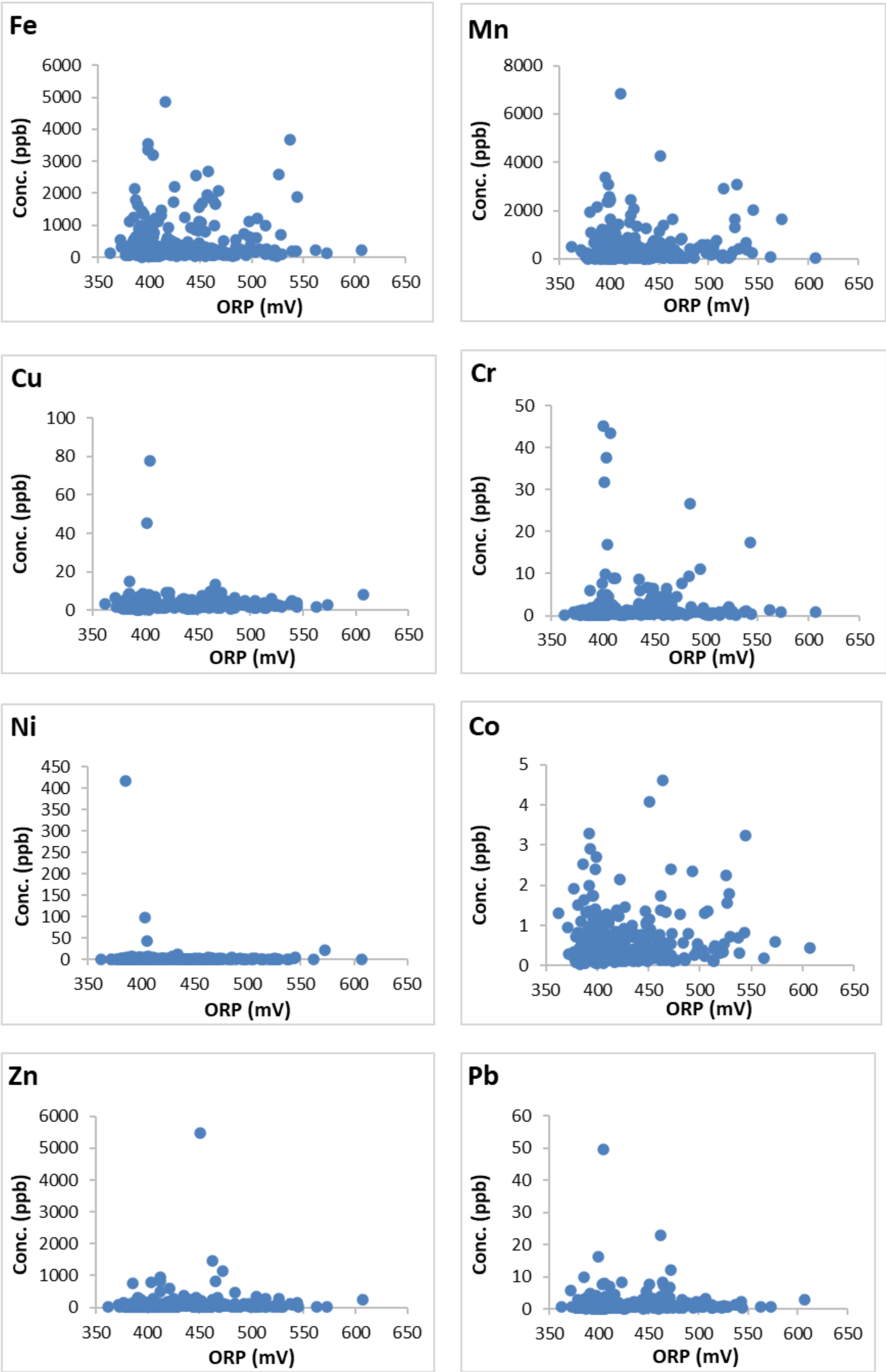
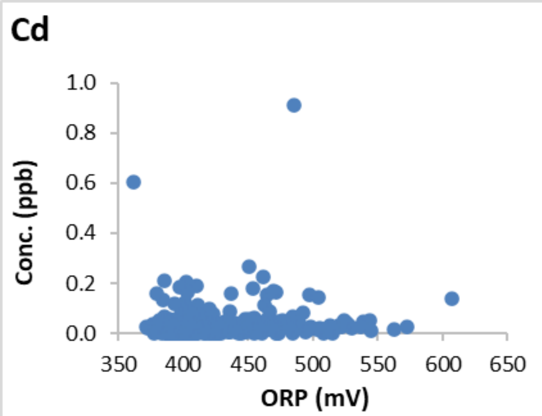
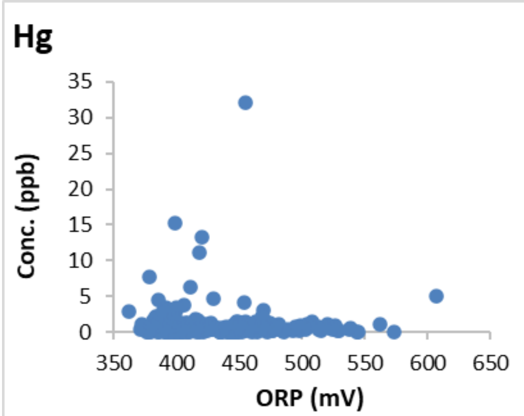
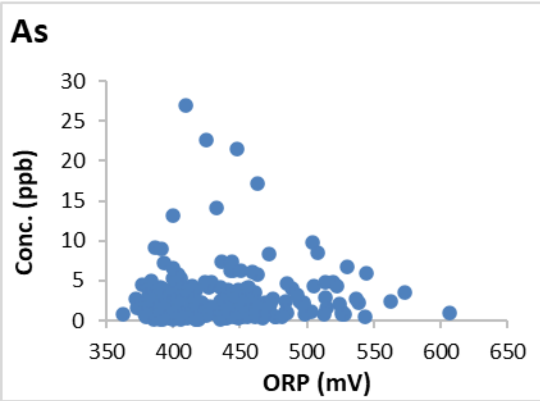


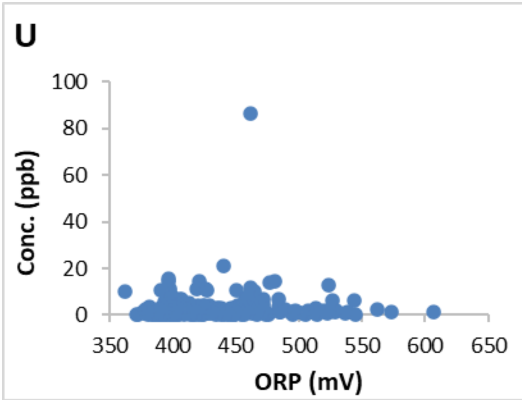
Fig. 28. Relationship of metal concentration in Groundwater with pH

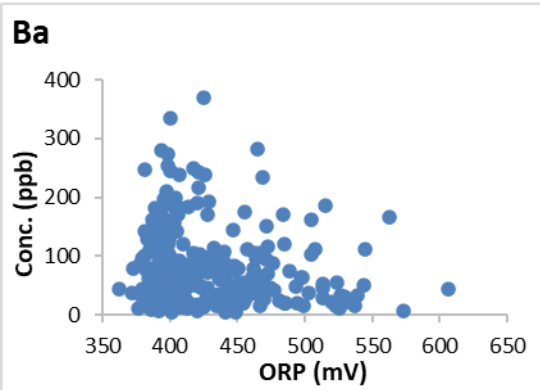

Fe
Conc. (ppb)
0
1000
2000
3000
4000
5000
6000
350
400
450
500
550
600
650
ORP (mV)
Mn
Conc. (ppb)
0
2000
4000
6000
8000
350
400
450
500
550
600
650
ORP (mV)
Cu
Conc. (ppb)
0
20
40
60
80
100
350
400
450
500
550
600
650
ORP (mV)
Cr
Conc. (ppb)
0
10
20
30
40
50
350
400
450
500
550
600
650
ORP (mV)
Ni
Conc. (ppb)
0
50
100
150
200
250
300
350
400
450
350
400
450
500
550
600
650
ORP (mV)
Co
Conc. (ppb)
0
1
2
3
4
5
350
400
450
500
550
600
650
ORP (mV)
Zn
Conc. (ppb)
0
1000
2000
3000
4000
5000
6000
350
400
450
500
550
600
650
ORP (mV)
Pb
Conc. (ppb)
0
10
20
30
40
50
60
350
400
450
500
550
600
650
ORP (mV)

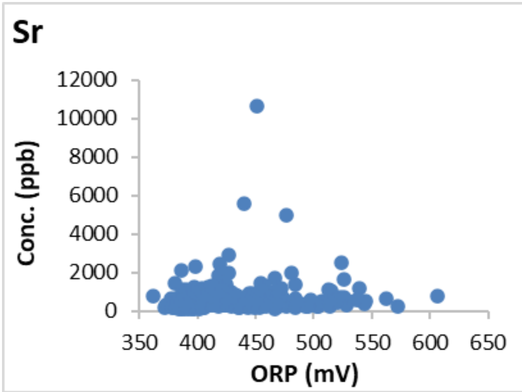

Cd
1.0
0.8
0.6
0.4
0.2
0.0
Conc. (ppb)
350 400 450 500 550 600 650
ORP (mV)

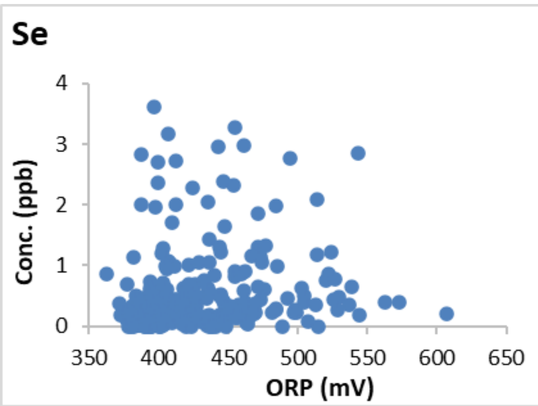

Hg
35
30
25
20
15
10
5
0
Conc. (ppb)
350 400 450 500 550 600 650
ORP (mV)

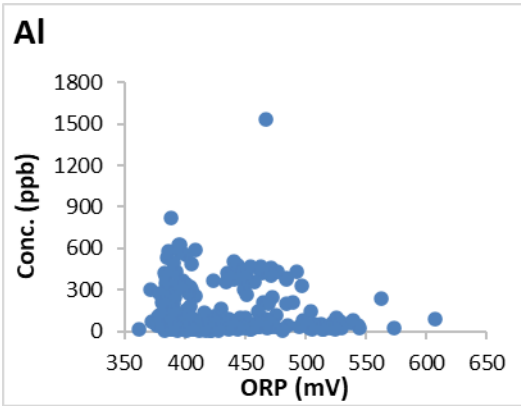

As
30
25
20
15
10
5
0
Conc. (ppb)
350 400 450 500 550 600 650
ORP (mV)


U
100
80
60
40
20
0
Conc. (ppb)
350 400 450 500 550 600 650
ORP (mV)


Ba
400
300
200
100
0
Conc. (ppb)
350 400 450 500 550 600 650
ORP (mV)


Sr
12000
10000
8000
6000
4000
2000
0
Conc. (ppb)
350 400 450 500 550 600 650
ORP (mV)


Se
4
3
2
1
0
Conc. (ppb)
350 400 450 500 550 600 650
ORP (mV)


Al
1800
1500
1200
900
600
300
0
Conc. (ppb)
350 400 450 500 550 600 650
ORP (mV)

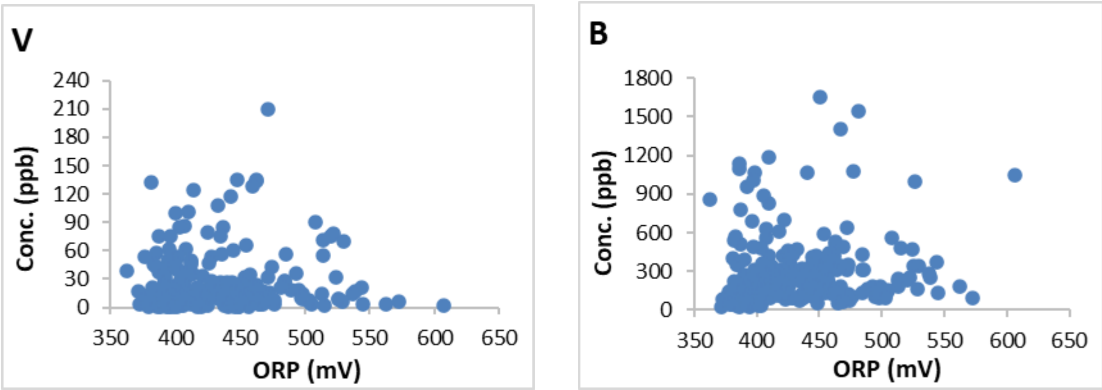


Fig. 29. Relationship of metal concentration in Groundwater with ORP

5.3 Hydrogeochemical Characteristics of Groundwater of Study Area

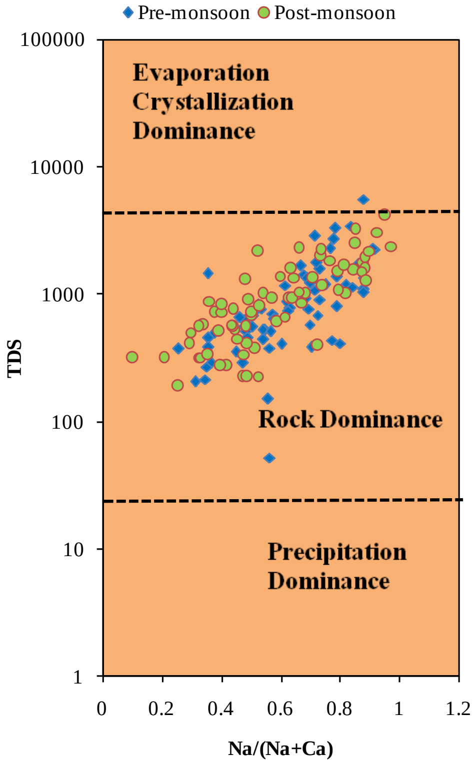
Geo-environmental conditions have a marked influence on the groundwater quality. Hydrogeochemical studies relevant to the water quality explain the relationship of water chemistry to aquifer lithology. Such relationship would help not only to explain the origin and distribution of dissolved constituents but also to elucidate the factors controlling the groundwater chemistry. Gibbs (1970) proposed a hypothesis to elucidate the major natural mechanisms controlling world water chemistry. Three mechanisms – atmospheric precipitation, rock dominance and the evaporation-crystallization process – are the major factors controlling the composition of dissolved salts of the world waters. Other second-order factors, such as relief, vegetation and composition of material in the basin dictate only minor deviations within the zones dominated by the three prime factors. Gibbs plot is a diagrammatic representation of the mechanisms responsible for controlling the chemical composition of various bodies of water on the surface of the earth. The major cations that characterize the end-member of the world surface waters are Ca for freshwater bodies and Na for high-saline water bodies. Gibbs plotted the weight ratio Na/(Na+Ca) on the x-axis and the variation in total salinity on the y-axis. This ordered arrangement can serve as a basis for discussion of the several mechanisms that control world water chemistry. The first of these mechanisms is the atmospheric precipitation. The chemical compositions of low-salinity waters are controlled by the amount of dissolved salts furnished by precipitation. These waters consist mainly of the rivers having sources in thoroughly leached areas of low relief in which the rate of supply of dissolved salts to the rivers is very low and the amount of rainfall is high – much greater in proportion to the low amount of dissolved salts supplied from the rocks. In addition, the composition of this precipitation differs from that of rock-derived dissolved salts. The second mechanism is the rock dominance controlling world water chemistry. The waters of this rock-dominated end-members are more or less in partial equilibrium with the materials in their basins. Their positions within this grouping are dependent on the relief and climate of each basin and the composition of each basin. The third major mechanism that controls the chemical composition of the earth's surface waters is the evaporation-fractional crystallization process. This mechanism produces a series extending from the Ca-rich, medium-salinity (freshwater), 'rock source' end-member grouping to the opposite, Na-rich, high-salinity end-member.

Godavari Delta

Almost all collected groundwater samples from study area in both seasons for the year 2022, fall in rock dominance zone suggesting precipitation induced chemical weathering along with dissolution of rock forming minerals (Fig. 30).

Scatter Plots between Ions

The ion ratio among the major ions of groundwater is widely used to illustrate the controlling processes of the groundwater system. The scatter plot of (Ca+Mg) vs TZ^+ shows that all the points fall above 1:1 equiline [Fig. 31(a-b)]. The relatively high contribution of (Ca+Mg) to the total cations (TZ^+) and high (Ca+Mg)/(Na+K) ratio indicate that carbonate weathering is a major source of dissolved ions in the groundwater of the study area [Fig. 31(a-b)]. The relatively high contributions of HCO_3 to Ca ratio indicate that carbonate weathering play major role in the chemistry of groundwater in Godavari delta basin. In addition, the scatter plot of (Ca vs Mg) displays that majority of the water samples fall in the zone of calcite dissolution as compare to silicate weathering zone, which illustrates that calcite rock weathering with less silicate weathering were main rock weathering factors controlling the chemistry of groundwater in Godavari delta basin. The scatter plot of (Na+K) vs TZ^+ shows that all the points fall above 1:1 equiline with a low ratio indicating a relatively low contribution of dissolved ions from silicate weathering [Fig. 31(a-b)]. Na^+, K^+ and dissolved silica in the drainage basin are mainly derived from the weathering of silicate minerals, with clay minerals as by-products. The plot of Na vs Cl indicates most of the points lie below the 1:1 equiline and on the 1:1 equiline reflecting halite dissolution through silicate weathering through the release of Na [Fig. 31(a-b)]. The plot of (Ca+Mg) vs HCO_3 for most of the samples in the study area indicates an excess of Ca+Mg over HCO_3 suggesting an extra source of Ca and Mg. This requires that a portion of the (Ca+Mg) has to be balanced by other anions like SO_4 and/or Cl. The plot of (Ca+Mg) vs HCO_3+SO_4 is a major indicator to identify the ion exchange process activated in the study area. If ion exchange is the process, the points shift to right side of the plot due to excess of HCO_3+SO_4. If reverse ions exchange is the process, points shift left due to excess Ca+Mg. Plot of (Ca+Mg) vs HCO_3+SO_4 shows that most of the plotted points clusters around the 1:1 equiline and fall in HCO_3+SO_4 indicating the ion exchange process which may be due to the excess of HCO_3+SO_4 [Fig. 31(a-b)]. In plot of Na vs (Ca+Mg), the most of the points fall below the 1:1 equiline with excess of Na over (Ca+Mg), also indicating the ion exchange process in the aquifer system. Moreover, plot of (Na+K-Cl) vs (HCO_3+SO_4-Ca-Mg) shows that most of water samples concentrated on or very close to 1:1 line, thereby indicating that cation exchange also plays main hydrogeochemical factor controlling the chemistry of groundwater of Godavari delta basin. The plot of Ca vs SO_4 indicates most of the points lie below the 1:1 equiline and showing the excess of Ca over SO_4, reflecting gypsum dissolution not occurring and there might be some other source of Ca in groundwater of the study area. The EC vs (Na/Cl) plot is used for evaporation process occurring in the water system by yielding a horizontal line. It is clearly depicted that the scattered points concentrated to form a bunch that reflecting the evaporation is not occurring in the groundwater system [Fig. 31(a-b)].



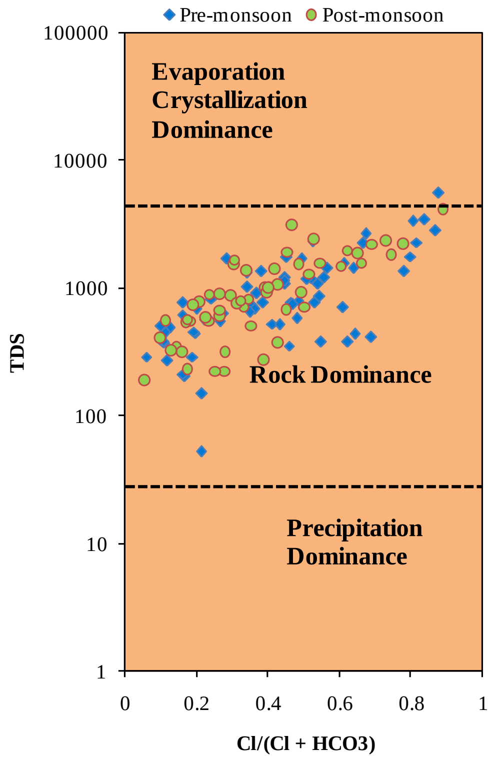


Fig. 30 Gibbs plot explaining the mechanism controlling the groundwater chemistry in Godavari delta

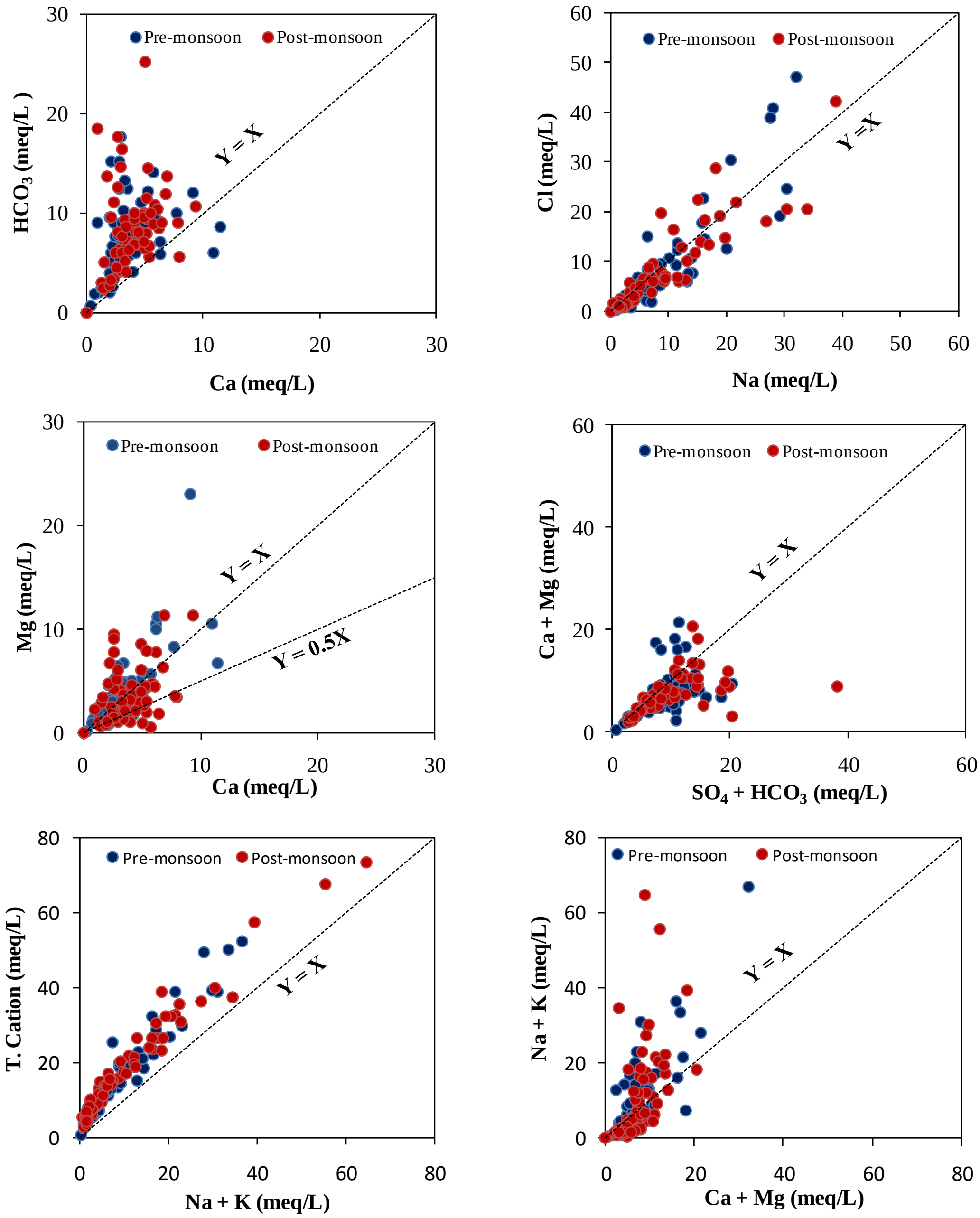


Fig. 31(a) Scatter plots of groundwater of Godavari delta

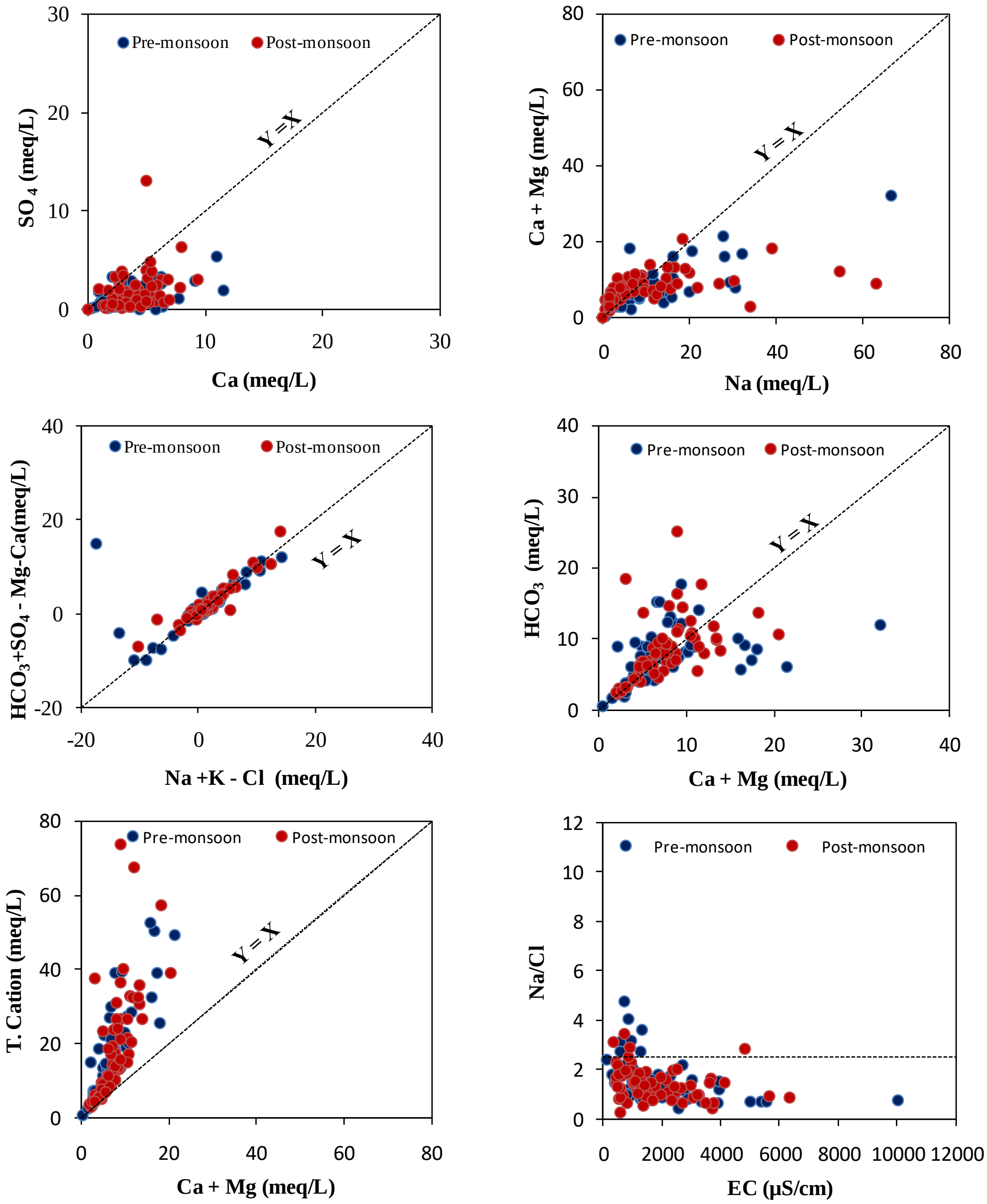


Fig. 31(b) Scatter plots of groundwater of Godavari delta

Krishna Delta

Almost all collected groundwater samples from study area in both seasons for the year 2022, fall in rock dominance zone suggesting precipitation induced chemical weathering along with dissolution of rock forming minerals. Few samples are away from this zone reflecting the contribution from evaporation crystallization process responsible for chemical composition of ground water of the study area (Fig. 32).

