

Research Paper

Trace Elements in Groundwater of Coastal Aquifers of Pondicherry Region, India

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Abstract

Totally forty three representative groundwater samples were collected from various aquifers of Pondicherry region covering urban, rural and industrial areas and analyzed for trace elements concentration using Atomic Absorption Spectrophotometer. Also, eleven sediment samples at different depths from two bore holes, representing various aquifer systems were collected and analyzed for various minerals using XRD techniques. Concentrations of Arsenic and Iron were higher than the permissible limits of World Health Organisation. The higher concentration of these two trace elements must be due to presence of arsenic and iron bearing minerals and their continuous interaction with pore water. The higher concentration of boron in the coastal ground water of the study area is due to the geological formations of marine origin. The concentration of rest of the elements in almost all samples is less than the permissible levels prescribed by World Health Organization. The complex geological environment present in the study area plays a dominant role on the concentration and spatial distribution of trace metals in ground water.

Keywords: India, Groundwater, Pollution, Pondicherry, Trace Elements

1. Introduction

The trace metals are probably the most harmful and insidious pollutants because of their non-biodegradable nature and their potential to cause adverse effects on human beings at certain levels of exposure and absorption. There is an increase in epidemiological and other evidences, indicating an association between water quality and mortality from cardio vascular and other chronic diseases. Trace elements designate a group of elements that occur in natural system in minute concentration and when present in sufficient quantities, are toxic to living organisms. The behaviour of metals in ground water is complicated than surface water. It depends on source and many bio- and geochemical processes that control macro chemical and trace element conditions (Edmunds, 1973; Edmunds et al, 1987; Stuyfzand, 1991; Stuyfzand, 1992 and Drever, 1998). The major controls are pH and Eh, speciation, dissolution and equilibrium solubility control,

sorption, precipitation, uptake by vegetation and release through mineralization (Stuyfzand, 1992 and Levin & Gosk, 2008).

Aquifer contamination by trace metals has become a striking problem in the last few decades, due to increasing pollution of the environment. Widespread high concentration generally results from natural processes, although human activities locally increase trace metals. The problem is especially delicate if bank filtration has to be applied in urban regions, where the aquifer is under the permanent influence of (mostly polluted) river water and also under the influence of other pollution source (industrial plants, sewers, airborne pollution, etc.). Bank filtration is regarded as an accumulator of heavy metals. The changes in pH, redox potential and ionic strength initiate the remobilization of accumulated heavy metals

and cause severe deterioration of aquifer water quality. Municipal sewage also adds trace metals to surface and ground water (Robards et al, 1994).

General studies describing the mobility of trace metals are scarce. Tanji & Valoppi (1989) gave an overview of trace element behaviour in agriculturally controlled systems and differentiated trace elements from natural sources from these agricultural induced contaminations. Stuyfzand (1991 and 1992) has published a general study on contamination ranges and possible mobilisation processes in many groundwater types in Netherlands. Many researchers like Aiuppa et al (2003), Ahmed et al (2004), Bodenat et al (2004), Goh & Lim (2005), Nickson et al (2005), Raju (2006), Govindaradjane et al (2007) and Reddy et al (2007) etc. have also reported the presence of trace metal in natural waters.

Pondicherry is one of the regions in India that depends solely on groundwater to meet the needs of drinking, irrigation and industry. Excessive mining of groundwater, intense agricultural practices and the geological environment prompted to study trace metal concentration in groundwater.

2. Study Area

The Pondicherry region is the largest among the four isolated domains of the union territory of Pondicherry and is located on the east coast of India, forming enclaves within the Cuddalore district of Tamil Nadu state (Figure 1). The region covers an area of 293 sq. km, consisting of 179 villages with a total population of 0.6 Million as per 2001 census (Govindaradjane et al, 2007). Physiographic-ally, the study area is a flat plain with an average elevation of about 15 m above MSL (CGWB, 1993).

