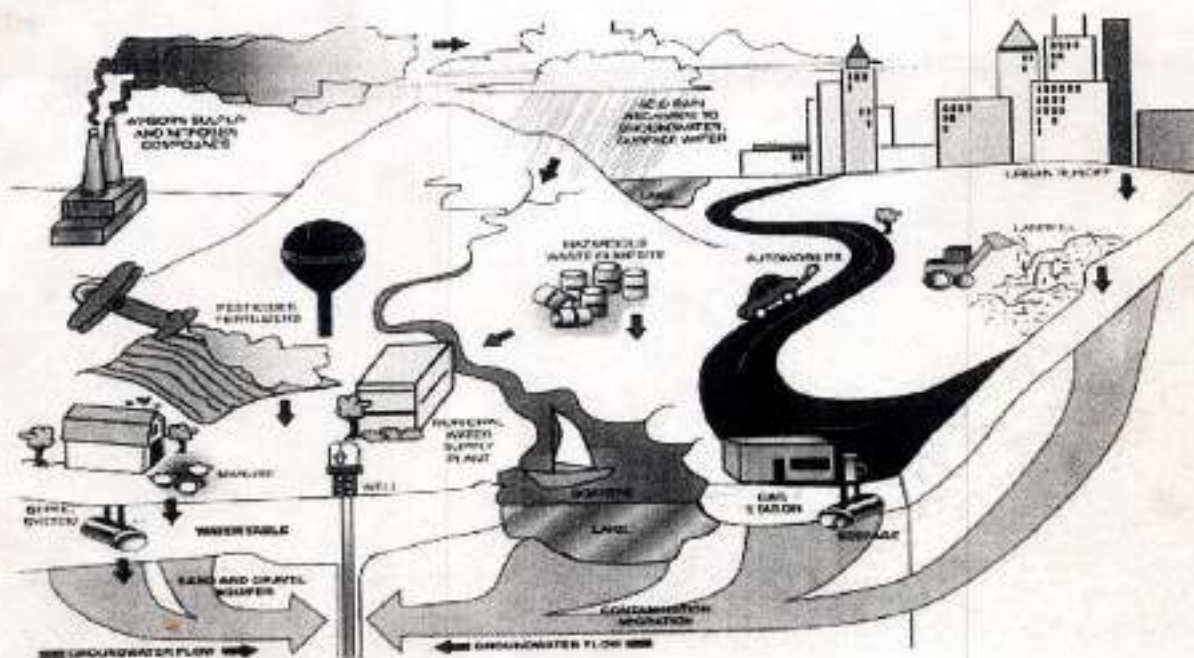


**MINISTRY OF WATER RESOURCES
GOVERNMENT OF INDIA
&
INDIAN NATIONAL COMMITTEE ON
HYDROLOGY**

***Research Project Report on*
WATER QUALITY ASSESSMENT
AND CHARACTERIZATION IN
PONDICHERRY REGION**



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WATER QUALITY ASSESSMENT AND CHARACTERIZATION IN THE PONDICHERRY REGION

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WATER QUALITY ASSESSMENT AND CHARACTERIZATION IN PONDICHERRY REGION

1.0 PROJECT SUMMARY

Presently, there is a growing awareness that development of water resources, must be sustainable, which implies that the natural resources must be managed and conserved in such a way as to meet the needs for present and future generations. Accurate information on the condition and trends of groundwater quality and quantity is required as a basis for economic and social development and for maintenance of environmental quality through a proper perception of the physical processes controlling the hydrological cycle in time and space. Pondicherry region, with an aerial extent of 293 km² and agriculture being the predominant sector followed by industrial sector, depends only on the groundwater source. In order to better understand the water quality, nature of the source and pollutant migration and distribution, the present study investigates the several aspects of groundwater of the entire Pondicherry region from three major aquifers.

The first aspect of the present work deals with the hydro geochemistry of groundwater where major ion distribution and the processes controlling the seasonal variation of these ions were studied. The dominant cations and anions of the groundwater in Pondicherry region were found to be in the order of Na>Ca>Mg>K and HCO₃>Cl>SO₄ (meq l⁻¹) respectively. The predominant hydrochemical facies of groundwater were identified as Na+KHCO₃, CaHCO₃ and MgHCO₃. Also the classification of groundwater based on total dissolved solids, hardness, salinity and sodium concentration were made. Rock-water interaction was found to be the mechanism controlling the major ion chemistry. It is seen that the major ion concentrations are predominantly influenced by natural agencies than the anthropogenic activities. Also the findings reveal that the over exploitation of groundwater has invited the problem of sea water intrusion along the coast line and results in the increase of major ions such as Na and Cl.

The second aspect of the study is concerned with the nutrient biogeochemistry, emphasizing the impact of agricultural fertilizers on the groundwater quality. The

distribution of nutrient concentration indicates that leaching of the fertilizers applied to croplands resulted in the enrichment of nutrients in groundwater of agriculture area in Pondicherry region. The spatial variation of nutrient concentration reveals that the nitrogenous nutrients are enriched by about 2 to 3 times in well waters of urban area than in agriculture area, indicating the abundant leaching nutrients from municipal waste and sewage effluents through the urban soil.

The third aspect of the investigation is focused on the trace element concentration and distribution in groundwater. The study indicates that the trace elements are mostly derived from anthropogenic sources (industrial and municipal waste discharges), which are being delivered into the hydrological systems either directly or indirectly. Good correlations observed for a number of trace metals point out to their origin is due to human activities. Spatial variation in concentration of organochlorine pesticides in Pondicherry region has been studied for the samples collected in surface water, shallow and deep wells. The total residual level of organochlorine pesticides in different sources are in the order of tanks (36 ng l^{-1}) > shallow wells (20.8 ng l^{-1}) > deep wells (15.1 ng l^{-1}). The residual level of organochlorine pesticides are found to be 3 to 4 times more in agriculture area than in urban area. On the basis of the present analyses, mean organochlorine pesticide content of Pondicherry groundwater has been computed. Comparisons have been made with water from lakes, rivers, estuary and ocean in India. There is a striking similarity between the DDT concentration of Pondicherry water and river Cauvery and Vellar estuary.

Finally, the pattern and extent of seawater intrusion in fresh water aquifer has been studied by applying numerical modeling. The study reveals that the salt water has intruded into the coastal alluvial aquifer for about 3000 meters irreversibly. The zone between 3000 meters and 6000 meters from the coastline will always be under the dynamic influence of salt water and fresh water. The study also suggests that the development of groundwater from the alluvial aquifer can be planned only after a distance of 6000 meters from the coastline. The results of the study reveals that the over exploitation of groundwater and improper management of natural resources, led to the unequal distribution of major and trace elements in the Pondicherry region.

2.0 INTRODUCTION

Freshwater for human consumption is a fragile, finite resource and the demand for freshwater continues to grow with human population. The diversion of fresh water supply to agriculture, industrial and domestic needs stretch hydrological system to the limit. Within a nation, these needs compete for a supply of freshwater that may already be scarce and may vary drastically both seasonally and geographically. In India the pressure on land has been enormous as can be judged from the fact that in 1961, the urban population was 78 million and the figures now available on the basis of 1991 census show 217 million, representing 27.7% of the total population, as against 18%, 30 years ago. In view of the increasing population, the rivers and groundwater resources can easily become polluted with untreated domestic and industrial waste as well as agricultural chemicals let into them.

Agriculture, as the single largest user of freshwater on a global basis and as a major cause of degradation of surface and groundwater resources through erosion and chemical runoff, has cause to be concerned about the global implications of water quality. The associated agrofood-processing industry is also a significant source of organic pollution in most countries. Aquaculture is now recognized as a major problem in freshwater, estuarine and coastal environments, leading to eutrophication and ecosystem damage. The principal environmental and public health dimensions of the global freshwater quality problem are highlighted below:

- Five million people die annually from water-borne diseases
- Ecosystem dysfunction and loss of biodiversity
- Contamination of marine ecosystems from land-based activities
- Contamination of groundwater resources
- Global contamination by persistent organic pollutants

Experts predict that, because pollution can no longer be remedied by dilution (i.e. the flow regime is fully utilized), freshwater quality will become the principal limitation for sustainable development in the future. Groundwater contamination incidentally,

occurs primarily through non-point sources such as seepage from overlying surface waters and runoff. Non-point source pollutants, irrespective of source, are transported overland and through the soil by rainwater and recharge. These pollutants ultimately find their way into groundwater, wetlands, rivers and lakes and, finally, to oceans in the form of sediment and chemical loads carried by rivers. As discussed below, the ecological impact of these pollutants range from simple nuisance substances to severe ecological impacts involving fish, birds and mammals, and on human health. The range and relative complexity of agricultural non-point source pollution are illustrated in Figure 1.

Fig. 1: Complexity of non-point source pollution in groundwater



Non-point source water pollution, once known as "diffuse" source pollution, arises from a broad group of human activities for which the pollutants have no obvious point of entry into receiving watercourses. In contrast, point source pollution represents those activities where wastewater is routed directly into receiving water bodies by, for example, discharge pipes, where they can be easily measured and controlled. Obviously, non-point source pollution is much more difficult to identify, measure and control than point sources.

The term "point source" means any discernible, confined and discrete conveyance, including but not limited to any pipe, ditch, channel, tunnel, conduit, well, discrete fissure, container, rolling stock, concentrated animal feeding operation, or vessel or other floating craft, from which pollutants are or may be discharged. This term does not include agricultural storm water discharges and return flows from irrigated agriculture." The reference to "agricultural storm water discharges" is taken to mean that pollutant runoff from agriculture occurs primarily during storm flow conditions.

Sources of contamination that can cause groundwater contamination

Point sources:

- On-site septic systems
- Leaky tanks or pipelines
- Leaks or spills of industrial chemicals at manufacturing facilities
- Underground injection wells (industrial waste)
- Municipal landfills
- Livestock wastes
- Leaky sewer lines
- Fly ash from coal-fired power plants
- Sludge disposal areas at petroleum refineries
- Land spreading of sewage or sewage sludge
- Graveyards

Non-point (distributed) sources

- Fertilizers on agricultural land
- Pesticides on agricultural land and forests
- Contaminants in rain and dry atmospheric fallout

The pollution due to the non-point source is greatly influenced by meteorological, hydrological and geological conditions, in addition to the land-use pattern. The ecological impact of the pollutants affects human health, flora and fauna. Sewer overflows and run-off threatens the life sustainable properties of our water, endanger human health and have an ecological impact over flora and fauna.

3.0 IMPORTANCE OF THE STUDY

Many groundwater basins are used at such rates that the groundwater is being mined. This contributes to the growing interest in enhanced ("artificial") groundwater recharge to stabilize the position of the water table, and in some instances to return the water table to levels existing before the overdraft. In addition, water development projects that had been focused largely on the development of surface water reservoirs for water storage are being refocused on water conservation and the development of groundwater storage of surface waters (conjunctive use) owing to difficulties in constructing new surface water reservoirs. Water utilities and districts in many areas of the country are participating in and/or planning for conjunctive use projects in which surplus surface waters obtained during wet periods are recharged to the aquifer for use during dry periods/droughts. There is considerable discussion today about the potential impact of contaminants in waters used for enhanced recharge on groundwater and aquifer quality (i.e., the ability of the aquifer to serve as a reliable water supply source or conjunctive use aquifer).

The widespread finding that many groundwater basins have been polluted by contaminants derived from industrial, municipal, and agricultural activities, coupled with the conclusion that once a groundwater and aquifer area are polluted it is difficult (if not impossible at least in the near-term) to restore the aquifer to unrestricted use, provides justification for concern about the potential impacts of contaminants in recharge waters on groundwater and aquifer quality. Regulatory agencies at the central and state levels are establishing concentration limits for contaminants in waters used for enhanced recharge, that are designed to protect groundwater and aquifer quality. In addition there is growing concern about the quality of "incidental recharge" waters such as river water that pass to the groundwater aquifer through the river bed. Wastewater discharges to rivers are not typically being evaluated and regulated with regard to potential impacts of contaminants on groundwater and aquifer quality. Therefore, it becomes necessary to focus on issues pertaining to water quality for not only optimizing the available resource but also to maintain a quality that is usable in the future. In evaluating the potential impacts of chemical and biological contaminants

in recharge waters it is necessary to determine whether the contaminants in such waters could:

- Pollute an aquifer to impair its use for water supply,
- Lead to the pollution of waters recovered from the aquifer due to contaminants already present in the aquifer from natural and anthropogenic sources and
- Limit the ability to recharge and recover water from the aquifer – impact aquifer hydraulic quality

Surface waters that recharge aquifers include relatively poorly treated domestic and industrial wastewaters, agricultural waters, and urban and rural storm waters. Each of those sources contains a wide variety of chemical contaminants that can be adverse to groundwater and aquifer quality.

In many parts of the world, tremendous increase in demand for freshwater has occurred due to population growth and industrial and intense agricultural activities. In order to meet the demand, groundwater commonly has been overexploited and the quality is being affected. The geochemistry of groundwater is largely a function of the mineral composition of the aquifer through which the water flows. Thus differences in aquifer composition are reflected as differences in the ground water chemistry. Though several researchers/organizations have attempted to characterize the quantity and quality of groundwater in Pondicherry region, India (Central Ground Water Board, [CGWB] report, 1993), no systematic temporal and spatial variations in the water chemistry have been studied. Hence, in this study, a concerted effort was undertaken to evaluate the quality of groundwater, with reference to domestic and irrigational purposes, by studying major ion distributions and their variations with seasons and water type by identifying inter-elemental correlations.

4.0 OBJECTIVES

The primary aim of this research work is to assess the quality of the available water resources, health hazards as a result of toxic accumulation and their impact on environment. The detailed objectives are to:

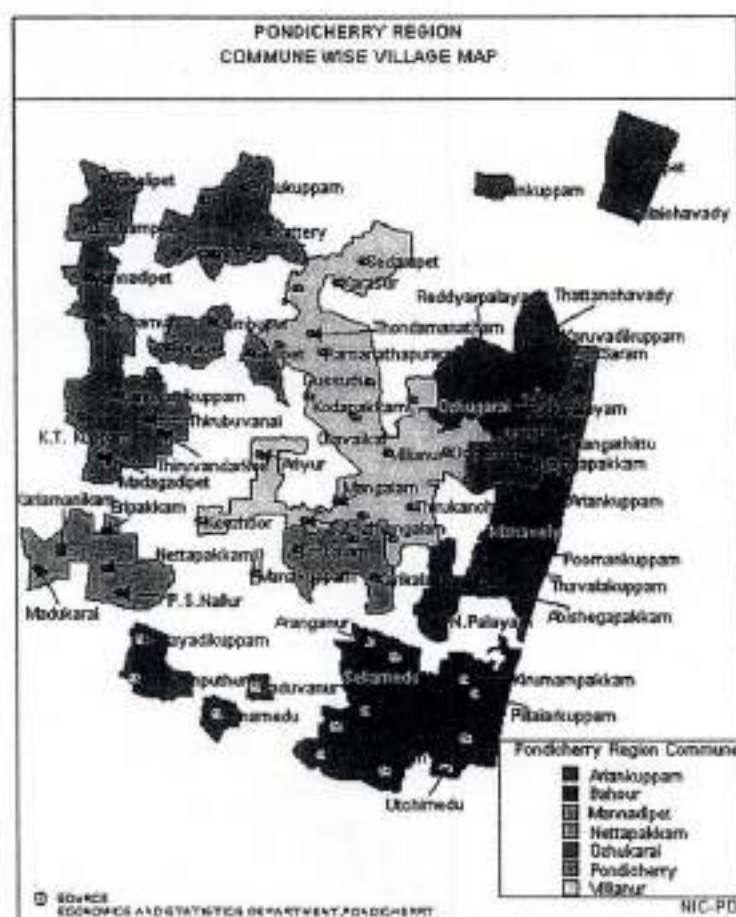
- Assess the spatial and temporal variation of major and trace elements in the ground water and surface water of Pondicherry Region and to understand the process controlling the seasonal variation of these elements
- Determine the spatial variation of the various forms of inorganic nutrients (NO_3 ; NO_2 ; NH_4 and PO_4) in ground water to evaluate the impacts of agriculture activity in this region
- Evaluate the residue levels of organochlorine pesticides in surface and ground waters of this region
- Predict the dispersion and migration patterns of the metals and to establish the geochemical pattern and hydro chemical facies of ground water of this region
- Study the pattern and extent of salt-water intrusion into the fresh water aquifer system using solute-transport modeling
- Propose the possible water management practices limiting seawater intrusion and to create a comprehensive assessment of pollution with a scientific database.

5.0 STUDY AREA

Background on land use in Pondicherry

Pondicherry region is one among the four isolated domains of the Union Territory of Pondicherry along the east coast (Fig.2) and has an aerial extent of 293 km². The climate of the region is humid and tropical and receives an average rainfall of 1254 mm, which is mostly contributed by northeast monsoon. The groundwater is the sole source of water supply for domestic, industrial and agricultural activities. Agriculture being the major economic activity of the rural population, it also has its effects on the groundwater quality of this region. Hence, a multidisciplinary approach involving the major ion chemistry, trace elements and nutrients, the residual level of organochlorine pesticides in groundwater are the primary foci of this study.

Fig. 2: Base Map of Pondicherry



As Pondicherry economy has grown, economic activity has moved away from agriculture to industries and services. Agriculture now accounts for less than 10% of GSDP in Pondicherry as opposed to 30% only three decades ago. In spite of this change, which is indicative of the transition to a more diversified economy, agriculture continues to be a main source of livelihood, i.e. 25% of the workforce still depends on agriculture and allied activities.

Sources of Irrigation

Despite Pondicherry's achievements in terms of irrigation (reflected by relatively high irrigation intensities), the fact that the intensity ratio has actually declined over time suggests that there are certain constraints in terms of irrigation. The different regions of the Union Territory not only have different sources of irrigation, but are also confronted with different problems. While Karaikal depends significantly on canal irrigation, tank irrigation is more prominent in the Pondicherry region. Groundwater irrigation, however, has become the major source of irrigation in the Union Territory as a whole.

Groundwater

Since the 70s, groundwater irrigation has expanded phenomenally in Pondicherry. There are over 8000 tubewells in the Pondicherry and Karaikal regions. Most of these tubewells are deep tubewells averaging a depth of 100 meters and often being as deep as 200 meters. The net area commanded by the wells is about 15000 ha. Thus, for every 2 ha there is a tubewell. Getting an electrical connection for the tube wells is quite easy. Moreover, now most of the tubewells are with submersible pumpsets and electricity supply is available 24 hours a day. Groundwater is, therefore, often used without any restriction. A recent study by the Agriculture Department revealed that about 40% of excess water is utilized which has resulted in the decline of the water table. Besides for declining water tables, excessive pumping of groundwater can result in intrusion of seawater in the coastal areas. This is slowly becoming a major issue of concern in both the coastal belts of Pondicherry and Karaikal. Although groundwater use is very difficult to monitor, effective steps will have to be taken if the depletion of the groundwater table is to be stopped in the future such as charging for use of electricity.

Pollution

Groundwater

The quality of groundwater has also deteriorated, especially near industrial areas. Industrial pollution confronts agriculture in two ways: through groundwater pollution

and surface water pollution. The problem in Pondicherry is particularly bad because industrial areas are spread throughout the Pondicherry and Karaikal regions and often are located close to agricultural areas. For example, groundwater resources of the Pillyarkuppam-Kirumambakkam region is contaminated with toxic chemicals such as arsenic, mercury, nickel and lead. Major polluting industries include the paper, paint and sugar industries. Paper mills are releasing untreated effluents in closed conduits; effluents consequently seep through pipes and mix with the groundwater. The paint industry has stocked coal tar (a raw material) in open areas, which have leached into the groundwater. Other negative externalities also exist. In areas where industries are manufacturing calcium chloride, water has a strong chlorine smell and is white in color.

Surface Water

Surface irrigation systems are also being polluted. The major culprit in terms of surface water pollution has been the sugar mills. Sugar mills have been releasing effluents into canals, which are feeding irrigation tanks. In one case, effluents have been released into a canal, which feeds 21 irrigation tanks in the region and the adjoining Villupuram district tanks. While these are individual examples, they are symptomatic of the wider problem of industrial pollution, which needs to be addressed so that agriculture does not have to bear the brunt of the negative externalities.

Fertilizers

The intensity of fertilizer use in Pondicherry is also very high. Generally, increases in productivity have been associated (at least partly) with increasing use of chemical fertilizers. What is noticeable in the case of Pondicherry is that despite the declining area under agriculture, the use of fertilizers has increased from the late eighties to the present. Table 1 gives details of the amount of fertilizers used in the Union Territory. While in the short run, chemical fertilizers might indeed increase overall productivity, in the long run there are potential negative effects of too much fertilizer use, especially in terms of declining land productivity, but also in terms of other negative externalities such as water pollution.

Table 1: Quantity of different fertilizers used in Pondicherry (in tonnes)

Year	Nitrogen	Phosphorous	Potassium	Total
1988-89	10,033	3,259	4,896	18,188
1990-91	11,180	4,291	6,430	21,905
1993-94	11,526	3,820	3,933	19,269
1996-97	13,760	4,109	4,356	22,225
1999-2000	12,469	5,673	5,177	23,319

Source: Directorate of Economics and Statistics, Government of Pondicherry, Various issues of the Abstract of Statistics.

The indication already is that the benefits of chemical fertilizer use have been exhausted and the negative impact increasingly apparent and requires more attention. Therefore, this study has been undertaken to assess the contamination groundwater in the Pondicherry region, with special emphasis on water quality and its characterization.

Study area (Fig. 2) in general, is a flat peneplain with an average elevation of about 15m above M.S.L. The climate of Pondicherry region is humid and tropical. The mean annual temperature ranges between 22 and 33°C. It receives an annual rainfall of 1254 mm during both the southwest (June-September) and intense northeast (October-December) monsoon (CGWB report, 1993). Pondicherry region is basically an agricultural area and the land used for crop production is 56 percent. Due to industrialization and urbanization, the land use for non-agricultural use is on the increase.