Scatter Plots between Ions

The ion ratio among the major ions of groundwater is widely used to illustrate the controlling processes of the groundwater system. The scatter plot of (Ca+Mg) vs TZ^+ shows that all the points fall above 1:1 equiline [Fig. 33(a-b)]. The relatively high contribution of (Ca+Mg) to the total cations (TZ^+) and high (Ca+Mg)/(Na+K) ratio indicate that carbonate weathering is a major source of dissolved ions in the groundwater of the study area [Fig. 33(a-b)]. The relatively high contributions of HCO_3 to Ca ratio indicate that carbonate weathering play major role in the chemistry of groundwater in Godavari delta basin. In addition, the scatter plot of (Ca vs Mg) displays that majority of the water samples fall in the zone of calcite dissolution, which illustrates that calcite rock weathering was main rock weathering factors controlling the chemistry of groundwater in Krishna delta basin. The scatter plot of (Na+K) vs TZ^+ shows that all the points fall above 1:1 equiline with a low ratio indicating a relatively low contribution of dissolved ions from silicate weathering [Fig. 33(a-b)]. Na^+, K^+ and dissolved silica in the drainage basin are mainly derived from the weathering of silicate minerals, with clay minerals as by-products. The plot of Na vs Cl indicates most of the points lie below the 1:1 equiline and on the 1:1 equiline reflecting halite dissolution through silicate weathering through the release of Na [Fig. 33(a-b)]. The plot of (Ca+Mg) vs HCO_3 for most of the samples in the study area indicates an excess of Ca+Mg over HCO_3 suggesting an extra source of Ca and Mg. This requires that a portion of the (Ca+Mg) has to be balanced by other anions like SO_4 and/or Cl. The plot of (Ca+Mg) vs HCO_3+SO_4 is a major indicator to identify the ion exchange process activated in the study area. If ion exchange is the process, the points shift to right side of the plot due to excess of HCO3+SO4. If reverse ions exchange is the process, points shift left due to excess Ca+Mg. Plot of (Ca+Mg) vs HCO_3+SO_4 shows that most of the plotted points clusters around the 1:1 equiline and fall in HCO_3+SO_4 indicating the ion exchange process which may be due to the excess of HCO_3+SO_4 [Fig. 33(a-b)]. In plot of Na vs (Ca+Mg), the most of the points fall below the 1:1 equiline with excess of Na over (Ca+Mg), also indicating the ion exchange process in the aquifer system. Moreover, plot of (Na+K-Cl) vs (HCO_3+SO_4-Ca-Mg) shows that most of water samples concentrated on or very close to 1:1 line, thereby indicating that cation exchange also plays main hydrogeochemical factor controlling the chemistry of groundwater of Krishna delta basin. The plot of Ca vs SO4 indicates most of the points lie below the 1:1 equiline and showing the excess of Ca over SO4, reflecting gypsum dissolution not occurring and there might be some other source of Ca in groundwater of the study area.n The EC vs (Na/Cl) plot is used for evaporation process occurring in the water system by yielding a horizontal line. It is clearly depicted that the scattered points formed almost a horizontal line that reflecting the evaporation process in the groundwater system [Fig. 33(a-b)].

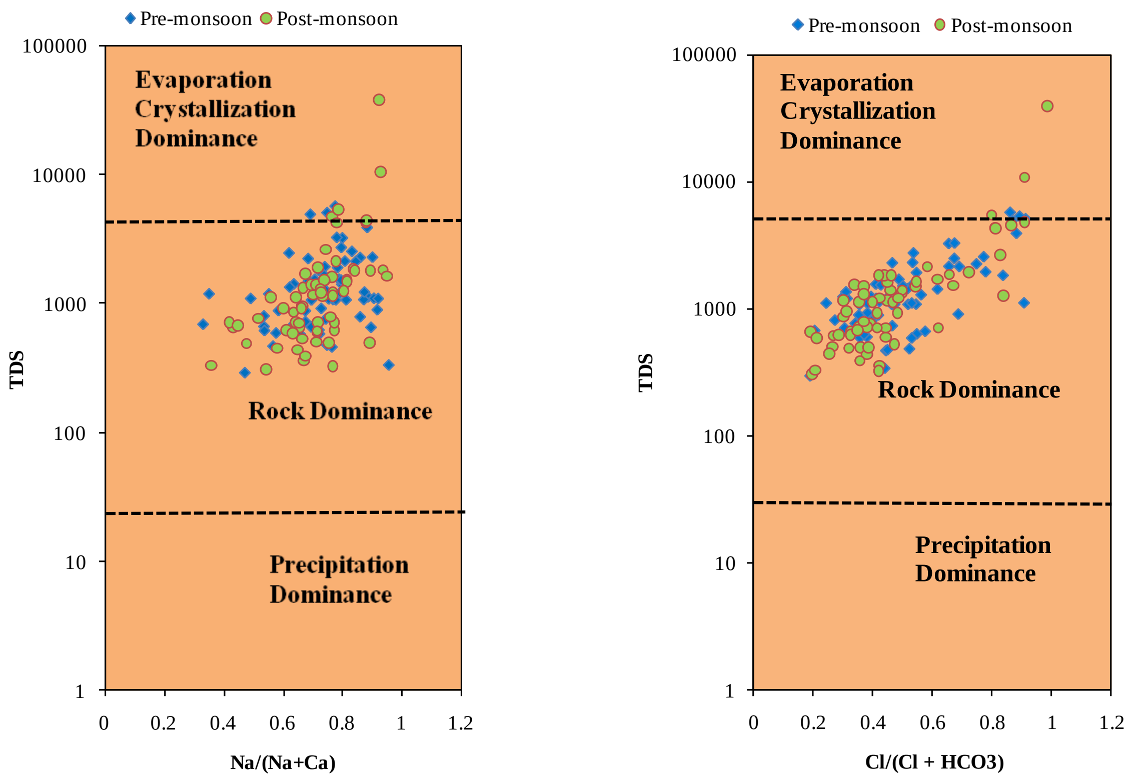


Fig. 32 Gibbs plot explaining the mechanism controlling the groundwater chemistry in Krishna delta

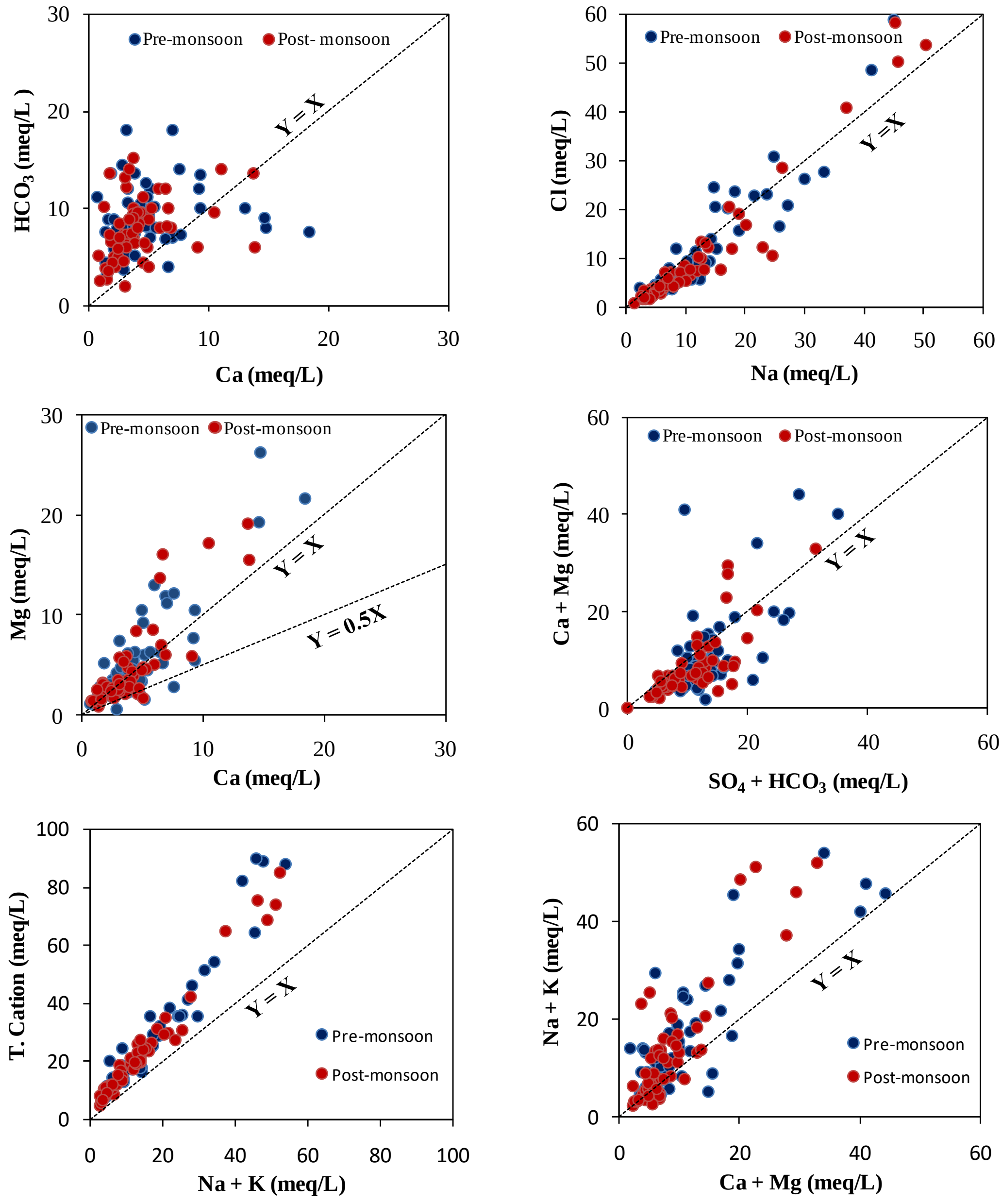


Fig. 33(a). Scatter plots of groundwater of Krishna delta

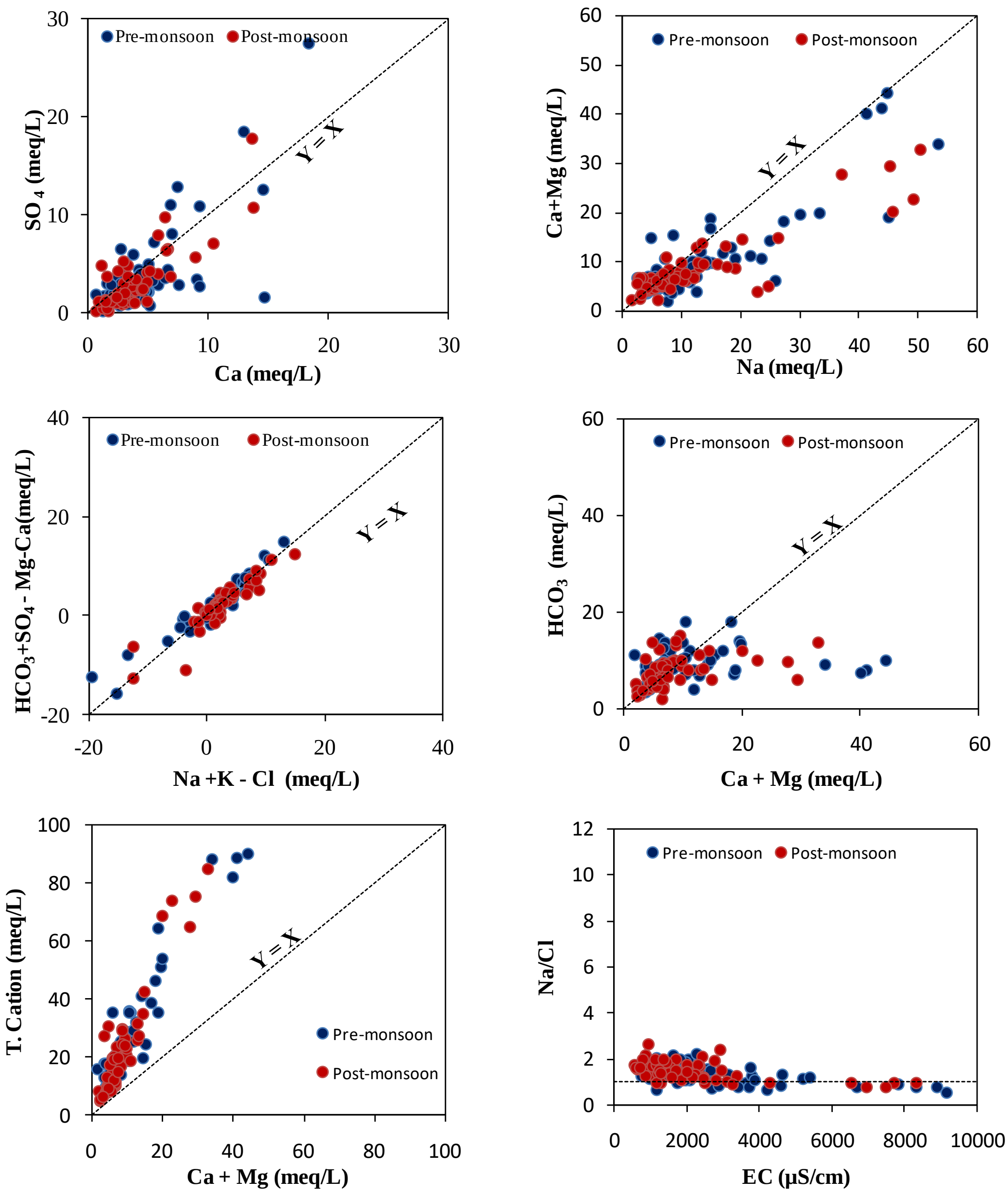


Fig. 33(b) Scatter plots of groundwater of Krishna delta

5.4 Classification of Groundwater of Study Area

Different accepted and widely used graphical methods such as Piper trilinear diagram and Chadha's diagram have been used in the present study to classify the ground water of the study area. Piper trilinear diagram (Piper, 1944) and Chadha's diagram (Chadha, 1999) are used to express similarity and dissimilarity in the chemistry of water based on major cations and anions.

Piper Trilinear Classification

Piper (1944) has developed a form of trilinear diagram, which is an effective tool in segregating analysis data with respect to sources of the dissolved constituents in ground water, modifications in the character of water as it passes through an area and related geochemical problems. The diagram is useful in presenting graphically a group of analysis on the same plot. The Piper trilinear diagram combines three areas of plotting, two triangular areas (cations and anions) and an intervening diamond-shaped area (combined field). Using this diagram water can be classified into different hydrochemical facies. The chemical analysis data of ground water samples of the study area (Godavari and Krishna delta) have been plotted on trilinear diagram for both the season (Pre- & Post-monsoon) for the year 2022 [Fig. 34(a-b)]. It is evident from the results that majority of the samples of the study area belong to Na-Cl-SO_4 and Ca-Mg-HCO_3 hydrochemical facies in both the basin during pre- and post-monsoon seasons.

Chadha's diagram

Modified version of the piper trilinear diagram is developed by Chadha (1999). In the piper diagram the milliequivalent percentages of the major cations and anions are plotted in two base triangles and the type of water is determined on the basis of position of the data in the respective cationic and anionic triangular fields. The plottings from triangular fields are projected further into the central diamond field, which represents the overall character of the water. Piper diagram allow comparisons to be made among numerous analyses, but this type of diagram has a drawback, as all trilinear diagram do, in that it does not portray actual ion concentration. The distribution of ions within the main field is unsystematic in hydrochemical process terms, so the diagram lacks certain logic. This method is not very convenient when plotting a large volume of data. Nevertheless, this shortcoming does not lessen the usefulness of the Piper diagram in the representation of some geochemical processes. In contrast, in Chadha's diagram, the difference in milliequivalent percentage between alkaline earths (calcium plus magnesium) and alkali metals (sodium plus potassium), expressed as percentage reacting values, is plotted on the X axis and the difference in milliequivalent percentage between weak acidic anions (carbonate plus bicarbonate) and strong acidic anions (chloride plus sulphate) is plotted on the Y axis. The resulting field of study is a square or rectangle depending upon the size of the scales chosen for X and Y coordinates. The milliequivalent percentage differences between alkaline earth and alkali metals and between weak acidic anions and strong acidic anions would plot in one of the four possible sub-fields of the diagram. The main advantage of this diagram is that it can be made simply on most spreadsheet software packages. In order to define the primary character of water, the rectangular field is divided into eight sub-fields, each of which represents a water type, as follows: 1. Alkaline earth exceeds alkali metals. 2. Alkali metals exceed alkaline earth. 3. Weak acidic anions exceed strong acidic anions. 4. Strong acidic anions exceed weak acidic anions. 5. Alkaline earths and weak acidic anions exceed both alkali metals and strong acidic anions respectively. Such water has temporary hardness. The position of data points in the diagram represent Ca^{2+}-Mg^{2+}-HCO_3^- type, Ca^{2+}-Mg^{2+}- dominant HCO_3 - type, or HCO_3^- - dominant Ca^{2+}-Mg^{2+}- type waters. 6.

Alkaline earths exceed alkali metals and strong acidic anions exceed weak acidic anions. Such water has permanent hardness and does not deposit residual sodium carbonate in irrigation use. The position of data points in the diagram represents Ca^{2+}-Mg^{2+}-Cl - type, Ca^{2+}-Mg^{2+}- dominant Cl^- - type or Cl^- - dominant Ca^{2+}-Mg^{2+}- type waters. 7. Alkali metals exceed alkaline earths and strong acidic anions exceed weak acidic anions. Such water generally creates salinity problems both in irrigation and drinking uses. The position of data points in the diagram represent Na^+ - Cl^- - type, Na_2SO_4- type, Na^+ -dominant Cl^- -type, or Cl^- -dominant Na^+ -type waters. 8. Alkali metals exceed alkaline earths and weak acidic anions exceed strong acidic anions. Such waters deposit residual sodium carbonate in irrigation use and cause foaming problems. The positions of data points in the diagram represent Na^+ - HCO_3^- - type, Na^+ -dominant HCO_3^- -type, or HCO_3^- -dominant Na^+ -type waters. The chemical analysis data of ground water samples of the study area have been plotted using Chadha's diagram for both the basin (Godavari and Krishna delta) for the year 2022 [Fig. 35(a-d)]. It is evident from the results that majority of the samples of both the basin belong to Na-Cl-SO_4 or Ca-Mg-HCO_3 hydrochemical facies in both pre- and post-monsoon seasons.