The climate of Pondicherry region is humid and tropical. The mean monthly temperature ranges between 22 and 33 degree Celsius. It receives an annual rainfall of 1281 mm. The position of groundwater table varies from 1.5 to 27 meters. The Pondicherry region is basically an agriculture area and the land used for crop production is around 56 %. The area is covered with Quaternary, Tertiary and Mesozoic sediments with Archaeans as the basement rocks (CGWB, 1993). The stratigraphic succession of the study area is given in Table 1.

3. Methodology

Forty three representative groundwater samples, in total, were collected from the aquifers of Pondicherry region covering urban, rural and industrial areas. The locations of groundwater samples are shown in Figure 1. The collection, preservation and analyses of water samples

were carried out following the procedure prescribed by APHA (1998). The ground water samples were analysed for trace metals using Atomic Absorption Spectrophotometer. Also, eleven representative sediment samples were collected from various depths at two boreholes, one at Pillaichavady and another at Ashram Lake Estate, covering all aquifer systems such as Cuddalore, Kadaperikuppam, Manaveli, Ottai clay and Vanur sandstone formations. The lithologs and depth at which sediment samples collected are shown in Figure 2. The sediment samples were analyzed using XRD technique ("PANalytical XPert Pro X-ray powder diffractometer" in the 2θ range of $15-75^\circ$ using $\text{CuK}\alpha$ radiation by powder diffraction method) to identify minerals having trace metals as constituents.

4. Results and Discussion

The X-ray diffractograms of sediment samples (Figure 3a and 3b) indicate the presence of minerals such as Quartz (Qz), Microcline (Mc), Calcite (Ca), Dolomite (Do), Pyrite (Py), Realgar (Rg), Arsenolite (Ae), Claudetite (Ct), Lautite (Lt), Covellite (Cv), Mimitite (Mi), Atelestite (At), Elpasolite (El) and Sarkinite (Sk). The arsenic, iron, manganese, copper, lead etc. bearing minerals present in the aquifers act as source of these elements in groundwater in the study area.

The study area consists of sedimentary formations such as sandstone, limestone, shale, peat and unconsolidated sediments of marine origin. Also, the iron sulphides such as pyrite and marcasite are reported to be present in the aquifer materials (CGWB, 1993). Further, lignite is present in the form of seams in cuddalore sandstone formation. The geological formations present in the study area are of marine origin and hence there is every possibility for the presence of trace metal in groundwater. The excessive pumping of groundwater leading to sea water intrusion (CGWB, 1993) and spurt in industrial activity further enhance the scope for higher concentrations of trace metals. The chief mechanism controlling chemistry of ground water of Pondicherry region is rock water interaction (Sivasankaran et al, 2005). Further, it has already been reported that sulphide minerals such as pyrite, claudetite, arsenolite, marcasite etc. are present in the aquifer sediments in the study area (Reddy et al, 2007). Also, the higher concentration of arsenic in the ground water is mainly due to lithology of geological setup coupled with excessive mining of ground water (Govindaradjane et al, 2007).

The collected water samples were analyzed for trace elements (having different biogeochemical characteristics). The results show wide spatial variations in the concentration of most of the trace elements in the study area (Figures 4a-d and Figures 4e-h).