Geology

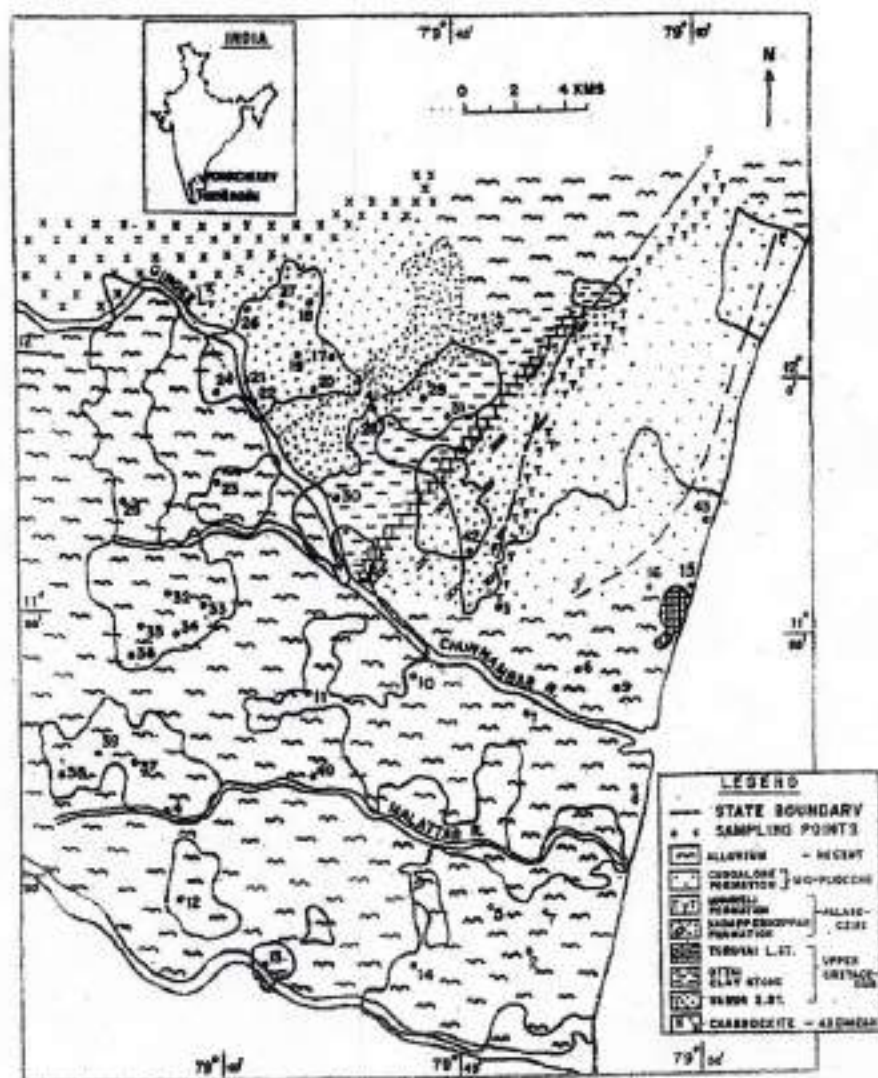
The entire area of Pondicherry region is covered by sedimentary formations, ranging in age from Cretaceous to Recent. The detailed geological investigations were carried out by oil and natural Gas commission (ONGC) (Nair, 1971) and CGWB (1993). Table 2 depicts the stratigraphy of the study area. It is evident from the geological map (Fig. 3), that outcrops of the different formations have been found with NE-SW trend only in the north of the Gingee river is covered with recent alluvium. The investigated area is covered with the Quaternary, Tertiary and the Mesozoic sediments with the Achacan as the basement. The general strike of these sediments is towards southeast. The area is also affected by tectonic disturbances. In the north eastern

region, three faults have been identified by CGWB (Raghava Rao et al, 1976). One fault runs along the stream course of the Gingee river and the other two faults around north eastern elevated grounds. Based on the geology and formations from which the water samples were collected (Fig.3) for investigation, the entire area may be divided into three zones namely; Zone I (Alluvial formations) and Zone II (Tertiary formations) and Zone III (Cretaceous formations). Since Zone I is recently formed alluvium, it overlies Zone II. The Cretaceous aquifer (Zone III) refers to the "Lower Cretaceous aquifer. The thickness of the aquifer is very small (10-15 m) containing predominantly clay and silt, and it is not a potential aquifer. Hence, our samplings were restricted to lower Cretaceous aquifer.

Table 2: Stratigraphy of Pondicherry Region (after Nair and Rao, 1971)

Era/ Period	Epoch	Formation	Lithology
Quaternary	Recent	Alluvium (10 to 55 m)	Sands, clays, kankar gravels
Tertiary	Mio- Pliocene	Cuddalore (30 to 450 m)	Sandstone, pebbly, gravelly and coarse grained with minor clays and siltstones and thin seams of lignite
Unconformity			
Tertiary	Paleocene	Manaveli (41 to 71 m)	Yellow and yellowish brown, grey calcareous siltstone and clay stone and shale with thin bands of lime stone
Tertiary	Paleocene	Kadapperkuppam (31 to 185 m)	Yellowish white to dirty white, sandy, hard-fossiliferous limestone, calcareous sandstone and clay.
Unconformity			
Mesozoic	Upper Cretaceous	Thuruvai Limestone (10 to 15 m)	Highly fossiliferous limestone, conglomeratic at places, calcareous sandstone and clay
Mesozoic	Upper Cretaceous	Ottai claystone (88 to 231 m)	Greyish to grayish green claystone, siltstone with thin bands of sandy limestone and fine grained calcareous sandstone
Mesozoic	Upper Cretaceous	Vanur Sandstone (52 to 106 m)	Quartzos sandstone, hard coarse grained, occasionally feldspathic or calcareous with minor clays
Mesozoic	Upper Cretaceous	Ramanathapuram (unexposed 55 m)	Black carbonaceous, silty clays and fine to medium grained sands with bands of lignite and sandstone, medium to coarse grained
Unconformity			
Archeans		Eastern Ghat Complex	Charnokite and biotite hornblend gneisses

Fig. 3. Geology of the Pondicherry Region and the sampling locations



Hydrogeology

Extensive hydrogeological investigations were carried out by the Central Ground Water Board in the study area (Raghava Rao et al, 1976 and 1978). Out of eight stratigraphic units the alluvium, the Cuddalore, the Vanur and the Ramanthapuram formations are potential aquifers, where as the Ottai claystone, the Kadapperikuppam and the Manaveli formations are less potential aquifers. The groundwater occurs both under water table conditions. In the alluvial formations groundwater occurs mostly under table conditions with a transmissivity coefficient of around $275 \text{ m}^3/\text{d}/\text{m}$. The Cuddalore formation is the most potential aquifer in the study area occupying approximately an area of 115 km^2 as outcrops and about 375 km^2 underlies the alluvial deposits. Groundwater occurs under unconfined, semi-confined and also at some places under confined conditions. The transmissivity of the aquifer ranges from 4000 to $9000 \text{ m}^3/\text{d}/\text{m}$. The Vanur and Ramanathapuram aquifers are mainly of medium grained compact sandstone and yield about 350 to 400 litres /min. The aquifers of this region are recharged by precipitation, irrigation return, monsoon flow from watercourses and surface water bodies

6.0 METHODOLOGY

A list of wells tapping the various aquifers has been prepared by consulting the Central Ground Water Wing of Agriculture Department of Government of Pondicherry. Seasonal water samples during summer (June), pre-monsoon (October) and post-monsoon (February) seasons were collected from 41 wells representing the entire Pondicherry region. In addition, one surface water sample was collected. These locations cover various sections such as domestic, irrigation and industrial sectors. In Zone I (Alluvial formation) only very few samples were collected because of the difficulty in locating shallow wells (due to non availability of wells). Water samples were collected in acid washed new 1-litre polyethylene bottles from borewells that were flowing continuously.

All samples were flushed with several volumes of water before the samples were collected. Separate 500 ml samples were collected for analysis of cations and anions and filtered immediately through 0.45 μm Millipore filters and cation aliquot acidified to $\text{pH} < 1.5$. Temperature, pH and Electrical Conductance were measured *insitu* using portable meter (CHECKMATE 90). In the laboratory, water samples were analysed for major ion concentrations such as Ca, Mg, Na, K, HCO_3 , CO_3 , Cl and SO_4 , nutrients, pesticides following the standard procedures (Apha, 1989 and Ramesh, and Anbu 1996) and the details are tabulated in Table 3.

The data quality of the chemical analysis of various ionic constituents of the groundwater samples have been checked and verified. The difference between the sum of the cations and the sum of anions when expressed in milli equivalents per litre are well within the limits (ionic balance) (APHA, 1989). The analytical data processed with various computer programmes for statistical evaluation. The inter elemental correlation and factor analysis were performed by using STATGRAPHICS programme and the contour diagrams of some of the major elements were drawn using SURFER programme and are shown in 4a, 4b and 5. The different elemental concentrations, their source and distribution are discussed in the following section.

Table 3. Methods adopted for chemical analysis in the present study

ANALYSIS	METHOD	INSTRUMENT USED
A. SURFACE WATER		
1. Major ion chemistry		
<i>i) Anion</i>		
Bicarbonate (HCO_3)	H_2SO_4 Titration	
Chloride (Cl)	Mohr's Titration	
Sulfate (SO_4)	Barium chloride	UV-Spectrophotometer
<i>ii) Cation</i>		
Calcium (Ca) & Magnesium (Mg)	EDTA method	Titration
Sodium (Na) & Pottasium (K)	Photometric	Flame photometer
2. Nutrients		
Nitrate-Nitrogen ($\text{NO}_3\text{-N}$)	Cadmium reduction	Spectrophotometer
Nitrite ($\text{NO}_2\text{-N}$)		"
Ammonia ($\text{NH}_4\text{-N}$)	Nesslerisation	"
Ortho Phosphate ($\text{PO}_4\text{-P}$)	Ascorbic acid	"
Total Dissolved Phosphate (TDP)	"	"
Dissolved Silica (H_4SiO_4)	Molybdo-silicate	"
3. Pesticides		
HCH & DDT	Solvent Extraction	GC-ECD
C. GEOGRAPHICAL INFORMATION SYSTEM	IDRISI	

Fig.4a: Concentration Contour Map of Chloride

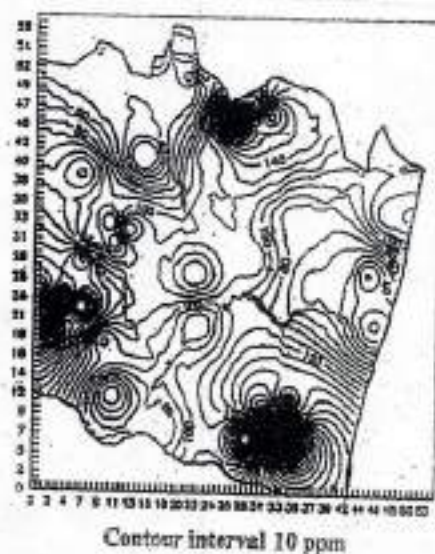
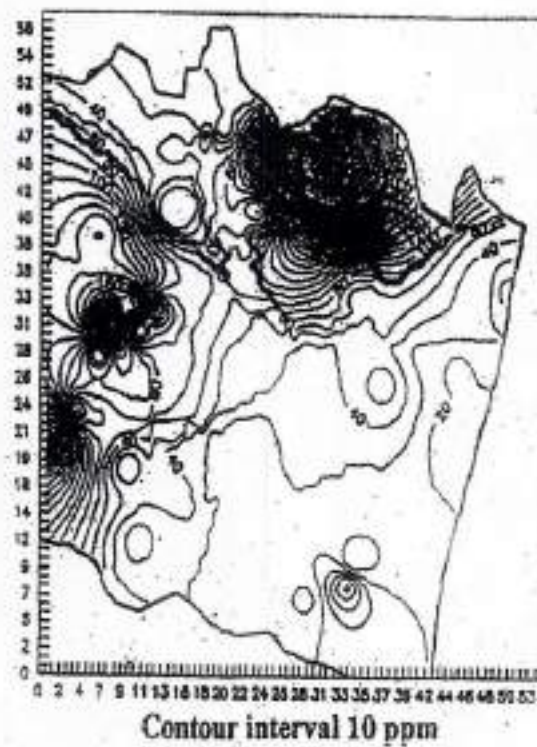


Fig.4b: Concentration Contour Map of Sodium



Fig.5: Concentration Contour Map of Sulphate



7.0 RESULTS AND DISCUSSION

7.1 Spatial and Seasonal Variations of Major Ions

The average annual concentration of the major ions of groundwater samples is presented in the Table 4. The inter-elemental correlations among these chemical parameters are presented aquifer wise in the Table 5.

Table 4. Major ion concentration (mg l^{-1}) in the groundwater of Pondicherry region

S.Nr.	EC	PH	Ca	Mg	Na	K	HCO ₃	CO ₃	Cl	SO ₄	TDS
<i>Zone I: Alluvial Aquifer</i>											
2	2254	6.70	65	63	258	4	275	8	604	74	1336
5	1153	7.0	22	18	93	2	184	0	152	17	602
37	1719	7.43	82	41	154	3	375	33	225	67	946
38	2322	7.43	122	52	237	3	320	30	372	301	1427
43	1598	7.56	107	21	104	31	313	28	162	106	1022
<i>Zone II: Tertiary Aquifer</i>											
1	835	7.46	45	31	95	2	296	38	56	56	580
3	766	7.30	35	29	88	3	241	16	72	54	522
4	992	7.53	55	29	105	2	429	23	87	31	702
6	746	7.60	34	17	90	1	211	17	58	28	541
7	366	7.15	23	16	23	2	177	0	18	9	266
8	400	7.00	29	14	26	1	215	5	18	4	308
9	342	7.10	12	6	55	1	174	17	18	17	283
10	1109	7.46	51	26	123	2	314	49	117	37	670
11	1263	7.66	43	34	147	1	341	37	149	42	759
12	688	7.66	36	37	87	1	343	29	33	25	566
14	397	7.00	13	11	60	2	182	9	17	17	302
15	985	7.56	49	16	117	6	265	33	134	15	573
16	1024	7.25	42	34	112	2	306	17	127	36	688
40	1023	7.63	74	37	81	3	437	27	72	22	727
S.Nr.	EC	PH	Ca	Mg	Na	K	HCO ₃	CO ₃	Cl	SO ₄	TDS
<i>Zone III: Cretaceous Aquifer</i>											
13	996	7.43	46	27	111	1	430	27	70	30	714
17	1055	7.56	87	62	27	3	499	22	87	14	778
18	209	7.00	18	9	8	2	133	0	11	2	181
19	696	7.50	65	43	15	3	343	33	23	5	486
20	848	7.37	63	38	38	3	386	27	41	9	578
21	828	7.33	52	45	48	4	412	27	46	26	634
22	755	7.10	43	30	77	6	326	8	44	62	585
24	666	7.13	46	21	73	3	312	8	39	45	488
25	1315	7.20	79	32	133	4	316	22	132	151	849

Zone III: Cretaceous Aquifer (Cont...)											
26	893	7.20	88	27	63	32	444	10	70	27	722
27	270	7.20	20	15	10	3	119	17	7	4	176
28	1035	7.40	57	30	101	2	362	39	36	76	664
29	2963	7.40	187	66	301	1	453	19	322	525	1856
30	1014	7.46	87	34	66	5	297	14	117	39	670
31	2146	7.30	170	83	214	4	356	28	195	682	1712
32	1361	7.70	33	39	178	2	439	41	68	204	964
33	1099	7.56	55	12	124	2	294	25	144	20	651
34	899	7.60	43	21	95	3	281	30	70	22	526
35	1588	7.70	54	34	189	2	226	33	88	315	972
36	1332	7.75	10	14	169	3	351	46	185	56	784
39	1075	7.60	48	32	105	4	465	34	77	42	773
41	2133	7.56	93	36	253	3	333	17	211	421	1383
*42	343	8.63	15	17	29		140	18	26	2	232
WHO		6.5	200	125	200		500		250	250	1000

S. Nr: Sample location number – Refer Fig.2 for sampling locations. EC: S/cm

Table 5 Inter-elemental Correlation matrices

Variable	EC	PH	Ca	Mg	Na	K	HCO ₃	Cl	SO ₄
a. Alluvial aquifer									
EC	1								
pH	-0.2	1							
Ca	0.62	0.65	1						
Mg	0.8	0.1	0.6	1					
Na	0.95	-0.41	0.35	0.75	1				
K	0.2	0.49	0.41	-0.4	-0.44	1			
HCO ₃	0.48	0.57	0.76	0.3	0.28	0.18	1		
Cl	0.83	-0.67	0.11	0.49	0.93	-0.37	0.07	1	
SO ₄	0.69	0.41	0.8	0.92	0.54	-0.03	0.4	0.24	1
b. Tertiary aquifer									
Variable	EC	PH	Ca	Mg	Na	K	HCO ₃	Cl	SO ₄
EC	1								
pH	0.77	1							
Ca	0.81	0.75	1						
Mg	0.72	0.7	0.72	1					
Na	0.92	0.72	0.57	0.58	1				
K	0.29	0.2	0.39	0	0.24	1			
HCO ₃	0.76	0.72	0.9	0.82	0.58	0.12	1		
Cl	0.92	0.58	0.61	0.49	0.9	0.41	0.52	1	
SO ₄	0.57	0.41	0.32	0.61	0.64	0	0.34	0.45	1

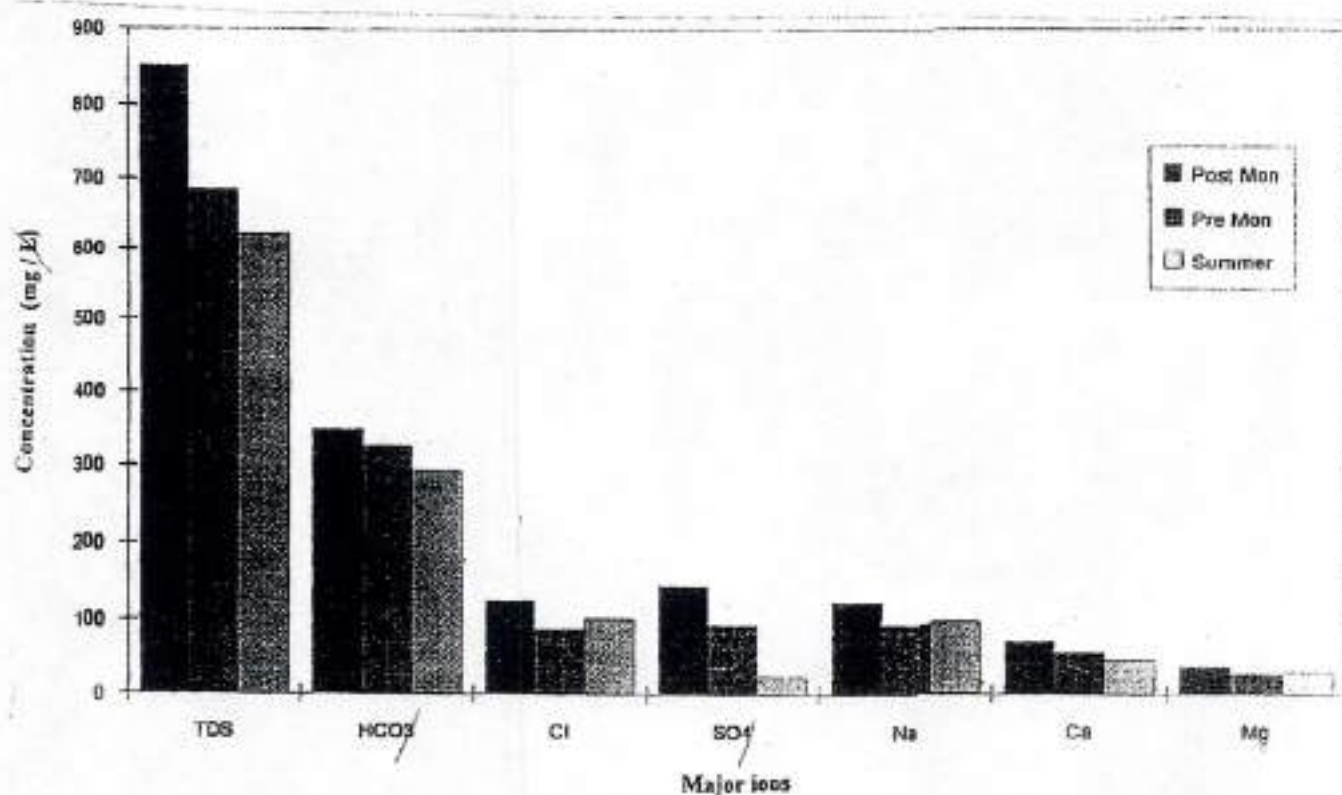
c. Cretaceous aquifer									
Variable	EC	pH	Ca	Mg	Na	K	HCO ₃	Cl	SO ₄
EC	1								
pH	0.02	1							
Ca	0.79	-0.22	1						
Mg	0.65	-0.09	0.83	1					
Na	0.94	0.09	0.58	0.41	1				
K	0.15	-0.13	0.17	0.39	0.15	1			
HCO ₃	0.45	-0.12	0.44	0.56	0.3	0.16	1		
Cl	0.92	0.05	0.73	0.48	0.86	0	0.34	1	
SO ₄	0.87	-0.04	0.77	0.69	0.84	0.35	0.16	0.74	1

The relative concentration of the major cations in groundwater of silicate terrains depends largely on the relative abundance of the various rock types and their degree of alteration. In well-drained areas, where the degree of weathering is modest, the abundance of major cations in groundwater depends chiefly on the relative mobilities (Garrels, 1967; Kowda and Somoilova, 1969). The dominant cations and anions of the average ground water of Pondicherry region are in the order of Na>Ca>Mg>K and HCO₃>Cl>SO₄ (mg l⁻¹) respectively. In certain places of interior Pondicherry region (Sample numbers 29, 31, 38 & 41) and along the coastal line (Sample numbers 2 & 43), the major ion concentrations are higher than that of the average groundwater observed in the rest of Pondicherry region (Table 4). This may be due to continuous withdrawal of groundwater for irrigation through borewells, which leads to seawater intrusion into the freshwater zone, along the coastline. In the interior Pondicherry region, the increase in concentration may be due to the geology and sub-surface soil characteristics.

The temporal variation in the concentrations of major ions is shown in Figure 6. From the figure it is evident that the concentrations of all the ions in summer season were low and exhibiting increasing trend towards pre-monsoon and post-monsoon seasons. The reason for these changes could be the dissolution of salts and minerals in soils due to the increase in water table during monsoon. Ramesam (1982) has reported similar trend in groundwater of a typical hard rock terrain and Kripanidhi (1984) also has observed the same trend in waters of village wells in Karnataka state, India. The examination of the seasonal data of major ion concentration also reveals that 1) the

HCO_3^- is the dominant ion irrespective of the season because it is mainly derived from rock weathering 2) large variation is observed in SO_4 concentration because considerable amount of SO_4 is added to hydrologic cycle from precipitation and 3) only minor variation is observed in Ca and Mg concentration due to their low mobility in groundwater system.