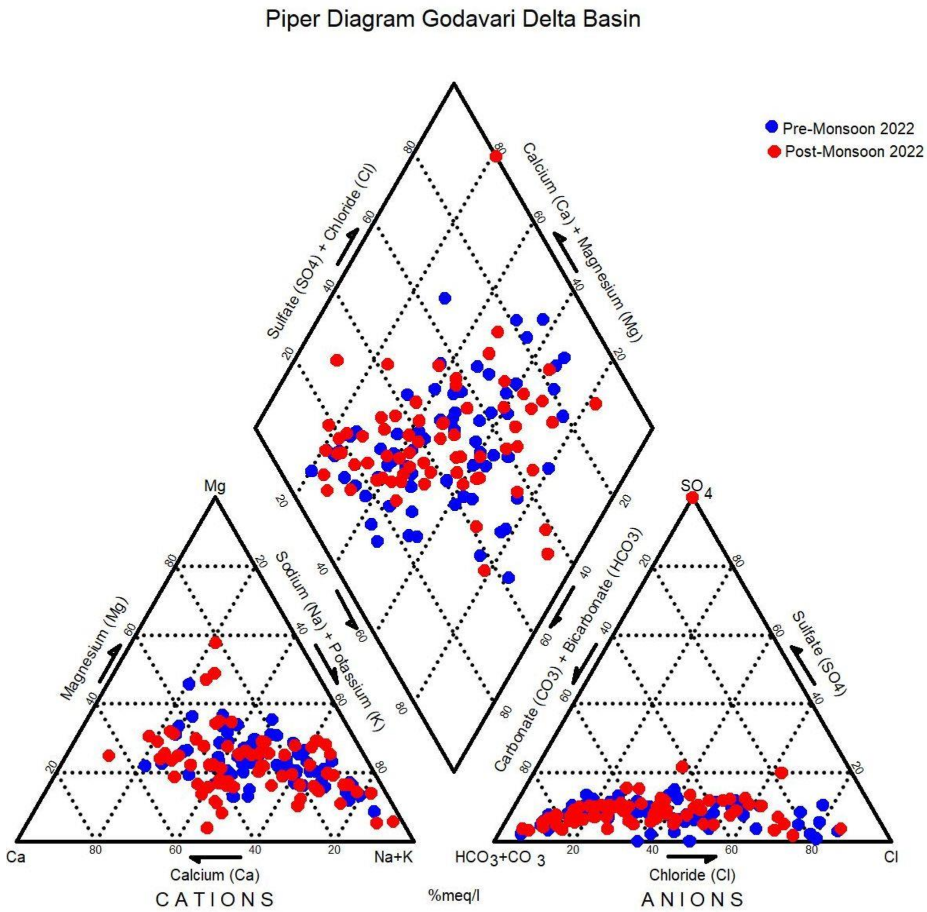


Fig. 34(a) Piper Trilinear Diagram for Godavari delta

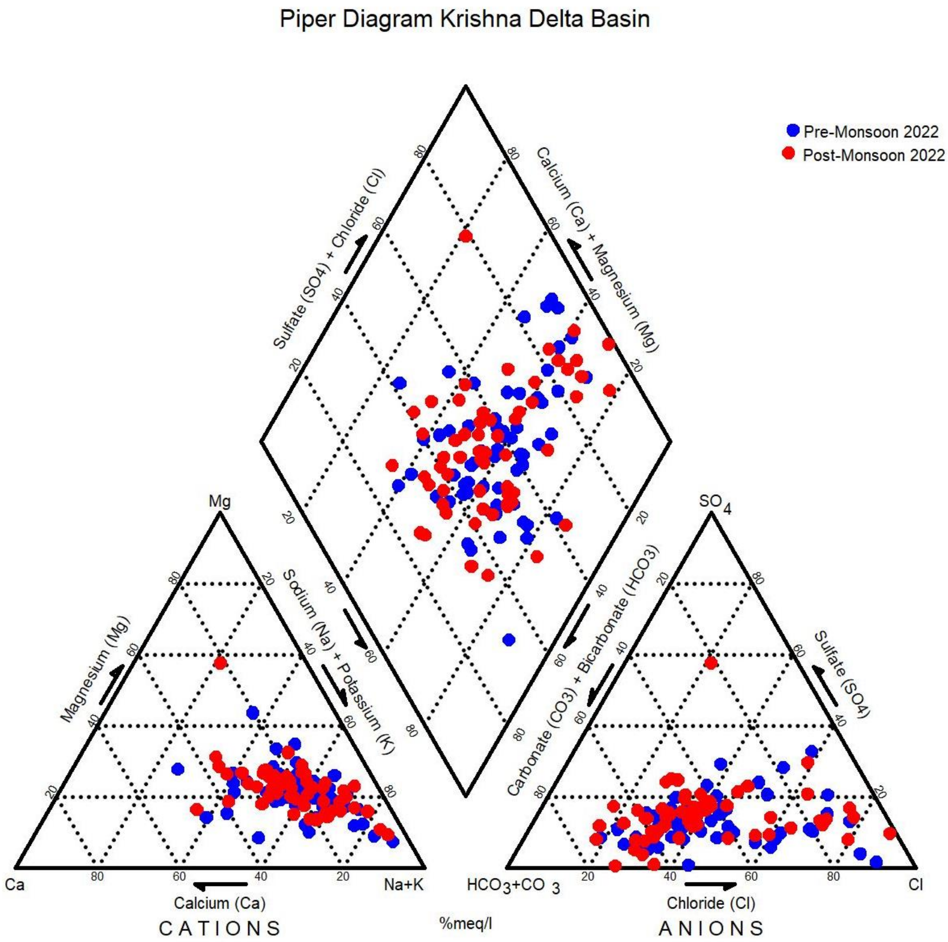


Fig. 34(b) Piper Trilinear Diagram for Krishna delta

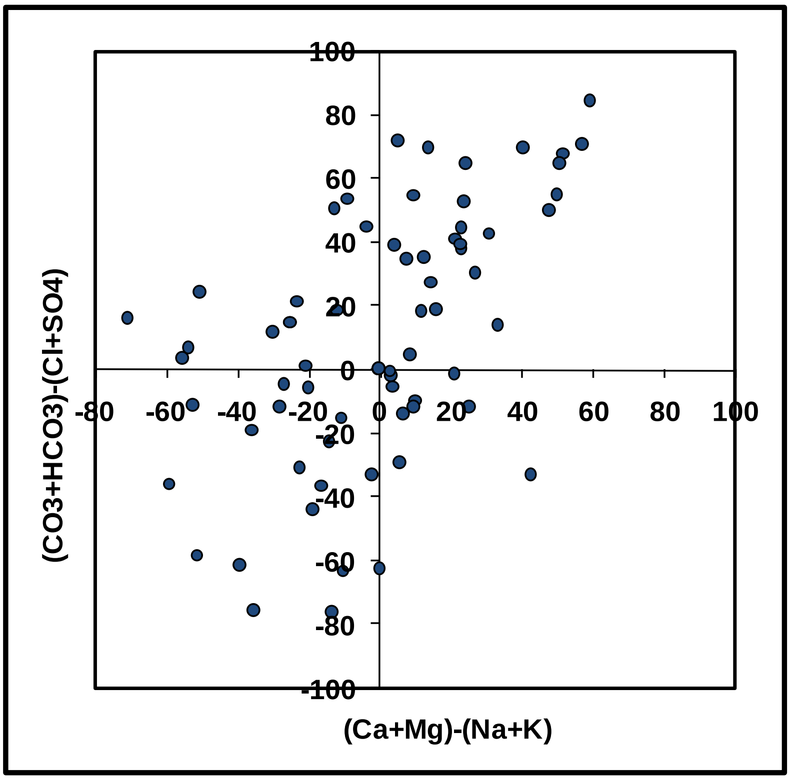


Fig. 35(a). Chadha's Diagram (Pre-monsoon 2022) for Godavari delta

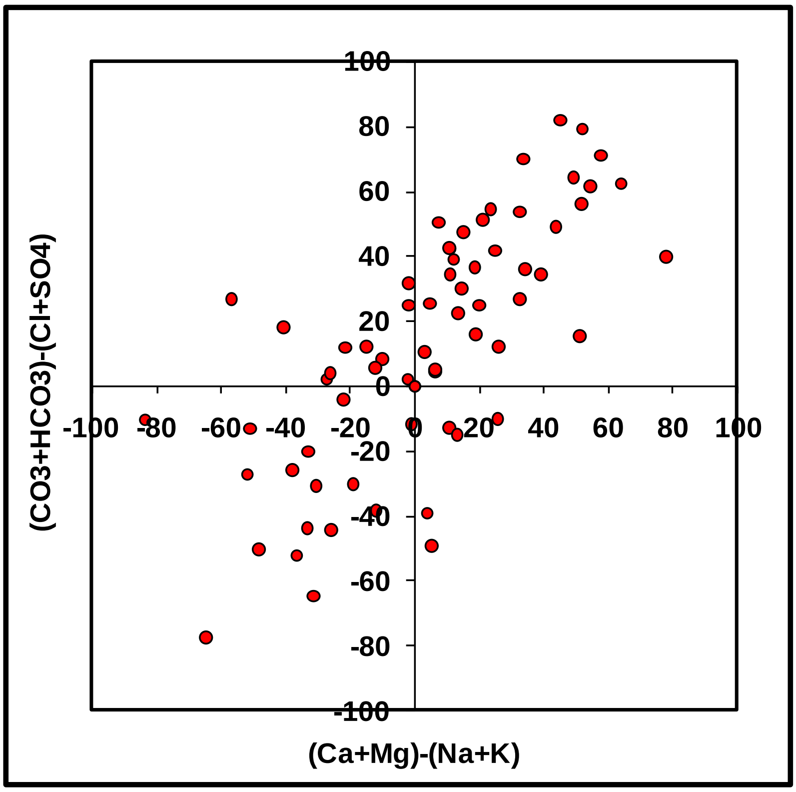


Fig. 35(b). Chadha's Diagram (Post-monsoon 2022) for Godavari delta

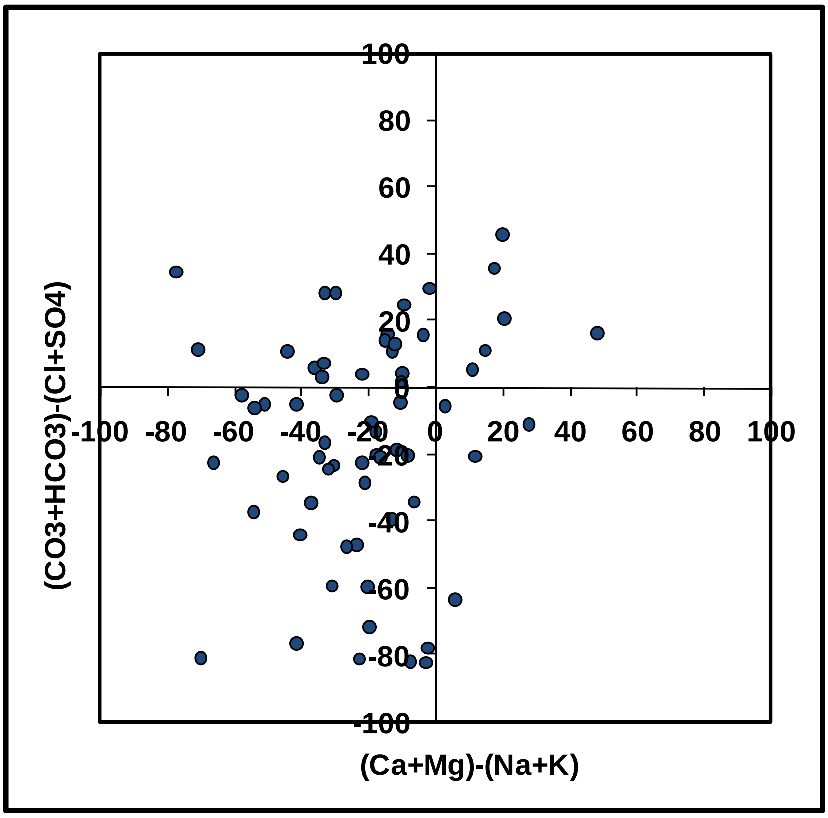


Fig. 35(c). Chadha's Diagram (Pre-monsoon 2022) for Krishna delta

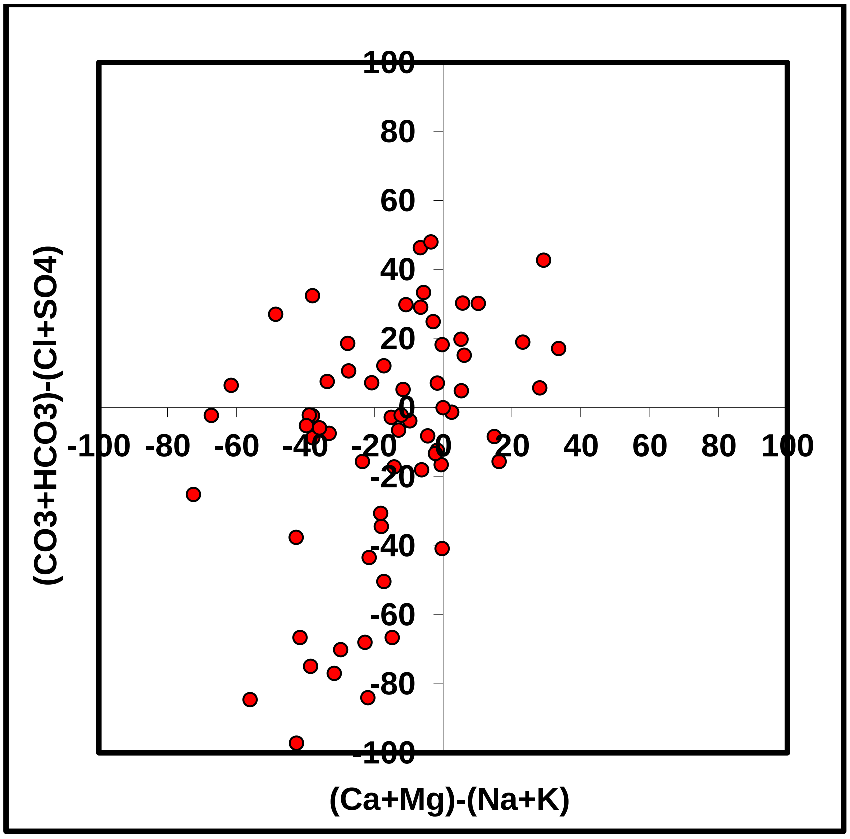


Fig. 35(d). Chadha's Diagram (Post-monsoon 2022) for Krishna delta

5.5 Stable Isotopic Characterization of Shallow Groundwater in the Krishna and Godavari Deltas

To determine the sources of groundwater recharge and salinity in the Krishna-Godavari (KG) deltas, stable isotope ($\delta^{18}O$ and $\delta^{2}H$) analysis has been conducted on groundwater samples collected from the CGWB monitoring network. The locations of these wells are shown in Fig 36. The Godavari delta is primarily located in the East Godavari and West Godavari districts. Similarly, the Krishna delta is distributed in Krishna and Guntur districts. A total of 137 groundwater samples have been collected in the month of June 2023 for stable isotope analysis, out of which 32 samples were analyzed (based on the depth of the well) for tritium dating. The range of depth of wells among 137 wells varies between 4 to 15 m except in a few wells (4 No.) which are between 200 to 300 m.

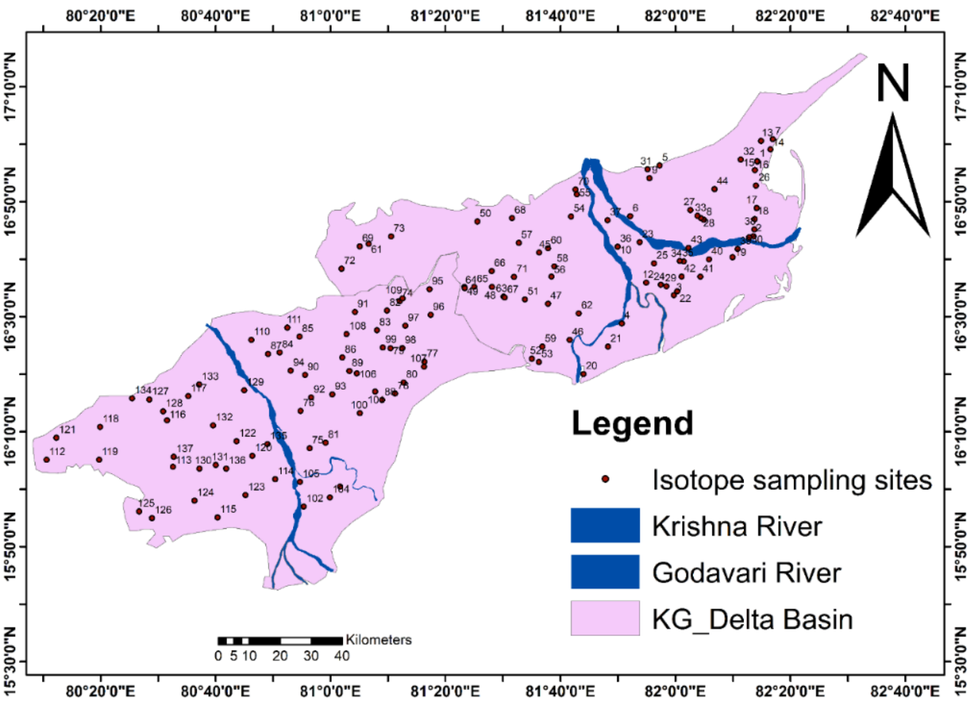


Fig. 36. Location of Groundwater observation well network of CGWB in the KG deltas

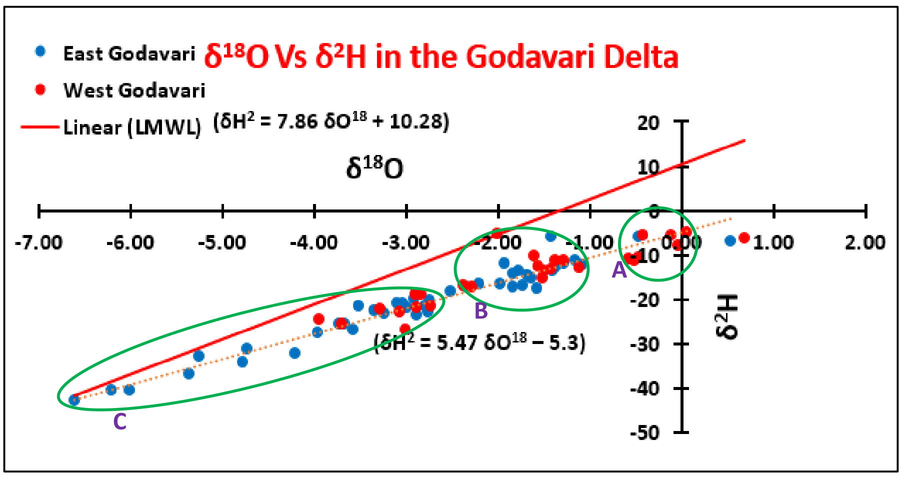


Fig. 37. $\delta^{18}O$–$\delta^{2}H$ relationship of shallow wells in the East and West Godavari districts

Fig. 37 shows the isotopic trend lines for groundwater data of shallow wells in the Godavari delta. The plot is compared with the Local Meteoritic Water line (LMWL) and a slope of 5.47 occurred for the stable isotopes. Fig. 37 clearly shows that there is no direct rainfall recharge into groundwater in the Godavari delta. A few of the shallow wells of West Godavari fell in Group A similar to the seawater characteristics representing the seawater mixing process. The shallow wells that fell in Group B have enriched isotopic signatures, representing the evaporation process during infiltration. Most of the shallow wells in the East and West Godavari districts with high depletion of stable isotopes ($\delta^{18}O$: -4 to -7) represent the fresh surface water recharge by canals.

The plot between $\delta^{18}O$ and $\delta^{2}H$ for the shallow groundwater samples is shown in Fig. 38 for Krishna delta and also compared with the Local Meteoritic Water Line (LMWL). The low slope (4.9) in the shallow wells of the Krishna delta (Krishna and Guntur districts) indicated more evaporation, whereas the high slope (5.47) represents low evaporation process in the Godavari delta (East and West Godavari districts). Fig. 38 also shows that there is no direct rainfall recharge into groundwater in the Krishna delta. In the case of the Krishna delta, eight shallow wells of Krishna district fell in group 'A' which are far away from the seawater zone and showed very high isotopic enrichment due to the dominance of high evaporation process. Few of the shallow wells of Krishna and Guntur districts have fallen in Group B enriched stable isotopes and have similar to the seawater characteristics representing the seawater mixing process. Most of the shallow wells of Krishna and Guntur districts fallen in Group C show enriched stable isotopes shows evaporation dominance.

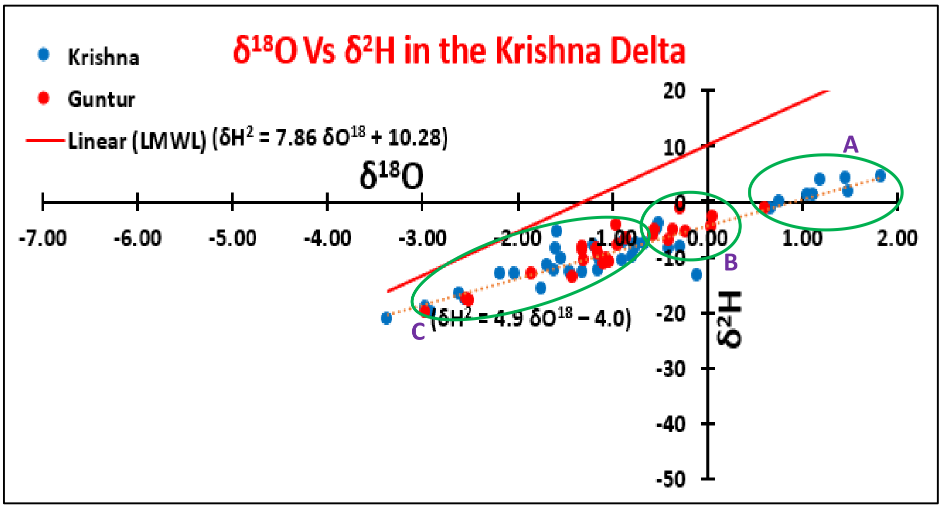


Fig. 38. $\delta^{18}O$–$\delta^{2}H$ relationship of shallow wells in the Krishna and Guntur districts

The origin of salinity in the shallow wells of East and West Godavari districts (Godavari Delta) is explained by the $\delta^{18}O$–EC relation (Fig. 39). Most of the shallow wells have very low EC values (<1000 µS/cm) and have a large variation in $\delta^{18}O$ content (0 to -7 ‰) represent recharged surface water. Few shallow wells of East and West Godavari districts in Group B have low EC values (1000-2000 µS/cm) with large variations in $\delta^{18}O$ values, showing a mixing process (freshwater with saline soils) during infiltration. A narrow change in $\delta^{18}O$ values (0 to -3.5‰) with a large variation in EC values (2000-5800 mg/L) in Group 'C' represents the leaching process of chloride from the land surface due to seepage of intermixed brackish water into shallow groundwater.

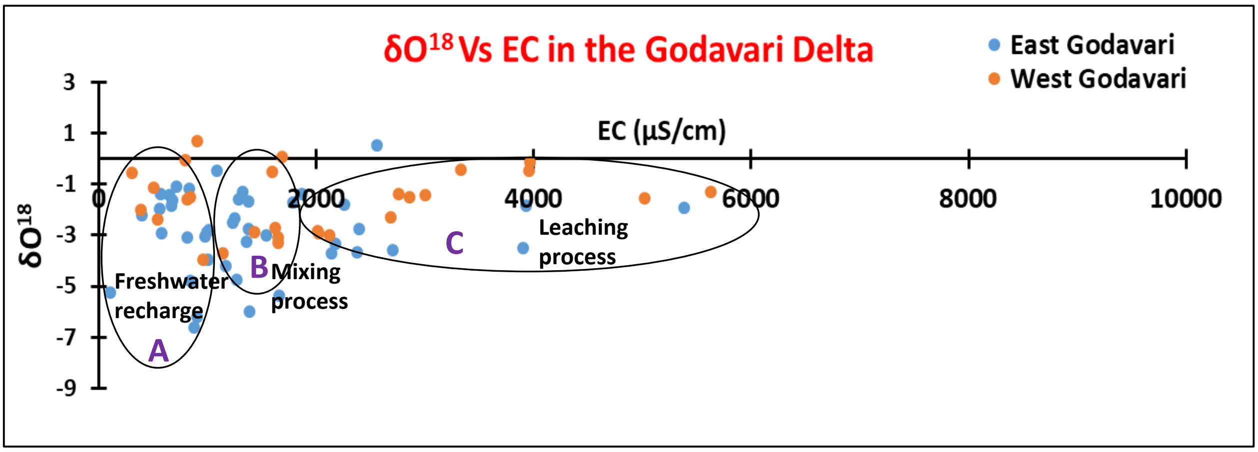


Fig. 39. Scatter plot of EC versus δ^{18}O of shallow wells in the East and West Godavari districts

The scatter plot of δ^{18}O–EC of shallow wells in the Krishna and Guntur districts (Krishna Delta) is shown in the Fig. 40. Group 'A' represents highly enriched δ^{18}O values with moderate to high EC values (1000-6800 µS/cm) representing evaporation dominance. Group B denotes enriched δ^{18}O isotopic content with moderate EC values (EC: 1000-2000 µS/cm) and have a large variation in δ^{18}O content represent the mixing process by the recharged surface water with saline soils. A narrow change in δ^{18}O values (-1 to -3.5‰) with a large variation in chloride content (2000-5000 mg/L) in Group 'C' represents the leaching process of chloride from the land surface. No freshwater zone appeared, and mixing, leaching & evaporation enrichment are the dominant processes for obtaining salinity in the Krishna delta. It is observed from the stable isotope analysis that the groundwater salinity due to saline water mixing is more in the Krishna delta than in Godavari delta. The comparison of these scatter plots (δ^{18}O–EC in Fig. 39 and Fig. 40) indicated that the stable isotopes are enriched in the Krishna delta than in the Godavari delta. This may be due to denser canal network and fresh water availability in the Godavari Delta than in Krishna delta.

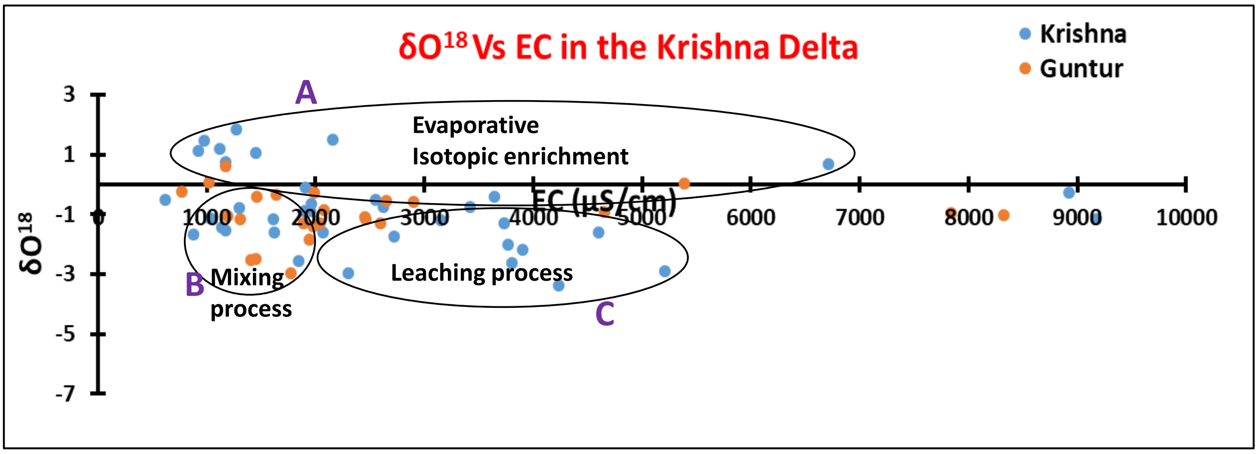


Fig. 40. Scatter plot of EC versus δ^{18}O of shallow wells in the Krishna and Guntur districts

A total of 32 groundwater samples are analyzed for the tritium analysis, and the locations are shown in Fig. 41. Out of 32 wells, 28 wells are shallow wells (< 12 m depth), and 4 wells are deep wells (190-300 m depth). All the deep wells are located in the Krishna district.