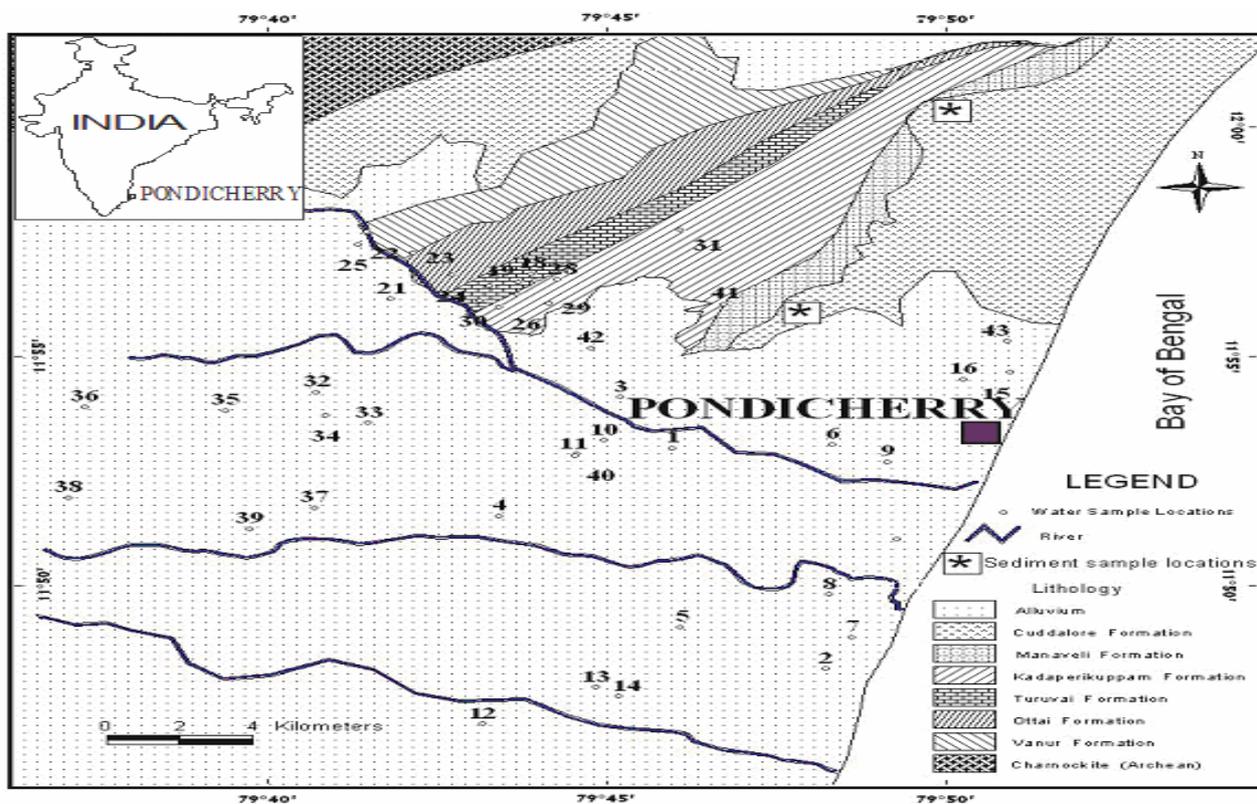


Figure 1. Study Area with Sample Locations and Lithology

4.1. Metalloids

The spatial distribution of total dissolved Arsenic (As) gradually increased from 3 to the maximum of 99 $\mu\text{g/l}$ at location 43 with a mean value of 20.5 $\mu\text{g/l}$. The observation made here for dissolved As seems to be higher than 10 $\mu\text{g/l}$, a provisional guide line value prescribed by WHO, in almost 47% of the samples (WHO, 1993). The concentration of As in natural water usually associates with sedimentary rocks of marine origin, weathering of volcanic rocks, fossil fuels, mineral deposits, mining waste, agricultural waste and irrigation practices (Hunt & Howard, 1994). Anthropogenic source of As are numerous both in the form of organic metal complexes and inorganic ions. Mandal et al (1996) indicated that the source of arsenic may also be due to the geology of the area. The sedimentary geological formations of marine origin and presence of arsenic and iron bearing minerals such as Pyrite, Realgar, Arsenolite, Claudetite, Scorodite, Covellite, Enargite and Prosprite are the sources of arsenic in the study area. The redox conditions prevailing in the study area might have favoured the release of Arsenic from the source to ground water.

Selenium (Se) with an average crystal abundance of 0.01 mg/kg, occurs in most types of rocks, but is enriched in shale. Geochemically, selenium resembles sulphur and

these two are often found in the association with one another. Selenium concentration typically ranges from less than 0.01-5.00 $\mu\text{g/l}$ when there are no major anthropogenic inputs. In the study area, Se concentration ranged from 12-355 $\mu\text{g/l}$. The clay / shale present in aquifer systems of the study area must be the source of Se present in ground water.