Fig.6. Seasonal variation of major ions



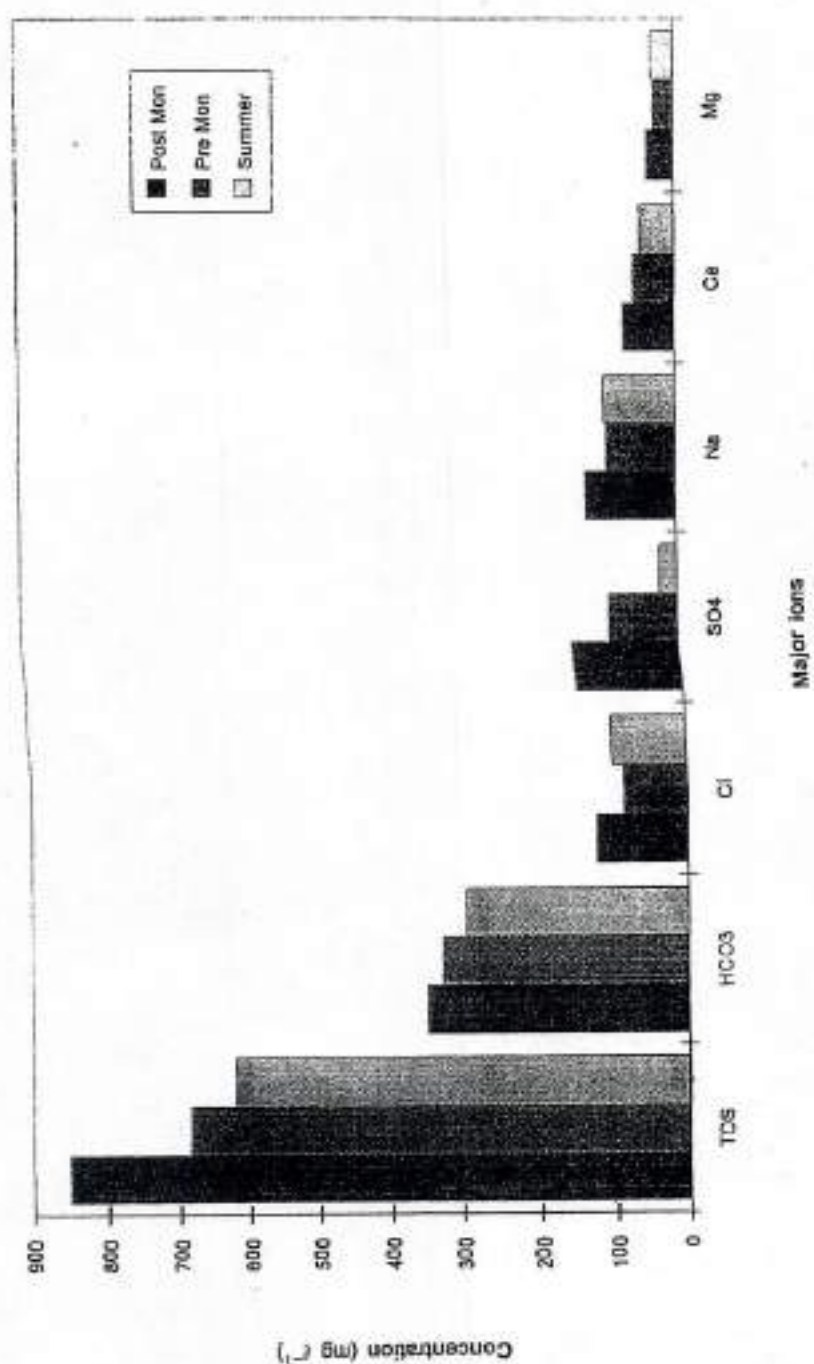


Fig. 4: Seasonal Variation of Major Ions

Spatial Distribution of Major Ions

Alluvial Aquifer (Zone I)

pH and Electrical Conductance

In alluvial aquifer, high ionic concentrations were observed when compared with other aquifers. The pH value ranged from 6.7 to 7.56. Excepting well number 2, the other four wells (nos. 5, 37, 38 and 43) indicate marginal alkalinity. The specific electrical conductance (EC) ranged from 1153 to 2322 $\mu\text{S}/\text{cm}$. The Total Dissolved Solids (TDS) varied from 602 to 1427 mg l^{-1} . Higher values of EC have been observed for the samples collected from the wells located in this alluvial formation (Zone I), which may be due to the extraction of the groundwater from the shallow alluvial aquifer system leading to the intrusion of seawater. Also the reversal in hydraulic gradient along the coast confirms that the groundwater is being over exploited and thereby invites the problem of seawater intrusion. This is also evident from the correlation with Na (0.95) and Cl (0.83). In interior Pondicherry region (well location nos. 37 and 38) the higher values of EC may be due to the formational salinity because of this formation having poor aquifer characteristics. Low values of Na/Cl ratio (0.42-0.68) have been observed in this aquifer compared to the Na/Cl ratios of the water samples collected from other aquifer formations (0.87-3.00). Also the decrease in HCO_3/Cl ratio (1.12-0.26) and increase in Na% in the groundwater of alluvial aquifer indicates the predominance of chloride waters (Rosenthal, 1988). Therefore, it can be concluded that the water in the alluvial aquifer has been contaminated with salt water. The modeling study for seawater intrusion in Pondicherry coast using a numerical model SUTRA (Saturated-Unsaturated Transport) has been conducted. (Please refer the final section of this study). This study also confirms that the seawater has intruded into the fresh water aquifer along the coast. Also, the groundwater level contours indicate that there is a reversal in hydraulic gradient of groundwater flow and results in the saline water intrusion.

Bicarbonate

Bicarbonate (HCO_3) concentration ranged from 184 to 375 mg l^{-1} and more or less uniform throughout all the Zones in the study area. HCO_3 is the primary anion in the groundwater, which is mainly derived from carbon dioxide released by organic decomposition in the soil (Todd, 1979). Most of the HCO_3 must have been derived

from the soil CO_2 . Two sources generally contribute to the CO_2 load of groundwater; 1) CO_2 present in the soil environment, that is derived from the respiration of plant roots and decay of organic matter; and 2) CO_2 resulting from the oxidation of organic matter in the unsaturated zone of fluctuating water table (Wallik, 1981). The observed higher concentrations of HCO_3 were due to the oxidation of organic matter in the alluvial zone.

Chloride

The annual average concentrations of chloride varied from 152 to 604 mg l^{-1} and variation pattern resembles that of EC. From the chloride contour diagram (Fig 4a) it is observed that higher values of chloride were present in the waters of alluvial aquifer. Chloride shows very good correlation with Na and EC (Table 5). The higher values of chloride in groundwater indicate the admixture of mineralized water or pollution (Narayana and Suresh, 1989). In the alluvial aquifer, the concentration of Cl in groundwater is mainly due to saltwater intrusion. It is also evident from the occurrence of Na+K and CaCl type waters in summer seasons and transformed into HCO_3 type water during monsoon and post-monsoon seasons.

Sodium

The average Na concentration ranged 93 to 258 mg l^{-1} . higher concentrations of Na was observed in Zone I (Alluvial aquifer). The variation pattern is presented in contour map (Fig. 4b). The influencing factors may be natural agencies such as storms, high tide and intrusion of seawater in the coastal aquifer system. Na shows very good correlation with EC and moderate correlation with Ca and Mg (Table 5). In general, Na is dominant cation in most mineralized ground water. In humid environments, Na is flushed from the soil and unsaturated zones, whereas in more arid climates, the concentration of Na in groundwater may be due to salt-water intrusion and humid environment.

Sulphate

The concentration of SO_4 exhibits wide variation (17 to 301 mg l^{-1}) and shows strong positive correlation with EC, Ca, Mg and Na (Table 5). The concentration contour map represents the trend factors. Considerable amount of SO_4 is added to the hydrologic cycle from precipitation. This comes from dried sea spray as cyclic salt,

continental dust, oxidation of H_2S that enters the atmosphere from coastal marshes and air pollution (Matthess, 1982). Further addition of sulphate to groundwater takes place from the breakdown of organic substances in the soil, leachable sulphates present in fertilizers and other human influences (Alexander, 1961). It seems that the SO_4 in ground water in the alluvial aquifer is mainly due to seawater intrusion and partly due to leachable fertilizers etc.

Potassium

Potassium varies from 2 to 4 $mg\ l^{-1}$, but a very high value of 31 $mg\ l^{-1}$ was observed in well number 43 (Table 4). The reason for this high concentration may be due to urban pollution into the alluvial aquifer system in Zone I. Potassium exhibits positive correlation only with Ca. Because of its lower geochemical mobility in freshwater, K is seldom found in greater resistance of the K-feldspars and K-silicates to the weathering, K ions are released by weathering. However, after prolonged migration they tend to become fixed again through sorption on clay minerals and formation of secondary minerals (Matthess, 1982).

Calcium and Magnesium

Calcium varied from 22 to 122 $mg\ l^{-1}$ and Mg ranged from 18 to 63 $mg\ l^{-1}$ and both of these show good correlation with EC and other ions (Table 5). The relative mobility of Ca is an order of magnitude greater than that of Na and Na in turn five times more mobile than K. The difference in the relative mobility of Ca, Mg, Na, and K is more pronounced in groundwater from granite terrains (Holland, 1978). The concentration of solutes in the groundwater of silicate terrain is mainly controlled by very few parameters. Among these, the most important is probably the quantity of CO_2 and organic acids generated in soil zones by root respiration and by bacterial decay of organic matter (Silverman and Munoz, 1970). Virtually all the CO_2 that dissolves in groundwater is neutralized to HCO_3 by reaction with silicate minerals.

Tertiary aquifer (Zone II)

The quality of ground water tapped from this aquifer was almost neutral to alkaline with an annual average pH ranging from 7.00 to 7.66. Carbonate was relatively low, ranging between 0 to 49 $mg\ l^{-1}$ in water samples analyzed. EC ranged from 342 to

1263 μS and TDS varied from 266 to 759 mg l^{-1} . The average annual concentrations of all major ions are well within the limits prescribed by WHO (1992) as shown in the Table 4. Tertiary aquifer resembles the same as the correlation matrix of alluvial aquifer (Table 5) except for pH and HCO_3 . These major elements show good correlation with each other. The water type present in this aquifer is HCO_3 type because of the presence of calcareous silt and sandstone, limestone and clay in the Tertiary zone (Table 6). Among the different hydrostratigraphic units, the water from the Cuddalore sandstone group (Tertiary aquifer system) of Mio-Pliocene is comparatively better in quality than other aquifer formations. However, the quality of the water tapped from the upper tertiary formations along the coast shows an increase in the major ion concentrations indicating that the upper layer of the tertiary aquifer is also affected by seawater intrusion and intermixing of water between the alluvial and tertiary aquifer.

Cretaceous aquifer (Zone III)

The quality of groundwater in the Cretaceous aquifer system was slightly alkaline with pH ranging from 7.00 to 7.75. EC ranged from 270 to 2146 μS and TDS varied from 176 to 1712 mg l^{-1} . There was an anomalous increase of EC and other major ion concentrations in well number 29,31 (Table 4) and 39 are located in this aquifer. This may be possibly due to the intermixing of deep and shallow water and lithological characteristics of subsurface formations (fossiliferous limestone, calcareous sandstone and clay). The mixing takes place because of improper and insufficient casing provided to tubewells. Though all major ion concentration is within limits, sulphate exhibits higher concentrations in many locations (Fig.5) and show good positive correlation with most of the ions. The reason may be due to the presence of highly fossiliferous limestone, calcareous limestone, calcareous sandstone and clay. Although some limestones are very pure and consist almost wholly of one or more carbonate minerals, others have smaller content of silica, feldspar and minor constituents such as glauconite, collophane and pyrite (Pettijohn, 1984). Sulphur compounds are frequently present in shales, clay, mudstones and marls. When sulphide minerals such as pyrite and marcasite undergo oxidation, they give rise to anhydrous and hydrous sulphates (Bell, 1983).

Table 6: Classification of water types

Zone Nr/ S. Nr.	Handa's classification (Hardness, Salinity, Sod. Haz)			Facies Classification		
	Summer	Pre- Monsoon	Post- Monsoon	Summer	Pre- Monsoon	Post- Monsoon
I-2	A3C3S1		A3C5S3	Na + K Cl		Na + K Cl
5	A3C3S1	B2C2S1		Na + K Cl	Na + K HCO ₃	
37	A1C3S1	B3C3S1	A2C3S1	Ca HCO ₃	Na + K mixed	Ca mixed
38	A2C3S1	A2C4S2	B3C3S2	Ca Cl	Ca mixed	Na + K mixed
43	A1C3S1	A2C3S1	B2C3S1	Ca HCO ₃	Ca mixed	Na + K HCO ₃
II- 1	B1C3S1	B1C3S1	B1C3S1	Ca HCO ₃	Mg HCO ₃	Mg HCO ₃
3	B2C2S1	B1C3S1	B1C3S1	Na + K HCO ₃	Mg HCO ₃	Ca HCO ₃
4	B2C3S1	B1C3S1	B1C3S1	Na + K HCO ₃	Ca HCO ₃	Ca HCO ₃
6	A1C2S1	B2C2S1	B2C3S1	Na + K HCO ₃	Na + K HCO ₃	Ca HCO ₃
7		B1C2S1	B1C2S1		Mg HCO ₃	Ca HCO ₃
8	B1C2S1	B1C2S1	B1C2S1	Mg HCO ₃	Ca HCO ₃	Ca HCO ₃
9	B2C2S1			Na + K HCO ₃		
10	A2C3S1	B2C3S1	B2C3S1	Ca mixed	Na + K HCO ₃	Na + K HCO ₃
11	B1C3S1	B3C3S2	B1C3S1	Mg HCO ₃	Na + K mixed	Mg HCO ₃
12	B2C2S1	B1C3S1	B1C3S1	Na + K HCO ₃	Mg HCO ₃	Mg HCO ₃
14	B2C2S1	B2C2S1		Na + K HCO ₃	Na + K HCO ₃	
15	B2C2S1	B2C2S1	B3C3S1	Na + K HCO ₃	Na + K HCO ₃	Na + K Cl
16	B2C3S1		A1C3S1	Na + K HCO ₃		Mg HCO ₃
40	B1C3S1	B1C3S1	B1C3S1	Mg HCO ₃	Ca HCO ₃	Ca HCO ₃
III -13	B2C3S1	B2C3S1	B1C3S1	Na + K HCO ₃	Ca HCO ₃	Ca HCO ₃
17	A1C3S1	A1C3S1	A1C3S1	Mg HCO ₃	Ca HCO ₃	Mg HCO ₃
18	B1C1S1	B1C1S1	B1C1S1	Mg HCO ₃	Ca HCO ₃	Ca HCO ₃
19	B1C3S1	B1C2S1	A1C3S1	Mg HCO ₃	Ca HCO ₃	Mg HCO ₃
20	B1C3S1	B1C2S1	B1C3S1	Mg HCO ₃	Mg HCO ₃	Ca HCO ₃
21	A1C2S1	B1C3S1	B1C3S1	Mg HCO ₃	Ca HCO ₃	Mg HCO ₃
22	B1C2S1	B1C3S1	B1C3S1	Mg HCO ₃	Ca HCO ₃	Ca HCO ₃
24	B2C2S1	B1C3S1	B1C2S1	Na + K HCO ₃	Ca HCO ₃	Ca HCO ₃
25	B1C3S1	A2C3S1	A2C3S1	Ca HCO ₃	Ca mixed	Ca mixed
26	B1C3S1	B1C3S1	B1C3S1	Ca HCO ₃	Ca HCO ₃	Ca HCO ₃
27	B1C2S1	B1C2S1	B1C1S1	Mg HCO ₃	Mg HCO ₃	Ca HCO ₃
28	B1C3S1	B1C3S1	B1C3S1	Ca HCO ₃	Mg HCO ₃	Ca HCO ₃
29	A2C5S2	A2C2S2	A3C5S3	Ca mixed	Ca mixed	Na + K mixed
30	A1C3S1	A1C3S1	A1C3S1	Ca HCO ₃	Ca HCO ₃	Ca HCO ₃
31	B1C3S1	B2C3S1	A2C5S3	Ca HCO ₃	Na + K HCO ₃	Ca SO ₄
32	B2C3S1	B2C3S1	B3C3S2	Na + K HCO ₃	Na + K HCO ₃	Na + K mixed
33	B2C3S1	B2C3S1	B1C3S1	Na + K HCO ₃	Na + K HCO ₃	Ca HCO ₃
34	B2C3S1	B2C3S1		Na + K HCO ₃	Na + K HCO ₃	
35	B2C3S1	A3C3S1	A3C3S2	Na + K HCO ₃	Na + K SO ₄	Na + K SO ₄
36	B2C3S2	B3C3S2		Na + K HCO ₃	Na + K mixed	
39	B2C3S1	B1C3S1		Na + K HCO ₃	Ca HCO ₃	
41	A3C3S1	A3C3S2	A3C3S3	Na + K mixed	Na + K mixed	Na + K SO ₄

Factor Analysis

Factor analysis, as applied to widely differing sets of groundwater hydrochemical data, appear to be moderately successful as statistical tool for revealing hydrochemical and hydrogeological features. Jayakumar (1993) and Ramesh et al (1995) have provided excellent descriptions of factor analysis applied to geochemical problems. Similar statistical technique has been used aquifer-wise for groundwater of Pondicherry region and presented in Tables 7a-c. In alluvial aquifer, only five shallow wells could be located for collection of water samples. Therefore, factor analysis was performed considering only four variables (Ca, Na, HCO₃ and Cl) selected at random (Table 7a). Factor I of the Varimax rotated factor matrix is characterized by strong loadings on Na and Cl and accounts for 64 % of the variance. The dominance of these ions could be related to the marine origin.

Table 7a. Varimax Rotated Factor Matrix for Alluvial Aquifer

Variable	Factor 1	Factor 2	Factor 3	Communality
Ca	0.3873	0.7674	-0.0282	0.6730
Na	0.9777	-0.0545	-0.1204	0.9310
HCO ₃	0.3270	0.7438	0.0062	0.5904
Cl	0.9150	-0.3051	0.1699	0.9222
Eigen value	2.1003	1.1921	-0.0404	
Percent Variance	63.8	36.2	0.0	
Cumulative Percent Variance	6.8	100.0	100.0	

Table 7b. Varimax Rotated Factor Matrix for Tertiary Aquifer

Variable	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Communality
EC	0.5699	0.7468	0.275	0.1407	0.1278	0.9965
PH	0.6139	0.3828	0.1859	0.0941	0.5411	0.8607
Ca	0.8652	0.2954	0.0863	0.3300	0.0931	0.9819
Mg	0.7621	0.2206	0.4703	-0.0984	0.0950	0.8812
Na	0.2863	0.8132	0.3813	0.0899	0.2825	0.9809
K	0.0692	0.1814	-0.0568	0.8783	0.0294	0.8179
HCO ₃	0.9111	0.2782	0.1065	-0.0028	0.0887	0.9379
Cl	0.2868	0.8913	0.1822	0.2726	0.0033	0.9869
SO ₄	0.1869	0.306	0.8304	-0.0567	0.0651	0.8239
Eigen value	5.6660	1.078	0.9092	0.3516	0.2073	
Percent Variance	68.1	13	10.9	4.2	2.5	
Cumulative Percent Variance	68.1	81.1	92.0	96.2	98.7	

Table 7C. Varimax Rotated Factor Matrix for Cretaceous Aquifer

Variable	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Communality
EC	0.9074	0.32	0.25	0.0879	0.0285	0.992
pH	0.0473	-0.0572	-0.0573	-0.086	0.5635	0.3237
Ca	0.5861	0.686	0.1857	0.0409	-0.3224	0.9319
Mg	0.3141	0.7796	0.3506	0.3845	-0.0385	0.963
Na	0.9719	0.0145	0.132	0.156	0.104	0.9915
K	0.051	0.1114	0.0676	0.65	-0.1085	0.4449
HCO ₃	0.181	0.1977	0.8829	0.0891	-0.1091	0.868
Cl	0.8869	0.2698	0.1569	-0.163	0.0213	0.9075
SO ₄	0.8095	0.4043	-0.1106	0.3998	-0.0447	0.9791
Eigen value	4.9543	1.1323	0.6904	0.4259	0.2878	
Percent Variance	66.1	15.1	9.2	5.7	3.8	
Cumulative Percent Variance	66.1	81.3	90.5	96.2	100	

In the case of tertiary aquifer, from the varimax rotated factor matrix, the factor 1 is dominated by pH, Ca, Mg and HCO₃ (Table 7). This contributes 68% of the variance of the samples, which suggests the close association amongst Ca, Mg and HCO₃. This indicates that the variance in the chemical composition of the hydrochemical system is controlled by the presence of calcareous silt and sandstone, limestone and clay in the tertiary zone. The second factor shows enrichment of Na and Cl suggesting that this aquifer is influenced by seawater intrusion due to intermixing of water between alluvial and tertiary aquifer.

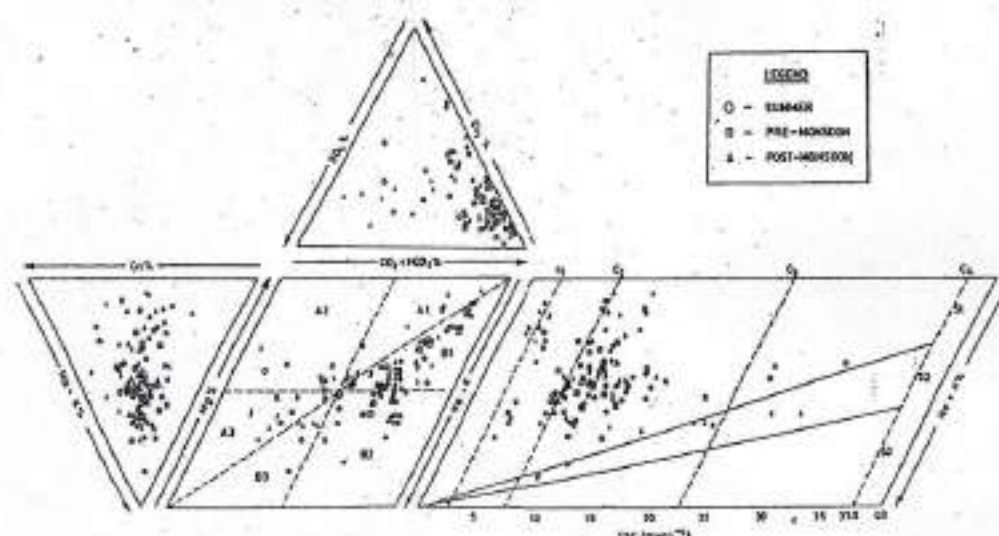
Similarly, factor 1 for cretaceous aquifer accounts for 66% of the variance. This factor is characterized by very strong positive loadings on Ca, Na, Cl and SO₄ and contributes to the major dissolved solids of ground water. All these ions could be associated with the presence of highly fossiliferous limestone, calcareous sandstone and clays in this zone.

Classification of Pondicherry Groundwater

The Cation and anion data are represented on a Hill-Piper diagram as suggested by Handa (1965) for classification of ground water with respect to its suitability for not only domestic purposes, but also for irrigational use. Handa had combined the trilinear plot and the U.S. Salinity Research Laboratory diagram with some modifications.

Hence, water could be classified into A1, A2, A3 or B1, B2, B3 (based on hardness and other ionic relations), C1, C2, C3, C4 and C5 classes (based on salinity) and S1, S2 and S3 classes (based on sodium hazard). Based on the above classification, the chemical quality of groundwater of Pondicherry region given in Fig.7 represents the characteristic on the modified Hill-Piper diagram. From the above classification the following observations may be deduced:

Fig.7. Modified Hill-Piper Diagram for Classification of groundwater



About 75% of the samples have temporary hardness

1. Most of the samples are having low to medium salinity
2. All the samples are of sodium water type
3. Sample number 29 shows permanent hardness, extremely high salinity and medium sodium content due to mixing of shallow water and evaporation takes place in the presence of gypsiferous soil as evidenced from Table 2
4. Samples collected from the wells along the coastal line (Zone I-Alluvial aquifer show permanent hardness and high salinity content
5. In most of the places of the study area, the water is suitable for drinking and irrigational purposes except of bore well locations 2, 29, 31, 38 and 41

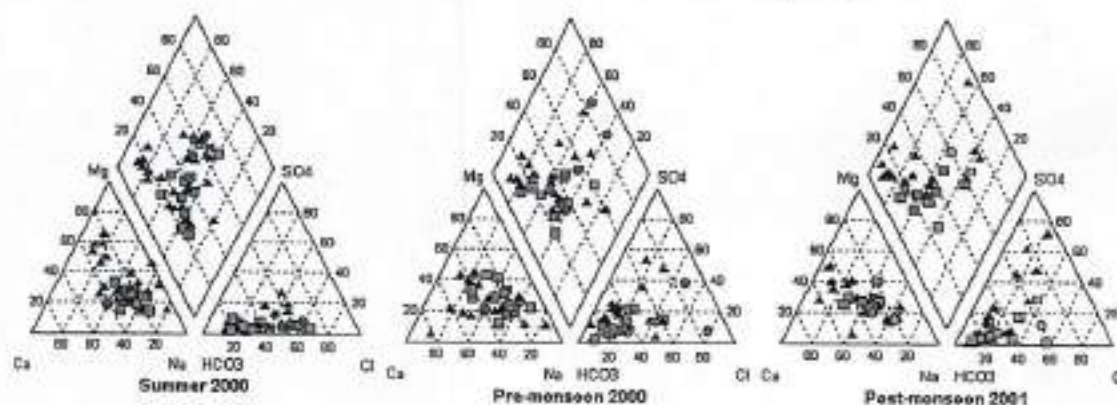
Geochemical Facies

The chemical composition of groundwater in the aquifer system in Pondicherry region is controlled by the composition of its recharge components such as, rainfall, leakage from the adjacent formations or from various waste disposal pits and wells and by the

geological and hydrogeological variations within the aquifer (lithology, porosity and thickness of the saturated and unsaturated zones). Hydrochemical facies are named after the ions that make up more than 50 percent of the total concentration (meq l^{-1}) (Piper, 1944; Nativ and Smith, 1987). A mixed cation and anion facies also have been observed in different zones (Table 6, Fig. 8)

- Zone I - Na + K Cl and Na + K HCO_3 facies are dominant
 Zone II - Na + K HCO_3 , Mg HCO_3 and Ca HCO_3 facies are dominant
 Zone III - Mg HCO_3 and Ca HCO_3 facies are dominant

Fig. 8. Zone-wise Variation of Major Ions in the Pondicherry Region



Zone 1 (Alluvial Aquifer): Na + K Cl and Na + K HCO_3 facies are dominant

Zone 2 (Tertiary Aquifer): Na + K HCO_3 , Mg HCO_3 and Ca HCO_3 facies are Dominant

Zone 3 (Cretaceous Aquifer): Mg HCO_3 and Ca HCO_3 facies are dominant

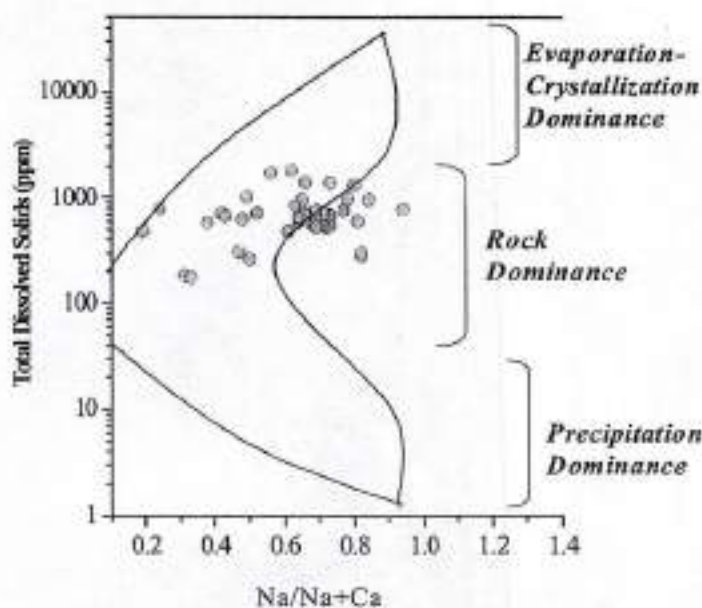
From the geochemical facies, which are dominant in different zones, it further supports the following observations:

- The water in the alluvial aquifer system (Zone I) has been affected by seawater intrusion.
- The water in the tertiary aquifer system (Zone II) is influenced by the nature of geological formations and to some extent by seawater intrusion.
- The water type in the Cretaceous aquifer (Zone III) is mainly due to the dissolution of minerals from subsurface formations. A mixed cation - SO_4 facies are also noticed in the northeastern area of Pondicherry region.