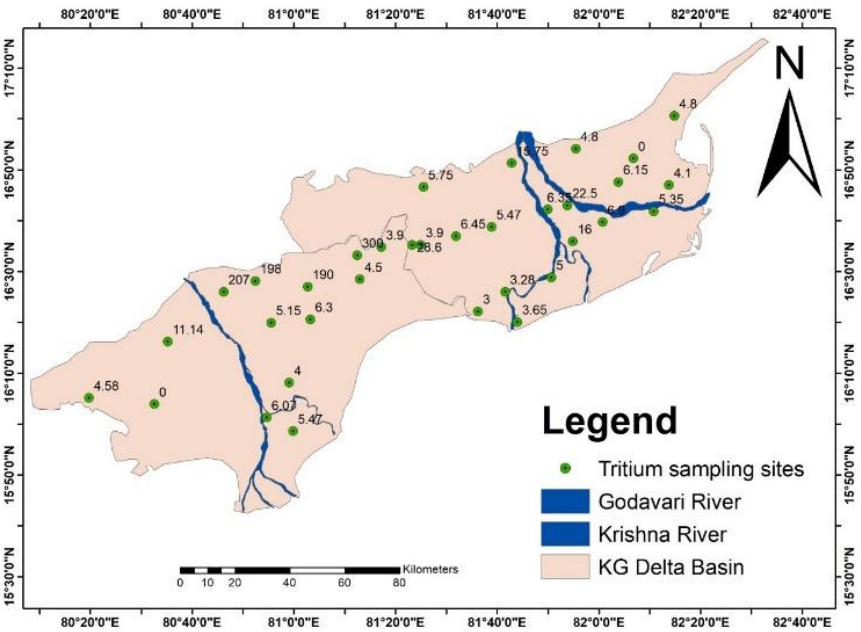


Fig. 41. Spatial network wells considered for Tritium (TU) in KG Deltas

Shallow groundwater levels (m, amsl) and EC values are plotted in Fig. 42. Except one well, remaining groundwater levels are in the range of 2-20 m (amsl) and EC values are in the range of 500-3500 µS/cm). No proper relation has been established between groundwater levels and EC values (Fig. 42).

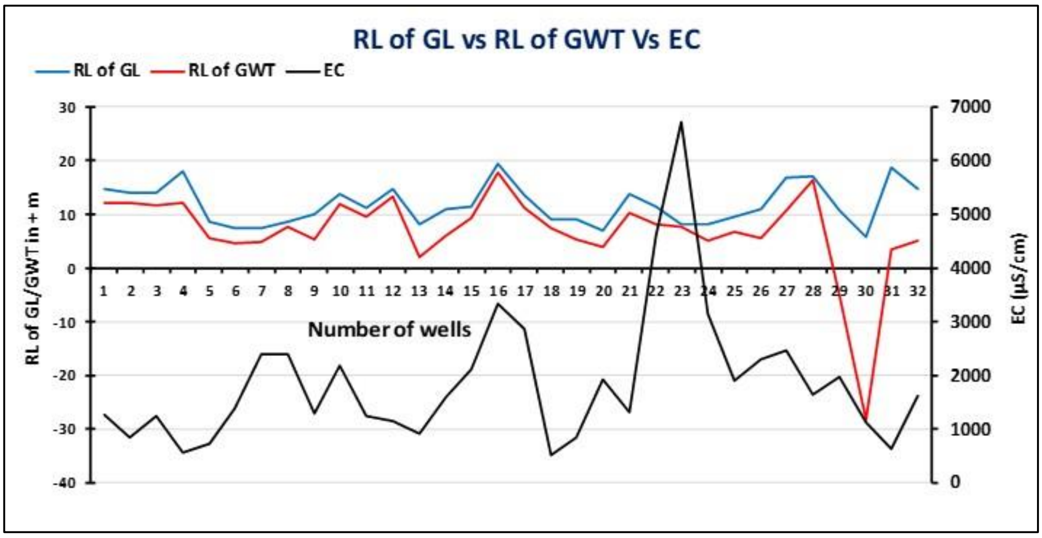


Fig. 42. Plot of groundwater level (amsl) and corresponding EC values

Spatial distribution of Tritium (TU) of groundwater samples (21 shallow and 4 deep wells) are shown in Fig. 43. Tritium is used for determining the relative ages of groundwater. 1 TU is equal to one tritium atom per 10^{18} hydrogen atoms, corresponding to 0.120 Bq/L for water at standard temperature and pressure. It is a standard dating tool for groundwater up to the age range of 100 years. Tritium content in water with less than 1 TU are at least 45 year old and less than 0.25 TU are more than 60 year old.

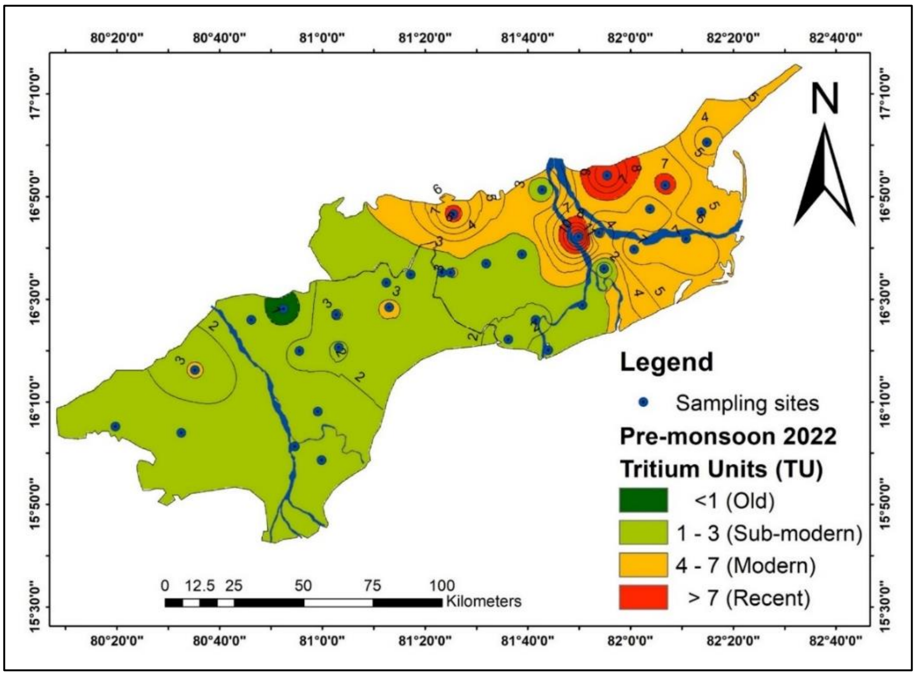


Fig. 43 Spatial distribution of Tritium (TU) in groundwater in the KG deltas

The plot of tritium contents versus depth is presented in Fig. 44. From the plot, it can be seen that seven shallow groundwater samples have tritium content in the range of 7–11.5 TU, indicating that groundwater is modern recharged by canals in the Godavari delta. Some of the shallow groundwater in the Godavari delta, as well as all shallow and deep groundwater in the Krishna delta, have less tritium content (1-3 TU), showing that this groundwater is older than 25–30 years. Only one deep groundwater sample in the Krishna delta has tritium content less than 1, indicating it is nearly 45 years old.

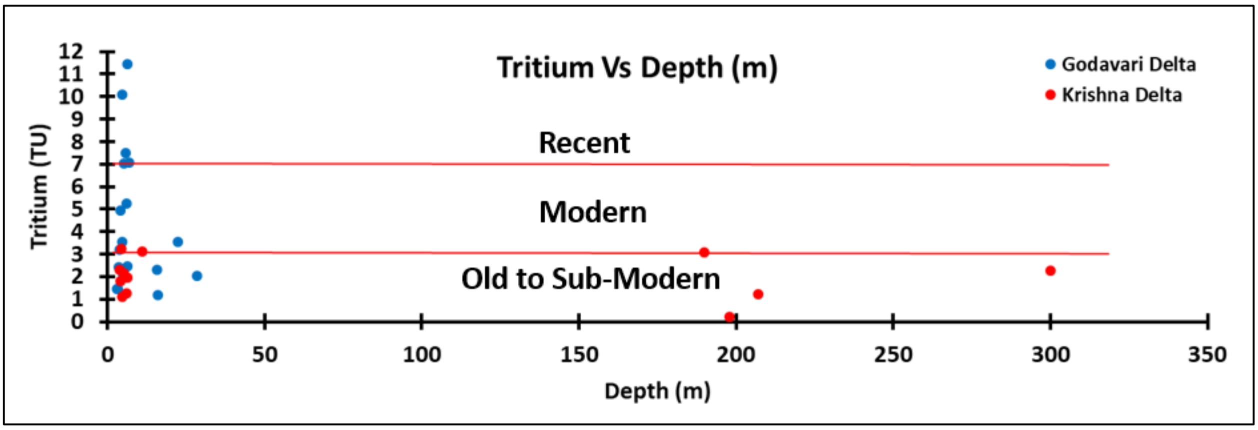


Fig. 44. Tritium content versus depth plot of groundwater in the KG deltas

Stable isotopes of these 32 groundwater samples are shown separately in the $\delta^{18}O–\delta^{2}H$ relationship (Fig. 45). Similar to the Fig. 37 and Fig. 38, significant evaporation occurred in the Krishna delta (slope: 3.6) than in Godavari delta (slope 5.5). Additionally, shallow groundwater of Krishna delta in the Group A is close to the seawater zone which implies groundwater of Krishna delta has dominance of mixing processes with saline water over Godavari delta. More depletion of stable isotopes have lesser salinity (Zone A in Fig. 39) and recent recharge by canals of Godavari delta represented in Group B in Fig. 45.

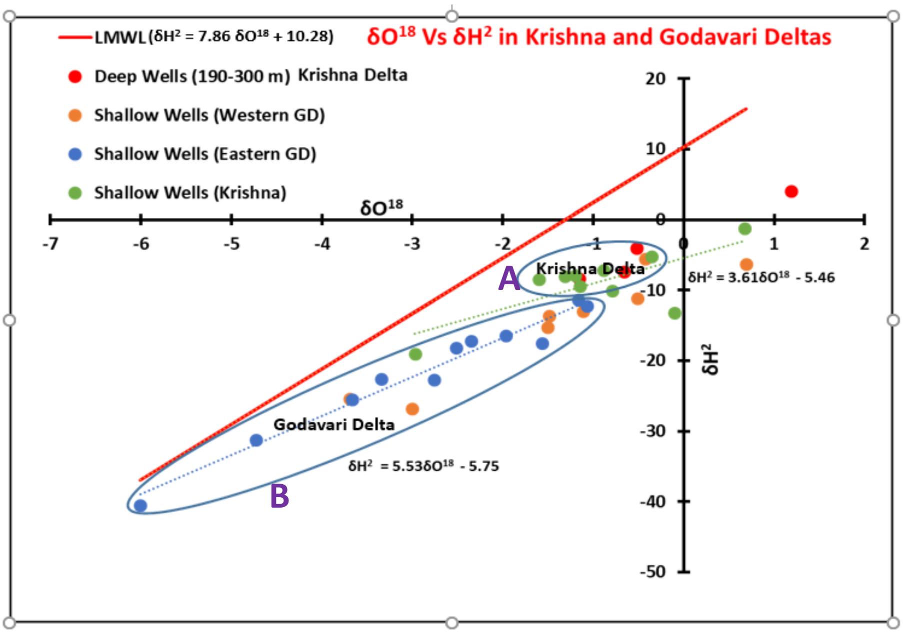


Fig. 45. $\delta^{18}O$–$\delta^{2}H$ relationship of shallow (28 No.) and deep (4 No.) wells in the KG deltas

It is observed from the Fig. 46 that the d-excess of most of the shallow wells in the Krishna and Godavari deltas have negative values, suggesting old recharge and mixing process with saline water seepage. The negative d-excess values are associated with heavier values of $\delta^{18}O$. The d-excess of very few shallow wells are characterized by positive values indicating recent recharge with evaporation process.

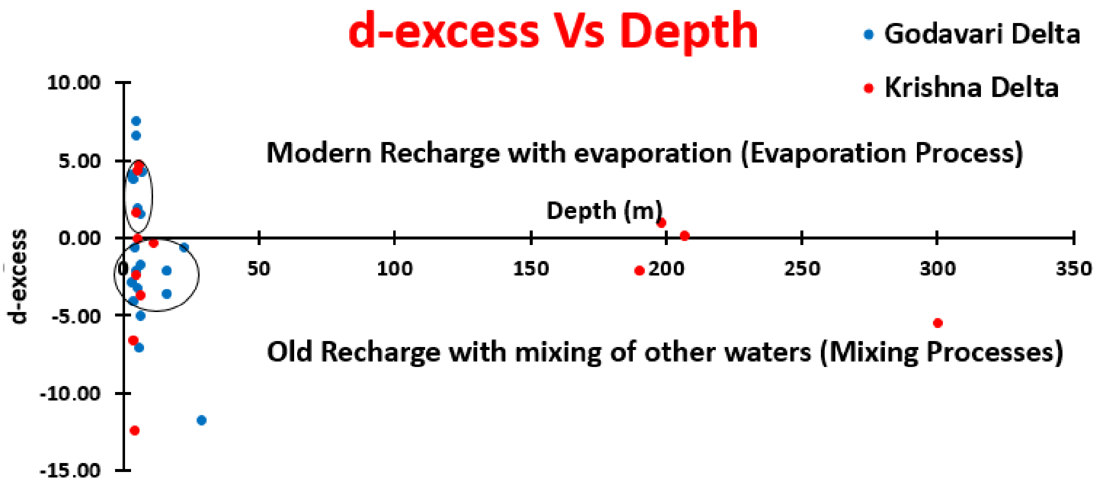


Fig. 46. d-excess versus depth (m) of groundwater in KG deltas

5.6 Emerging Contaminants in Groundwater of Study Area

5.6.1 Pesticide Residue Concentrations

Pesticides contamination in natural water is a worldwide problem and has become a challenge for the all world scientists. In recent years increasing population pressure, evolving industrial chemical society and advances in science and technology resulted in many questions about the safety of drinking water in countries, like India China and many other countries, where the majority of population live in villages with bare infrastructure facilities, illiteracy and lack of awareness.

The term pesticide is used to cover a range of chemicals that kill organisms that humans consider undesirable and includes the more specific categories of insecticides, herbicides, rodenticides, and fungicides. However, the chemical pesticides are usually not target specific and therefore, may cause harm to non-target species and many of them are quite persistent for long periods in the environment. The indiscriminate application of pesticides provides the pollutional effect to a considerable extent. The pesticides join the water courses through the runoff from agricultural lands, industrial and urban effluents, spray operations for crop and disease vector control etc and may ultimately reach to the ground water through percolation. The pesticides may impart toxicity to the ground water and causes various health hazards. The unused pesticides and their degradation product and metabolites in the various compartments are known as Pesticide Residue.

Presently, synthetic organic pesticides are largely used to control insects and other pests. There are three main groups of synthetic organic insecticides:

i) Organo-Chlorine Pesicides: Also known as chlorinated hydrocarbons includes polychlorinated organic compounds mainly
   - Dichloro diphenyl trichloroethane (DDT) (o,p′-DDT, p,p′-DDT, p,p′-DDD, p,p′-DDE)
   - Diene group e.g. Benzene Hexa Chloride (BHC) isomers (α-BHC, β-BHC, γ-BHC & δ-BHC)
   - Endosulfan
   - Aldrin
   - Methoxychlor

ii) Organo-Phosphorous Pesticides: Phosphorous containing organic compounds e.g.
   - Ethion
   - Dimethoate,
   - Malathion
   - Methyl Parathion

iii) Carbamates: Nitrogen containing organic compounds used as insecticides (derivatives of carbamic acid) e.g. propoxur, carbaryl, and aldicarb

In addition, a number of herbicides, including the chlorophenoxy compounds 2,4,5-T (which contains the impurity dioxin, which is one of the most potent toxins known) and 2,4-D are common water pollutants.

One of the most well-known organochlorine pesticides was DDT (dichlorodiphenyltrichloroethane) which had been widely used to control insects that carry such diseases such as malaria, typhus, and plague. It was its impact on food chains, rather than human toxicity, that led to its ban even in India also. The main properties of organochlorine pesticides, that cause them to be particularly disruptive to food chains, are i) they are very persistent, which means they last a long time in the environment before being broken down into other substances, and ii) they are quite soluble in lipids, which means they easily accumulate in fatty tissue.

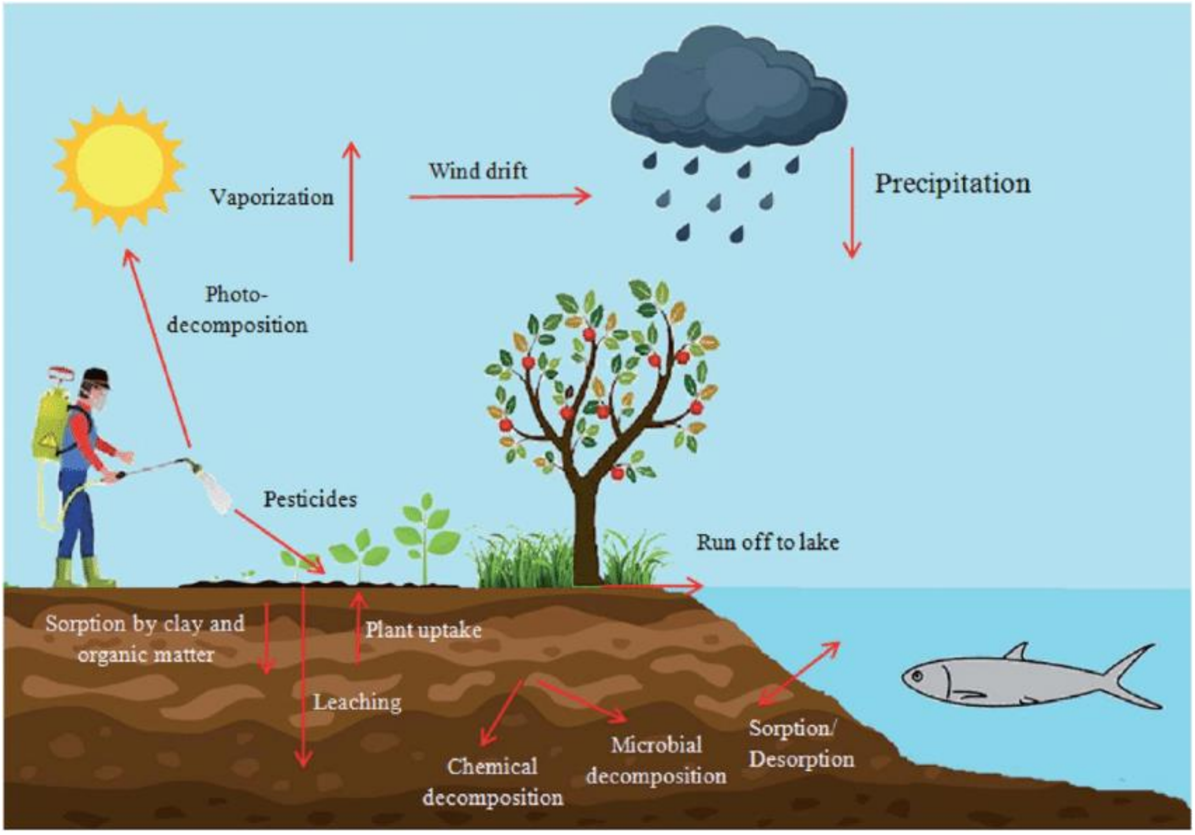


Fig. 47. Pesticides in Food Chain

Organochlorine pesticides (OCPs), also existing as typical persistent toxic substances (PTS), have been of increasing concerns the world due to their salient features of persistence, bioaccumulation, and toxicity. In the twelfth Stockholm Convention, nine organochlorine pesticides, including aldrin, toxaphene, DDTs, chlordane, dieldrin, endrin, heptachlor, mirex, and hexachlorobenzene, were proposed to be controlled as persistent organic pollutants (POPs), a variety of organic chemicals which have lasting harms to environment and eco-system (Fig. 47). Due to their intensive utilization in agricultural and industrial activities, residues of the OCPs have been widely identified and reported across the world, even in Antarctica and the Arctic Zone. Moreover, a majority of these pesticides belongs to endocrine-disrupting chemicals, which have been well proved as a series of most harmful substances to the endocrine system of human being and wild animals.

The organophosphates, such as parathion, malathion, diazinon, TEPP (tetraethyl prophosphate), and dimethoate, are effective against a wide range of insects and they are not persistent. However, the toxicity is much more than the organochlorines that they have replaced. They are rapidly absorbed through the skin, lungs, and gastrointestinal tract and, hence, unless proper precautions are taken, they are very hazardous to those who use them. Some of organo-chlorines are quite stable and persistent in aquatic medium while some of organo-phosphorous are significantly unstable in water and may degrade, hydrolyse or transform to other forms. The DDT metabolites are very stable.

Humans exposed to excessive amounts have shown a range of symptoms including tremor, confusion, slurred speech, muscle twitching, and convulsions. Acute human exposure to carbamates has led to a range of symptoms, such as nausea, vomiting, blurred vision, and in extreme cases, convulsions.

The solubility of pesticides in water besides their chemical structure (polarity) depends upon a number of factors e.g. pH, temperature, salt concentration, extent of agitation, organic matter (humic acid etc.), concentration of the medium and on partition between water and sediment phases and biotic activity. Most of the organo-chlorine pesticides are non-polar in nature and have a tendency to dissolve in water to a very low extent and in general, the solubility of organo-chlorines in water range between 0.001 mg/L for DDT to 10.0 mg/L for γ-BHC (lindane). While the organo-phosphorous pesticides largely vary in their polar nature from almost non-polar to highly polar ones and subsequently, from sparingly soluble to highly soluble in water they are. In general the solubility range of organo-phosphorous pesticides may be from 24 mg/L for parathion to 25 g/L for dimethoate. However, all of them are soluble in most of the organic solvents making their handling easier.

The maximum permissible limit of Pesticide residues as prescribed by BIS (2012) for drinking purpose is provided in Table 7. In the present investigation, 18 pesticides viz; Monocroptophos, Phorate, BHC-Alfa, Atrazine, BHC-beta, BHC-Gamma, BHC-Delta, Parathionmethyl, Alachlor, Isoproturon, Malathion, Aldrin, Chlorpyrifos, DDT, Butachlor, Endosulfan, Dieldrin and Ethion were analysed in the collected groundwater samples from study area using Agilent GC-MS/MS. Analysis result reveals that there is a presence of BHC-Alfa, Atrazine, BHC-beta, BHC-Delta, Parathionmethyl, Alachlor, Malathion, Chlorpyrifos, DDT, Endosulfan, Dieldrin and Ethion in 73 samples collected from Godavari Delta and BHC-Alfa exceeded the maximum limit in 10 samples and Chlorpyrifos exceeded the maximum limit in one sample during pre-monsoon season (2022) (Table 8). Further, there is a presence of BHC-Alfa, Atrazine, BHC-beta, BHC-Delta, Alachlor, Malathion, Aldrin, Chlorpyrifos, DDT, Butachlor, Endosulfan, Dieldrin and Ethion in 64 samples collected from Krishna Delta and BHC-Alfa exceeded the maximum limit in 15 samples during pre-monsoon season (2022) (Table 10).

Analysis result reveals that there is a presence of Monocroptophos, Phorate, BHC-Alfa, Atrazine, BHC-beta, BHC-Delta, Parathionmethyl, Alachlor, Isoproturon, Malathion, Aldrin, Chlorpyrifos, DDT, Butachlor, Endosulfan, and Ethion in 73 samples collected from Godavari Delta and BHC-Alfa exceeded the maximum limit in 68 samples, BHC-delta in one sample, Phorate in one sample and Chlorpyrifos exceeded the maximum limit in two sample during post-monsoon season (2022) (Table 9). Further, there is a presence of Monocroptophos, Phorate, BHC-Alfa, Atrazine, BHC-beta, Alachlor, Isoproturon, Malathion, Aldrin, Chlorpyrifos, DDT, Butachlor, Endosulfan, and Ethion in 64 samples collected from Krishna Delta and BHC-Alfa exceeded the maximum limit in 61 samples, Phorate in one sample and Chlorpyrifos exceeded the maximum limit in two sample during post-monsoon season (2022) (Table 11). Spatial distribution maps of pesticides are shown in Fig. 48 to Fig. 55.

Table 7. Maximum Prescribed Limit of Pesticides as BIS (2012) for Drinking Purpose

S. No.	Pesticide Residue	Prescribed Limit (μg/L)
1.	Alachlor	20
2.	Atrazine	2
3.	Aldrin/Dieldrin	0.03
4.	Alpha HCH	0.01
5.	Beta HCH	0.04
6.	Butachlor	125
7.	Chlorpyriphos	30
8.	Delta HCH	0.04
9.	2,4-Dichlorophenoxyacetic acid	30
10.	DDT (*o,p* and *p,p* – Isomers of DDT, DDE and DDD)	1
11.	Endosulfan (alpha, beta and sulphate)	0.4
12.	Ethion	3
13.	Gamma – HCH (Lindane)	2
14.	Isoproturon	9
15.	Malathion	190
16.	Methyl parathion	0.3
17.	Monocrotophos	1
18.	Phorate	2

Table 8. Pesticide Residue Concentrations in Groundwater of Godavari delta (Pre-monsoon 2022)

S.No.	Pesticide residue	Min.	Max.	Sample Number
1	Monocroptophos	BDL	BDL	None
2	Phorate	BDL	BDL	None
3	BHC-Alfa	BDL	0.017	Ten (8,9,11,25,33,40,48, 58,71,72)
4	Atrazine	BDL	0.020	Four (44,47,62,64)
5	BHC-beta	BDL	0.014	Sixty (1,4,5,6,7,8,9,10,12,13,14,16,17,18,19,20,22, 25,26,28,31,32, 33,35,36,37,38,40,41,42,43,44,45, 46,47,48,49,50,51,52,53,54,55,56,58,59,60,61,62, 63,64,65,66,67,68,69,70,71,72,73)
6	BHC-Gamma	BDL	BDL	None
7	BHC-Delta	BDL	0.023	Five (6,8,30,54,60)
8	Parathionmethyl	BDL	0.001	One (39)
9	Alachlor	BDL	0.063	Twenty Four (4,5,11,14,19,24,25,38,4346,48,51,55, 58,59,60,61,62,63, 65,66,67,69,70,71,73)
10	Isoproturon	BDL	BDL	None
11	Malathion	BDL	0.021	One (15)
12	Aldrin	BDL	BDL	None
13	Chlorpyrifos	BDL	30.349	Thirty eight (1,2,3,9,11,13,17,18,20,23,25,27,29,30, 31,32,35,36,38,41,43,44,45,47,48,49,50,51,53,54,55, 56,65,69,70,71,72,73)
14	DDT	BDL	0.060	Sixty eight (1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16, 17,18,19,20,21,22,23,24,25,26,27,28,29,31,32,33,34, 35,36,37,38,39,40,41,42,43,44,45,46,47,48,49,51,52, 53,54,55,58,59,60,61,62,63,64,66,67,68,69,70,71, 72,73)
15	Butachlor	BDL	BDL	None
16	Endosulfan	BDL	0.054	Sixty six (1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16,17, 18,20,21,22,24,25,26,27,28,29,31,32,33,34,35,36,37, 38,39,40,41,42,43,44,45,46,47,48,49,51,52,53,54,55, 58,59,60,61,62,63,64,66,67,68,69,70,71,72,73)
17	Dieldrin	BDL	0.011	Twelve (5,13,14,15,20,26,27,28,40,49,64,66)
18	Ethion	BDL	1.951	Thirty seven (1,3,4,5,6,7,8,9,10,11,12,13,14,20,21, 22,25,26, 27,29,31,32,33,35,37,41,42,43,44,49,55, 62,64,70,71,72)

*Sample number given in **Red** represents the sample having value more than the permissible limit.