Silver (Ag) concentration in ground water ranged from 0.02-0.1 $\mu\text{g/l}$. Silver is relatively rare element, with an average concentration in the earth's crust of 0.7 mg/kg. Although silver can occur in the elemental form in the environment, several ores contain silver, including argenite (Ag_2S) and homesilver (AgCl). Some times, it associates with complex sulphides present in the subsurface environment. The WHO has stipulated a guidelines value of 50 $\mu\text{g/l}$ for Ag in drinking water. The observed value in the study area is well within the limits. The presence of various types of sulphide minerals in the aquifer systems and their interaction with pore water release the Ag in to ground water in the study area.

4.2. Nutrients Type Traces Elements

In the ground water system, certain trace metals such as Cd, Cu, Ni and Zn are involved in biogeochemical cycles similar to nutrients. The evidence for this is the covariance

in concentration of metals such as Cd, Cu, Ni, Zn with PO_4 , NO_3 , SiO_2 in water column profiles (Martin & Windom, 1991). This indicates that these metals are incorporated into phytoplankton in the surface euphotic zone along with nutrients and released at the depth due to microbial degradation of organic detritus.

manure and the acid in rain dissolves minerals, changes cation exchange complex occupation. This leads to higher concentration of trace metals such as Cd, Cu, Co, Ni and Zn in ground water. Also, the elevated concentrations are due to the fact that Cu has strong affinity for clays, iron, manganese hydroxides, sulphide, and carbonate minerals

Table 1. Stratigraphic Succession of Pondicherry Area

Era	Period	Epoch	Formations	Lithology
Cenozoic	Quaternary	Recent	Alluvium, laterite	Sands, clays, silts, kankar and gravels, laterite
		Mio-Pliocene	Cuddalore Formation	Pebbly & gravelly & coarse grained sandstones with minor clays & siltstones with thin seams of lignite
Unconformity				
Cenozoic	Tertiary	Palaeocene	Manaveli Formation	Yellow & yellowish brown, grey calcareous siltstones and claystone & shale with thin bands of limestone
			Kadaperikuppam Formation	Yellowish white to dirty white sand. Hard fossiliferous limestone, calcareous sandstone and clays
Unconformity				
Mesozoic	Upper Cretaceous		Thuruvai Formation	Highly fossiliferous limestone, conglomerate at places, calcareous sandstone and clays
			Ottai Claystone	Grey to grayish green claystones, silts with thin bands of sandy limestone and fine grained calcareous sandstone
	Lower Cretaceous		Vanur Sandstone	Quartzitic sandstone, hard coarse grained, occasionally feldspathic or calcareous with minor clays
			Ramanathapuram Formation	Black carbonaceous silty clays and fine to medium grained sands with bands of lignite and medium to coarse grained sandstone
Unconformity				
	Archaean		Eastern Ghat complex	Charnockite and Biotite hornblende gneisses

Reference: CGWB, 1993

The concentration of Cadmium (Cd) in the lithosphere is low, normally ranges from 0.1-0.2 μ g/l. It is concentrated in sulphide minerals of other metals like zinc sulphide, lead sulphide, mercuric sulphide, etc., (Manahan, 1979 and Nraigu, 1980). The Cd also associates with various types of sulphide minerals, sedimentary environment as one of the impurities. The Cd concentration in ground water of the study area varies from 0.10 μ g/l to 4 μ g/l with mean value of 1.62 μ g/l. The Cd concentrations in ground water of the study area were well within the limit of WHO and MINAS standards (1993). The slightly higher range of Cd must be due to its release from aquifer sediments.

The copper (Cu) concentration ranged from 1.14-33.8 μ g/l with a mean value of 5.81 μ g/l. A slightly elevated concentration of dissolved Cu was observed in the study area. Generally, oxidation of reduced N and S in the

(Purvaja, 1995). Hence, Cu shows a pronounced tendency to form complexes with carbonate, nitrate, sulphate, chlorides and ammonia. The higher concentration of Cu in ground water in the study area is predominantly due to the presence of Covellite (CuS), a copper bearing sulphide mineral in clay layers and their interaction with pore water.