Mechanism Controlling the Chemistry of Groundwater

Gibbs (1970) discussed some of the mechanisms that control the composition of the major dissolved salts of water. The hydrochemical studies are being used to establish the relationship of water composition to aquifer lithology. This helps not only to explain the origin and distribution of the dissolved constituents but also to elucidate the factors controlling the groundwater chemistry. As per the classification of Gibbs (1970), the major natural mechanisms controlling world surface-groundwater chemistry are 1) atmospheric precipitation 2) rock weathering and 3) evaporation and fractional crystallization. A boomerang-shaped diagram resulted when Gibbs plotted the ratio of two major cations as $\text{Na}/(\text{Na}+\text{Ca})$ of the groundwater samples have been plotted against TDS and is shown in Fig. 9.

Fig. 9 Mechanism controlling the Groundwater Chemistry of Pondicherry



The density of distribution of points is high above the centerline of enveloping curve and this indicated that the mechanism controlling the chemistry of groundwater is predominantly is due to evaporation in the subsurface environment. Further the groundwater types and CaCO_3 saturation indices that the

groundwater has had a longer residence time in the Tertiary and Cretaceous aquifers could confirm it. The density of distribution of points are more above the centerline of enveloping curve and this indicated that the mechanism controlling the chemistry of groundwater is predominantly is due to evaporation in the subsurface environment. Further the groundwater types and CaCO_3 saturation indices that the groundwater has had a longer residence time in the Tertiary and Cretaceous aquifers could confirm it.

7.2 SPATIAL DISTRIBUTION OF TRACE ELEMENTS

Trace elements designate a group of elements that occur in natural system in minute concentrations and when present in sufficient quantities, are toxic to living organisms. Compared with the behavior of metals in rivers and oceans, the behavior of trace elements in ground water is complicated, and is related to sources of ground water (rain water, river water and sea water; sometimes anthropogenically influenced) and to many bio and Geochemical processes that control macro-chemical and trace element conditions (Edmunds 1973,1987; Drever 1988; Stuyfzand 1991a, 1992). The major controls are pH and Eh, speciation (complexing agents are organic matter and inorganic ligands), dissolution and equilibrium solubility control, sorption and precipitation, uptake by vegetation and release through mineralization.

General studies describing the mobility of trace elements are scarce. Tanki and Valoppi (1989) gave an overview of trace element behaviour in agriculturally controlled systems and differentiated trace elements from natural sources from these agriculture-induced contaminations. Stuyfzand (1991a, 1992) has published a general study on contamination ranges and possible mobilization processes in many ground water types in Netherlands. Hence, studying the behaviour of trace elements, their sources and major active processes that control the trace element concentration levels in ground water of the study area, is important to understand trace element biogeochemistry and their transformations. Representative ground water samples were collected from various locations covering the major sections of Pondicherry region during June (pre-monsoon) and February (post-monsoon). The average results of the analyses are presented in Table 8. The mean elemental concentration contour diagrams for the trace elements are presented in Figures 10 to 15.

Concentration of trace elements in groundwater of Pondicherry region

Aquifer contamination by trace metals has become a striking problem in the last few decades, as a result of increasing pollution of the environment. 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

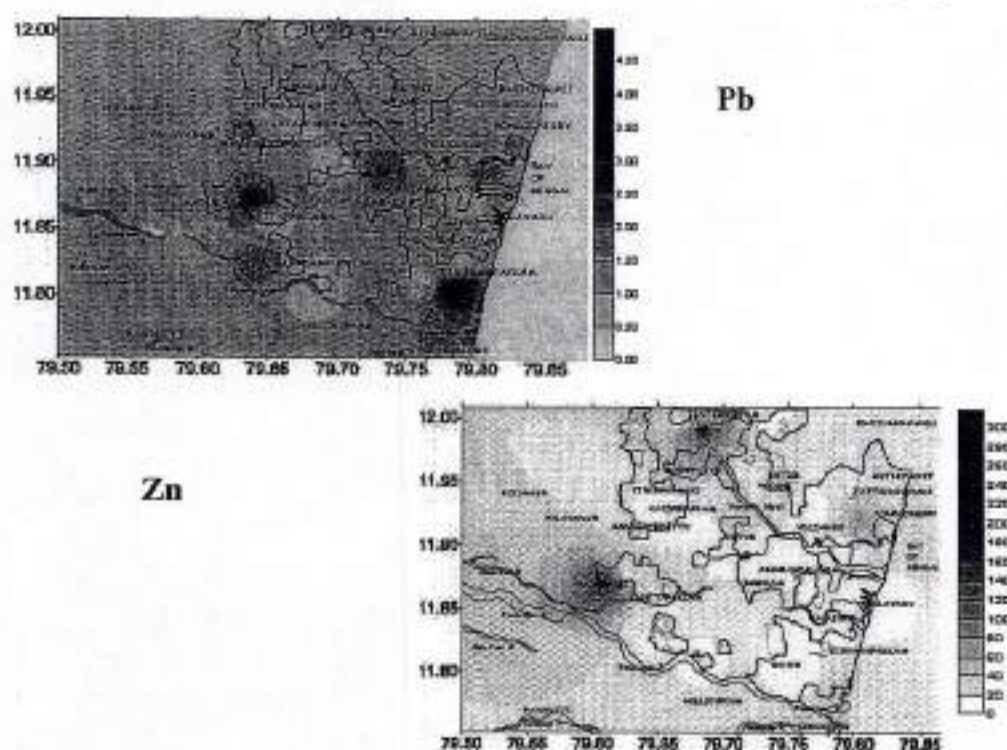
under the influence of other pollution sources (industrial plants, sewers, airborne pollutants, etc.). Bank infiltration, which is regarded as an accumulator of heavy metals and changes in pH, redox potential and ionic strength initiate the remobilization of accumulated heavy metals and cause severe deterioration of aquifer water quality (Predrag and Peter 1994).

Table 8. Average trace element concentration in groundwater of Pondicherry Region

As	Ag	Cd	Cu	Ni	Zn	Co	Pb	Fe	Mn	Cr	Mo	B	V	Se
5.00	0.05	0.22	4.84	8.05	10.80	2.08	0.22	282	10.69	20.25	2.00	49.00	12.00	14.00
19.00	0.05	0.68	15.69	9.00	35.76	3.13	5.02	1693	393	40.20	3.00	228.00	26.00	74.00
-	0.04	0.85	2.08	8.01	3.78	1.62	1.00	-	1.68	25.00	-	-	-	-
12.00	0.05	0.26	5.06	6.60	11.25	0.26	0.25	695	1.69	21.31	0.20	57.00	37.00	46.00
-	0.06	0.10	3.88	6.89	21.69	0.26	1.02	-	1.71	15.00	-	-	-	-
7.00	0.04	0.15	1.41	6.50	6.30	0.46	1.02	634	1.54	19.00	2.00	72.00	12.00	24.00
4.00	-	4.00	2.00	7.00	12.00	0.80	0.50	404	10	20.00	2.00	89.00	12.00	15.00
3.00	0.05	1.50	2.01	7.00	4.44	1.11	1.01	375	2.55	17.70	3.00	74.00	12.00	16.00
-	0.05	0.28	5.04	4.48	19.79	0.58	2.10	-	0.85	15.00	-	-	-	-
8.00	0.04	2.70	2.94	7.58	7.72	0.49	2.22	334	9.41	18.36	3.00	76.00	18.00	25.00
10.00	0.06	3.38	3.94	2.53	8.17	0.39	0.53	378	2.14	18.56	1.30	58.00	62.00	30.00
8.00	0.07	3.00	6.91	7.88	13.27	0.52	2.01	345	0.9	17.73	2.00	44.00	58.00	24.00
16.00	0.04	0.45	7.66	9.43	13.58	0.72	0.33	674	2.85	27.12	3.00	51.00	74.00	49.00
-	0.04	0.74	1.14	3.70	2.90	0.58	0.28	-	1.68	12.00	-	-	-	-
9.00	0.05	2.90	3.17	4.21	20.53	0.37	1.04	563	5.78	16.66	1.00	218.00	14.00	33.00
31.00	0.04	1.75	12.20	22.60	92.73	0.95	1.04	-	5.33	19.50	-	-	-	-
14.00	0.05	0.32	3.40	10.75	15.27	0.47	1.00	1121	3.68	22.50	1.00	66.00	26.00	43.00
5.00	0.04	3.40	2.04	3.27	8.16	0.47	2.02	264	5.62	9.32	1.00	51.00	26.00	14.00
6.00	0.04	2.15	2.28	3.10	193.75	1.09	2.04	385	3.44	15.18	2.00	49.00	24.00	23.00
26.00	0.05	1.75	3.70	10.60	10.08	1.19	1.01	1086	4.22	21.78	1.00	84.00	58.00	96.00
9.00	0.04	0.70	5.30	7.86	18.08	1.17	1.00	868	4.06	33.78	1.00	79.00	12.00	22.00
5.00	0.04	0.50	2.12	9.93	312.37	1.06	1.58	602	48.1	16.20	1.00	102.00	12.00	20.00
6.00	0.03	0.71	2.44	8.38	14.70	1.06	0.51	641	86.63	15.77	1.00	75.00	14.00	27.00
11.00	0.03	1.80	4.25	13.46	32.12	1.08	1.51	925	18.54	15.13	2.00	139.00	19.00	38.00
20.00	0.03	1.36	3.19	19.40	13.14	1.11	1.50	1373	26.04	16.14	1.00	83.00	26.00	75.00
3.00	0.03	1.75	2.72	5.90	28.00	0.53	1.00	348	3.69	14.90	1.00	60.00	16.00	12.00
14.00	0.02	1.17	3.60	16.40	6.56	1.53	1.02	6460	7.51	43.50	2.00	161.00	92.00	94.00
24.00	0.03	2.61	13.75	76.56	5.88	3.40	1.00	12440	3.06	52.90	1.00	169.00	123.00	124.00
24.00	0.03	2.02	8.30	11.28	27.35	0.28	1.50	2569	5.56	22.84	1.00	89.00	32.00	83.00
54.00	0.04	1.69	11.03	130.21	41.35	5.06	1.00	21990	4.04	54.26	2.00	252.00	126.00	228.00
4.00	0.04	2.20	2.10	4.24	7.37	0.29	0.50	618	0.64	26.70	0.60	378.00	21.00	19.00
-	0.04	0.76	3.57	4.13	2.22	0.25	0.50	-	0	33.69	-	-	-	-
-	0.09	1.17	1.78	3.00	2.29	0.30	1.02	-	1.62	16.76	-	-	-	-
13.00	0.10	2.36	12.50	18.04	19.56	1.44	2.28	3228	20.4	34.60	2.00	2595.00	64.00	71.00

As	Ag	Cd	Cu	Ni	Zn	Co	Pb	Fe	Mn	Cr	Mo	B	V	Se
-	0.21	1.16	4.95	3.03	5.48	0.30	1.06	-	4.2	32.42	-	-	-	-
72.00	0.09	2.35	15.78	30.00	15.00	1.69	3.53	4813	7.62	30.00	2.00	106.00	175.00	289.00
26.00	0.09	3.22	33.81	23.25	249.06	1.28	1.07	3982	3.16	36.30	1.00	269.00	156.00	113.00
-	0.07	0.60	3.12	8.08	1.01	1.10	1.02	-	2.06	34.00	-	-	-	-
18.00	0.08	2.39	4.04	16.00	6.16	0.80	1.03	2363	6.54	30.00	1.00	67.00	101.00	94.00
65.00	0.10	3.19	8.70	37.54	82.67	1.72	1.09	5164	4.14	30.00	3.00	362.00	265.00	244.00
37.00	0.10	1.41	3.22	10.35	6.81	0.86	1.11	1506	5.62	30.00	2.00	40.00	135.00	132.00
99.00	0.10	2.47	2.85	13.03	9.42	0.65	1.53	6547	0.98	15.33	0.60	167.00	176.00	355.00

For this study, specific trace elements that serve as representative of groups having different biogeochemical characteristics are considered. The first group, 'metalloids' is represented by Arsenic (As), Selenium (Se) and Silver (Ag). A group referred to as 'nutrient type' elements is represented by elements such as Cadmium (Cd), Copper (Cu), Nickel (Ni) and Zinc (Zn). These elements exhibit strong relationships to nutrients suggesting that their cycles in the ground waters are influenced predominantly by biological processes. 'Geochemically controlled' elements are those whose fates are dominantly influenced by inorganic processes and these include elements such as Cobalt (Co), Iron (Fe), Lead (Pb), Manganese (Mn) and Vanadium (V). The distributions of all these elements in ground water of Pondicherry region have been studied. In addition to these naturally bound trace elements, Chromium (Cr), derived mainly from human activities has also been studied.

Figs.10-11: Distribution of Zn ($\mu\text{g l}^{-1}$) in the groundwater of Pondicherry region

This represents an “anthropogenic source” adding a human dimension to trace metal biogeochemistry. Trace metals have interested researches for a variety of reasons ranging from a need for identification of the origin of trace metals, metal transport as related to public health, to the problem of biomagnifications of these toxic elements in the food chain. It is thus, imperative to understand the basic routes and distribution pattern of elements that are critical for life process.

Metalloids

Arsenic (As), Selenium (Se) and Silver (Ag)

The spatial distribution of total dissolved As gradually increased from a minimum of $3 \mu\text{g l}^{-1}$ at Location 8 to a maximum of $99 \mu\text{g l}^{-1}$ at Location 43 with a mean value of $20.50 \mu\text{g l}^{-1}$. The observation made here for dissolved As, seems to be higher than $50 \mu\text{g l}^{-1}$ (WHO 1984) in only few locations, which are mostly from agriculture area. The occurrence of As in natural water is usually associated with sedimentary rocks of marine origin, weathering of volcanic rocks, fossil fuels, mineral deposits, mining wastes, agricultural wastes and irrigational practices (Hunt and Howard 1994). Anthropogenic sources of As are numerous both in the form of organic metal

complexes and inorganic ions. Until the past decade, inorganic forms of As were used extensively in agriculture as insecticides, fungicides, herbicides and desiccants in this area. Although inorganic arsenicals are no longer widely used in agriculture, there is still concern about the residual effects of its high application in the past. Adriano (1986) points out that as residue can accumulate to high levels in locations adjacent to agricultural areas where as pesticides or defoliants were repeatedly used, causing surface soil accumulation of 600 mg l^{-1} or more. The leaching of resident As from the soil, coupled with historical anthropogenic input contributes to the distribution of dissolved As in the study area. Badal et al 1996, indicated that the source of arsenic might also be due to the geology of the area. Over extraction of ground water, especially during summer enhances the liberalization of As into the water column, which eventually surfaces by forming volatile complexes. There is sufficient evidence to suggest that there is a geological control in the distribution of as with alluvium sediments.

Arsenic becomes toxic when its concentration reaches $50 \text{ } \mu\text{g l}^{-1}$ in water used for drinking purposes (Table 9). It accumulates in the biota and other inorganic materials because of its low mobilization factor of 3.3 and soon becomes poisonous. Grantham and Jones (1978) suggested that As may cause neurological damage when water contaminated with arsenic greater than $100 \text{ } \mu\text{g l}^{-1}$ is consumed. Selenium, with an average crystal abundance of 0.1 mg kg^{-1} , occurs in most types of rocks, but it is enriched in shale. Geochemically, selenium resembles sulfur and the two are often found in association with one and another. Selenium is released in relatively large amounts as a by-product of various industrial and other anthropogenic sources. Selenium concentrations typically range from $<0.1 \text{ } \mu\text{g l}^{-1}$ to $5.00 \text{ } \mu\text{g l}^{-1}$ when there are major anthropogenic inputs. In the study area, a Se concentration ranges from $12 \text{ } \mu\text{g l}^{-1}$ to $96 \text{ } \mu\text{g l}^{-1}$. In certain locations of shallow waters a maximum concentration of $355 \text{ } \mu\text{g l}^{-1}$ were observed due to industrial and agricultural activities.

Nutrient Type Trace Elements

In the ground water system, certain trace metals are involved in biogeochemical cycles similar to nutrients. The evidence for this is the covariance in concentration of metals such as Cd, Cu, Ni, and Zn with PO_4 , NO_3 , and SiO_2 in water column profiles (Martin and Windom 1991). This indicates that these metals are incorporated into phytoplankton in the surface euphotic zone along with nutrients and released at depth

Cadmium (Cd), Copper (Cu), Nickel (Ni) and Zinc (Zn)

The concentration of cadmium in lithosphere is low, normally ranges from $0.1 \mu\text{g l}^{-1}$ to $0.2 \mu\text{g l}^{-1}$. It is concentrated in sulphide minerals of other metals like zinc sulphide, lead sulphide, mercuric sulphide, etc. (Manahan 1979 and Nraigu 1980). The main sources of Cd pollution are industrial activities as the metal is widely used in electroplating, pigments, plastic stabilizers and battery industries. Cadmium concentration in ground water of study area ranged from $0.10 \mu\text{g l}^{-1}$ to $4 \mu\text{g l}^{-1}$ with a mean value of $1.62 \mu\text{g l}^{-1}$. It can be seen from our analyses that the cadmium concentrations in ground water of the study area were well within the limits of WHO standards. The very low exchangeable Cd Contents, with only a slight dominance in few samples indicate potential external influence on the aquifer. This may be due to the application of manure/fertilizer for agriculture. There are also no indications of any lithological preference of exchangeable cadmium. This is in accordance with the results of the other authors (Predrag and Peter 1994).

The copper concentration ranged from $1.14 \mu\text{g l}^{-1}$ to $33.81 \mu\text{g l}^{-1}$ with mean value of $5.81 \mu\text{g l}^{-1}$. The results indicate that Cu content in Pondicherry ground water along the river course is enriched. On the other hand the samples collected away from the river course are depleted in Cu concentration. A slightly elevated concentration of dissolved Cu observed in the present study, shows that it is derived as a result of oxidation of reduced N and S in manure and rain produces acid, which dissolves minerals, change Cation exchange complex occupation and lead to high concentration trace metals such as Cd, Co, Cu, Ni and Zn. The elevated concentration is also because; Cu has strong affinity for clays, iron and manganese hydroxides and carbonate minerals (Purvaja 1995). Hence, Cu residues are often in elevated concentrations in groundwater of subsurface environments. Further, Cu shows a pronounced tendency to form complexes with inorganic and organic ligands. At neutral pH, most of the inorganic Cu in solution is present as complexes with carbonate, nitrate, sulphate, chloride and ammonia.

The nickel concentration exhibits a wide variation and ranged from $3 \mu\text{g l}^{-1}$ to $130.21 \mu\text{g l}^{-1}$ with a mean value of $14.77 \mu\text{g l}^{-1}$ in the study area. More nickel concentrations

were observed in the shallow wells than in deeper wells and in the areas of intensive agriculture activities. The higher Ni contents were associated with organic rich soils and clay and loamy environments. In addition to these geologically bound sources, anthropogenic input of Ni through the application of phosphate fertilizers may also be an important source in this region. However, being a nutrient type element, it is taken up in significant quantities before being leached into the ground water. Zinc (Zn) is one of the most important trace nutrients for the vegetation. The concentration ranged from $1 \mu\text{g l}^{-1}$ to $93 \mu\text{g l}^{-1}$ and shows a wide variation in the contents. Higher concentrations of zinc were observed in the areas of intensive agriculture and industrial activities. The dissolved zinc concentration were minimum near the coastal zone and gradually increased inland. In few locations a maximum concentrations of $312 \mu\text{g l}^{-1}$ of Zn were observed due to the effluent discharges from the metal-based industries draining their effluents on land, in addition to the contribution through agricultural irrigation return. The concentration contour shows a thick cluster in the agricultural and industrial areas, highlighting the magnitude of human perturbations.

Geochemically Controlled Trace Elements

Cobalt (Co), Lead (Pb), Iron (Fe), Manganese (Mn) and Vanadium (V)

Cobalt concentration in ground water of study area ranged from $0.24 \mu\text{g l}^{-1}$ to $5.06 \mu\text{g l}^{-1}$. The Co concentration in drinking water generally found to be $0.02 \mu\text{g l}^{-1}$. The abundance of Co in sedimentary rocks ranges from 0.2 mg l^{-1} to 20 mg l^{-1} and seems to associate with clay and organic matter. In geochemical cycle, Co closely resembles Fe and Mn. Anthropogenic emissions; largely the burning of fossil fuel contributes to the Co contents. Municipal effluents may also contain relatively high residues, particularly in places dominated by metal processing industries. The concentration contour of Co in ground water is ranged from $0.22 \mu\text{g l}^{-1}$ to $5.02 \mu\text{g l}^{-1}$. The lead content of unpolluted natural surface waters worldwide has been estimated to be $1 \mu\text{g l}^{-1}$ to $10 \mu\text{g l}^{-1}$. 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 US Public Health Service has prescribed a limit of $50 \mu\text{g l}^{-1}$ and this has not been exceeded in our study. Iron is a non-conservative trace element found in significant concentration in

drinking waters because of its abundance in the earth's crust. The dissolved Fe content in the ground water of the study area ranged from $264 \mu\text{g l}^{-1}$ to $6547 \mu\text{g l}^{-1}$ with a mean value of $1685 \mu\text{g l}^{-1}$.