Table 9. Pesticide Residue Concentrations in Groundwater of Godavari delta (Post-monsoon 2022)

S.No.	Pesticide residue	Min.	Max.	Sample Number
1	Monocroptophos	BDL	0.5051	Fifteen (1,3,10,12,13,14,15,18,21,24,39,43,45,57,62)
2	Phorate	BDL	11.2435	Two (60,69)
3	BHC-Alfa	BDL	0.0254	Sixty Eight (1,2,4,5,6,7,8,10,11,12,13,14,15,16,17, 18,19,20,21,22,23,24,25,26,27,28,29,31,32,33,34,35,36,37, 38,39,40,41,42,43,45,46,47,48,49,50,51,52,53,54,55,56,57, 58,59,60,61,62,63,64,65,66,67,68,69,70,71,73)
4	Atrazine	BDL	0.0361	Nineteen (1,2,3,4,6,7,8,9,12,15,17,23,25,38,40,43,65,71,73)
5	BHC-beta	BDL	0.0252	Sixty two (1,4,5,6,7,8,10,11,12,13,14,15,16,17,18,19,20,21,22,23,24, 25,27,28,31,32, 33,34,35,36,37,38,40,41,42,43,45, 46,47,48,49,50,51,52,53,54,55,56,57,58,60,61,62, 63,64,65,66,67,68,69,70,71,73)
6	BHC-Gamma	BDL	BDL	None
7	BHC-Delta	BDL	0.0409	Three (3,9,35)
8	Parathionmethyl	BDL	0.0280	Two (1,3)
9	Alachlor	BDL	0.0316	One (16)
10	Isoproturon	BDL	0.5987	Sixteen (2,5,7,8,9,14,18,23,24,53,62,63,66,69,70,73)
11	Malathion	BDL	0.0595	Two (3,61)
12	Aldrin	BDL	0.0095	Three (1,69,73)
13	Chlorpyrifos	BDL	187.066	Sixty nine (1,2,3,4,5,6,7,8,10,11,12,13,14,15,16, 17,18,19,20,21,22,23,24,25,26,27,28,29,31,32,33,34, 35,36,37,38,39,40,41,42,43,45,46,47,48,49,50,51,52, 53,54,55,56,57,58,59,60,61,62,63,64,65,66,67,68,69, 70,71,73)
14	DDT	BDL	0.0636	Forty six (1,2,5,6,7,8,9,10,11,12,13,19,23,24,26,27,28,32,33, 34,35,37,38,39,40,41,43,45,46,49,51,53,54,56,57, 61,62,63,64,65,66,67,70,71,73)
15	Butachlor	BDL	0.0310	Twelve (8,10,23,26,27,33,41,45,53,62,63,65)
16	Endosulfan	BDL	0.0464	Eight (7,8,12,24,38,43,66,67)
17	Dieldrin	BDL	BDL	None
18	Ethion	BDL	0.509	Six (7,8,24,38,43,67)

*Sample number given in **Red** represents the sample having value more than the permissible limit.

Table 10. Pesticide Residue Concentrations in Groundwater of Krishna delta (Pre-monsoon 2022)

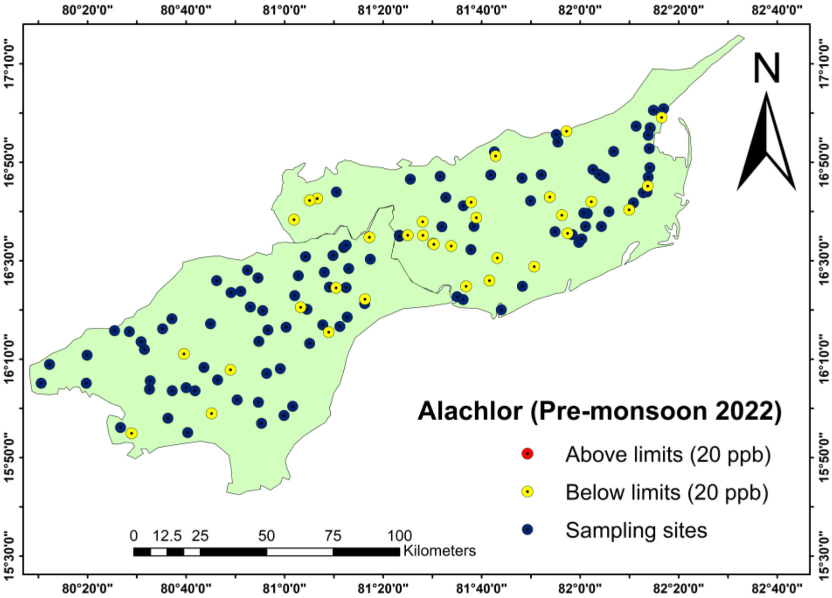
S.No.	Pesticide residue	Min.	Max.	Sample Number
1	Monocroptophos	BDL	0.011	One (115)
2	Phorate	BDL	BDL	None
3	BHC-Alfa	BDL	0.015	Fifteen (75,76,83,85,87,93,113,116,119,120,127,129, 131,135,136)
4	Atrazine	BDL	0.027	Twenty two (77,81,83,87,91,96,98,99,101,102,109, 111,112,115,116,117,119,123,125,126,127,131,137)
5	BHC-beta	BDL	0.011	Forty five (74,76,77,79,80,81,82,83,84,85,86,87,91, 96,101,102,103104,106,107,108,111,112,113,114, 115,116,117,118,119,120,121,122,124,125,126,127, 128,129,130,131,132,133,136,137)
6	BHC-Gamma	BDL	BDL	None
7	BHC-Delta	BDL	0.021	Six (79,80,83,93,101,128)
8	Parathionmethyl	BDL	BDL	None
9	Alachlor	BDL	0.010	Nine (77,79,88,89,95,123,126,132,135)
10	Isoproturon	BDL	BDL	None
11	Malathion	BDL	0.056	Four (102,103,119,123)
12	Aldrin	BDL	0.007	Five (76,97,104,115,116)
13	Chlorpyrifos	BDL	4.676	Fifty six (74,75,77,78,79,80,81,82,83,84,85,87,88, 89,91,92,96,97,99,100,101,102,103,104,105,106,107, 108,109,111,112,113,114,115,116,117,118,119,120, 121,122,123,124,125,126,127,128,129,130,131,132, 133,134,135,136,137)
14	DDT	BDL	0.065	Sixty (74,75,76,77,79,80,81,82,83,84,85,86,87,88, 89,91,93,94,95,96,97,98,99,100,101,102,103,104, 105,106,107,108,109,111,112,113,114,115,116,117, 118,119,120,121,122,123,124,125,126,127,128,129, 130,131,132,133,134,135,136,137)
15	Butachlor	BDL	0.037	One (83)
16	Endosulfan	BDL	0.030	Fifty nine (74,75,76,77,79,80,81,8283,84,85,86,87, 88,89,91,93,94,95,97,98,99,100,101,102,103,104,105 ,106,107,108,109,111,112,113,114,115,116,117,118, 119,120,121,122,123,124,125,126,127,128,129,130, 131,132,133,134,135,136,137)
17	Dieldrin	BDL	0.009	Two (102,117)
18	Ethion	BDL	0.728	Thirty two (75,84,86,91,93,96,97,99,101,102,104, 105,106,107,108,109,112,115,116,117,119, 120,121, 122,124,125,126,127,129,132,133,136)

*Sample number given in **Red** represents the sample having value more than the permissible limit.

Table 11. Pesticide Residue Concentrations in Groundwater of Krishna delta (Post-monsoon 2022)

S.No.	Pesticide residue	Min.	Max.	Sample Number
1	Monocroptophos	BDL	0.5361	Nineteen (74,81,86,95,99,103,106,109,110,111,117,119,121, 123,125,129,132,136,137)
2	Phorate	BDL	7.8671	Two (80,87)
3	BHC-Alfa	BDL	0.0239	Sixty one (74,75,76,77,78,79,80,81,82,83,84,85,86,87,88, 89,90,91,92,93,94,95,96,97,98,99,100,101,102,104, 105,106,107,108,109,110,111,112,113,114,115,117, 118,119,120,121,122,123,124,125,126,127,128,129, 130,131,132,134,135,136,137)
4	Atrazine	BDL	0.4793	Sixty three (74,75,76,77,78,79,80,81,82,83,84,85,86,87,88,89,90 ,91,92,93,94,95,96,97,98,99,100,101,102,103,104, 105,106,107,108,109,110,111,112,113,114,115,116, 117,118,119,120,121,122,123,124,125,126,127,128, 129,130,131,132,134,135,136,137)
5	BHC-beta	BDL	0.0135	Fifty four (74,75,76,77,78,79,80,81,82,83,85,86,87,88,89,90,91 ,92,93,94,95,96,98,99,100,101,102,103,104,105,106, 107,108,109,110,111,112,113,114,115,116,118,120,1 21,122,123,124,125,127,129,130,131,136,137)
6	BHC-Gamma	BDL	BDL	None
7	BHC-Delta	BDL	BDL	None
8	Parathionmethyl	BDL	BDL	None
9	Alachlor	BDL	0.0218	Two (106,116)
10	Isoproturon	BDL	0.3940	Twenty (75,76,79,81,82,86,90,91,93,99,100,102,105,107,110 ,112,119,129,134,135)
11	Malathion	BDL	0.2394	Five (92,132,134,135,136)
12	Aldrin	BDL	0.0097	One (88)
13	Chlorpyrifos	BDL	84.641	Sixty two (74,75,76,77,78,79,81,82,83,84,85,86,87,88,89,90,91 ,92,93,94,95,96,97,98,99,100,101,102,103,104,105, 106,107,108,109,111,112,113,114,115,116,117,118, 119,120,121,122,123,124,125,126,127,128,129,130, 131,132,134,135,136,137)
14	DDT	BDL	0.0669	Fifty five (74,75,76,77,78,81,82,83,84,85,86,87,88,89,90,91,92 ,93,94,95,96,97,98,99,100,101,102,103,104,105,106, 107,109,116,117,118,119,120,121,122,123,124,125, 126,127,128,129,130,131,132,133,134,135,136,137)
15	Butachlor	BDL	0.0286	Three (111,123,137)
16	Endosulfan	BDL	0.0618	Nine (85,92,100,105,120,125,128,135,137)
17	Dieldrin	BDL	BDL	None
18	Ethion	BDL	0.0624	Seven (92,100,105,120,125,128,137)

*Sample number given in **Red** represents the sample having value more than the permissible limit.



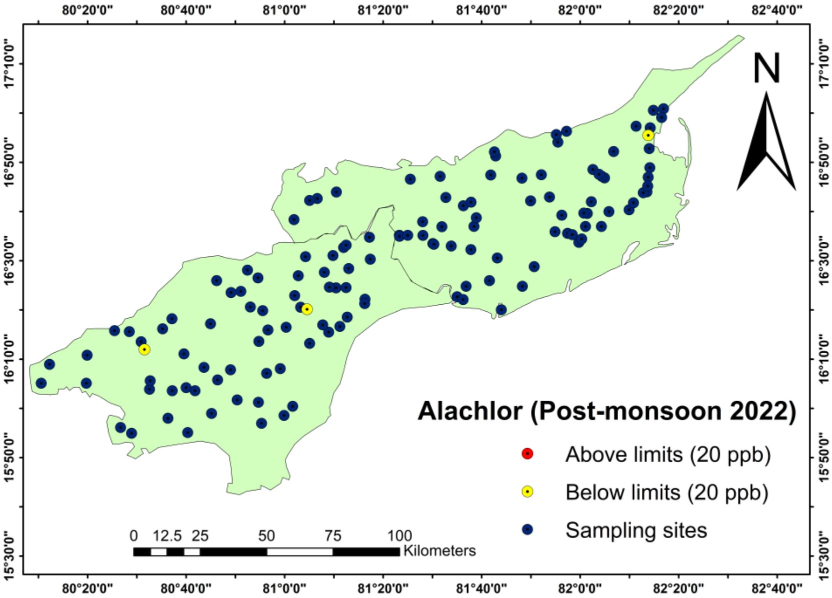


Fig. 48. Spatial distribution of Alachlor in groundwater of the study area

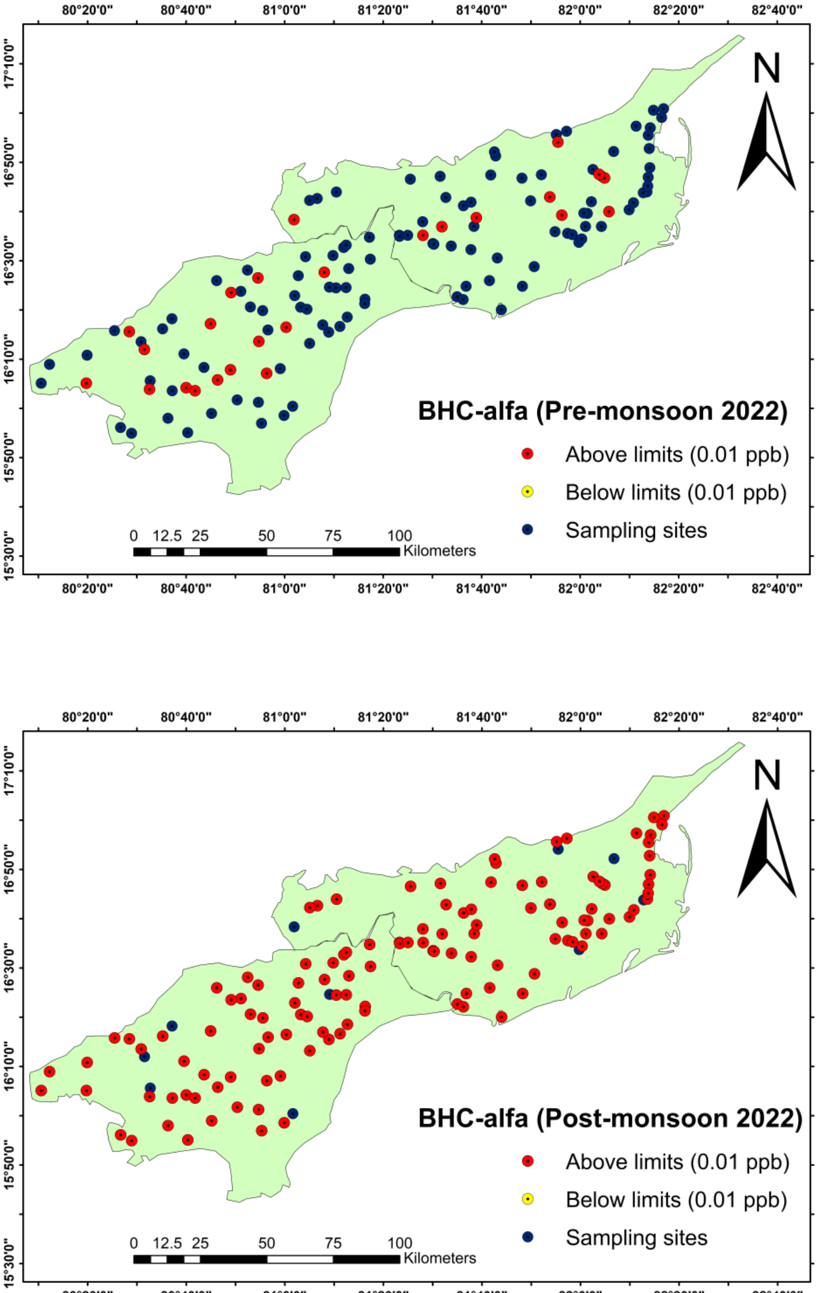
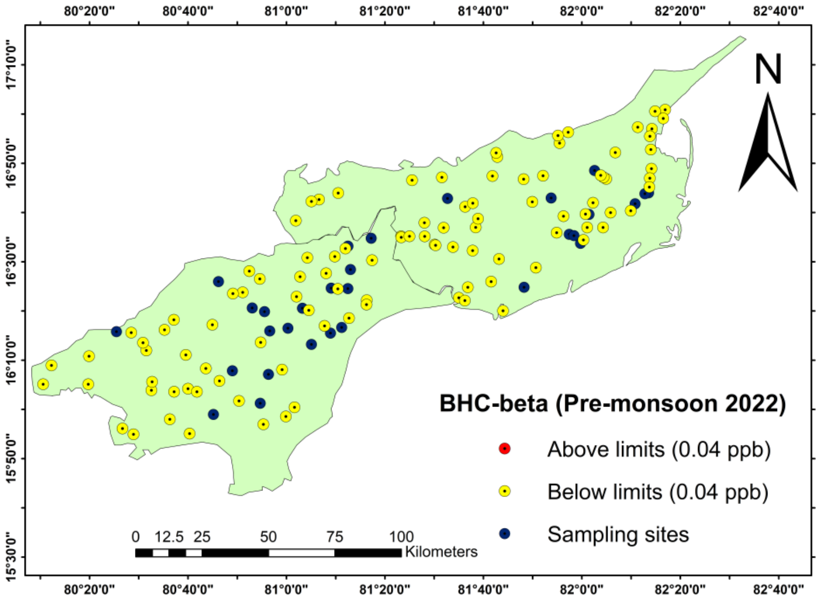


Fig. 49. Spatial distribution of BHC-alfa in groundwater of the study area



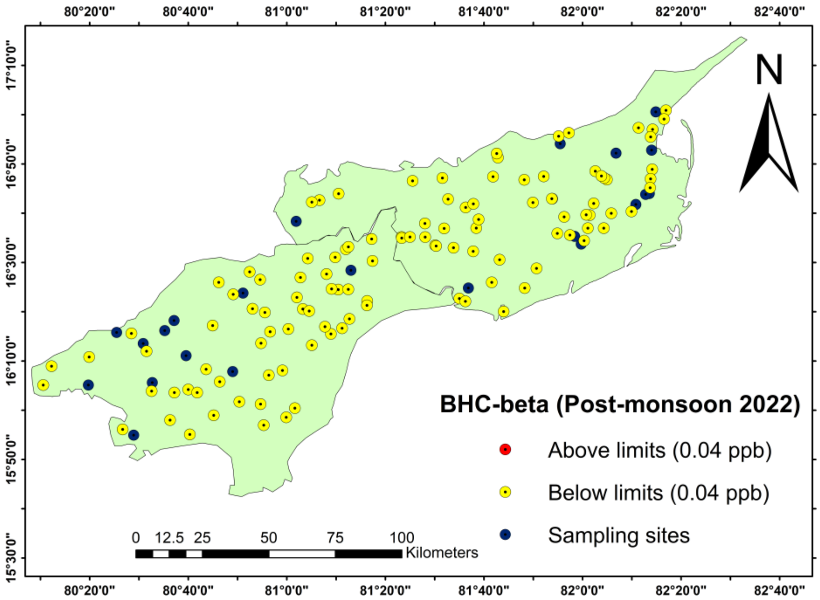
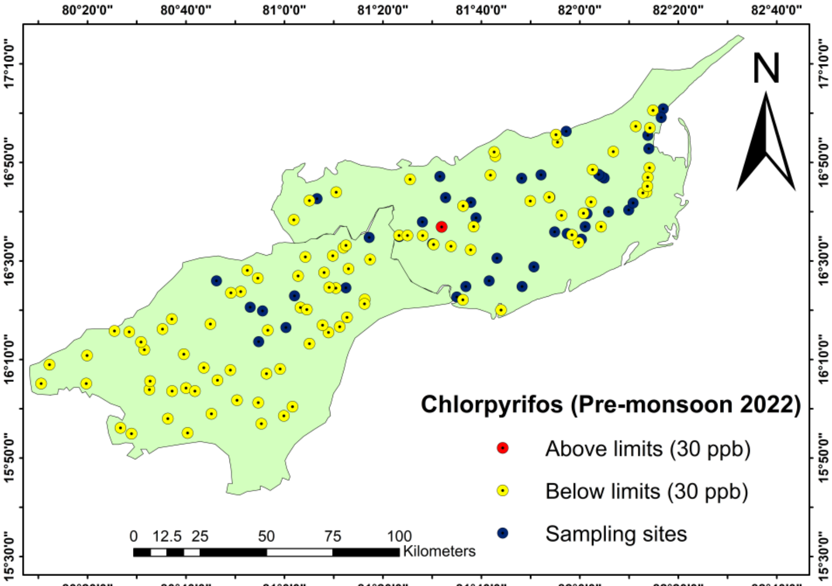


Fig. 50. Spatial distribution of BHC-beta in groundwater of the study area



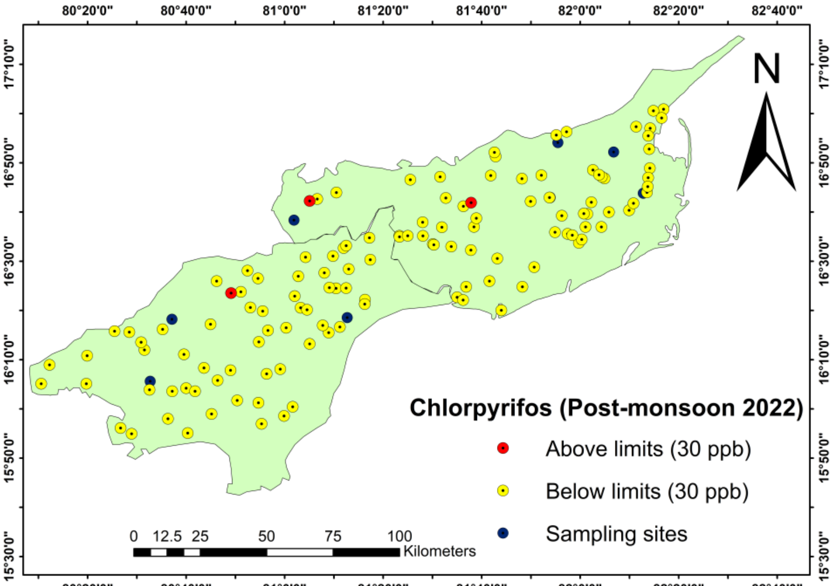
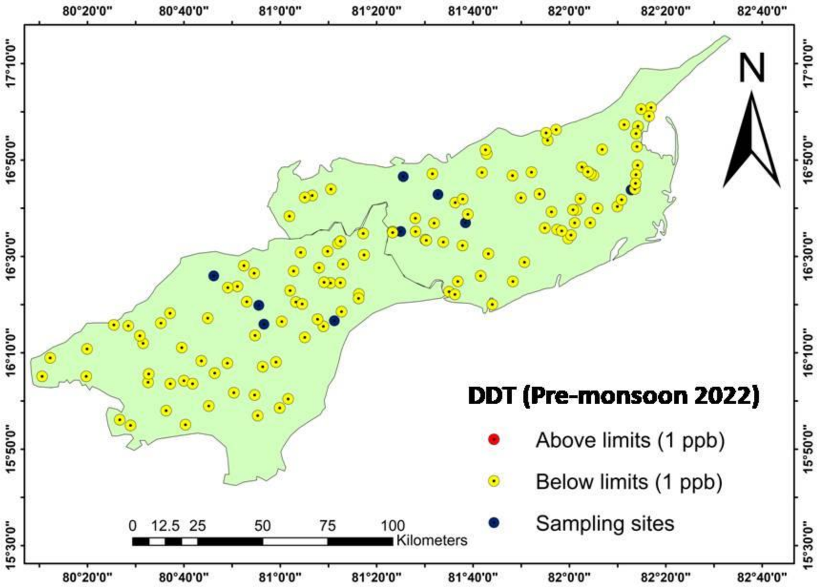