The Nickel (Ni) concentration exhibits a wide variation and ranged from 3-130.21 μ g/l with the average value of 14.7 μ g/l in the study area. Ni usually associates with organic rich soils, clay and loamy environment. In addition to these geologically bound sources, anthropogenic inputs of Ni through the application of phosphates fertilizers may also be important sources in this region.

Zinc (Zn) is the one of the most important trace nutrient for various types of vegetation. The concentration of Zn in

the study area ranged from 1-93 $\mu\text{g/l}$ and shows a wide variation in the contents. In the few locations, higher concentrations of Zn were observed. Generally, the industrial effluents and agriculture irrigation return contribute higher concentrations of Zn to ground water. The possibility of elevated contamination of nutrient type trace elements in ground water in the study area due to agriculture irrigation return is remote as the ground water table is at deeper levels in most part of the area and also presence of impervious clay layers in the subsurface environment.

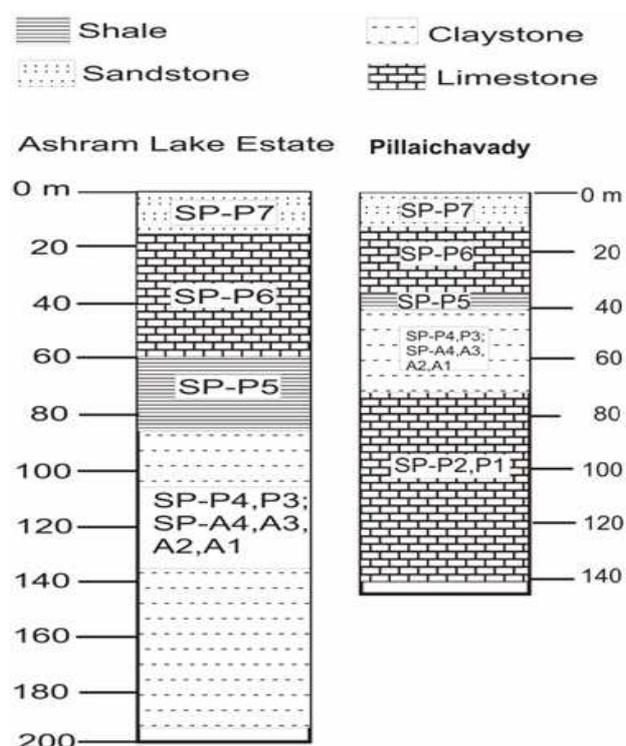


Figure 2. Lithologies of the two Borehole Samples with Depth Collected at Ashram Lake Estate and Pillaichavady

4.3. Geochemically Controlled Trace Elements

Cobalt (Co) concentration in ground water of the study area ranged from 0.24-5.06 $\mu\text{g/l}$. The abundance of Co in the sedimentary rocks ranges from 0.1-20 mg/l and seems to be associated with clay and organic matter. Also, Co commonly associates with arsenic-sulphur minerals. The presence of sedimentary formations having arsenic-sulphur mineral is the source for elevated concentration and spatial variations of Co in the study area.

Lead (Pb) concentration in the study area ranged from 0.22-5.02 $\mu\text{g/l}$. Lead content of unpolluted natural surface water world wide has been estimated to be 1 $\mu\text{g/l}$ to 10 $\mu\text{g/l}$. The level of lead content in the study area is less than the mean concentration of lead in public water supplies

elsewhere in the world. The Lead chloro-arsenate (Mimitite) present in the aquifer materials might be the source of lead in the groundwater in the study area.

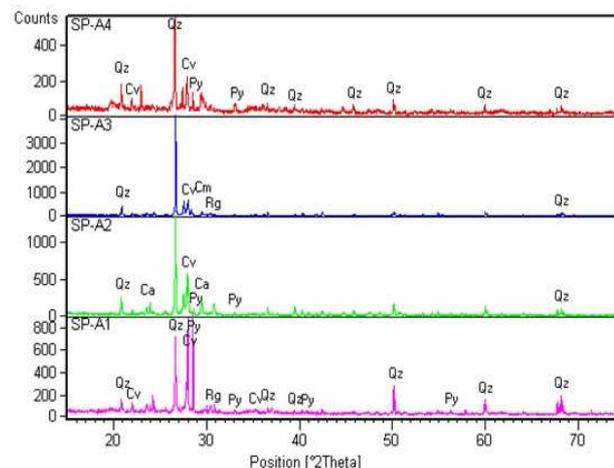


Figure 3a. The X-Ray Diffractograms of Sediment Samples Indicating the Presence of Various Minerals