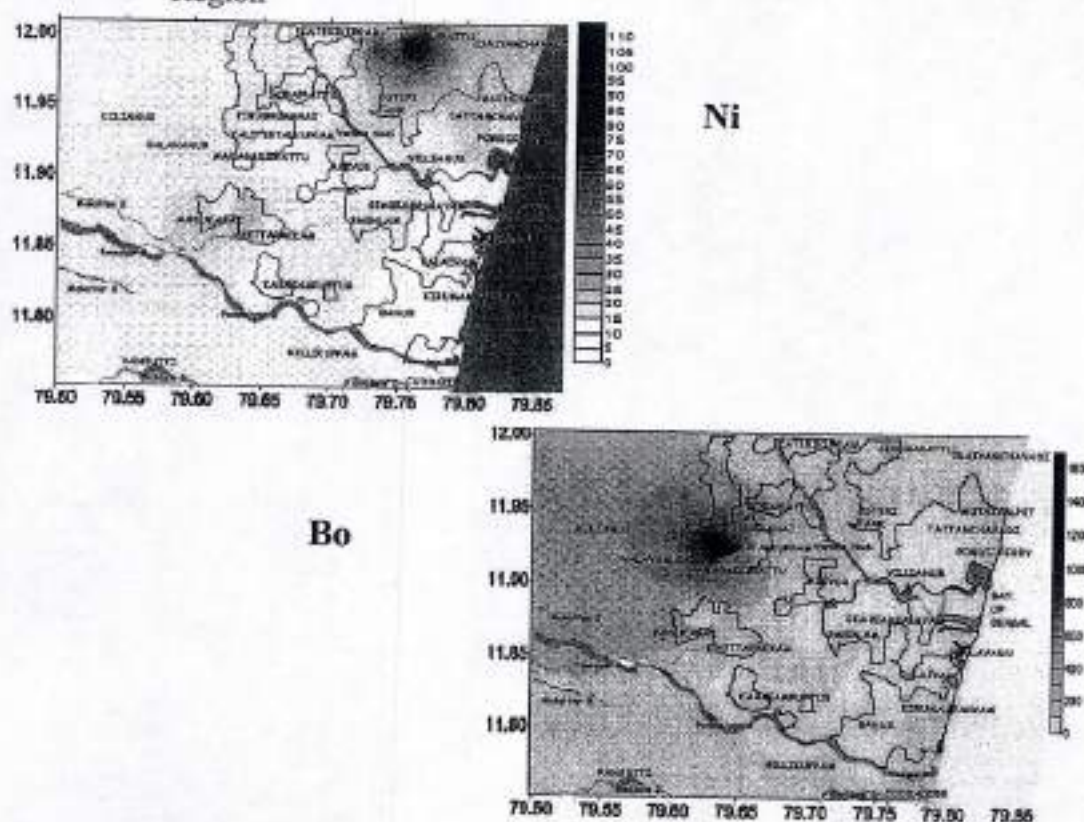
The distribution of Fe content in the study area exhibits a wide variation. The concentration of Fe in ground water is extremely variable, and in a few places a maximum concentration of $21,990 \mu\text{g l}^{-1}$ were observed, reflecting difference in underlying bedrock, erosion to lesser degree and industrial and municipal waste discharges into the ground water bodies. The higher concentrations were observed in the areas of intensive agriculture and industrial locations in the study area. Manganese is one of the most abundant trace elements in the lithosphere and its common range in rocks is 350 mg l^{-1} to 2000 mg l^{-1} . Manganese is an essential trace element required by both plants and animals. The manganese content of the ground water in the study is ranged from $0.90 \mu\text{g l}^{-1}$ to $48.10 \mu\text{g l}^{-1}$ with a mean value of $6.33 \mu\text{g l}^{-1}$. An anomalous concentration of $86.63 \mu\text{g l}^{-1}$ at Location 24 and $393 \mu\text{g l}^{-1}$ at Location 2 were observed. This may be due to the local anthropogenic influence (coal burning and incineration of municipal wastes) on the ground water. Vanadium is ubiquitous in nature. Its compounds commonly occur in the trivalent oxidation state. Vanadium concentration in the study area ranged from $12 \mu\text{g l}^{-1}$ to $265 \mu\text{g l}^{-1}$. Natural V occurs in igneous rocks, in titaniferous magnetite, in certain deposits of phosphate rock, in shales and in asphaltic deposits. V tends to be associated with organic matter and therefore its elevated concentrations in ground water are common.

Biological forms of trace metals

Chromium has been considered under this section because of its relative biological and/or pollutional significance. Chromium is ubiquitous in nature and most commonly found in the trivalent state, but hexavalent compounds are also found in small quantities. The trivalent form is an essential nutrient for man, required in amounts of $50 \mu\text{g day}^{-1}$ to $200 \mu\text{g day}^{-1}$ whereas the hexavalent form is carcinogenic to man and animals. In this study area, the Cr concentration ranged from $9.32 \mu\text{g l}^{-1}$ to $54.26 \mu\text{g l}^{-1}$ with a mean value of $24.50 \mu\text{g l}^{-1}$. Generally the natural content of Cr in drinking water is very low, containing between $1 \mu\text{g l}^{-1}$ and $10 \mu\text{g l}^{-1}$ except for regions with

substantial chromium deposits (Krishnamurthi and Pushpa 1995). Chromium chemicals are used as tanning agents, catalysts, pigments and plating industries and hence Cr found in excess quantities in the study is originating from human activities, seems acceptable. The concentration of other trace metal ions, which were not covered under the above classifications, such as Molybdenum (Mo) and Boron (B) were also determined in the ground water of the study area.

Figs. 14-15: Concentration of Ni and Bo ($\mu\text{g l}^{-1}$) in groundwater of Pondicherry Region



Molybdenum has been found in many surface and ground waters, usually in the range of a few $\mu\text{g l}^{-1}$, but on numerous occasions the levels would be below the detectable limits. Further Mo is non-toxic to humans based on their abundance in drinking water and natural foods. Among the micronutrients required for plant growth, Mo is required in the smallest amounts. Mining and milling of Mo is a potential source of Mo release into the environment. In the study area, the concentration of Mo ranged from 1 $\mu\text{g l}^{-1}$ to 3 $\mu\text{g l}^{-1}$, which is within the acceptable limits of WHO and MINAS. Boron

concentration in ground water of the study area ranged from $44 \mu\text{g l}^{-1}$ to $378 \mu\text{g l}^{-1}$ with an anomalous concentration of $2595 \mu\text{g l}^{-1}$ at Location 35. The high concentration levels may be attributed to the contamination of ground water with seawater intrusion in the study area. Boron behaves conservatively upon dissolution. It has very low concentration levels in sources other than of marine origin.

Statistical Analysis

In order to establish the natural processes and the source of pollution, r-mode factor analysis with rotation was applied to normalized trace element data of ground water. A correlation matrix from the normalized variables of trace element data was computed (Table 10) giving eleven components, contributing 100 percent of the total variable.

Table 10. Inter-elemental correlation matrix for trace elements

Elements	As	Se	Cd	Cu	Ni	Zn	Mn	Co	Pb	Cr	Fe
As	1.00										
Se	0.98	1.00									
Cd	0.54	0.09	1.00								
Cu	0.60	0.22	0.93	1.00							
Ni	0.62	0.51	0.52	0.60	1.00						
Zn	0.18	0.15	0.15	0.29	0.29	1.00					
Mn	0.11	0.02	0.19	0.27	0.07	0.10	1.00				
Co	0.54	0.10	0.99	0.93	0.55	0.16	0.23	1.00			
Pb	0.53	0.10	0.99	0.93	0.51	0.15	0.24	0.99	1.00		
Cr	0.54	0.30	0.73	0.81	0.76	0.17	0.28	0.75	0.73	1.00	
Fe	0.46	0.65	0.06	0.08	0.80	0.22	-0.04	-0.03	-0.03	0.41	1.00

Based on the point of inflection or minima point of cumulative Eigen value, three common factors were retained for subsequent varimax rotation and interpretation for trace element data. The factor loadings along with percent of trace and Eigen values for groundwater samples are presented in Table 11.

Inter-elemental Correlation

Table 10 shows the inter-elemental correlation for trace metals in ground water of Pondicherry region. In general, there is a strong positive correlation between the elemental pairs As-Se, As-Ni, Cd-Cu, Cd-Co, Cd-Pb, Cd-Cr, Fe-Ni, Fe-se, Cr-Ni, Cu-

Ni, Cu-Co, Cu-Pb, Cu-Cr, Co-Cr, Co-Pb and Cr-Pb exists, indicating that their possible precipitation/adsorption and further co-existence in the ground water system.

Table 11. Varimax Rotated Factor Matrices for trace elements

VARIABLE	FACTORS			COMMUNALITY
	Factor 1	Factor 2	Factor 3	
As	0.50	0.74	-0.05	0.99
Se	0.05	0.89	-0.07	0.98
Cd	0.98	0.05	0.06	0.99
Cu	0.92	0.19	0.22	0.93
Ni	0.46	0.74	0.21	0.96
Zn	0.04	0.22	0.76	0.28
Mn	0.21	-0.11	0.64	0.43
Co	0.98	0.07	0.09	0.99
Pb	0.99	0.04	0.09	0.99
Cr	0.74	0.41	0.22	0.84
Fe	-0.12	0.91	0.15	0.96
Eigen Values	5.73	2.34	0.84	
Variance %	52.11	21.28	8.99	
Cumulative Variance %	52.11	73.41	82.39	

It is also possible that the heavy toxic metals are moving as poly-metal complexes adsorbed on to the organic molecules, which are discharged into the ground water systems (Shivkumar and Biksham 1995). A strong positive correlation of Cu, Cd, Cr and As with most of the other elements suggests that the pollutants are mostly derived from anthropogenic sources (industrial and municipal waste discharges), which are being delivered to the hydrological system either directly or indirectly. Elements such as Cu, Cd and Ni exhibit strong correlation among themselves; indicate that they are derived from the oxidation of reduced N and S in manure/fertilizers in the agriculture area. Cr exhibits strong correlation with most of the metals indicates that they move together in the ground water system.

Factor Analysis

The Varimax Rotated Factor Matrix for the trace elements in groundwater is presented in Table 11. The first two factors account for nearly 73 % of the variance and hence only these two factors are considered for discussion

Factor 1

This factor is statistically dominant and accounts for 52% of the variance. This factor is characterized by very strong positive loadings on Cd, Cu, Co, Pb and Cr indicating that all these elements are of anthropogenic in origin. All these trace elements could be associated with only one factor: "Migration of pollutants from industrial outlets and input from agricultural activities". Hence, it can be categorically stated that the major source for Factor 1 is mainly due to the effluents from industries and agricultural inputs.

Factor 2

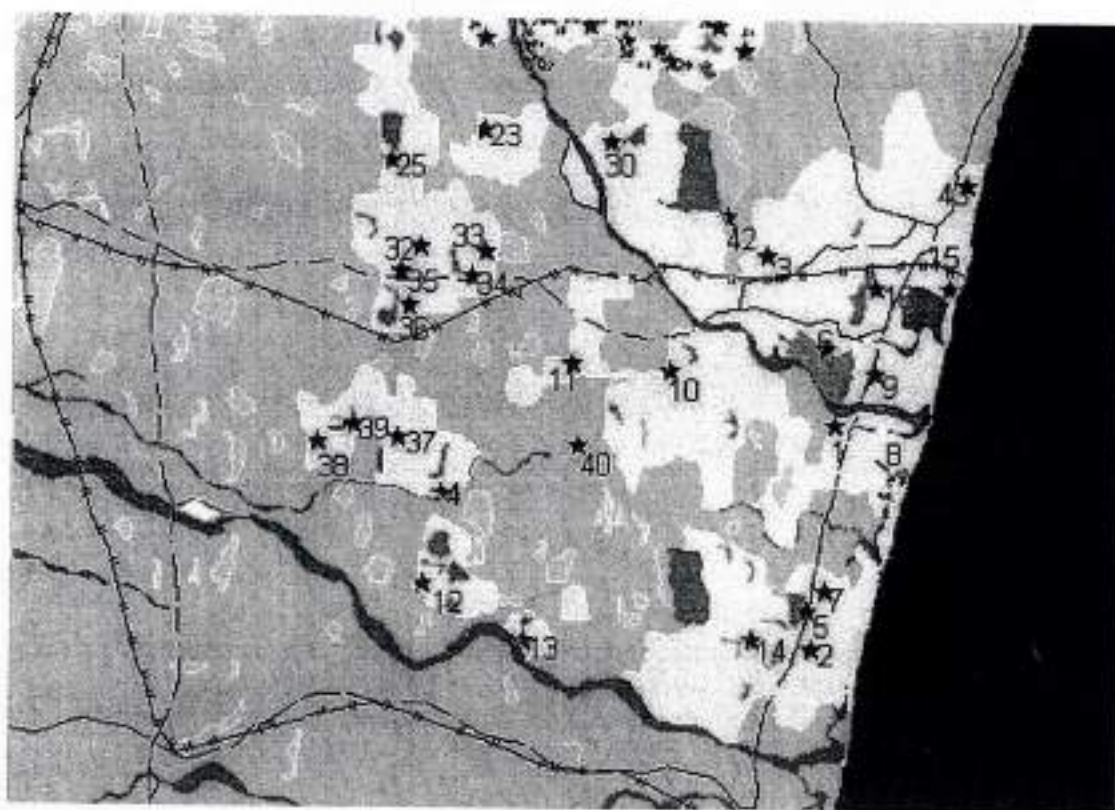
This factor accounts for 21% of the variance and shows positive loadings on As, Se, Ni and Fe. This factor can be termed as the "Mobilization factor". In Pondicherry region, it is possible that the mobilization factor also controls the distribution of trace elements in the groundwater system. A combination of industrial and agricultural pollutants discharged into the environment (Factor 1) and mobilization of heavy metals (Factor 2) can explain the trace element scenario in groundwater of Pondicherry region.

7.3 SPATIAL DISTRIBUTION OF DISSOLVED INORGANIC NUTRIENTS

Many natural chemical substances circulate through the environment and are important to the chemistry and biology of the Earth. The circulation of these substances is defined by its reservoirs, process affecting it and fluxes and is termed "Biogeochemical cycles". The biogeochemical cycles of Carbon(C), Nitrogen (N) and Phosphorus (P) at the earth's surface depend on the rates of the processes that control storage in and transfer between the various external reservoirs. The dynamics and thus, the response of biogeochemical cycles to perturbations are complicated by coupling of these cycles and numerous possible feedback mechanisms. For Example, nitrate concentrations in ground water on Long Island, New York, have increased markedly in the last 30 years and this increase has been attributed to lawn and garden fertilizers in addition to septic tank and cesspool discharges (Filpse et al 1985). To identify and quantify the process that control the cycling of nitrogen, phosphorus and silica, basic data is needed those includes not only proper inventory of the elements but also accurate estimates of present day fluxes between various external reservoirs. Speciation in aquatic systems has become increasingly important due to the realization that the environmental behavior of an element (i.e., bioavailability, bioaccumulation and biogeochemical transport) is dependent on its physico-chemical form (Roberts et al 1994). The monitoring of nitrogen and phosphorus in ground water that has been significantly distributed by humans such as polluted waters, application of organic and inorganic fertilizers for crops and coastal environments, has been critically surveyed in this study. The primary objective of this study is to determine the amount of nutrients (Nitrogen, Phosphorus and Silica) present in the ground water, their spatial variation in the study area and to identify the possible sources of nutrients.

Groundwater samples were collected from the aquifers of the Pondicherry region. Thirty-three wells were sampled of which 15 wells were from deep aquifers and 18 wells were from shallow aquifers. In addition, 4 samples were collected from irrigation tanks. The sampling locations are shown in the Fig. 16. The results of the analyses are presented in Table 12.

Fig.16: Sampling locations in the Pondicherry Region



Nitrogen

Nitrogen is known to be the one of the most important limiting nutrients, which could affect the quality of ground water. In view of this, there is a need to establish the forms in which nitrogen is present in this aquatic environment. Inorganic nitrogen in the aquatic environment occurs in a variety of oxidation states ranging from nitrate (NO_3^- most oxidized) to ammonium (NH_4^- most reduced). Besides the dissolved nitrogen gas, the major forms of nitrogen occurring in the ground water bodies are nitrate (NO_3), nitrite (NO_2), ammonium (NH_4) and organic nitrogen. The occurrence and distribution of these forms of nitrogen are governed by the chemistry of the subsoil, the geology, land use pattern, groundwater quality, etc. The formation of nitrates assumes greater importance in an aquatic system.

Nitrate nitrogen ($\text{NO}_3\text{-N}$) and nitrite nitrogen ($\text{NO}_2\text{-N}$)

The autotrophic oxidation of NH_4 is known to occur in two steps, the first to nitrite and then from nitrite to nitrate, which are discussed in detail below. Since, the formation of NO_3 and NO_2 are interlinked, the results are discussed together.

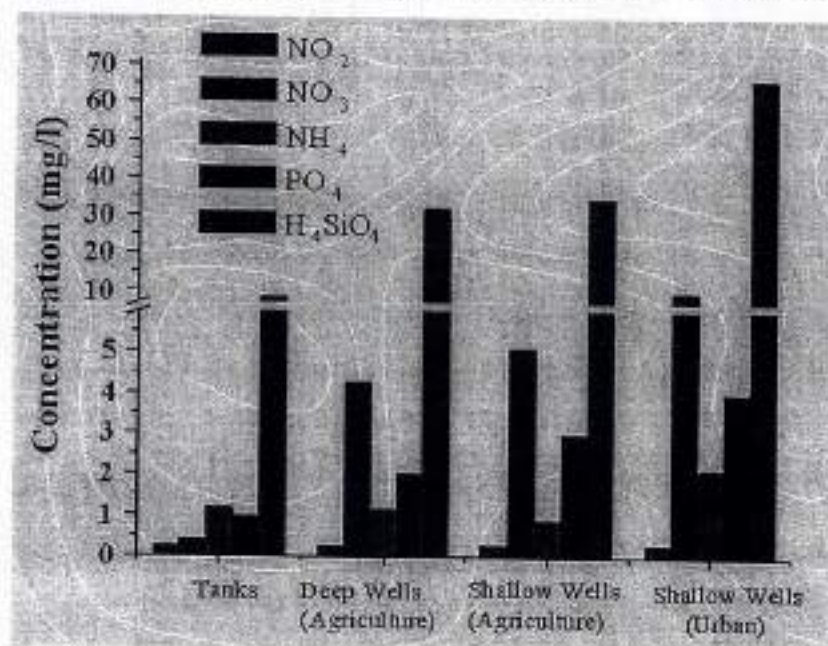
Table 12. Nutrient concentrations (mg l^{-1}) in ground water of Pondicherry region

Sample Nr.	$\text{NO}_2\text{-N}$	$\text{NO}_3\text{-N}$	$\text{NH}_4\text{-N}$	$\text{PO}_4\text{-P}$	H_4SiO_4
Deep wells (Agricultural Area)					
2	0.23	0.6	1.28	0.18	45
3	0.23	BDL	0.49	BDL	30
4	0.23	BDL	2.41	1.16	43
5	0.23	BDL	1.01	0.56	12
8	0.23	BDL	1.91	BDL	14
10	0.23	BDL	1.17	0.76	35
11	0.24	1.72	0.88	0.06	38
14	0.23	BDL	0.72	0.21	14
15	0.21	0.48	1.06	BDL	49
16	0.21	BDL	0.7	BDL	33
17	0.23	18.97	1.37	BDL	34
30	0.23	3.81	1.31	BDL	34
31	0.23	0.07	0.81	0.37	28
34	0.23	4.14	1.21	0.28	38
Shallow wells (Agricultural Area)					
1	0.24	2.88	1.27	BDL	33
1(s)	0.24	0.24	0.81	BDL	40
17	0.23	7.44	0.72	1.22	51
30	0.23	4.31	0.63	0.93	23
31	0.48	2.76	0.47	0.34	22
34	0.23	3.86	0.62	2.25	40
37	0.26	18.85	1.68	3.56	38
42	0.23	0.33	0.97	0.96	29
Shallow wells (Urban Area)					
Bypass road	0.24	0.14	0.95	BDL	36
Sewage PS	0.23	18.91	0.88	BDL	13
Sewage Farm	0.21	0.63	1.02	BDL	85
Venus theatre	0.31	8.24	2.04	BDL	77
Vivek school	0.39	10.63	1.32	BDL	100
PD residence	0.21	13.58	2.72	0.97	83
Govt. Workshop	0.51	21.65	2.97	BDL	66
VOC nagar	0.33	8.24	5.38	6.99	76
Muthialpet	0.33	20.89	1.13	2.91	73
St. Patricks School	0.21	0.28	1.46	BDL	46
Nainar	0.21	4.91	3.44	BDL	71
Tanks					
Karasoar	0.21	0.06	0.51	BDL	10
Kirumambakkam	0.23	BDL	1.47	BDL	12
Nallahur	0.23	0.88	1.49	BDL	3
Oosutteri	0.23	0.12	1.2	BDL	9

*BDL Below Detectable Limit ($<1\mu\text{g l}^{-1}$)

The nitrate concentrations were higher in the samples collected from the shallow well waters (0.14 mg l^{-1} to 21.65 mg l^{-1}), followed by deep well water (Trace- 18.97 mg l^{-1}) and tanks (0.06 mg l^{-1} to 0.88 mg l^{-1}). The nitrite concentrations were ranging from 0.21 mg l^{-1} to 0.50 mg l^{-1} in shallow well waters and a uniform concentration of 0.23 mg l^{-1} in deep well waters and tanks (Figure 17). The nitrate ($\text{NO}_3\text{-N}$) concentrations were an order of magnitude higher than nitrite ($\text{NO}_2\text{-N}$) concentrations in the study area and they displayed a trend of higher

Figure 17. Concentration of Nutrients (mg l^{-1}) in Groundwater of Pondicherry Region



Recent literature indicates that fertilizer application has been causing elevated nitrate concentrations in ground water in many areas of the United States and around the world (Beck et al 1985). Research over the last decade has

clearly shown that agriculture is the most extensive source of nitrate delivered to ground water and surface waters. The expanded, intensive use of nitrogen fertilizers over the last 20 to 30 years has profitably increased agriculture production, but it has also had an adverse impact on water quality in many of the major agricultural areas particularly in developing countries such as India. Studies, ranging in scale from research plots to regional inventories, have shown that nitrate concentrations in ground water can be related directly to agricultural areas (George 1989). Typically, these studies show a range from 3 fold to a 60-fold increase in nitrate concentration ground water moving from more natural, background conditions to agricultural areas. Background areas such as forest and grasslands and often even pasture and rangeland,

commonly show $<2 \text{ mg l}^{-1} \text{ NO}_3\text{-N}$ in ground water, under stable conditions. Many agriculture areas exhibit over 10 mg l^{-1} in shallow ground water. Nitrate in ground water may arise from waste lagoons, septic systems and feedlots (point sources) or be a result of precipitation, Mineralization and fertilizer application (non-point sources). Numerous reports are available on nitrate contaminations from point sources and also from non-point sources (e.g., Henry et al 1984).

The observed higher concentrations of nitrate in ground water in the study area may be attributed to anthropogenic sources. Major agriculture activities with intensive irrigation and application of fertilizers may be the source for higher level of nitrate concentration in the ground water of Pondicherry region. The elevated concentration of 10 fold increase against a background concentration of $<2 \text{ mg l}^{-1}$ of nitrates in ground water are associated primarily with crop land. Further the higher levels of nitrate concentrations in shallow well waters were due to resistance and movements of fertilizers in soil, better adsorbing capacity of the soils and solubility of the fertilizers etc. The maximum nitrate concentration (22 mg l^{-1}) in the ground water of this region is well with in the limits of 45 mg l^{-1} (WHO 1992) because of the following reasons:

- a) The application rate of nitrogen fertilizers in this area is low ($\sim 50 \text{ kg ha}^{-1}$) against 150 to 200 kg ha^{-1} in developed countries;
- b) being a tropical region, the denitrification in subsoil may be pronounced;
- c) the intensive irrigation in these areas has started only since last 20 years so that the accumulation of nitrate in ground water is not significant and;
- d) the heavy monsoon rains might have washed away the excess nitrates if any.