Fig. 51. Spatial distribution of Chlorpyrifos in groundwater of the study area



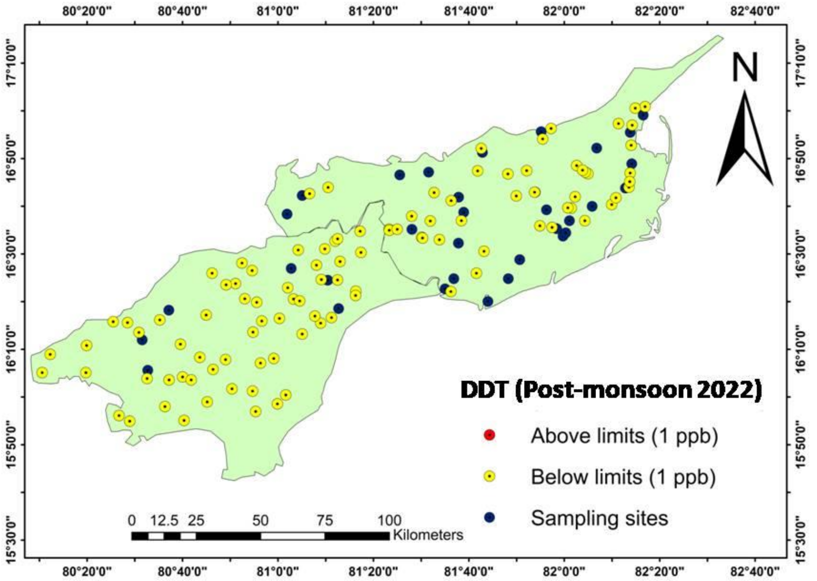
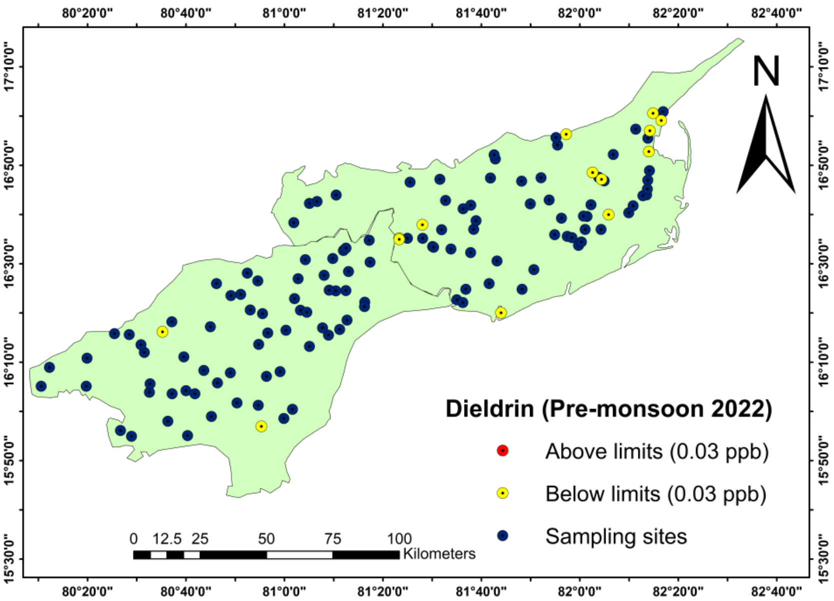


Fig. 52. Spatial distribution of DDT in groundwater of the study area



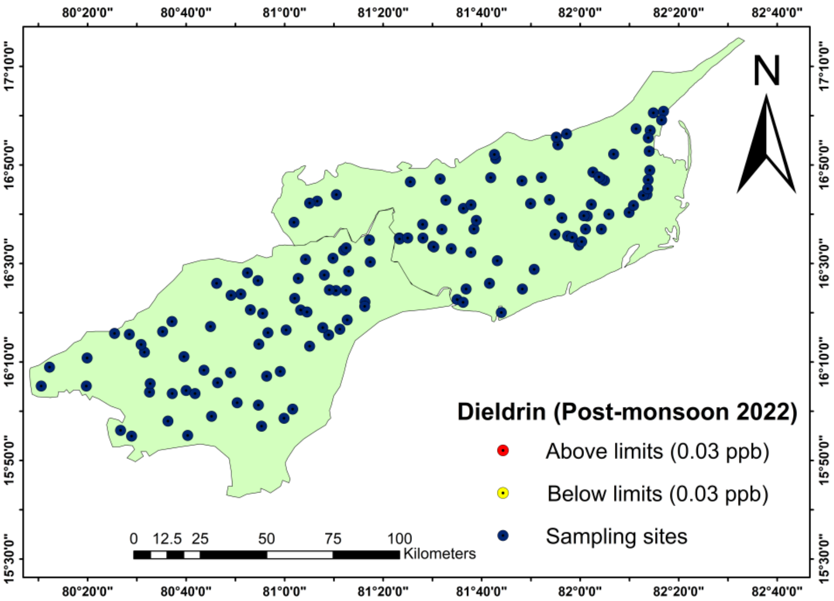
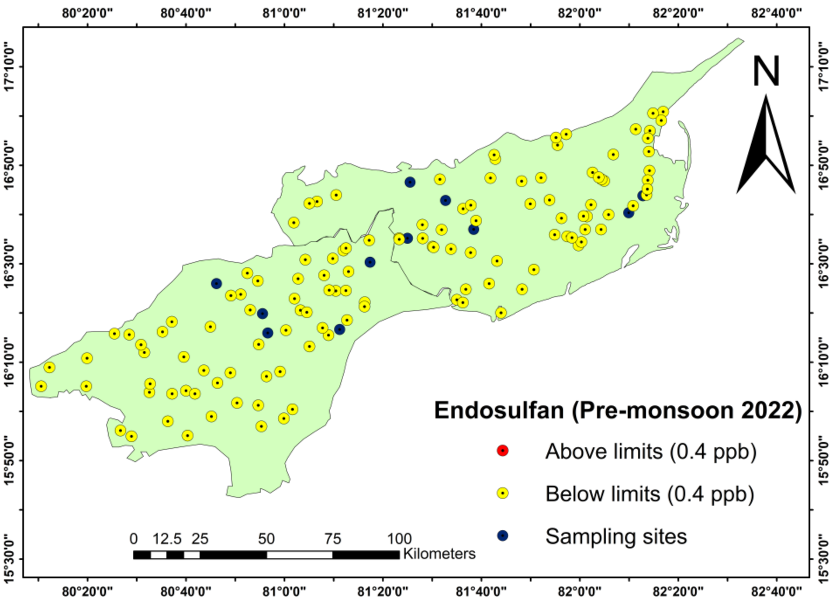


Fig. 53. Spatial distribution of Dieldrin in groundwater of the study area



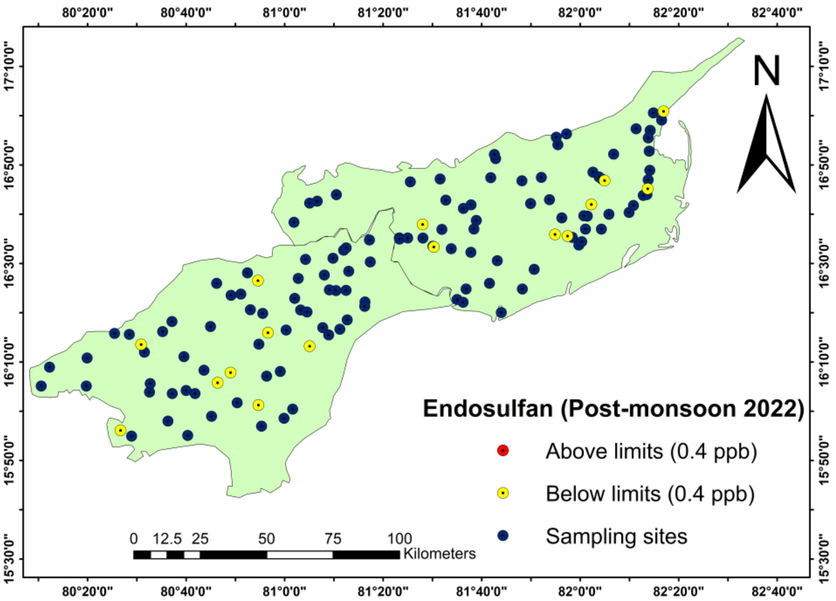
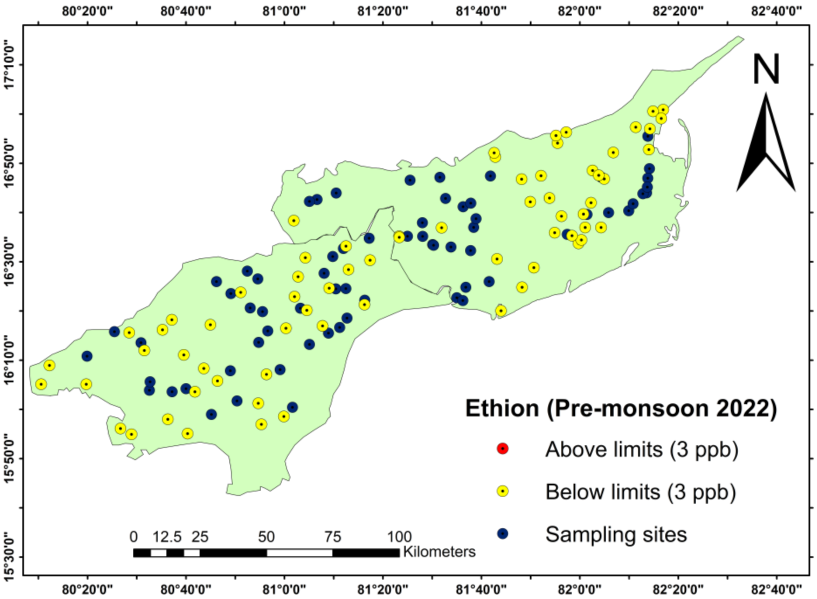


Fig. 54. Spatial distribution of Endosulfan in groundwater of the study area



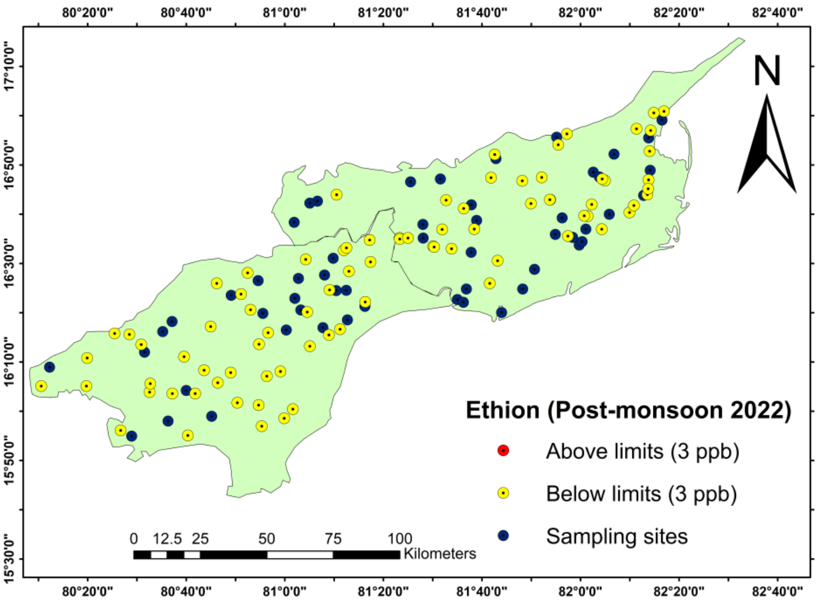


Fig. 55. Spatial distribution of Ethion in groundwater of the study area

5.6.2 Polychlorinated Biphenyls (PCBs) Concentrations in Groundwater of Study Area

Polychlorinated Biphenyls (PCBs) are deployed as dielectric and coolant fluids in electrical apparatus, carbonless copy paper and in heat transfer fluids. These are used as plasticizers in paints and cements, stabilizing additives in flexible PVC coatings of electrical cables and electronic components, pesticide extenders, reactive flame retardents and sealants for adhesives, wood floor finishes. The maximum permissible limit of PCBs of 0.5 µg/L has been prescribed by BIS (2012) for drinking purpose. Higher concentration more than permissible limit of these may cause birth defects, developmental delays, and liver changes. In the present investigation, 8 PCBs viz; 2-Chlorobiphenyl (BZ #1), 2,3-Dichlorobiphenyl (BZ #5), 2,2',5-Trichlorobiphenyl (BZ #18), 2,4',5-Trichlorobiphenyl (BZ #31), 2,2',3,5'-Tetrachlorobiphenyl (BZ#44), 2,2',5,5'-Tetrachlorobiphenyl (BZ#52), 2,3,4,4'-Tetrachlorobiphenyl (BZ#60), 2,2',4,5,5'-Pentachlorobiphenyl (BZ #101) were analysed in the collected groundwater samples from study area using Agilent GC-MS/MS. Analysis result reveals that there is a presence of PCBs in 62 groundwater samples out of 73 samples collected from Godavari Delta and 52 groundwater samples out of 64 samples collected from Krishna Delta during pre-monsoon season (2022). Total PCBs exceeded the maximum prescribed limit (0.5 µg/L) in only one groundwater sample out of 73 groundwater samples collected from Godavari Delta (Table 12) while none of groundwater samples was observed to exceed the permissible limit in 64 groundwater samples collected from Krishna Delta (Table 14).

Analysis result reveals that there is a presence of PCBs in 62 groundwater samples out of 73 samples collected from Godavari Delta and 64 groundwater samples out of 64 samples collected from Krishna Delta during post-monsoon season (2022). None of groundwater samples was observed to exceed the permissible limit in 73 groundwater samples collected from Godavari Delta (Table 13) and 64 groundwater samples collected from Krishna Delta (Table 15). Spatial distribution of Total PCBs in groundwater of the study area are shown in Fig. 56.

Table 12. Polychlorinated Biphenyls (PCBs) Concentrations in Groundwater of Godavari delta (Pre-monsoon 2022)

S.No.	PCBs	Min.	Max.	Sample Number
1	2-Chlorobiphenyl (BZ #1)	BDL	BDL	None
2	2,3-Dichlorobiphenyl (BZ #5)	BDL	BDL	None
3	2,2',5-Trichlorobiphenyl (BZ #18)	BDL	BDL	None
4	2,4',5-Trichlorobiphenyl (BZ #31)	BDL	0.0001	One (73)
5	2,2',3,5'-Tetrachlorobiphenyl (BZ#44)	BDL	BDL	None
6	2,2',5,5'-Tetrachlorobiphenyl (BZ#52)	BDL	BDL	None
7	2,3,4,4'-Tetrachlorobiphenyl (BZ#60)	BDL	0.007	Sixty two (1,2,3,4,5,6,7,8,9,10,11,12,13,14, 15,16,17,18,19,20,21,22,23,24,25,26,27,28, 29,30,31,32,33,34,35,36,37,38,39,40,41,42, 43,44,45,47,48,49,51,52,53,54,55,59,60,61, 62,64,66,69,71,72,73)
8	2,2',4,5,5'-Pentachlorobiphenyl (BZ #101)	BDL	0.024	Two (72,73)
9	Total PCBs	BDL	0.025	Sixty two (1,2,3,4,5,6,7,8,9,10,11,12,13,14, 15,16,17,18,19,20,21,22,23,24,25,26,27,28, 29,31,32,33,34,35,36,37,38,39,40,41,42,43, 44,45,47,48,49,51,52,53,54,55,59,60,61,62, 64,66,69,71,72,73)

Table 13 Polychlorinated Biphenyls (PCBs) Concentrations in Groundwater of Godavari delta (Post-monsoon 2022)

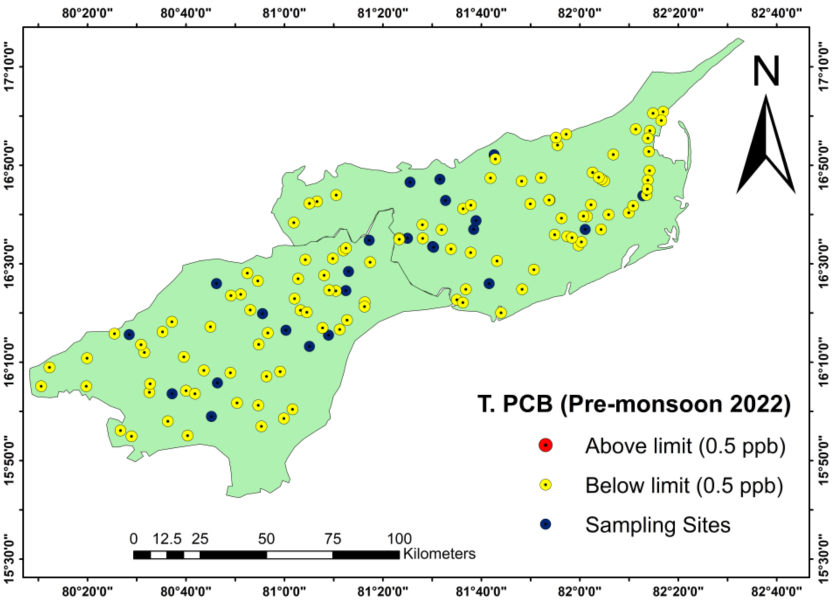
S.No.	PCBs	Min.	Max.	Sample Number
1	2-Chlorobiphenyl (BZ #1)	BDL	BDL	None
2	2,3-Dichlorobiphenyl (BZ #5)	BDL	BDL	None
3	2,2',5-Trichlorobiphenyl (BZ #18)	BDL	BDL	None
4	2,4',5-Trichlorobiphenyl (BZ #31)	BDL	0.0013	Twenty nine (5,7,8,10,11,12,14,15,16,18,20,24,25,26,31, 32,33,34,39,43,46,47,50,56,57,58,62,64,65)
5	2,2',3,5'-Tetrachlorobiphenyl (BZ#44)	BDL	BDL	None
6	2,2',5,5'-Tetrachlorobiphenyl (BZ#52)	BDL	BDL	None
7	2,3,4,4'-Tetrachlorobiphenyl (BZ#60)	BDL	0.0019	Sixty eight (1,2,4,5,6,7,8,9,10,11,12,13,14, 15,16,17,18,20,21,22,23,24,25,26,27,28, 29,31,32,33,34,35,36,37,38,39,40,41,42, 43,45,46,47,48,49,50,51,52,53,54,55,56,57 ,58,59,60,61,62,63,64,65,66,67,68,69,70,71,73)
8	2,2',4,5,5'-Pentachlorobiphenyl (BZ #101)	BDL	BDL	None
9	Total PCBs	BDL	0.0032	Sixty two (1,2,3,4,5,6,7,8,9,10,11,12,13,14, 15,16,17,18,19,20,21,22,23,24,25,26,27,28, 29,31,32,33,34,35,36,37,38,39,40,41,42,43, 44,45,47,48,49,51,52,53,54,55,59,60,61,62, 64,66,69,71,72,73)

Table 14 Polychlorinated Biphenyls (PCBs) Concentrations in Groundwater of Krishna delta (Pre-monsoon 2022)

S.No.	PCBs	Min.	Max.	Sample Number
1	2-Chlorobiphenyl (BZ #1)	**BDL**	**BDL**	**None**
2	2,3-Dichlorobiphenyl (BZ #5)	BDL	BDL	None
3	2,2',5-Trichlorobiphenyl (BZ #18)	BDL	BDL	None
4	2,4',5-Trichlorobiphenyl (BZ #31)	BDL	0.014	One (83)
5	2,2',3,5'-Tetrachlorobiphenyl (BZ#44)	BDL	BDL	None
6	2,2',5,5'-Tetrachlorobiphenyl (BZ#52)	BDL	BDL	None
7	2,3,4,4'-Tetrachlorobiphenyl (BZ#60)	BDL	0.001	Fifty two (74,75,76,77,78,79,80,81,82,83, 84,85,86,87,89,91,92,94,96,99,101,102,103, 104,105,106,107,108,109,111,112,113,114, 115,116,117,118,119,121,122,124,125,126, 128,129,131,132,133,134,135,136,137)
8	2,2',4,5,5'-Pentachlorobiphenyl (BZ #101)	BDL	BDL	None
9	Total PCBs	BDL	0.014	Fifty two (74,75,76,77,78,79,80,81,82,83,84, 85,86,87,89,91,92,94,96,99,101,102,103,104, 105,106,107,108,109,111,112,113,114,115, 116,117,118,119,121,122,124,125,126,128, 129,131,132,133,134,135,136,137)

Table 15 Polychlorinated Biphenyls (PCBs) Concentrations in Groundwater of Krishna delta (Post-monsoon 2022)

S.No.	PCBs	Min.	Max.	Sample Number
1	2-Chlorobiphenyl (BZ #1)	BDL	BDL	None
2	2,3-Dichlorobiphenyl (BZ #5)	BDL	BDL	None
3	2,2',5-Trichlorobiphenyl (BZ #18)	BDL	BDL	None
4	2,4',5-Trichlorobiphenyl (BZ #31)	BDL	0.0003	Six (76,81,88,108,111,124)
5	2,2',3,5'-Tetrachlorobiphenyl (BZ#44)	BDL	BDL	None
6	2,2',5,5'-Tetrachlorobiphenyl (BZ#52)	BDL	BDL	None
7	2,3,4,4'-Tetrachlorobiphenyl (BZ#60)	BDL	0.0017	Sixty four (74,75,76,77,78,79,80,81,82,83, 84,85,86,87,88,89,90,91,92,93,94,95,96,97, 98,99,100,101,102,103,104,105,106,107,108, 109,110,111,112,113,114,115,116,117,118,119, 120,121,122,123,124,125,126,127,128,129,130, 131,132,133,134,135,136,137)
8	2,2',4,5,5'-Pentachlorobiphenyl (BZ #101)	BDL	BDL	None
9	Total PCBs	BDL	0.0028	Sixty four (74,75,76,77,78,79,80,81,82,83, 84,85,86,87,88,89,90,91,92,93,94,95,96,97, 98,99,100,101,102,103,104,105,106,107,108, 109,110,111,112,113,114,115,116,117,118,119, 120,121,122,123,124,125,126,127,128,129,130, 131,132,133,134,135,136,137)



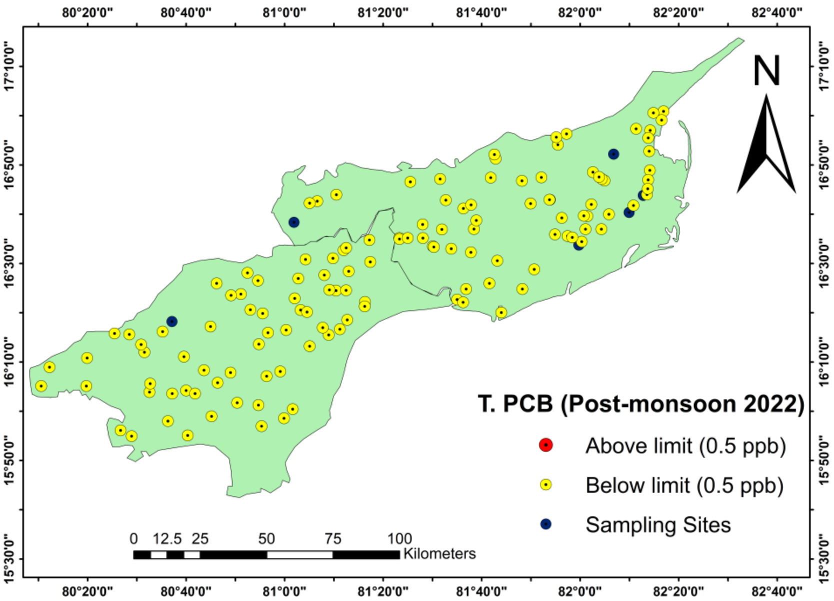


Fig. 56. Spatial distribution of Total PCBs in groundwater of the study area

5.6.3 Polynuclear Aromatic Hydrocarbons (PAHs) Concentrations in Groundwater of Study Area

Polynuclear Aromatic Hydrocarbons (PAHs) are generally present in water through air and mainly through industrial discharges (Fig. 57). These are shown to be mutagenic and carcinogenic pollutants even at trace level and are the byproducts of petroleum processing or formed as a result of incomplete combustion of organic compounds. Although these are insoluble in water but, sometimes, contaminate water system. The maximum permissible limit of PAHs of 0.1 µg/L has been prescribed by BIS (2012) for drinking purpose. In the present investigation, 16 PAHs viz; Naphthalene, Acenaphthylene, Acenaphthene, Pyrene, Flourene, Fluoranthene, Phenanthrene, Anthracene, Benz[a]anthracene, Chrysene, Benzo[k]fluoranthene, Benzo[b]fluoranthene, Benzo[a]pyrene, Indeno[1,2,3-cd]pyrene, Dibenz[a,h]anthracene and Benzo[g,h,i]perylene were analysed in the collected groundwater samples from study area during pre- and post-monsoon season (2022) using Agilent GC-MS/MS. Analysis result reveals that there is a presence of PAHs in all 73 groundwater samples of Godavari Delta Basin and 64 groundwater samples of Krishna Delta Basin. Total PAHs exceeded the maximum prescribed limit (0.1 µg/L) in 46 groundwater samples out of 73 groundwater samples collected from Godavari Delta Basin (Table 16) while three groundwater samples were observed to exceed the permissible limit out of 64 groundwater samples collected from Krishna Delta during the pre-monsoon (Table 18).

In case of post-monsoon season, Total PAHs exceeded the maximum prescribed limit (0.1 µg/L) in 61 groundwater samples out of 73 groundwater samples collected from Godavari Delta Basin (Table 17) while 58 groundwater samples were observed to exceed the permissible limit out of 64 groundwater samples collected from Krishna Delta (Table 19). Spatial distributions of total PAH in groundwater of the study area are shown in Fig. 58.