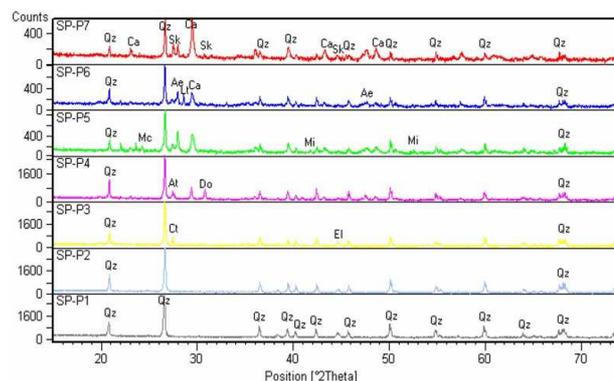


Figure 3b. The X-Ray Diffractograms of Sediment Samples Indicating the Presence of Various Minerals

Iron (Fe) is a non-conservative trace element found in significant concentrations in drinking water because of its abundance in earth's crust. It was observed that concentration of Fe in ground water in the study area vary from 264-21990 $\mu\text{g/l}$ with an average of 1685 $\mu\text{g/l}$. About 73 % of the samples shown concentration of iron more than the provisional guideline value of 300 $\mu\text{g/l}$ prescribed by WHO (1993). The higher concentration and extreme spatial variations of Fe in groundwater reflects abundance of iron bearing minerals such as pyrite, realgar etc. and their variation in aquifer systems. The higher concentration of Fe in groundwater of the study area is essentially geogenic.

The concentration of Mn in groundwater in the study area varies from 0.85-393 $\mu\text{g/l}$ with mean value of 6.33 $\mu\text{g/l}$. An anomalous concentration of 86.63 $\mu\text{g/l}$ at the location

24 and 393 $\mu\text{g/l}$ at the location 2 were observed. The Manganese associate with complex sulphide minerals present in sedimentary rocks. The presence of Sarkinite in the aquifer systems is the source of Mn in the groundwater.

value of 24.50 $\mu\text{g/l}$. Generally, the natural content of chromium in drinking water is very low, containing between 1-10 $\mu\text{g/l}$ except for region with substantial chromium deposits (Krishna Murthi & Viswanathan, 1995).