Ammonium nitrogen ($\text{NH}_4\text{-N}$)

Two types of nitrate reduction can occur in nature. They are i) dissimilative nitrate reduction (or the reduction of nitrogen oxides-nitrate, nitric oxide and nitrous oxide) and ii) assimilative nitrate reduction in which the reduced product NH_4 is formed. The main process by which formed and released to the surface and ground water include the breakdown of amino acids and other organic nitrogen compounds, excretion by zooplankton and bacterial reduction of nitrate. The ammonia nitrogen concentration ranged between 0.47 mg l^{-1} and 5.38 mg l^{-1} in shallow well waters; 0.49 mg l^{-1} to 2.41 mg l^{-1} in deep well water; and 0.51 mg l^{-1} to 1.49 mg l^{-1} in tank water. The relatively

higher values NH_4 in shallow well water indicate that active denitrification processes are occurring in the shallow depth, reducing the NO_3 and NO_2 concentrations significantly. It can also be concluded that in general, the nitrogenous nutrients were about 2 to 3 times higher in well waters of urban area than in rural area, suggesting that the abundant leaching of nutrients from municipal waste and sewage effluents through the urban soil. This is in accordance with the findings of Appleyard (1995) that nitrate concentrations are significantly higher in urban areas than in the non-urban areas in a study conducted in a coastal aquifer near Perth, Western Australia.

Phosphorus

Phosphorus, like nitrogen, is also an essential element for sustained primary productivity in the ecosystem. The form of phosphorus discussed here is orthophosphate ($\text{PO}_4\text{-P}$). Orthophosphate levels in natural waters are low, between $1.0 \mu\text{g l}^{-1}$ and $24.0 \mu\text{g l}^{-1}$ (Meybeck 1982) with an average concentration of $12.0 \mu\text{g l}^{-1}$, in the tropical rivers. Of the inorganic forms, the commonly referred orthophosphate is critically important, being the only form of phosphorus that is capable of being taken up by autotrophic organisms. There is a marked increase of nutrient levels in rivers particularly of N and P as a consequence of man's activities and hence, high dissolved load of these nutrient reach the ground water. The level of PO_4 in ground water of Pondicherry region ranged from 0.34 mg l^{-1} to 6.99 mg l^{-1} in shallow ground water, 0.06 mg l^{-1} to 1.16 mg l^{-1} in deep well waters and it was found in trace levels in tank waters. Phosphate is slightly soluble and strongly adsorbed in most soil systems (Lindsey 1979). Generally, it doesn't infiltrate, except under abnormal circumstances. High phosphate concentrations in subsurface water under cropland were reported by Pionke and Urban (1985). The $\text{PO}_4\text{-P}$ contaminated ground water generally ranged from $50 \mu\text{g l}^{-1}$ to $170 \mu\text{g l}^{-1}$ where as background was from $3.0 \mu\text{g l}^{-1}$ to $50 \mu\text{g l}^{-1}$, depending on specific sites (Pionke and Urban 1985). The higher level of $\text{PO}_4\text{-P}$ observed in the shallow and deep wells are mainly attributed to: i) systems that have special features overriding normal controls on phosphorus movement to subsurface water such as heavily irrigated sandy soils overlying shallow water tables; ii) due to the stream flow recharge into the ground water systems; iii) due to high natural soil

and geologic P levels; and iv) due to sampling of existing wells, rather than appropriately constructed wells.

Dissolved Silica

Analysis of ground water often include silica as it is an easy constituent to measure; however, interpretation of the results has been limited due to the absence of information regarding the behaviour and controls on silica in ground water. Because of its non-toxic nature to humans, animals and plant life, has escaped the attention of early hydro chemists: although in industry silica has assumed some importance because silica and other precipitates are undesirable in high-pressure systems. More recent investigations have recognized the importance of silica in ground water studies (Haines and Lloyd 1985; and Pucci and Owens 1989).

Silica generally exists in solution as the monomeric form, Si(OH)_4 (Haines 1984). In normal ground waters silica is relatively unreactive and doesn't readily form compounds and complexes with other dissolved constituents. Silica is particularly inert with respect to the major cations and anions and will only undergo reactions with the dissolved cations (Calcium and magnesium) under conditions of high pH and cation activity. Anionic species, in general, don't react with silica in ground waters (Haines and Lloyd 1985). A concentration of approximately $5 \text{ mg l}^{-1} \text{ SiO}_2$ may be expected as a background level in ground water of unreactive aquifers. In the study area, the concentration of H_4SiO_4 ranged from 13.0 mg l^{-1} to 100 mg l^{-1} in shallow waters, 12.0 mg l^{-1} to 49.0 mg l^{-1} in deep well waters and 3.0 mg l^{-1} to 12.0 mg l^{-1} in tank waters. The higher concentrations of dissolved silica in ground water of Pondicherry region may be due to the release of amorphous silica within the soil zone. Table 8 shows the average concentration of nutrients in ground water of Pondicherry region along with the composition of the natural waters such as river, estuary and sea. This table reveals that; i) the nitrate concentration in the shallow wells of agriculture area shows a marginal increase than the other natural waters, indicating the impact of agricultural activities on the ground water quality; and ii) the higher concentrations of silica in both shallow and deep wells indicate the release of amorphous silica with in the soil zone.

7.4 Spatial Variation of Organochlorine Pesticides

The environmental contaminations by pesticide residues are of great concern due to their toxicity, bioaccumulation and persistent nature. Organochlorine pesticides such as HCH (hexachlorocyclohexane) and DDT (dichlorodiphenyl-trichloroethane), Endrin, Lindane and Aldrin are among the most persistent and globally distributed organic pollutants. These pesticides are long-lived organic compounds that become concentrated as they move through the food chain and have toxic effects on reproduction and immunological function. Since the introduction of organochlorine pesticides in late 1930s the residues of these compounds have been found in many parts of the World (Hattula et al 1978). Along with other chlorinated micro pollutants, persistent pesticides such as HCH, DDT, Endrin, Lindane and Aldrin have become widely distributed around the planet. Pesticides are unique in that they are purposefully released in to the environment to control the selected species. The chlorinated pesticides are now largely banned chemicals, which may still pose a threat to human health as well as the wider environment.

In India, the organochlorine insecticides, DDT and HCH were used extensively for agriculture and other public health programs accounting for ~ 77% of the total consumption (Gupta 1986). The pesticide transport can occur in three ways, i) movement in the vapor phase, ii) surface runoff and iii) leaching. The tropical warm temperatures favor evaporation from earth's surface. Among them surface runoff can contribute maximum load from the non-point source through streams and canals. Hence the logic is to dictate that the concentration will be highest near the point of release and decline with distance. Relatively mobile organochlorine compounds have the exception with the distance because of their tendency to partition for easy movement. In spite of their persistence nature, organochlorine insecticides were reported in major world rivers (Oliver and Nicol 1984; El-Dip and Badawy 1985; Agarwal et al 1986; Jhonson et al 1988; Halder et al 1989; Ramesh et al 1990; Haut et al 1991; and Hernandez et al 1992; Agnihotri et al 1994; Rajendran and Subramanian 1997; Yamashita et al 1997; Baun et al 1998 and Wu et al 1999).

Global Distribution of organochlorine residues in surface waters

A comparison of published levels of organochlorine from the surface waters of sea, river and lake water gives a good indication of the typical contamination that might be expected in different water types. Very little information exists with respect to contamination of surface seawater, although it is acknowledged that the gas-phase exchange of the semi-volatile organochlorines from the atmosphere will probably influence their occurrence more than direct riverine discharges. Recent studies (Schreitmuller and Ballschmiter 1995) suggest that global distribution will be largely controlled by gas-phase equilibrium between the ocean and the atmosphere. A logical extension of this is the probability that the ocean will become a different source of such compounds for many years as increasing restriction reduces their release. Recent reports on HCH levels in the atmosphere have indicated a net source of this compound in the northern hemisphere (Iwata et al 1993). A selected published result in surface waters from different region is given in Table 13. The Great lake and Lake Baikal data reveal generally greater contamination, especially for the DDT compounds due to additional influence of adsorption onto eroded suspended sediments.

Table 13: Global distribution of organochlorine residues in surface waters

Name	Chlordane	α HCH	Lindane	DDE	DDT	Reference
Mediterranean	3.7	180	150	1.2	1.3	Iwata et al (1993)
South China Sea	9.3	380	97	1.0	6	Iwata et al (1993)
Arctic	3.7	5970	824	--	--	Cotham (1991)
Bay of Bengal	7.9	610	110	1.4	8.6	Iwata et al (1993)
Southern Ocean	3.4	28	8.2	0.5	0.5	Iwata et al (1993)
Bering Sea	3.4	1500	190	0.9	0.1	Iwata et al (1993)
Lake Baikal	46.4	1100	240	--	--	Kucklick et al (1994)
Great Lakes	36-100	1300	420	45	--	Kucklick et al (1994)

Pesticide pollution in Indian rivers

The organochlorine usages are the more among the pesticide used in India, which includes HCH, DDT, malathion, methyl parathion and endosulfan. About 25-32 % of the total pesticide consumption in India is in public health applications. Many of these compounds have been banned in industrialized countries due to their toxicity, bioaccumulation and persistent nature in environment. However organochlorine pesticides are still used extensively in India due to their effectiveness and low cost

(Postel 1988 and Goldberg 1991). The pesticide pollution and their impacts on Indian rivers are reported by several researchers (Rajendran 1984; Agarwal et al 1986; Subba Rao et al 1986; Thakkar and Sarin 1987; Karthikeyan 1988; Bakre et al 1989; Halder et al 1990; Ramesh et al 1990; Rajendran and Subramanian 1997 and Sujatha et al 1998). The present study aims to identify and measure the concentration of organochlorine insecticides HCH and DDT in both water and sediment samples of the entire river basin, to assess the impact of agricultural inputs on the river system.

Growing demand for food as a result of increasing population has led to a substantial rise in the production and utilization of wide variety of pesticides in Agriculture. The constant usage of these pesticides leads to a continued contamination of our environment including the water resources (Kaushik et al 1987, Ramesh et al 1989; 1990; Ngebe and Biddleman 1992 and Iwata et al 1993; 1994). At present, ground water contamination by pesticides is a major environmental concern due to health effects and the difficulty in evaluating the fate and ecotoxicological effects of these pollutants. The transmigration of organochlorines through food and drinking water may lead to higher accumulation in human system leading to pathophysiological and related health effects. Among these pesticides, organochlorine insecticides such as Hexachlorocyclohexane (HCH) and Dichlorodiphenyltrichloroethane (DDT) are being used intensively in India for Agriculture and public health programmes because of their semi volatile, highly persistent and toxic nature. In spite of restrictions or ban on organochlorine compounds (OC) usage in western countries since 1970s; these man made chemicals are still present at considerable levels worldwide especially in tropical countries.

In Pondicherry region, paddy being the major crop cultivated, the following pesticides are extensively used to control pests. Among the insecticides HCH (30.76 MT), Endosulphan (6.32), Malathion (4.73), Monocrotophos (14.40 MT), Phosphomidan (8.00 MT), Carbaryl (3.00 MT), Carbofuran (1.50 MT) are fungicides used in this region. Weedicides (Butachlor and Atrazin) are also used in small quantities for weed control (Source: Agriculture Department, Government of Pondicherry). In total, on an average about 113MT of pesticides are used in a year in this region for agriculture and public health programmes. The residual concentrations of HCH isomers (alpha, beta, gamma and delta), Aldrin and p,p' - DDT metabolites, which were analyzed in water samples collected from Pondicherry region and are given in Table 14.

Table 14: Residual levels of HCH, Aldrin and DDT (ng l^{-1})

S.No	Alpha	Beta	Gama	Delta	Total HCH	Aldrin	pp'-DDD	Total Pesticides
Tanks								
1	-	32.5	0.78	6.9	40.2	-	1.59	41.8
2	-	24.8	0.52	3.9	29.3	-	0.99	30.21
Shallow Wells - Agricultural Area								
3	-	8.93	0.43	14.30	23.6	1.28	1.53	26.44
4	1.63	-	0.31	9.49	11.4	0.32	-	11.76
5	-	10.2	0.76	2.38	13.3	6.75	-	20.08
6	-	13.1	0.46	11.50	25.1	-	-	25.11
7	-	36.1	4.92	19.80	60.82	-	-	60.82
Deep Wells - Agricultural Area								
8	-	6.63	0.32	8.26	15.2	-	-	15.22
9	-	4.05	0.23	7.5	11.8	0.51	0.54	12.88
10	-	5.6	0.24	12	17.8	0.66	-	18.5
11	13.6	-	0.22	-	13.8	-	-	13.79
Shallow Wells - Urban Area								
12	2.67	-	0.38	1.51	4.56	0.33	-	4.88
13	-	1.22	0.27	-	1.49	0.34	-	1.83
14	-	6.02	0.57	-	6.6	2.86	-	9.46
15	0.91	-	0.24	4	5.15	0.54	-	5.69
16	-	4.71	0.11	2.5	7.33	-	0.35	7.67
17	2.8	-	0.26	38.5	41.6	1.27	-	42.83
Deep Wells - Urban Area								
18	-	1.79	0.52	10.3	12.6	0.65	-	13.26
19	-	-	42.5	17	59.5	13.9	-	73.4

Surface Water

The OCs transported through the atmosphere as gases and/or particulate phases enter surface waters by gas exchange across the air – water interface and by deposition along with aerosols, rain and snow (Iwata et al 1994). In the study area, the total concentration of HCH isomers in water samples collected from two irrigation tanks was found to be 29.3 ng l^{-1} and 40.2 ng l^{-1} . Among the DDT metabolites only p,p'-DDD was identified and the values were 0.99 ng l^{-1} and 1.59 ng l^{-1} . Dikshit et al (1990) recorded very high values of HCH and DDT in well ($4654000 \text{ ng l}^{-1}$ and $5194000 \text{ ng l}^{-1}$) and pond waters ($9941000 \text{ ng l}^{-1}$ and $16059000 \text{ ng l}^{-1}$) collected in and around Bhopal city. The other compound aldrin was below the detection limit in both the samples of the study area. The total residual level of organochlorine pesticides ranged from 30.21 ng l^{-1} to 41.80 ng l^{-1} with an average of 36 ng l^{-1} . Among all the pesticides, the residue levels of total HCH isomers were more. This may be due to the constant use of HCH isomers for agricultural purposes and due to rain, run-off and by deposition along with aerosol it could have been reached the surface water bodies.

Groundwater

The increased concentration of pesticide residues to ground water bodies are influenced by irrigated environment, lighter soil texture and wet season rice culture. The depth of the tube wells, from which the water samples collected from agriculture and urban area were considered here while discussing the residue levels.

Agriculture Area

In the water collected from shallow bore wells, the residue levels of total HCH varied from 11.4 ng l^{-1} to 26.44 ng l^{-1} with an average of 18.44 ng l^{-1} . *p, p'* - DDD was recorded in only one sample (1.53 ng five samples). The residual concentration of Aldrin ranged between $0.32 \text{ ng ng l}^{-1}$ and 6.75 ng l^{-1} . At one location, where the water was collected from open dug well, a maximum residual level of HCH isomers of 60.82 ng l^{-1} was quantified. The reason for the higher level is due to the contamination of well water by surface run off. The water samples collected from deep wells showed a lesser concentration of pesticide residues when compared to shallow wells. The residual concentration of total HCH ranged from 11.80 ng l^{-1} to 17.80 ng l^{-1} with an average of 14.70 ng l^{-1} . In the case of DDT only *p, p'* - DDD alone was identified and quantified (0.54 ng l^{-1}) in only one sample among four samples. Aldrin was recorded in only two samples and the concentrations were 0.51 ng l^{-1} and 0.66 ng l^{-1} .

In all the above three sources (tanks, shallow wells and deep wells) of water samples, Aldrin were rarely identified. It was not quantified to surface water samples (Tanks) and very low concentrations were quantified in shallow and deep well water samples. Though Aldrin has been banned for agriculture use, the reason for the trace quantities are due to the seepage/percolation into the subsoil water that were used earlier and persistence in the ground water. Among the three organochlorine compounds, HCH isomers were quantified more than the other compounds (Figures 18, 19 and 20).

Our study reveals that total residual levels of organochlorine pesticides in different sources are in the order of tanks (36.00 ng l^{-1}) > shallow wells (20.80 ng l^{-1}) > deep wells (15.10 ng l^{-1}). The residue level of HCH, DDT and Aldrin in Pondicherry region is very low when compared to the ground water found in Indo-Gangetic region. The above observation is in good agreement with the reports published by Dogheim et al (1996) and Castaneda et al (1996); who have reported increased of HCHs and DDTs

in the ground water within rice field boundaries in irrigated and rainfed areas. It could also be stated that the detection of pesticides was associated with the well depth with a higher probability of detecting a pesticide in the shallow unconfined aquifer than in the deeper aquifers (Bruggeman 1995). Among the Isomers of HCH, beta-isomer was predominant in Tank and Shallow Water samples followed by Delta and Gamma isomers. Alpha-Isomer was not quantified in tank waters and recorded in only one shallow water sample. But in the waters of deep wells, the trend is quite different that Delta- HCH predominates Alpha and Beta-HCH. Alpha-Isomer was recorded in only one location (3D-PASIC FARM) where very high concentration of (13.6 ng l^{-1}) was recorded (Table 14). Variation in the isomeric composition of HCH is greatly influenced by season as well as usage pattern. The behavior of HCH is largely controlled by the Physico-chemical properties of the individual isomers. High concentration of Beta-HCH might be due to the isomerization of Gamma-HCH to Beta-HCH in Water and sediment as suggested by Hayes (1982). Moreover Beta-HCH has lowest vapour pressure, water solubility, more stable among all the isomers and also resistance to microbial degradation. Therefore, the concentration of this isomer in water is likely to remain at high level. The isomeric composition of water samples in the present study is quite different from Indo-Gangetic and Bhopal region where Alpha-HCH was the predominant one (Table 15).

Table 15: Concentration (ng l^{-1}) of organochlorine pesticide residues in groundwater of some major Indian cities

Site	HCH	DDT	Aldrin + Dieldrin	Reference
Bhopal	43,20,000 87,18,000 (61,30,000)	103,92,000 223,48,000 (145,48,000)	-	Dikshith et al (1990)
Ahmedabad	24 – 2489 (257)	11 – 315 (48)	-	Jani et al (1991)
North Madras	161 – 1081 (576)	-	-	Ramachandran et al (1995)
Gangetic Plains	BDL – 978 (217)	BDL – 1657 (279)	BDL – 908 (109)	Mohapatra et al (1995)
Himalayan Range	52 – 118 (32)	BDL – 700 (88)	BDL - 40 12	Kumar et al (1995)

(BDL- Below detectable level)

Fig. 18: Residue levels of organochlorines in agricultural area

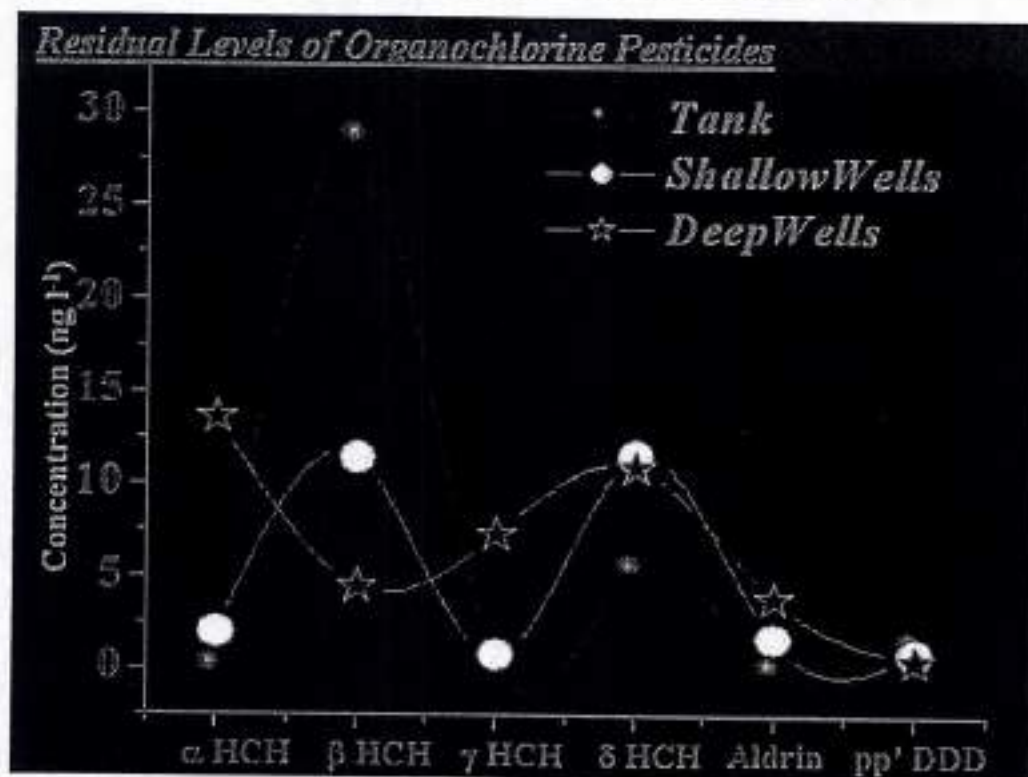


Fig.19: Residue levels of Organochlorines in Shallow wells

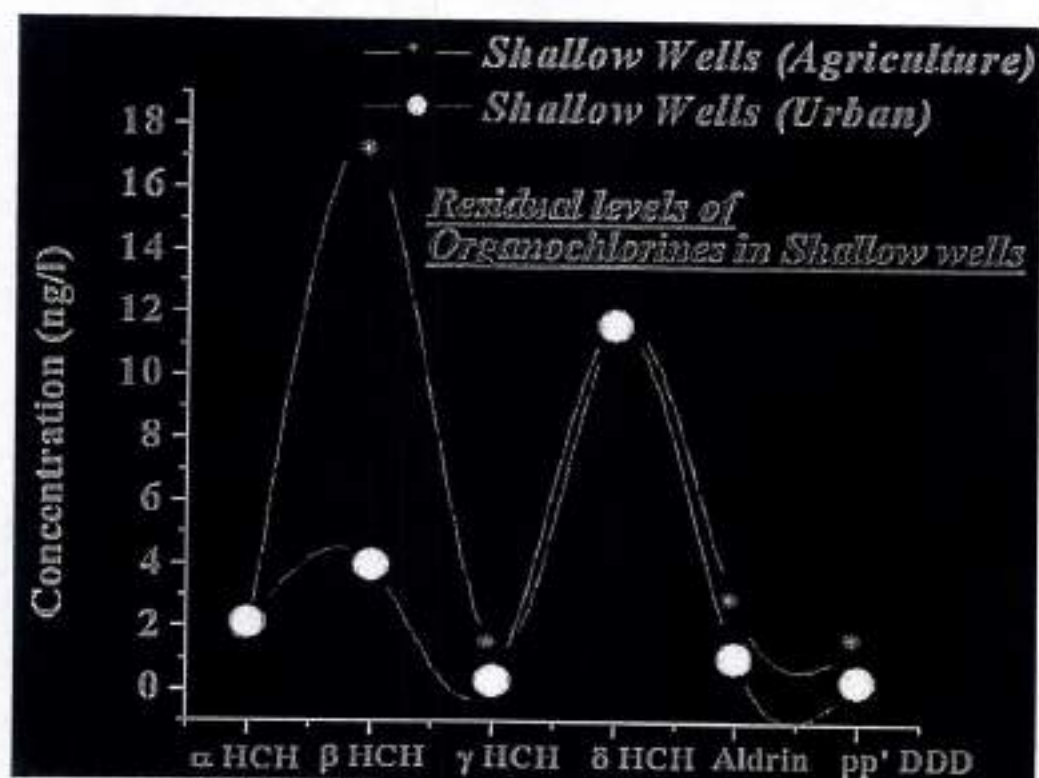
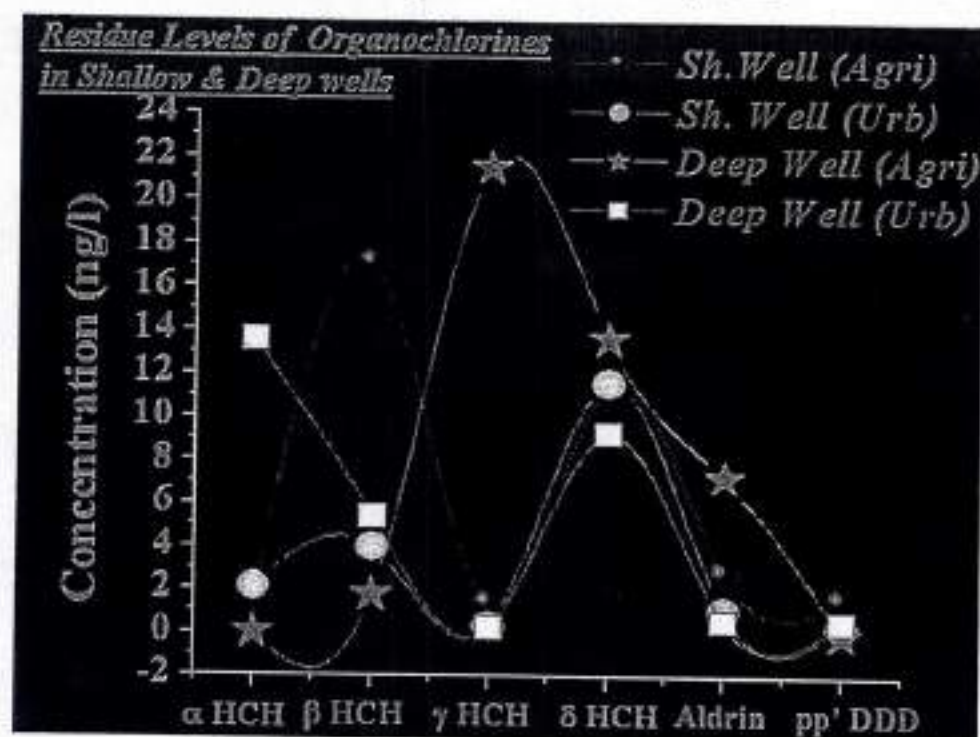


Fig.20: Residue levels of Organochlorines in Deep wells



Among DDT metabolites, only p,p' DDD was identified and quantified in 25% of the total number of samples. p,p' DDD is the metabolite of DDT compounds, formed during the reductive dechlorination in anaerobic conditions in the subsoil environment. Mostly in the ground water samples the presence of p,p' DDD alone is possible because of the anaerobic conditions prevails in the soil zone. Dikshith et al (1990) and Mohapatra et al (1995) recorded high concentration of DDT than HCH in ground waters of Bhopal and Indo-Gangetic region respectively during 1989-1992. But in the present study HCH predominates DDT in almost all the samples analyzed. The reason for high concentration observed by Dikshith et al (1990) and Mohapatra et al (1995) might be due to the excessive use of DDT in those days before it was banned. Mohapatra et al (1995) recorded high values of p,p'- DDD in water samples and it shows that recent use of DDT compounds in vector control and/or illegal use in agriculture in Indo-Gangetic region. They have reasoned out that still some farmers even now use DDT, despite the ban, because it is available at cheaper cost.