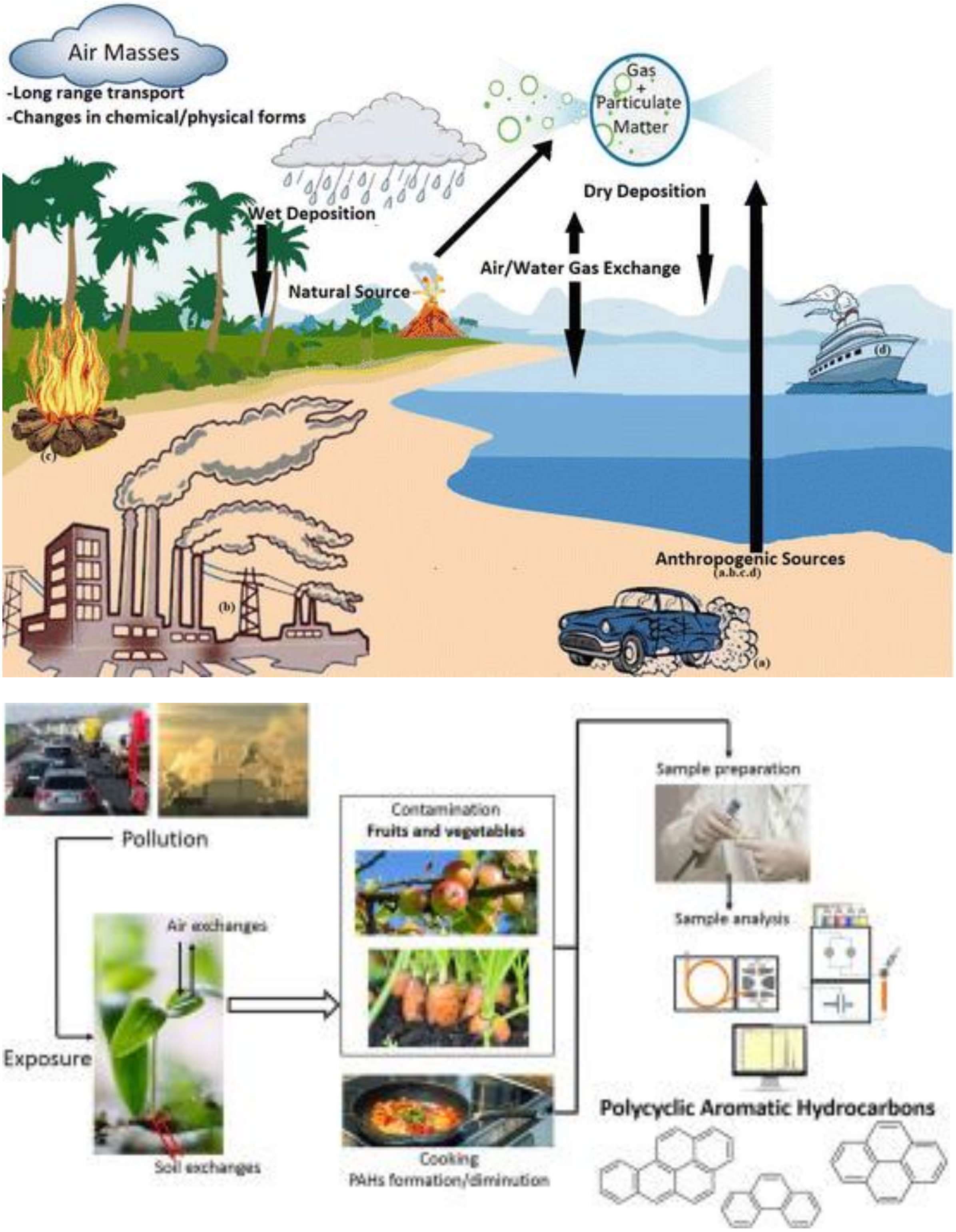


Fig. 57. Sources of PAHs in the Environment and in the Food Chain

Table 16. Polynuclear Aromatic Hydrocarbons (PAHs) Concentrations in Groundwater of Godavari delta (Pre-monsoon 2022)

S.No.	PAHs	Min.	Max.	Sample Number
1	Naphthalene	BDL	1.555	Seventy two (1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16,17,18,19,20,21,22,23,24,25,26,27,28,29,30,31,32,33,34,35,36,37,38,39,40,41,42,43,44,45,46,47,48,49,50,51,52,53,54,55,56,58,59,60,61,62,63,64,65,66,67,68,69,70,71,72,73)
2	Acenaphthylene	BDL	0.020	Fifty six (1,3,4,5,6,7,8,9,10,11,12,13,14,15,16,17,19,21,22,24,25,26,27,28,29,31,32,33,34,35,36,37,38,39,40,41,42,43,44,46,47,48,49,51,54,55,56,58,59,62,63,64,65,66,71,72)
3	Acenaphthene	BDL	0.031	Fifty nine (1,2,3,4,5,6,7,8,10,11,13,1415,16,17,18,19,20,21,22,24,25,26,27,28,29,31,32,33,34,35,36,37,38,39,40,41,42,43,44,45,46,48,49,50,52,54,58,59,60,61,62,65,66,67,68,69,70,71,72,)
4	Pyrene	BDL	0.063	Three (24,30,72)
5	Flourene	BDL	0.011	Fifteen (11,12,15,18,20,22,24,25,26,27,29,31,34,36,39)
6	Fluoranthene	BDL	0.013	One (72)
7	Phenanthrene	BDL	0.076	Seventy two (1,2,4,5,6,7,8,9,10,11,12,13,14,15,16,17,18,19,20,21,22,23,24,25,26,27,28,29,30,31,32,33,34,35,36,37,38,39,40,41,42,43,44,45,46,47,48,49,50,51,52,53,54,55,56,57,58,59,60,61,62,63,64,65,66,67,68,69,70,71,72,73)
8	Anthracene	BDL	0.077	Seventy three (1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16,17,18,19,20,21,22,23,24,25,26,27,28,29,30,31,32,33,34,35,36,37,38,39,40,41,42,43,44,45,46,47,48,49,50,51,52,53,54,55,56,57,58,59,60,61,62,63,64,65,66,67,68,69,70,71,72,73)
9	Benz[a]anthracene	BDL	0.027	Twenty seven (6,7,8,9,12,14,15,18,20,22,23,25,28,29,32,39,40,41,42,50,51,52,54,58,67,69,73)
10	Chrysene	BDL	0.022	One (72)
11	Benzo[k]fluoranthene	BDL	0.038	Eight (3,10,28,41,45,56,58,65)
12	Benzo[b]fluoranthene	BDL	0.019	Five (14,24,33,41,62)
13	Benzo[a]pyrene	BDL	0.031	Thirty one (1,2,4,7,8,10,11,12,13,16,18,20,22,23,25,28,30,33,36,37,39,41,45,51,52,53,59,61,67,72,73)
14	Indeno[1,2,3-cd]pyrene	BDL	0.031	Ten (11,15,22,28,34,48,62,63,65,67)
15	Dibenz[a,h]anthracene	BDL	BDL	None
16	Benzo[g,h,i]perylene	BDL	0.008	Seven (4,7,10,13,32,50,66)
17	Total PAHs (Permissible Limit =0.1 µg/L)	BDL	1.722	Seventy three (1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16,17,18,19,20,21,22,23,24,25,26,27,28,29,30,31,32,33,34,35,36,37,38,39,40,41,42,43,44,45,46,47,48,49,50,51,52,53,54,55,56,57,58,59,60,61,62,63,64,65,66,67,68,69,70,71,72,73)

*Sample number given in **Red** represents the sample having value more than the permissible limit.

Table 17. Polynuclear Aromatic Hydrocarbons (PAHs) Concentrations in Groundwater of Godavari delta (Post-monsoon 2022)

S.No.	PAHs	Min.	Max.	Sample Number
1	Naphthalene	BDL	0.6383	Sixty seven (1,2,4,5,6,7,8,9,10,11,12,13, 14,15,16,17,18,20,21,22,23,24,25,26,27, 28,29,31,32,33,34,35,36,37,38,39,40,41, 42,43,45,46,47,48,49,50,51,52,53,54,55, 56,57,58,59,60,61,62,63,64,65,66,67,68, 69,70,71)
2	Acenaphthylene	BDL	0.0056	Fifty three (2,4,5,6,7,8,9,10,11,12,13,14,15,16,17,18, 24,25,27,28,31,32,33,34,35,36,37,38,39,40, 41,42,43,45,46,47,48,49,50,53,54,55,57,58, 59,61,63,64,65,66,68,70,71)
3	Acenaphthene	BDL	0.0217	Twelve (4,17,22,28,35,37,42,46,49,51,55,68)
4	Pyrene	BDL	0.0649	Twenty six (2,5,6,7,8,11,12,14,15,16,18,19,20,25,34,36, 37,41,43,46,48,50,56,65,71,73)
5	Flourene	BDL	0.0251	Nine (14,17,18,20,23,39,58,60,64)
6	Fluoranthene	BDL	BDL	None
7	Phenanthrene	BDL	0.0349	Five (2,4,28,36,53)
8	Anthracene	BDL	0.0813	Sixty three (1,5,6,7,8,9,11,12,13,14,15,16,17,18,19,20 21,22,23,24,25,26,27,28,29,31,32,33,34,35, 36,37,38,39,40,41,42,43,45,46,47,48,49,50, 52,53,56,57,58,59,60,61,62,63,64,65,66,67, 68,69,70,71,73)
9	Benz[a]anthracene	BDL	0.1223	Sixty six (1,2,4,5,6,7,8,9,10,11,12,13,14,15,16,17,18,19, 20,22,23,24,25,26,27,28,29,31,32,33,34,35,36, 37,38,39,41,42,43,45,46,47,48,49,50,51,52,53, 54,55,56,57,58,59,60,61,62,63,64,65,66,67,68, 69,70,71)
10	Chrysene	BDL	BDL	None
11	Benzo[k]fluoranthene	BDL	0.1187	Forty (1,2,5,6,10,11,12,13,14,15,16,18,20,21,23, 29,31,32,33,35,37,38,39,41,43,45,46,48,49, 51,52,53,54,58,62,64,65,68,70,71)
12	Benzo[b]fluoranthene	BDL	BDL	None
13	Benzo[a]pyrene	BDL	0.0292	Thirty three (5,7,8,11,12,14,15,16,18,20,21,23,24,25,26, 27,31,32,33,34,37,38,39,41,43,47,50,54,56, 62,63,67,68)
14	Indeno[1,2,3-cd]pyrene	BDL	0.0394	Eight (6,11,27,40,42,47,61,69)
15	Dibenz[a,h]anthracene	BDL	BDL	None
16	Benzo[g,h,i]perylene	BDL	0.0321	Nineteen (5,7,10,11,13,14,15,16,20,34,37,47,50,54,56,62, 65,67,69)
17	Total PAHs (Permissible Limit =0.1 µg/L)	BDL	0.7919	Seventy three (1,2,3,4,5,6,7,8,9,10,11,12,13, 14,15,16,17,18,19,20,21,22,23,24,25,26,27, 28,29,30,31,32,33,34,35,36,37,38,39,40,41, 42,43,44,45,46,47,48,49,50,51,52,53,54,55, 56,57,58,59,60,61,62,63,64,65,66,67,68,69, 70,71,72,73)

*Sample number given in **Red** represents the sample having value more than the permissible limit.

Table 18. Polynuclear Aromatic Hydrocarbons (PAHs) Concentrations in Groundwater of Krishna delta (Pre-monsoon 2022)

S.No.	PAHs	Min.	Max.	Sample Number
1	Naphthalene	BDL	0.045	Forty eight (74,75,76,77,78,79,80,81,82, 83,84,85,86,87,88,89,90,91,92,93,94,95, 96,97,98,100,101,102,103,105,106,107, 109,111,112,113,114,116,118,119,121,122, 123,126,131,135,136,137)
2	Acenaphthylene	BDL	0.009	Forty two (74,75,78,79,82,83,85,8687,88, 91,94,96,97,98,99,100,101,102,103,104, 105,106,109,110,111,112,113,114,116, 119,120,121,122,123,125,126,127,128, 131,133,136)
3	Acenaphthene	BDL	0.009	Thirty four (75,77,79,80,89,92,94,96,97,98, 99,101,103,104,105,107,108,109,111,113, 114,117,118,121,125,129,130,131,132,133, 134,135,136,137)
4	Pyrene	BDL	0.022	Fifty eight (74,75,76,77,79,80,81,82,84,85, 86,87,88,89,90,92,93,94,96,97,98,99,101, 102,103,104,105,106,107,108,109,111,112, 113,114,115,116,117,118,119,120,121,122, 123,124,125,126,127,128,129,130,131,132, 133,134,135,136,137)
5	Flourene	BDL	0.006	Twelve (76,91,96,97,101,106,110,122,130, 131,135,136)
6	Fluoranthene	BDL	BDL	None
7	Phenanthrene	BDL	0.020	Sixty four (74,75,76,77,78,79,80,81,82,83, 84,85,86,87,88,89,90,91,92,93,94,95,96,97, 98,99,100,101,102,103,104,105,106,107, 108,109,110,111,112,113,114,115,116,117, 118,119,120,121,122,123,124,125,126,127, 128,129,130,131,132,133,134,135,136,137)
8	Anthracene	BDL	0.019	Sixty three (74,75,76,77,78,79,80,81,82,84, 85,86,87,88,89,90,91,92,93,94,95,96,97,98, 99,100,101,102,103,104,105,106,107,108, 109,110,111,112,113,114,115,116,117,118, 119,120,121,122,123,124,125,126,127,128, 129,130,131,132,133,134,135,136,137)
9	Benz[a]anthracene	BDL	0.024	Fourteen (74,81,86,88,91,93,101,102,113, 124,129,131,135,136)
10	Chrysene	BDL	BDL	None
11	Benzo[k]fluoranthene	BDL	0.022	One (87)
12	Benzo[b]fluoranthene	BDL	0.019	Six (102,103,107,128,129,134)
13	Benzo[a]pyrene	BDL	0.016	Twelve (74,76,80,88,89,97,98,101,110,118, 124,127)
14	Indeno[1,2,3-cd]pyrene	BDL	0.030	Nine (74,88,102,109,118,128,129,131,133)
15	Dibenz[a,h]anthracene	BDL	0.008	Two (81,135)
16	Benzo[g,h,i]perylene	BDL	0.008	Seven (74,88,100,114,119, 128,131)
17	Total PAHs (Permissible Limit =0.1 µg/L)	BDL	0.122	Sixty four (74,75,76,77,78,79,80,81,82,83, 84,85,86,87,88,89,90,91,92,93,94,95,96,97, 98,99,100,101,102,103,104,105,106,107, 108,109,110,111,112,113,114,115,116,117, 118,119,120,121,122,123,124,125,126,127, 128,129,130,131,132,133,134,135,136,137)

*Sample number given in **Red** represents the sample having value more than the permissible limit.

Table 19. Polynuclear Aromatic Hydrocarbons (PAHs) Concentrations in Groundwater of Krishna delta (Post-monsoon 2022)

S.No.	PAHs	Min.	Max.	Sample Number
1	Naphthalene	BDL	0.6594	Sixty three (74,75,76,77,78,79,80,81,82,83, 84,85,86,87,88,89,90,91,92,93,94,95,96,97, 98,99,100,101,102,103,104,105,106,107, 108,109,110,111,112,113,114,115,116,117, 118,119,120,121,122,123,124,125,126,127, 128,129,130,131,132,134,135,136,137)
2	Acenaphthylene	BDL	0.0056	Forty eight (77,80,81,82,83,84,85,86,87,88,90,91, 92,93,94,95,96,97,99,100,101,102,103,104, 109,110,112,114,115,116,118,119,120,121, 122,123,124,125,127,128,129,130,131,132, 134,135,136,137)
3	Acenaphthene	BDL	0.0158	Eighteen (82,85,87,89,91,95,98,99,104,106, 110,111,112,113,117,129,131,136)
4	Pyrene	BDL	0.0611	Twenty (77,82,85,96,100,101,102,103,105,107,108, 111,114,120,126,128,129,134,136,137)
5	Flourene	BDL	0.0135	Five (81,86,88,90,125)
6	Fluoranthene	BDL	BDL	None
7	Phenanthrene	BDL	BDL	None
8	Anthracene	BDL	0.1097	Fifty nine (74,75,76,77,78,79,80,81,82,84, 86,87,88,90,91,92,93,94,95,96,97,98,99,100, 101,102,103,104,105,106,107,108,109,110, 111,112,113,114,115,116,117,118,119,120, 121,122,123,124,125,126,127,128,129,130, 131,132,134,135,136,137)
9	Benz[a]anthracene	BDL	0.06815	Forty nine (74,75,76,77,78,79,80,86,87,92,93,94, 96,98,99,101,102,103,104,105,106,107,108,109, 110,112,113,114,115,116,117,118,119,120,121, 122,123,124,125,126,128,129,130,131,132,134 ,135,136,137)
10	Chrysene	BDL	BDL	None
11	Benzo[k]fluoranthene	BDL	0.0708	Twenty four (74,75,80,83,85,89,90,102,103,104,105,109, 112,113,114,116,120,123,125,129,130,131, 132,135)
12	Benzo[b]fluoranthene	BDL	BDL	None
13	Benzo[a]pyrene	BDL	0.0427	Twenty three (78,80,83,84,92,96,98,99,104,105,106,108 ,109,110,112,116,118,122,124,126,131,132)
14	Indeno[1,2,3-cd]pyrene	BDL	0.0487	Thirteen (77,85,86,93,94,100,108,114,116,119,131,132,137)
15	Dibenz[a,h]anthracene	BDL	BDL	None
16	Benzo[g,h,i]perylene	BDL	0.0519	Twenty two (76,78,81,85,86,88,91,96,100,104,105,106,107,108,110, 116,117,118,121,130,131,137)
17	Total PAHs (Permissible Limit =0.1 µg/L)	BDL	0.9554	Sixty four (74,75,76,77,78,79,80,81,82,83, 84,85,86,87,88,89,90,91,92,93,94,95,96,97, 98,99,100,101,102,103,104,105,106,107, 108,109,110,111,112,113,114,115,116,117, 118,119,120,121,122,123,124,125,126,127, 128,129,130,131,132,133,134,135,136,137)

*Sample number given in **Red** represents the sample having value more than the permissible limit.

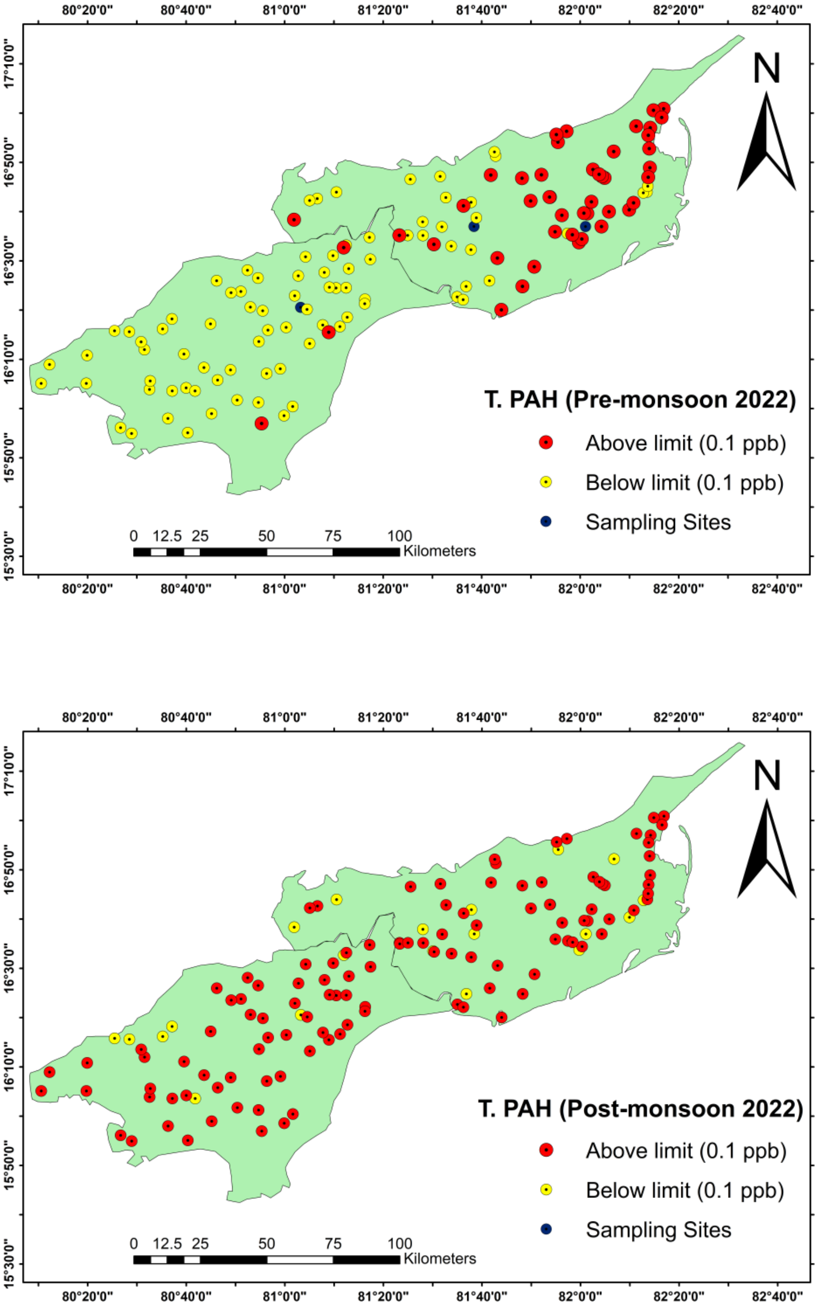


Fig. 58. Spatial distribution of Total PAH in groundwater of the study area

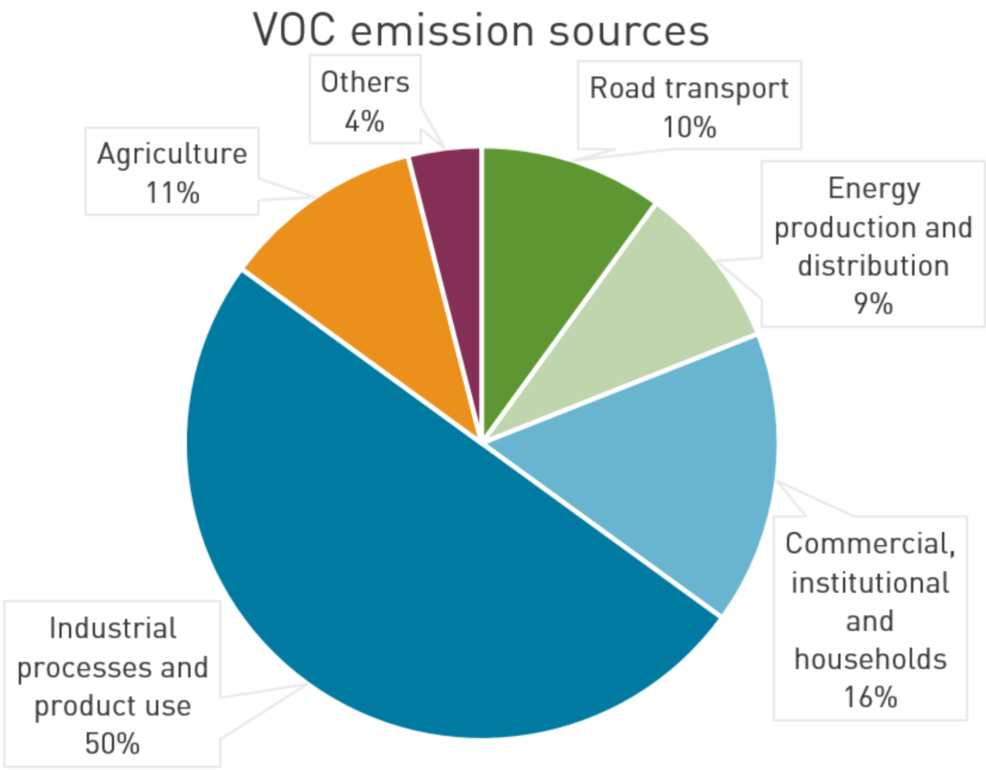
5.6.4 Volatile Organic Compounds (VOCs) Concentrations in Groundwater of Study Area

The main sources of Volatile Organic Compounds (VOCs) are industrial processes and product uses. Many household items viz; adhesives, air freshners, drapes, floor polishes, glue, carpet backing, dyes, liquid cleaners, markers, paint, toilet cleaners are also the source of VOCs (Fig. 59 & 60) (Table 20). No limit of VOCs has been prescribed by BIS (2012) for drinking purpose. In the present investigation, 9 VOCs viz; Benzene, Toluene, Butylacetate, Undecane, m-Xylene, o-Xylene, Ethylbenzene, p-Xylene and Styrene were analysed in the collected groundwater samples from study area during pre-and post-monsoon season (2022) using Agilent GC-MS/MS. Analysis revealed that only one VOC, Undecane was observed in four samples of Godavari delta and three samples of Krishna delta during the pre-monsoon period (Table 21 and Table 23). Moreover, Undecane & Benzene was observed in 2 & 36 samples of Godavari delta respectively and 3 & 13 samples of Krishna delta respectively during the post-monsoon period (Table 22 and Table 24).