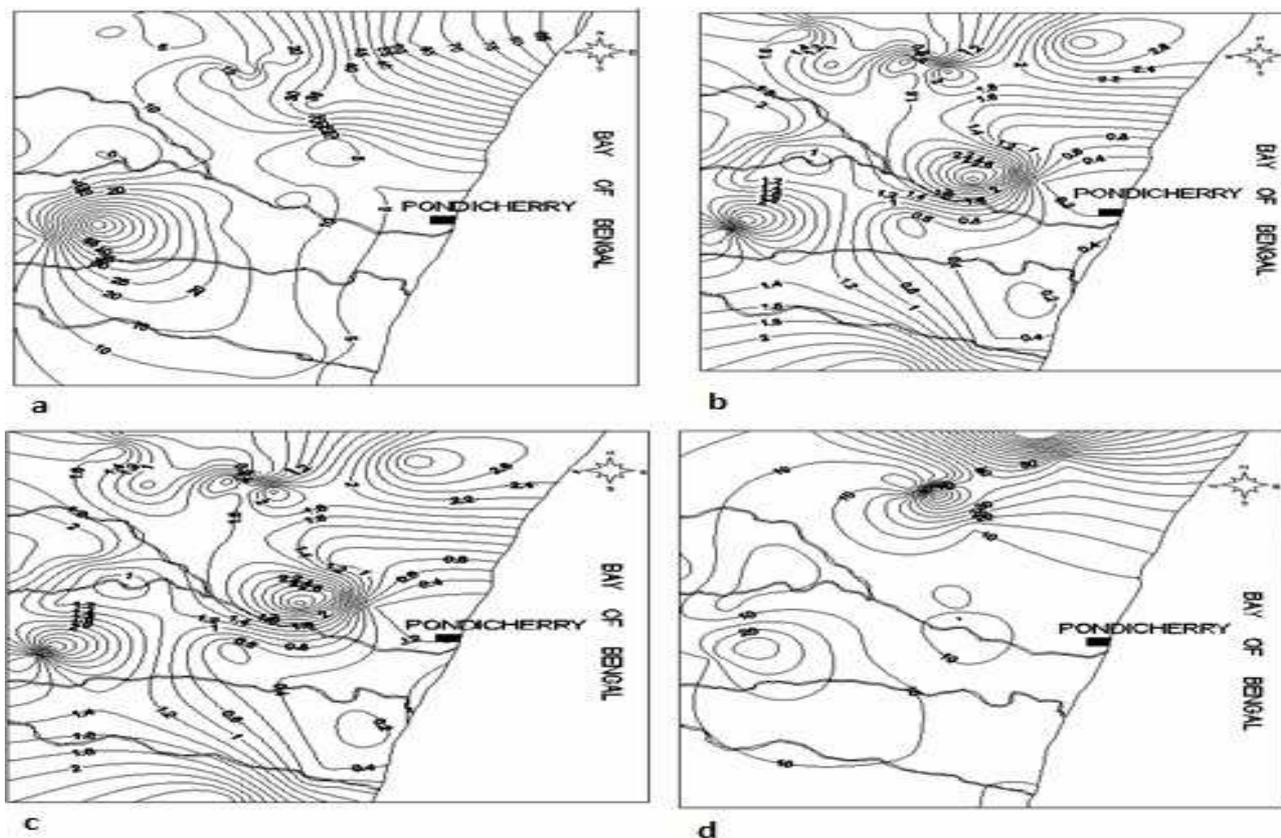


Figure 4a-4d. Spatial Variation of Trace Elements in the Study Area

Vanadium (V) concentration in the study area ranged from 12-265 $\mu\text{g/l}$. Natural V occurs in igneous rocks, in titaniferous magnetite, in the certain deposits of phosphate rocks in the shale and in asphaltic deposits. The V tends to be associated with organic matter and therefore, its elevated concentration in ground water is common. The presence of geochemically controlled trace elements, their concentration and spatial distribution is predominantly controlled by geological environment.

4.4. Biological / Pollutational Forms of Trace Metals

Chromium (Cr) is the ubiquitous in nature and most commonly found in the trivalent state, but hexavalent compound are also found in small quantities. The trivalent form is an essential nutrient for man, required in amount of 50 $\mu\text{g/day}$ to 200 $\mu\text{g/day}$, whereas, the hexavalent form is carcinogenic to man and animals. In the study area, the Cr concentration ranged from 9.32-54.26 $\mu\text{g/l}$ with a mean

Among the micro nutrient required for plant growth, Mo is required in the smallest amounts. Mining and milling of Mo is potential source of Mo release into the environment. Also, the Mo occasionally associates with complex sulphide minerals in sedimentary environment. The study area consists of sedimentary formations rich in sulphide minerals. In the study area, the concentration of Mo ranged from 1-3 $\mu\text{g/l}$, which is within the acceptable limit of WHO and MINAS.

Boron (B) concentration in the ground water of the study area ranged from 44-378 $\mu\text{g/l}$ with an anomalous concentration of 2595 $\mu\text{g/l}$ at location 35. Boron bearing salts associating with gypsum, anhydrite and clay are not uncommon. Usually, the boron is expected to be present in the sediments of marine origin. The higher concentration of boron in the coastal ground water of the study area is mainly due to the geological formations of marine origin.