Next to HCH compounds, Aldrin was identified in about 60% of the total number of samples. In tank water it was not identified but in shallow waters the concentration was little higher than deep well waters (Table 14). Relatively low concentration of

DDT metabolites (p,p' DDD) and high concentration of HCH recorded in the present study could be attributed to the quantities of these pesticides used in agriculture and public health activities (Vector Control Programmes). Though DDT has been banned for use in Agriculture in India, it is being used for public health activities (Singh et al.1988).

Urban Area

The total HCH concentration in water collected from shallow wells was ranged from 1.49 ng l^{-1} to 7.33 ng l^{-1} with an average of 5.03 ng l^{-1} . A high concentration of 41.6 ng l^{-1} of total HCH was observed in a shallow well situated in a sewage farm. The reason for this high concentration is due to irrigation of treated sewage effluents to the farm located around the treatment plant. The concentration of aldrin ranged from 0.33 ng l^{-1} to 2.86 ng l^{-1} , in shallow well water samples. p,p' - DDD of DDT compound was recorded in only one shallow well (Venus theatre - 0.35 ng l^{-1}). Only two samples were collected from deep aquifers in urban area. Out of which one sample showed a total residual level of 13.26 ng l^{-1} and the other showed a level of 73.40 ng l^{-1} . The anomalous increase in the residual level of the sample collected from Balabavan well is due to the leaching of pesticides because of the constant application of pesticides for plants in the nursery and also due to the leakage of contaminated water from the shallow aquifer to the deep aquifer. In deep well water sample the concentration of aldrin was 0.65 ng l^{-1} . p,p' - DDD of DDT compound was not recorded in deep well water samples.

The distribution pattern of HCH isomers in shallow and deep well water samples of urban area is almost similar to agricultural area. In shallow wells of urban area β -isomer predominates α , β and γ - HCH isomers. But in deep well waters α -HCH isomer predominates β and γ - HCH isomers (Table 14). Further, the total residue levels of organochlorine compounds in shallow well waters of agricultural area are 3 to 4 times more when compared to the total residue levels in shallow well waters of urban area. This shows that the continuous usage of pesticides for agricultural activities and hence the contamination of shallow ground water takes place in agricultural areas (Fig.19). The total residual levels of organochlorine pesticides in deep wells of both agricultural and urban area are more or less uniform (Fig.20), because water drawn from deep wells in these areas is from one and the same aquifer system (Tertiary formations - Cuddalore sandstones aquifer system). Hence, there is

no variation in the residual levels in deep aquifer wells between agricultural and urban areas.

When compared to the concentration of organochlorine pesticide residues in ground water of other Indian cities, the residual levels are depleted in Pondicherry region. Also, the residual levels of pesticides are well within the maximum acceptable limit of 100 ng l^{-1} for individual pesticide (ECC, 1980) for drinking purposes. In addition, the comparison of the mean organochlorine (HCH) residual data shows that the residual levels in ground water of Pondicherry region are depleted than in lakes, rivers and estuary except Arabian Sea (Table 16). The DDT values are comparable with Cauveri River and Vellar estuary but lower than Lakes and Rivers. The volatilization of pesticide residues from soil in South India and especially in the study area in more than leaching into the ground water column might be the reason for low concentration of DDT and HCH recorded. To conclude the ground water in Pondicherry region with respect to the concentration of pesticides of chlorinated nature is free from pollution at present and safe for consumption.

Migration of pollutants through ground water recharge with irrigation return and monsoon rains carrying integrated residues downwards from the soil surface are thought to be the important sources of pesticide contamination of ground water in this region. Though the residual levels of pesticides in the study area are well below the acute toxicological problems, the major concern is for long term, chronic exposure from compounds that may be carcinogenic or potentially mutagenic or teratogenic. The growing population of India will necessitate the use of even larger quantities of pesticides in future years as a result of the increased requirement to protect and improve the quality and quantity of its food and textile supplies, in addition to public health programmes.

With a view to environmental protection the Indian Government is giving high priority to biological control, and has launched Integrated Pest Management Programmes (IPM) to control pests in various crops. Large-scale field trials have been organized by the Indian Government to show the utility of biological control with training in mass rearing of biocontrol agents being offered to farmers (Mohapatra and Agnihotri 1996). Pesticide-free zones, where only biological control methods of pest control are used, are being developed. Several botanical and microbial pesticides have

been identified and examined for potential use on various crops (Sing 1993 and Battu et al 1993). Several formulations of *Bacillus thuringensis*, *Trichogramma sp.* And neem (*Azadirachta indica*) is commercially available.

Table 16: Concentration of organochlorines (ng l^{-1}) in natural waters of India.

Source	HCH	DDT	Reference
Yamuna River	660	120	Iwata et al (1994)
Cauveri river	79.3	2.16	Babu Rajendran & Subramanian (1996)
Lake-Mahalon Lake-Jal Mahal	50 - 9300 10 - 4600	70 - 24650 40 - 47400	Kumar et al (1998)
Vellar Estuary	14 - 2000	0.04 - 47400	Ramesh et al (1990)
Arabian Sea	2.7	115.2	Shailaja and Sarkar (1992)
Tanks	34.7	1.3	Present study
Groundwater (Shallow well in agriculture area)	18.4	0.4	Present study
Groundwater (Shallow wells in urban area)	5.1	0.1	Present study

Therefore, the problem of pesticides, and other agricultural impacts on ground water and the environment will require a new focus for research and farm management. More integrated farm management and more complete research into integrated farming system is needed, with a focus on efficiency and off-site impacts rather than just maximizing yields. Pesticides and fertilizers will remain as a needed tool for agricultural production but, clearly, less toxic compounds can be adopted: greater efficiencies and more judicious use can be employed. To resolve agricultural non-point source problems fully, policies for production must be integrated with policies for conservation and environmental protection, if we are to affect a satisfactory balance between efficient and economic agricultural production and protection of our water resources.

7.5 NUMERICAL MODELLING OF SALT WATER INTRUSION

Fresh groundwater systems are important sources of potable water throughout the world. Mostly, fresh groundwaters of coastal aquifers are in contact with saline water, which, if drawn into the fresh water aquifer system, can diminish the water potability as well as its usefulness for other purposes. Thus, a quantitative understanding of the patterns of movement and mixing between fresh and saline water, and of the factors that influence these processes, is necessary to manage and protect these resources for future use. The ability to mathematically describe the phenomenon of salt water – fresh water mixing and calculate the location of an approximate saltwater interface has progressed steadily since the late 19th century, but the mechanisms are still incompletely understood. Hydrogeologists have been using various numerical models to simulate how ground water moves in the subsurface. Models are useful for field investigations, for proper interpretation after the fieldwork and as a predictive tool how water quality or quantity may change in aquifer for the impinged conditions. Various models are available to predict the location and pattern of salt water-fresh water interface for a given set of hydrologic conditions. In this study, an attempt has been made to determine the pattern and location of the salt water – fresh water interface in the aquifer along the coast of Pondicherry region.

Aquifer Simulation Programme

Among is dispersed interface approaches, the widely used mathematical models are (i) the method of characteristics with variable pore water density (MOC DENCE) as proposed by Sanford and Konikow (1985) and (ii) the saturated unsaturated transport (SUTRA) modelling method as proposed by Voss (1984b). Balasubramanian (1992) has performed a variety of experimental simulations on an unconfined coastal aquifer and verified the results using different types of numerical techniques including the two above said approaches.

Both the methods are found to be of having high practical values. Subramanian (1994) has attempted simulating the saline intrusion problems along Tiruchendur coast, Tamil

Nadu using MOCDENCE. Lawrence (1995) attempted using SUTRA, the simulation of salt-water intrusion in ground water along Ramanathapuram coast, Tamil Nadu. Considering their grid network, domain specifications and time steps used, SUTRA was found to be more suitable to model the Pondicherry region. The details of simulation runs are given in the following sections.

General Numerical Procedures of Sutra

SUTRA (Saturated – Unsaturated Transport) is a mathematical modelling procedure, which has a high utility value in simulation of fluid movement and transport of either energy or dissolved substances in various subsurface conditions including saturated and unsaturated porous media (Voss 1984b). This modelling strategy employs a two-dimensional hybrid finite – element and integrated finite – difference method to approximate the governing equations that describe two independent processes that are simulated. The model could also consider the density – dependent flow over an areal domain or a cross – sectional area.

Simulation using SUTRA is in two space dimensions, although a three dimension quality is provided in that the thickness of the two dimensional region in the third direction may vary from point to point. Simulation may be done in either the areal plane or in a cross – sectional view. The spatial co-ordinate system may be either Cartesian (x, y) or radial cylindrical (r, z). Area simulation is usually physically unrealistic for variable density fluid mass balance equation. The ground water system may be either saturated or partly or completely unsaturated. Fluid density may be constant or vary as a function of solute concentrations or fluid temperature. SUTRA tracks the transport of either solute mass or energy in the flowing ground water through a unified equation, which represents the transport of either solute, or energy. Solute transport is simulated through numerical solution of a solute mass balance equation where solute concentration may effect fluid density. The single solute species may be transported conservatively or it may undergo equilibrium sorption (through linear Freundlich or Langmuir isotherms). In addition, the solute may be produced or decayed through first or zero order processes. The primary variable upon which the flow model is based is fluid pressure,

$$P [M/(L.S^2)] = p (x, y, t)$$

Pressure may vary spatially in the ground water system as well as with time. Pressure is expressed as a combination of fluid mass units [M], length units [L] and the time units in seconds [S]. Fluid density may vary depending on the local values of fluid temperature or solute concentration. Variation in fluid density, aside from fluid pressure differences, may itself drive flows. The effects of gravity acting on fluids with different density must therefore be accounted for in the flow field. The flow of ground water, in turn, is a fundamental mechanism upon which the physical models of energy transport and solute transport are based. The primary variable characterizing the state of solute distribution in a ground water system is solute mass fraction.

$$C [Ms/M] = C (x, y, t),$$

Which may also vary spatially and with time. The units are a ratio of solute mass [Ms] to fluid mass [M]. The term solute mass fraction may be used interchangeably with solute concentration and no difference should be implied. SUTRA simulation is carried out in a two space dimensions with parameters varying in these two directions. Fluid movement in the porous media where fluid density varies spatially may be driven either by differences in fluid pressure or by unstable variations in fluid density. Pressure driven flows for example, are directed from regions of higher than hydrostatic fluid pressure towards regions of lower hydrostatic pressure. Density driven flows occur when gravity forces act on denser regions of fluid causing them to flow towards fluid regions, which are less dense. A stable density configuration drives no flow and is one in which fluid density remains constant or increases with depth. The mechanisms of pressure and density driving forces for flow are expressed for SUTRA simulation by a general form of Darcy's law, which is commonly used to describe flow in porous media.

Where

$V (x,y,t)$ [L/s] average fluid velocity

$K (x,y)$ [L²] solid matrix permeability (2 X 2 tensor of values)

$K_r (x, y,t)$ [1] relative permeability to fluid flow (assume to be independent of direction)

G_g [L/s] gravitational acceleration (gravity vector) (1 X 2 vector of Values)

The gravity vector is defined in relation to the direction in which vertical elevation is measured.

$$\underline{g} = -|g| \underline{V}(\text{elevation})$$

Where $|g|$ is the magnitude of the gravitational acceleration vector. For example if y-space co-ordinate is oriented directly upwards, then $\underline{V}(\text{elevation})$ is a vector of values (for x and y directions, respectively): (0,1) and $|g| = (0,-|g|)$. If for example elevation increases in x,y plane at a 60° angle to the x-axis then

$$\underline{V}(\text{elevation}) = (1/2), (31/2/2) \text{ and } \underline{g} = -(1/2)|g|, -(31/2/2)|g|.$$

Fluid mobility depends on the combination of permeability, K_r , relative permeability, k_r and viscosity, μ . Even in the basic form of Darcy's law, flow may depend on solute concentration and temperature.

Permeability, k , is in most situations essentially independent of pressure, temperature and concentration and therefore is the appropriate fundamental parameter describing ease of flow in the SUTRA model.

The fluid mass balance is expressed as the sum of pure water and pure solute mass balance for a solid matrix in which there is negligible net movement.

Where $Q_p(x, y, t)$ [M/(L³.s)] is fluid mass source (including pure water mass plus solutes mass dissolved in source water) and $T(x, y, t)$ [M/L³.S] is solute mass source (e.g., dissolution of solid matrix or desorption).

The term on the left may be recognized as a total change in fluid mass contained in the void space with time. The term involving \underline{V} represents contributions to local fluid mass change due to excess of fluid inflows over outflows at a point. The fluid mass source term, Q_p accounts for external additions of fluid including pure water mass plus the mass of any solute dissolved in the source fluid. The pure solute mass source term, T , may account for external additions of pure solute mass, which are not associated with a fluid source. In most cases, this contribution to the total mass is small compared to the total pure water mass contributed by fluid sources, Q_p .

Solute mass is transported through the porous medium by flow of ground water (solute advection) and by molecular or ionic diffusion, which while small on a field scale, carries solute mass from areas of high to low concentrations. The actual flow

velocities of the ground water from point to point in three-dimensional space of an aquifer may vary considerably about an average, uniform two-dimensional velocity, \bar{V} , which is calculated from Darcy's law. As the true velocity field is usually too complex to measure in real systems, an additional transport mechanism approximating the effects of mixing of waters with different concentrations moving both faster and slower than the average velocity, $\bar{V}(x, y, t)$ is hypothesized. This mechanism, called solute dispersion, is employed in SUTRA as the best currently available description of the mixing process, though it is approximate. In the simple dispersion model employed, dispersion, in effect, significantly adds to the molecular diffusivity value of the fluid in particular directions dependent upon the direction.

Although SUTRA is two-dimensional model, the region of space in which flow and transport is to be simulated may be defined in three-space dimension. The three dimensional bounded volume of an aquifer, which is to be simulated by SUTRA, is completely divided up into a single layer of continuous blocks. These blocks are called finite elements. The subdivision is not done simple in a manner which creates one block (elements) ^{for} each portion of the aquifer system which has unique hydrogeological unit is ~~in~~ fact divided into many elements giving the subdivided aquifer region, the appearance of a finite net or mesh. These subdivisions of the aquifer region to be simulated into blocks are referred to as creating a finite element mesh (or finite element net).

The basic building block of a finite element mesh is a 'finite element'. The type of element employed by SUTRA for two-dimensional simulation is quadrilateral, which has a final thickness in the third space dimension. Each element has a three dimensional shape and four nodes. Nodal points are always shared by the element adjoining the node.

Aquifer parameter and coefficients, which vary from point to point in an aquifer, such as, specific storability, S_o , and hydraulic conductivity, K , are represented by an approximate way in SUTRA. Parameters are either assigned a particular constant value in each element of finite element mesh (element wise) or are assigned a

particular value at each node in a mesh in two possible ways (node wise or cellwise). In the water table aquifer, ~~for~~^{for} a simple example, a regular two-dimensional mesh is used. Nodewise assignment for head over this mesh results in a continuous surface of h value, with linear change in value between adjoining nodes along (projected) element edges. Cellwise assignment is employed for specific storativity, S_0 , and the time derivative, $\delta h / \delta t$. Each cell is centered on a node, not on an element. Cell boundaries are halfway between opposite sides of an element. Thus the spatial distribution of parameters, K , h and S are discretised (i.e., assigned discrete values) in three different ways: K element wise, h , nodewise and S_0 , cellwise.

Time is broken up into series of discrete steps or time step. The length of time step, Δt , is the difference in time between two discrete times at the beginning and end of a time step.

$$\Delta t_{n+1} = t^{n+1} - t^n$$

where Δt_{n+1} is the length of the $(n+1)$ the time step, t^n is the actual time at the beginning of the $(n+1)$ th time step and t^{n+1} is the actual time at the end of this time step. The time steps are chosen to discretise the time domain before a simulation just as a mesh (or 'spatial step') is chosen to discretise space. The time step length may vary from step to step.

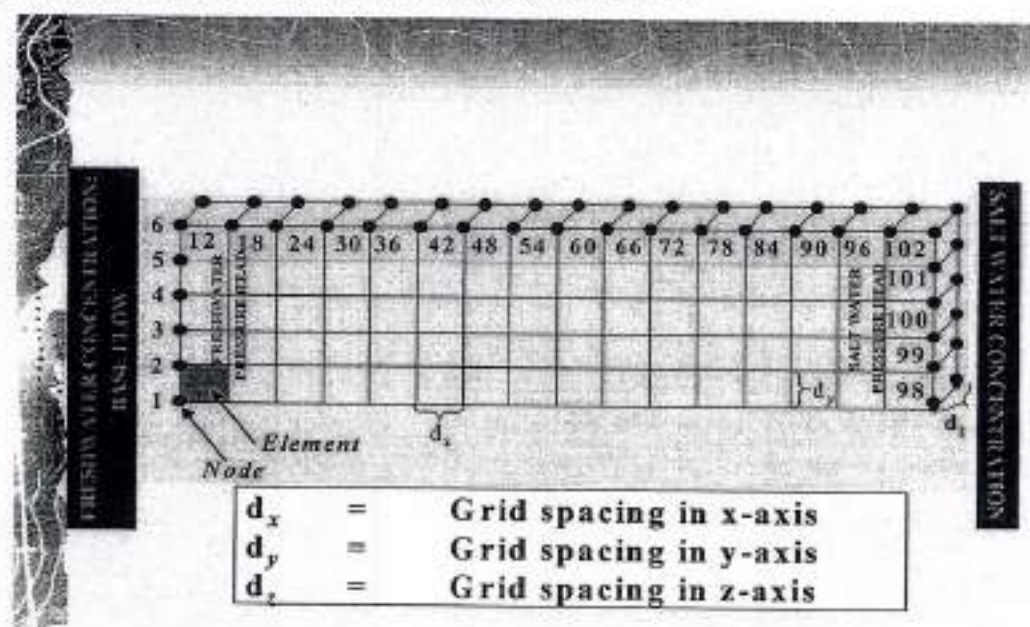
Before solving the matrix equations, information about boundary conditions must be included. In case of solving for heads, the boundary conditions take the form of either specified fluid fluxes across boundaries which are directly entered in the terms, Q , N or of particular head values specified at nodal locations. At a point of fixed head in an aquifer, a particular value of inflow or outflow occurs at the point in order to keep the head constant when the aquifer is stressed.

The interface of salt and fresh water fluctuates depending upon the recharge - discharge volumes. The recharge - discharge and base flow also control the water table elevation which, in turn, determines the pressure heads on both the finite elements of upstream and seaward side. The following are the sequence of the parameters used for SUTRA simulations.

Spatial Discretization of the Finite Elements

In the study area, an aquifer cross – section has been considered for a length of about 16,000 metres from the coastline. The depth of the aquifer considered was 50 metres below M.S.L. The section has been discretised into 102 nodes as shown in the Figure 21. The grid spacing in x direction was 1000 metres, in y direction was 10 metres and in the z direction it was kept as 1000 metres slice.

Fig 21 Elemental Network used for Interface Simulation



Representation of Coefficients in Space

The permeability considered for simulation runs was $1.02 \times 10^{-9} \text{ (m}^2\text{)}$ and the porosity of media assigned was 0.35. The other parameters used are:

Density of fresh water:	1000 kg/cu.m
Density of salt water:	1025 kg/cu.m
Fluid coefficient of density:	
Change with concentration:	700
Dispersivity:	$6.6 \times 10^{-4} \text{ m}^2 / \text{s}$

Flux Terms:

The fresh water heads and the net recharge – discharge have been assigned for all types of steady state solutions at all the top nodal points in the cross section considered in Pondicherry region.. The long-term average level of ground water was calculated month wise considering the ground water table for ten years (between 1986 to 1995).