Table 20. Commonly found Volatile Organic Compounds, their Sources and Health effect

S.No.	Contaminants	Source/Uses	Health Effect
1	Benzene	• Natural constituent of crude oil and one of the elementary petrochemicals &partially responsible for the aroma around petrol (gasoline) stations. • Used as a gasoline (petrol) additive, benzene increases the octane rating and reduces knocking. • Gasoline's benzene content with limits typically around 1%	Risk of cancer, Cause of Bone Marrow Failure, Cardiovascular disease
2	Toluene (Methyl Benzene)	• Paintthinner, permanent markers, contact cement and certain types of glue • Crude oil and byproduct in the production of gasoline by a catalytic reformer or ethylene cracker. • Byproduct of the production of coke from coal • Used as octane booster in gasoline fuels for internal combustion engines as well as jet fuel • Used as a coolant for its good heat transfer capabilities	Tiredness, confusion, weakness, drunken-type actions, memory loss, nausea, loss of appetite, hearing loss,Colour Vision loss
3	Butylacetate	• Used as a synthetic fruit flavoring in foods such as candy, ice cream, cheeses, and baked goods and solvent in nail polish	Highly Flammable

4	Undecane	• Used as a mild sex attractant for various types of moths and cockroaches, and an alert signal for a variety of ants	Hazardous nature
5	Ethyl Benzene	• Important in the petrochemical industry as an intermediate in the production of styrene, the precursor to polystyrene, a common plastic material. • Produced by burning of coal, gas, and oil • A constituent of tobacco smoke	Risk of cancer, Cause of Bone Marrow Failure, Dizziness, Cardiovascular disease, Adverse effect in children.
6	Xylene (Dimethyl Benzene) (o-, m-,p-)	• Byproduct of the production of coke from coal. • Used as a solvent in printing, rubber, and leather industries. • Occurs in crude oil in concentrations of about 0.5–1%. • Used in mass production of modern plastics	Headaches, irritability, depression, insomnia, agitation, extreme tiredness, tremors, hearing loss,impaired concentration and short-term memory loss
7	Styrene	• Occurs naturally in small quantities in some plants and foods • Found in coal tar • Used in rubber, plastic, insulation, fiberglass, pipes, automobile and boat parts, food containers, and carpet backing.	Toxin to the gastrointestinal tract, kidney, and respiratory system



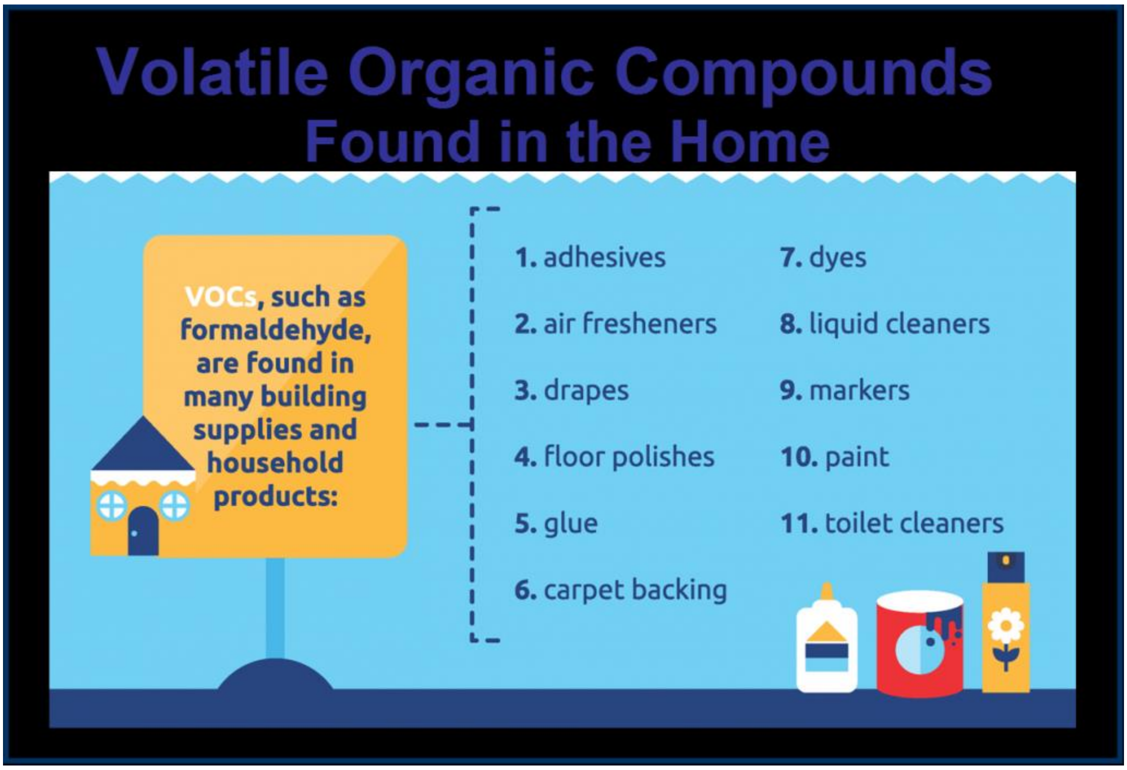


Fig. 59. VOC emmision sources from different sectors and sources from home

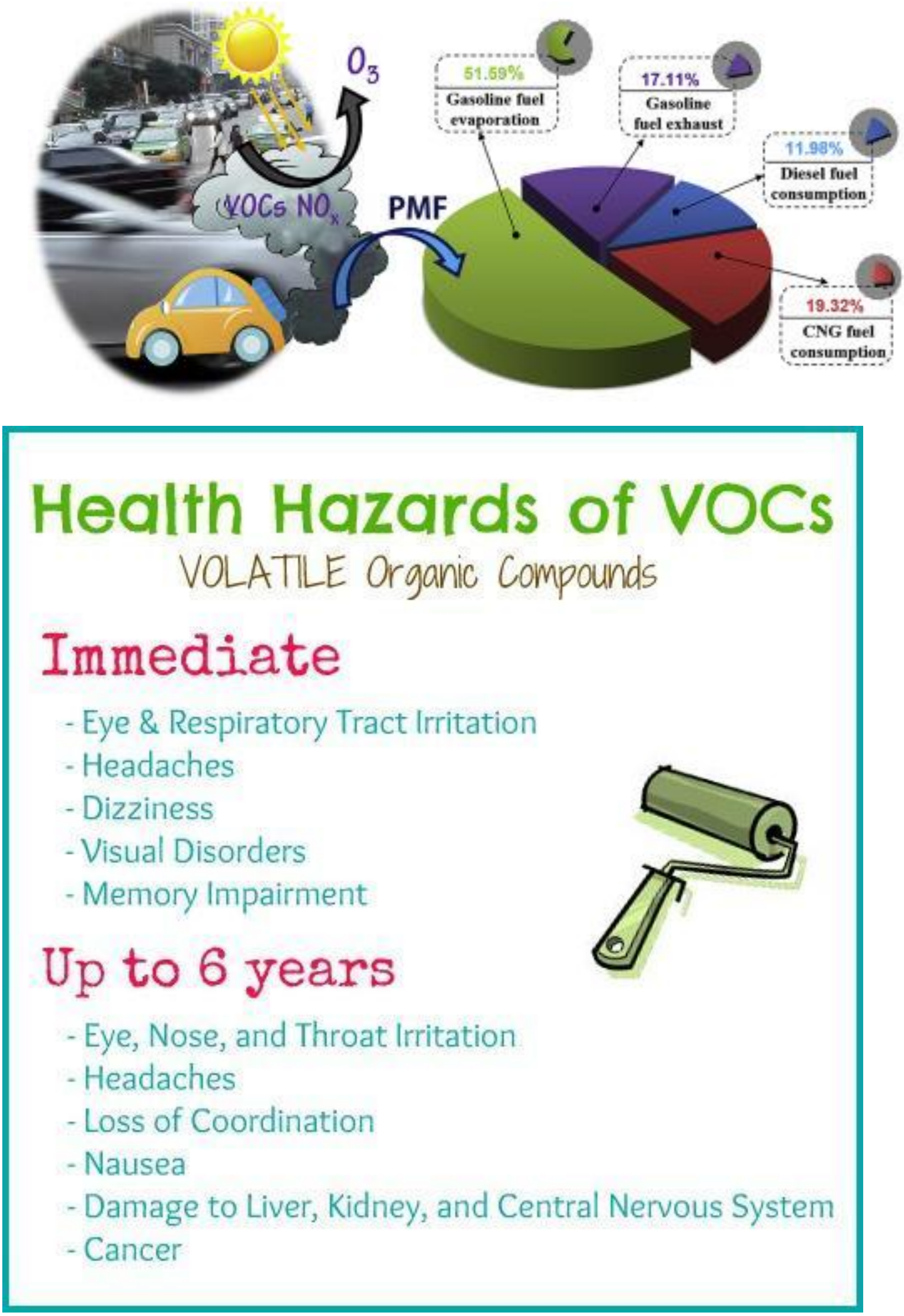


Fig. 60. Human health hazards of VOC

Table 21. Volatile Organic Compounds (VOCs) Concentrations in Groundwater of Godavari delta (Pre-monsoon 2022)

S. No.	VOCs	Min.	Max.	Sample Number
1	Benzene	BDL	BDL	None
2	Toluene	BDL	BDL	None
3	Butylacetate	BDL	BDL	None
4	Undecane	BDL	6.648	Four (7,14,35,73)
5	m-Xylene	BDL	BDL	None
6	o-Xylene	BDL	BDL	None
7	Ethylbenzene	BDL	BDL	None
8	P-Xylene	BDL	BDL	None
9	Styrene	BDL	BDL	None

Table 22. Volatile Organic Compounds (VOCs) Concentrations in Groundwater of Godavari delta (Post-monsoon 2022)

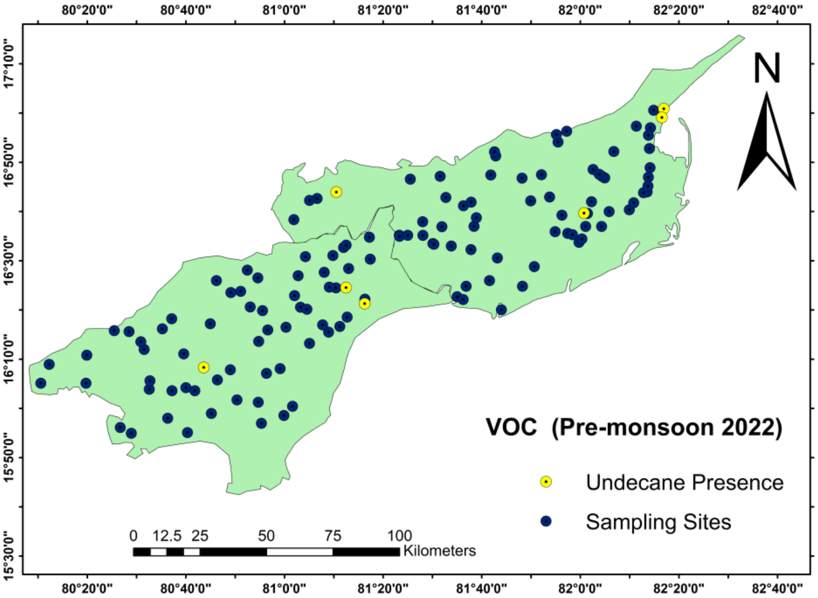
S. No.	VOCs	Min.	Max.	Sample Number
1	Benzene	BDL	0.6318	Thirty Six (3,6,7,8,11,12,18,21,25,37,39,40,41,42,43,45,46,47,48, 49,50,51,52,53,54,55,56,58,59,60,64,65,68,69,71,72)
2	Toluene	BDL	BDL	None
3	Butylacetate	BDL	BDL	None
4	Undecane	BDL	6.6494	Two (12,31)
5	m-Xylene	BDL	BDL	None
6	o-Xylene	BDL	BDL	None
7	Ethylbenzene	BDL	BDL	None
8	P-Xylene	BDL	BDL	None
9	Styrene	BDL	BDL	None

Table 23. Volatile Organic Compounds (VOCs) Concentrations in Groundwater of Krishna delta (Pre-monsoon 2022)

S. No.	VOCs	Min.	Max.	Sample Number
1	Benzene	BDL	0.617	Nine (93,109,115,118,120, 122,123,131,137)
2	Toluene	BDL	BDL	None
3	Butylacetate	BDL	BDL	None
4	Undecane	BDL	6.673	Three (98,107,122)
5	m-Xylene	BDL	BDL	None
6	o-Xylene	BDL	BDL	None
7	Ethylbenzene	BDL	BDL	None
8	P-Xylene	BDL	BDL	None
9	Styrene	BDL	BDL	None

Table 24. Volatile Organic Compounds (VOCs) Concentrations in Groundwater of Krishna delta (Post-monsoon 2022)

S. No.	VOCs	Min.	Max.	Sample Number
1	Benzene	BDL	0.6222	Thirteen (74,77,78,84,85,93,109,115,118,120,122,123,131)
2	Toluene	BDL	BDL	None
3	Butylacetate	BDL	BDL	None
4	Undecane	BDL	6.673	Three (98,107,122)
5	m-Xylene	BDL	BDL	None
6	o-Xylene	BDL	BDL	None
7	Ethylbenzene	BDL	BDL	None
8	P-Xylene	BDL	BDL	None
9	Styrene	BDL	BDL	None



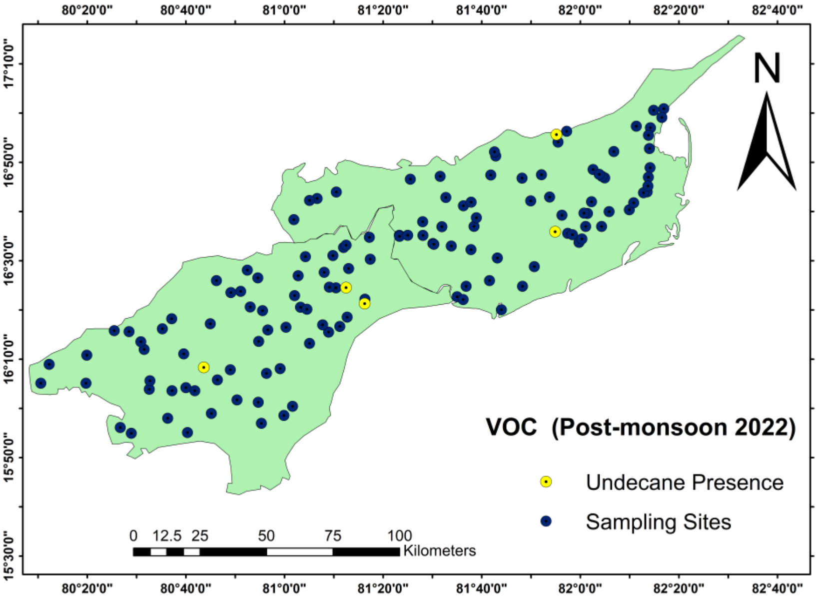
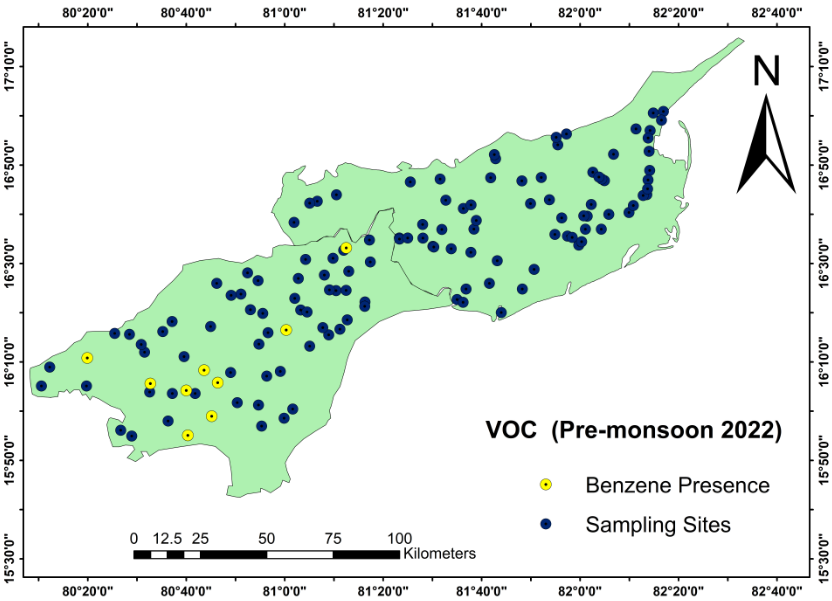


Fig. 61. Spatial distribution of Undecane in groundwater of the study area



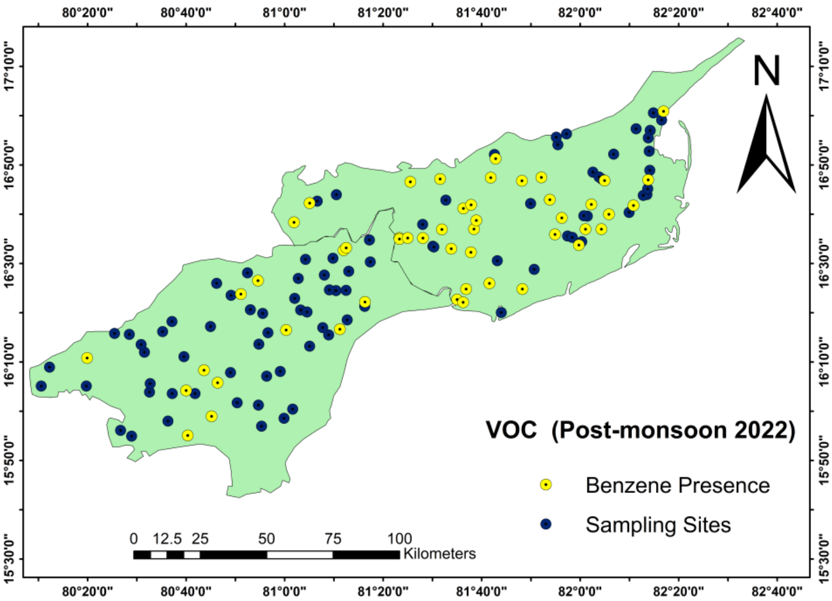


Fig. 62. Spatial distribution of Benzene in groundwater of the study area

5.7 Soil quality in KG Delta

Changes in ph and Eh have an enormous effect on chemical and biological processes in the soil substrate. Petroleum microseepage in the soil substrate causes several chemical reaction and microbial oxidation of hydrocarbons and also causes decrease in Eh and pH. Mineral stability in any environment is dependent on and is a function of pH and Eh. Hydrocarbons migrating into the near surface soils destablizes many compounds and increases the solubility of the trace and minor elements. Many metal elements are highly soluble in acid solutions but will be precipitated as oxides and hydroxides with increasing pH. Oxidation-reduction potential plays a major role on the mobility of elements. Anomalous amounts of V, Cr, Ni, Co, Mn, Hg, Cu, Mb, U, Zn, Pb & Zr are + indicators of petroleum deposits. Migrating hydrocarbons create a reducing environment in the soil and subsurface, which increases the solubility of many trace and major elements. In the present investigation, 12 soil samples were collected from different locations of KG Delta (Table 25) and analysed for V, Cr, Ni, Co, Cu, Zn, Ba & Sr concentrations. Normal values of these metals are given in Table 26. Variation of these metals in different soil samples is given in Fig. 63. The concentrations of all these metals in the collected soil samples were observed with in normal values of these metals and no anomalous behaviour was observed.

Table 25. Details of Soil Samples collected from KG Delta

S. No.	Sample ID	Location
1	1	Rally
2	2	Anaparthy
3	3	Garagaparru
4	4	Akiveedu-Pz
5	5	Appanapally
6	6	Antarvedi
7	7	Perupalem
8	8	Eluru (postal colony)
9	9	Munganda-Pz
10	10	Penumantra
11	11	Tatipaka
12	12	Pasalapudi

Table 26. Normal values of the metals V, Cr, Ni, Co, Cu, Zn, Ba, Sr in Soil

S. No.	Element	Normal Soil value (mg/kg)
1	V	90
2	Cr	70
3	Ni	50
4	Co	8
5	Cu	30
6	Zn	90
7	Ba	500
8	Sr	250

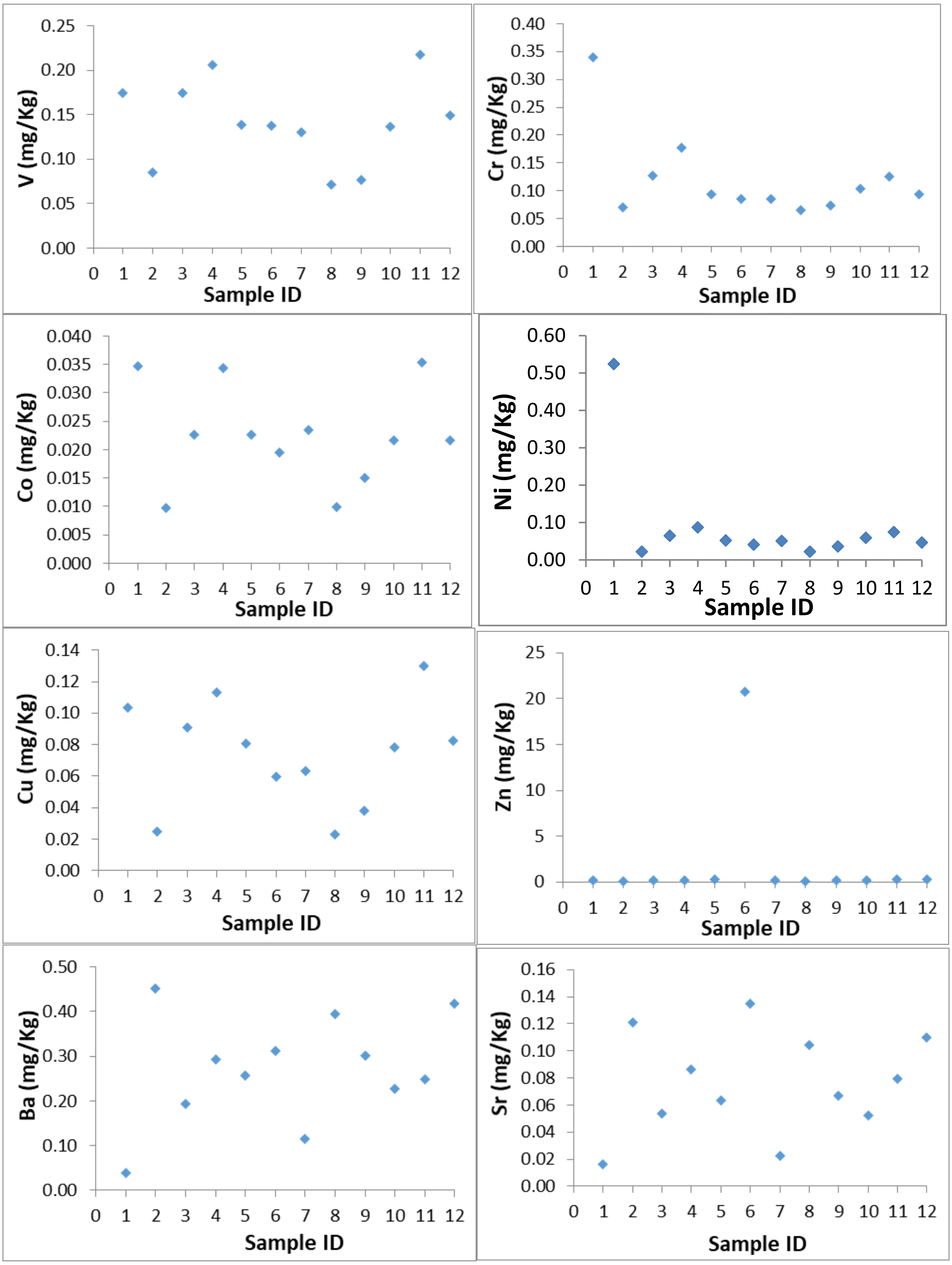


Fig. 63. Variation of the metals V, Cr, Ni, Co, Cu, Zn, Ba & Sr in different soil samples

6.0 UTILITY OF THE STUDY

The study has identified degraded groundwater quality zones, possible sources of pollution, understanding geochemical processes controlling the aquifer chemistry and suggested the measures for sustainable groundwater supply for drinking purpose in the study area, therefore enable better planning and management of groundwater resources.

7.0 CONCLUSIONS

The following conclusions may be drawn from the study:

- TDS, Alkalinity, Hardness, Ca, Mg, Cl, SO_4 and NO_3 in the groundwater of the few locations of study area exceeds the maximum permissible limit prescribed by BIS for drinking purposes.
- The presence of heavy metals has been recorded in many samples and the water quality standards have been violated for iron, aluminium, boron, manganese, nickel, lead, mercury and arsenic in few of the samples in Godavari basin delta while the concentrations of iron, aluminium, boron, mercury, manganese, lead, uranium and arsenic in few samples have been violated in Krishna basin delta.
- Carbonate weathering is a major source of dissolved ions in the groundwater of the study area. Cation exchange process and halite dissolution control the chemistry of groundwater of the region.
- Groundwater is more saline in Krishna Delta than Godavari delta which may be attributed to sea water mixing process.
- The comparison between LMWL and GWL indicates there is no direct rainfall recharge into shallow groundwater due to alluvial formations.
- The stable isotopes indicated that there is more evaporation in Krishna delta than in Godavari delta thus supports EC variations.
- The Tritium values (TU) of groundwater in KG deltas indicated that the Krishna delta groundwater is older than Godavari delta.
- d-excess vs well depth indicated that there are significant evaporation and mixing processes found in the KG Deltas.
- Presence of many pesticides were observed in many samples of the study area and BHC-Alfa has exceeded the maximum prescribed limit in more than 90% of the samples of the study area. Polychlorinated Biphenyls have also been detected in the samples of the study area but within the permissible limit of Total PCB.
- Total PAHs exceeded the maximum prescribed limit in more than 80% of the samples collected from Godavari basin delta.
- The presence of volatile organic compounds (Benzene) was also observed in few of the samples of Godavari and Krishna basin delta.
- Metal concentrations (Zn, Cu, Cr, Co, Ni, Ba, Sr, V, Se) in the soil samples of petroliferous regions of the study area were observed with in normal values of these metals and no anomalous behaviour was observed.

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