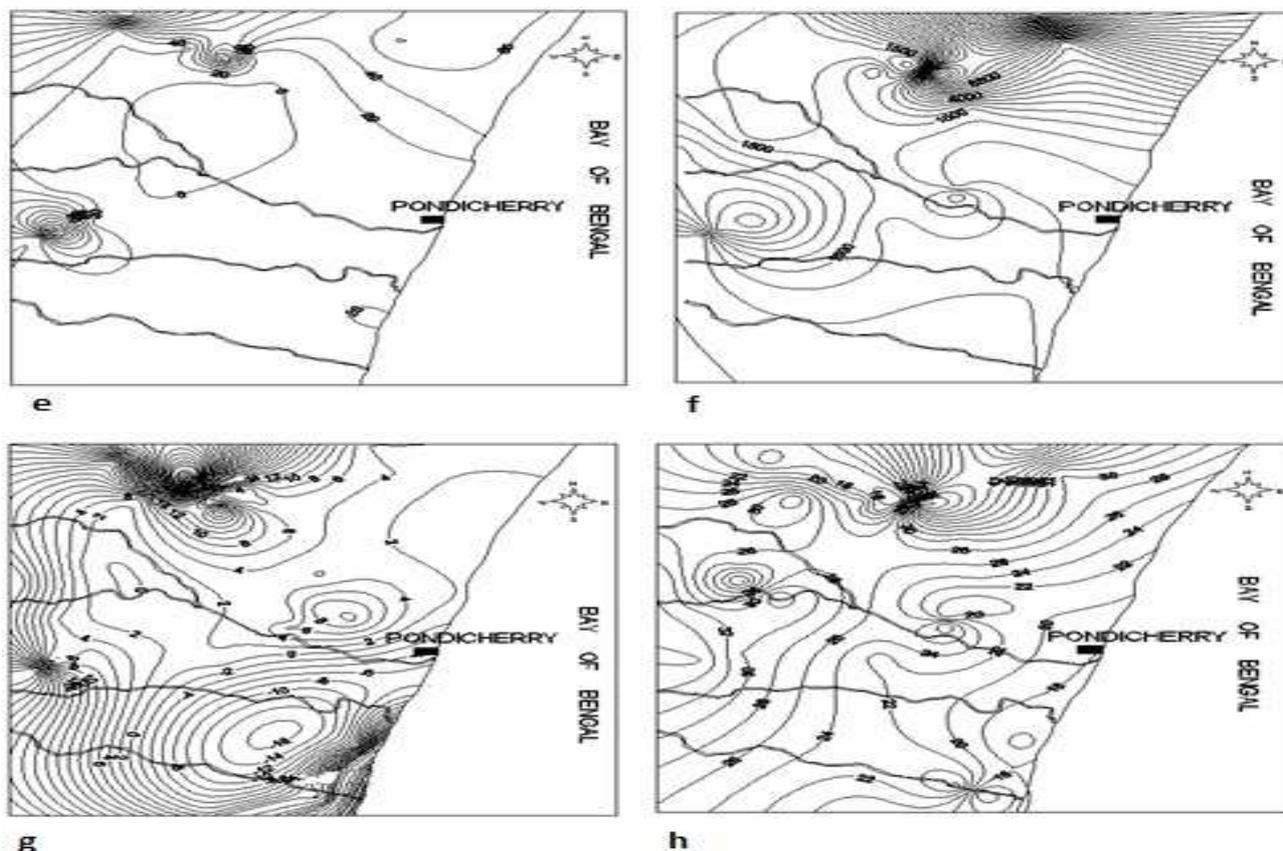


Figure 4e-4h. Spatial variation of trace elements in the Study Area

5. Conclusion

It was observed that 47% of As and 73% of Fe samples show higher concentration of As and Fe than the provisional guide line value of 10 $\mu\text{g/l}$ and 300 $\mu\text{g/l}$ respectively, prescribed by WHO (1993). Higher concentration of these trace elements must be due to presence of arsenic and iron bearing minerals and their continuous interaction with pore water. The higher concentration of boron in the coastal ground water of the study area is due to the geological formations of marine origin. The concentration of rest of the elements in almost all samples is less than the permissible levels prescribed by WHO. In general, the complex geological environment present in the study area plays a dominant role on the concentration and spatial distribution of trace metals in ground water.

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