Fig 22 Input Groundwater Levels and Recharge for various Simulation Runs

Simulation runs	Water table elevation at top nodal points (metre wrt MSL)																		Assigned net recharge
	00	12	18	24	30	36	42	48	54	60	66	72	78	84	90	96	102		
1 January	-6.98	-1.33	-1.70	-2.19	-2.60	-3.09	-3.48	-3.92	-4.30	-4.78	-5.21	-5.75	-6.30	-6.12	-1.74	-1.37	0.00	4.53E-09	
2 February	-1.51	-2.93	-3.35	-3.77	-4.18	-4.60	-5.01	-5.44	-5.85	-6.27	-6.69	-7.30	-6.60	-5.93	-3.38	-1.94	0.00	4.53E-09	
3 April	-1.89	-5.30	-5.70	-6.10	-6.50	-6.90	-7.30	-7.70	-8.10	-8.50	-8.97	-5.45	-7.90	-7.41	-5.80	-3.50	0.00	4.53E-09	
4 May	-6.33	-6.50	-6.75	-6.95	-7.20	-7.45	-7.75	-8.10	-8.40	-8.68	-8.90	-9.00	-7.85	-5.87	-4.50	-3.25	0.00	4.53E-09	
5 July	-6.45	-6.81	-7.14	-7.47	-7.79	-8.12	-8.44	-8.77	-9.10	-9.42	-9.74	-9.98	-7.50	-6.12	-4.90	-2.00	0.00	4.53E-09	
6 August	-6.45	-7.00	-7.20	-7.41	-7.71	-7.95	-8.10	-8.42	-8.60	-8.90	-9.14	-9.95	-8.00	-5.90	-4.90	-2.00	0.00	4.53E-09	
7 November	-3.73	-3.90	-4.19	-4.42	-4.65	-4.88	-5.12	-5.32	-5.55	-5.81	-5.94	-5.21	-1.48	-3.75	-2.48	-1.24	0.00	4.53E-09	
8 December	-6.35	-6.75	-1.11	-1.10	-1.54	-1.70	-2.50	-2.94	-3.30	-3.60	-4.04	-4.26	-3.65	-3.00	-2.00	-1.95	0.00	4.53E-09	
9 Average	-4.29	-4.04	-4.81	-4.92	-5.50	-5.88	-6.20	-6.52	-6.84	-7.10	-7.51	-8.00	-6.50	-6.33	-3.60	-1.30	0.00	4.53E-09	

Time Steps:

For steady state solutions a lengthy number of days has been kept as maximum time and daily time step sequence has been considered.

Digital Processing:

The preparation of the input data file required for SUTRA solute transport is a tedious procedure. A preprocessor, which can take only a few input details and create the entire data file.

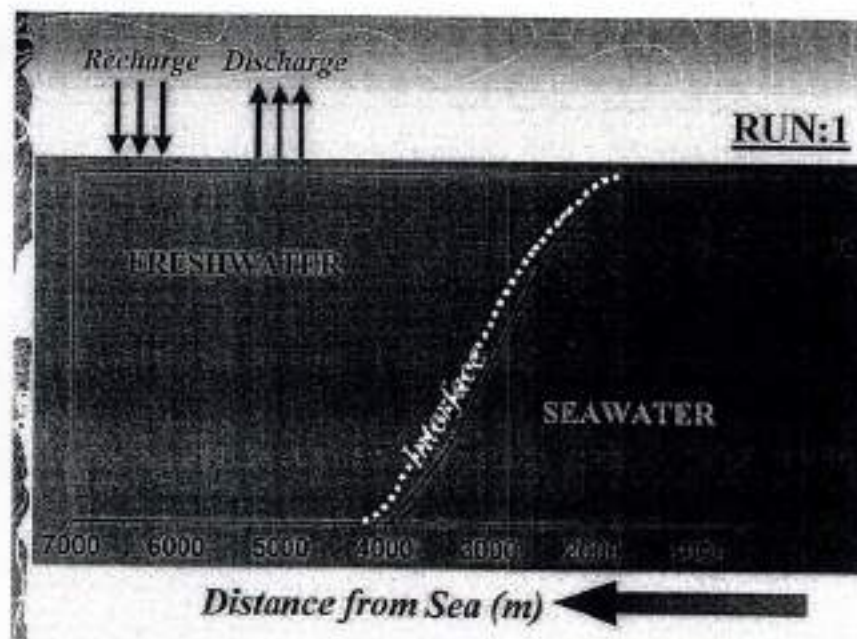
Discussion

SUTRA simulation runs were performed under constant recharge conditions with varying ground water table elevations. This has been done in order to assess the

movement of Salt-Water Water interface in Pondicherry region. The model was validated by comparing the simulated results and the actual values obtained.

The first simulation run was performed keeping the normal water table elevation with reference to the month of January. The lowest level of the ground water table was about 5.75 metres below MSL (long term average) during this period. The toe position of the interface was found to be located at about 4000 metres from the coastal. Fig 23 shows the results of the simulation run. The dotted line indicates the actual results while the simulated results are shown as the red line.

Fig 23 Results of Simulation Run 1



The second, third and fourth simulation runs were performed using the data of the ground water levels of February, April and May months respectively. The lowest water table elevation ranges from 7.50 metres to 9.00 metres during this period. Because of the steady decrease in ground water level, there is a movement in the toe position towards the landward side for about 5000 metres from the coastal line (Figure 24,25,26).

Fig24 Results of Simulation Run 2

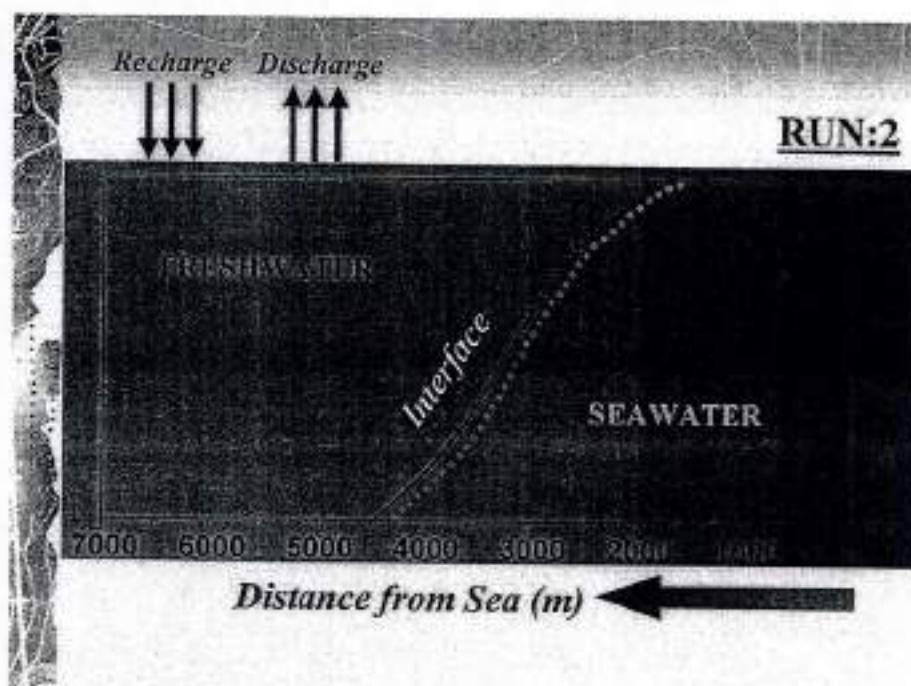


Fig 25 Results of Simulation Run 3

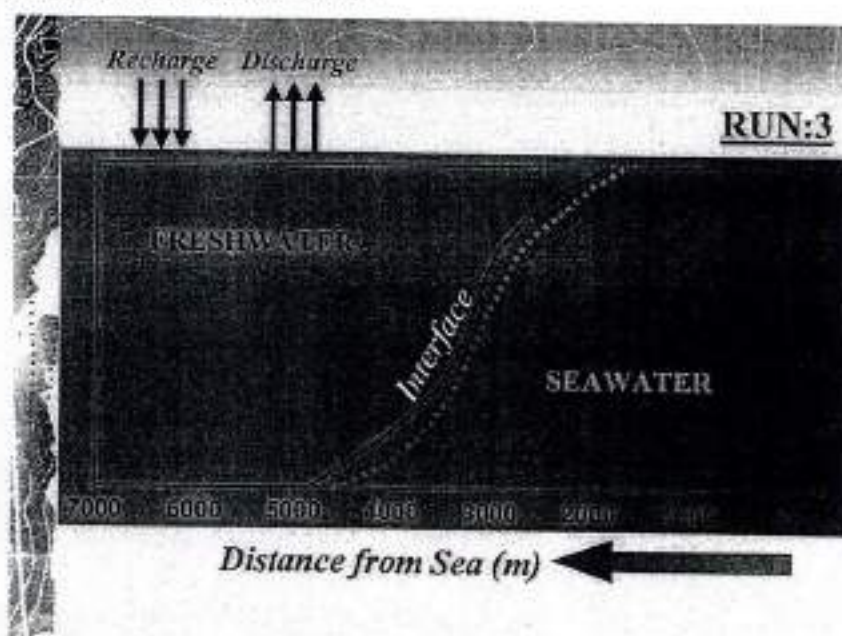
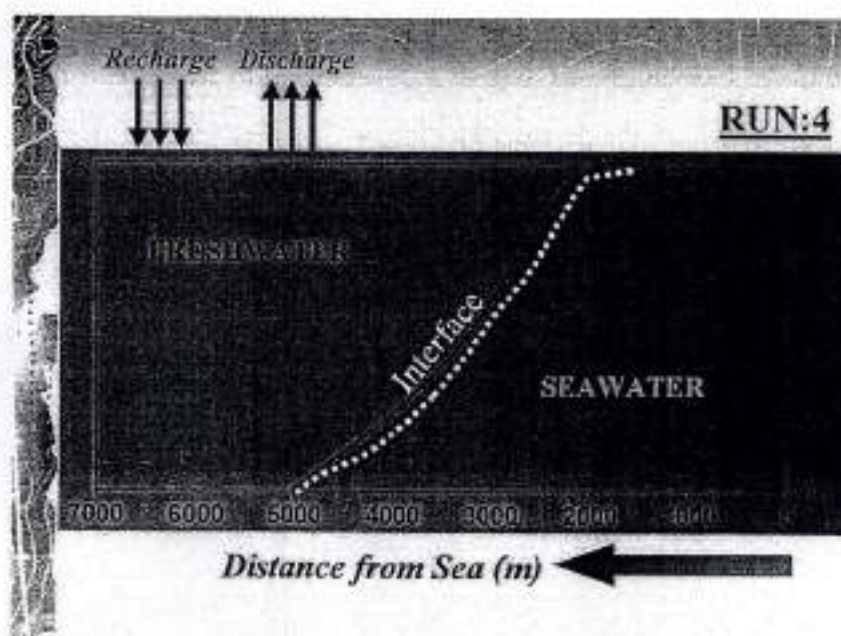


Fig 26 Results of Simulation Run 4



- i) The fifth and sixth simulation runs were performed for the months of July and August. The lowest ground water table was found to be about 9.98 meters below MSL. Because of further decrease in water level during summer which is normally due to over pumping of ground water, the interface had continued to move further landward to about 6000 meters from the coastal line (Figures 27 and 28).

Fig 27 Results of Simulation Run 5

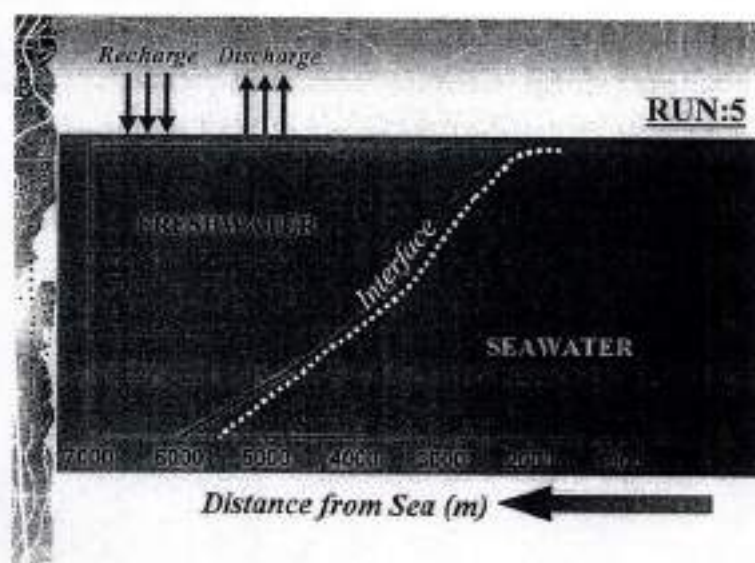
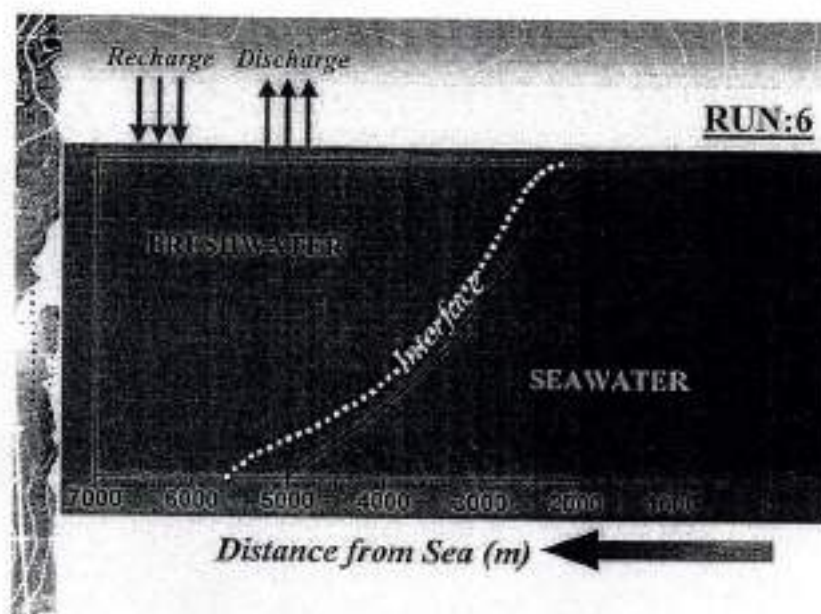


Fig 28 Results of Simulation Run 6



- ii) The seventh and eighth simulation runs were performed for the months of November and December. Because of the monsoon recharge, the ground water level raised and it was around 4.20 metres below MSL. Since, there was an increase in the ground water table the interface has moved towards seaward and the toe position was found to be at 3000 metres from the sea (Figures 29 and 30).

Fig29 Results of Simulation Run 7

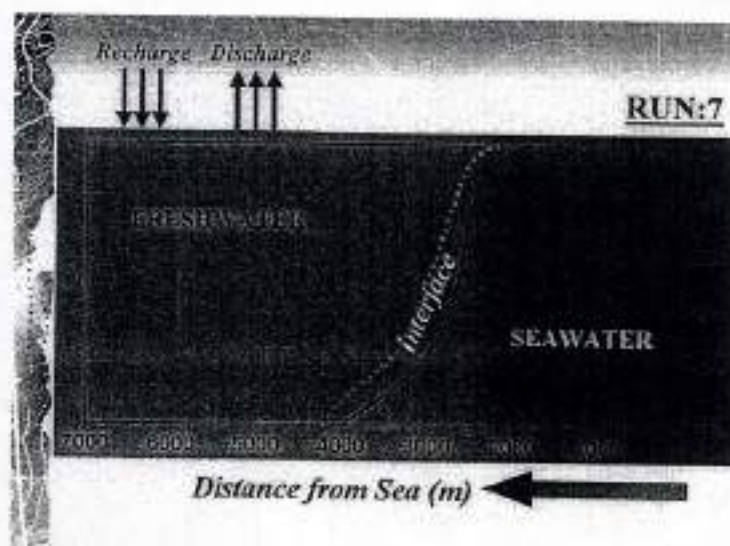
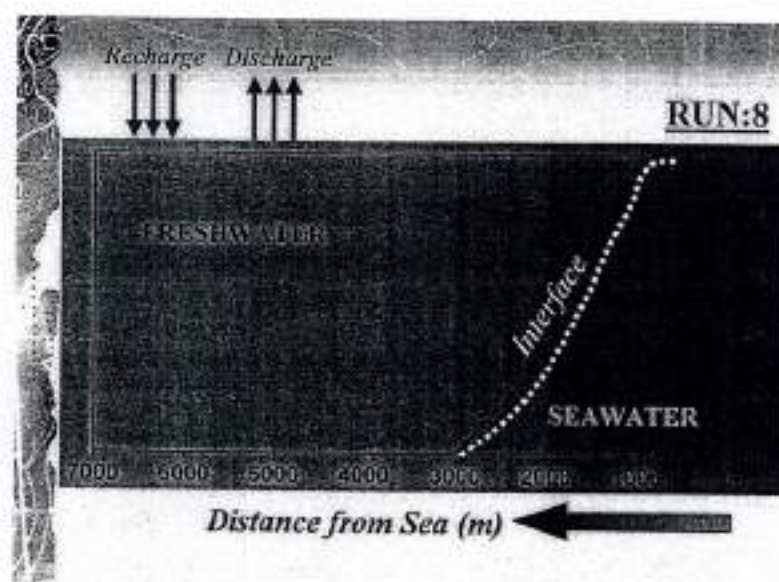
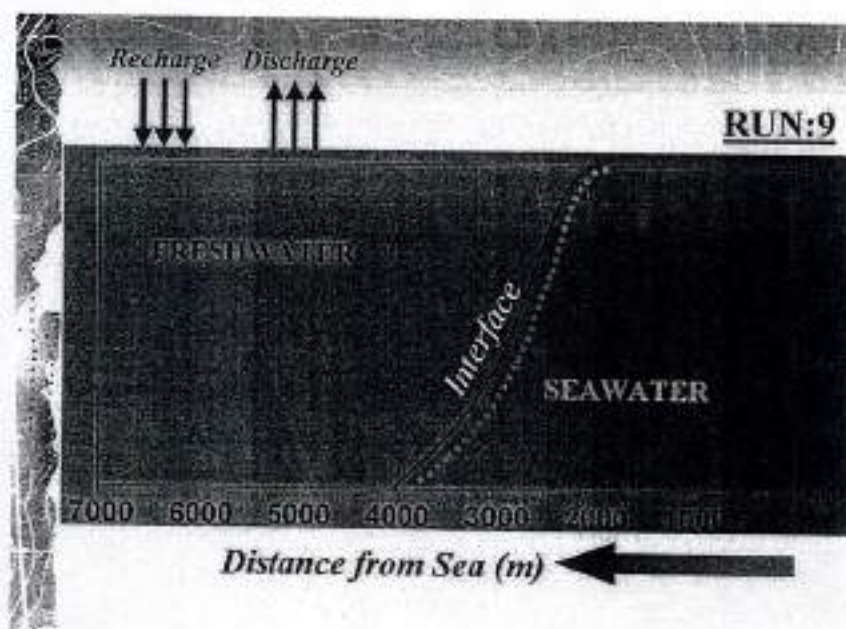


Fig30 Results of Simulation Run 8



- iii) Finally, a simulation run was performed considering a yearly long-term average ground water table condition. With a lowest water table level of 8.00 metres below MSL, the toe position of interface has been simulated and was found to be at a distance of about 4000 metres from the coast (Figure 31)

Fig31 Results of Simulation Run 9



Similar studies have been conducted by Balasubramanian et al (1993) and Lawrence (1995) in the coastal aquifers of Tuticorin and Ramanathapuram District, respectively

along the coast of Tamil Nadu, South India. Balasubramanian (1993) has concluded that the extent of salt-water intrusion was found to be varying from place to place depending upon the nature of formations, rainfall recharge, base flow etc. The linear distance of encroachment from the coastline varied from 5,000 metres to 12,000 metres from north to south and depth to the interface ranged from 20 metres to 80 metres (below ground level) from north to south. He has also suggested that the drilling of borewells between 5,000 metres and 10,000 metres near the coast line and beyond a depth of 20 metres within this area will always be dangerous and further deteriorate the existing water quality. Similar results were obtained by Lawrence (1995) in his study in the coastal aquifers of Ramanathapuram District, along the Tamil Nadu coast. He also found that the depth to the interface and the toe position of salt water - fresh water interface, depend upon the recharge and discharge characteristics of these aquifers.

From the results of the project study, it is evident that the behaviour of the coastal aquifers in Pondicherry region is similar to the coastal aquifers of Tuticorin and Ramanathapuram Districts. Therefore, to conclude, in Pondicherry region, the sea water- fresh water interface steadily moves in land during summer to a maximum extent of about 6000 metres and in monsoon it travels back towards the seaward side and keeps a toe position at about 3000 metres distance from the sea. The zone between 3000 metres and 6000 metres from the coastal line will always be under the dynamic influence salt water and fresh water. This area is the critical zone, which will always be having the diffused water quality. However, the situation will not be uniform as there are some layered aquifer conditions in this area. Therefore, the development of ground water can planned only after a distance of 6,000 metres from the coastal line. The existing surface water facilities should be widened all along the coastal line to maintain the fresh water availability. Unwarranted mining of water from the aquifer media will completely salinize the entire coastal aquifer and the reclamation of which will be very expensive.

8. SUMMARY AND CONCLUSIONS

Significant Results

- The dominant cations and anions of the average ground water of Pondicherry region are in the order of Sodium > calcium > magnesium > potassium > and bicarbonate > chloride > sulphate (meq l^{-1}) respectively.
- The groundwater of this region is mostly of $\text{Na}+\text{KHCO}_3$, $\text{Na}+\text{KCL}$, Ca HCO_3 and Mg HCO_3 types. From the geochemical pattern, it can be seen that the natural agencies are predominant in controlling the groundwater major ion chemistry than the anthropogenic activities / this in this region.
- The mechanism controlling the chemistry of ground water is predominantly by rock water interaction and partly due to evaporation in the sub surface environment.
- The study reveals that ^the ground water quality in the shallow alluvial aquifer system has been deteriorated due to seawater intrusion as a result of overexploitation of ground water. The upper layer of the tertiary aquifer is also affected by seawater intrusion.
- From the results of the second samples, it is observed that the concentration of the major ions in summer are low and exhibiting an increasing trend towards pre monsoon and post monsoon seasons due to the dissolution of salts and minerals in soils during the recharge of groundwater through precipitation i.e., rising water table in post-monsoon season dissolves more salts and minerals from the soils.
- The present study reveals that nearly 80% area (240 km^2) of the study area is suitable for drinking and irrigational purposes in comparison with national standards.
- The input of nitrogenous nutrients and phosphorus in the ground water system is primarily due to the leaching from the fertilizers applied to crop plants.
- The nitrate concentration ($\text{NO}_3\text{-N}$) concentration is an order of magnitude higher than nitrite concentration in the study area, and display a trend of higher concentrations in shallow well waters and lower concentrations in deep well

waters and tank waters. However the maximum (22 mg l^{-1}) nitrate concentrations in the groundwater of this region is well within the national standards (45 mg l^{-1})

- The relatively higher values (5.4 mg l^{-1}) of ammonia nitrogen ($\text{NH}_4\text{-N}$) Concentration in shallow well waters indicate that active denitrification process is occurring in the shallow depth, reducing ($\text{NO}_3\text{-N}$) and ($\text{NO}_2\text{-N}$) concentrations significantly.
- In general, the nitrogenous nutrients are observed about 2 to 3 times higher in well waters of urban area than in rural area, suggesting the abundant leaching of nutrients from municipal waste and sewage effluents through the urban soil.
- The high orthophosphate levels (0.18 mg l^{-1} to 6.99 mg l^{-1}) observed in the study area may be attributed to the system that have special features overriding normal controls on PO_4 movement to sub surface water such as heavily irrigated sandy soils overriding shallow water tables.
- Higher concentration of dissolved silica (13 mg l^{-1} to 100 mg l^{-1}) against an average concentration of 5 mg l^{-1} in the ground water of this region. This may be due to the release of amorphous silica within the soil zone.
- The higher concentration levels of boron ($44 \mu\text{g l}^{-1}$ to $2595 \mu\text{g l}^{-1}$) in the coastal ground water reveals that the ground water is contaminated by salt water intrusion.
- A strong positive correlation between the elemental pairs, such as As-Se, Cu-Co, Cu-Ni, Cd-Co, Cr-Cd, Cr-Cu, Fe-Ni and Co-Pd has been observed in this region which may be due to common anthropogenic sources.
- The impact of residue levels of organochlorine pesticides were found to be 3 to four times more in ground waters of agricultural area than in urban area.
- The total residual levels of organochlorine pesticides in different sources were in the order of tanks (36.0 ng l^{-1}) > shallow wells (20.8 ng l^{-1}) > deep wells (15.1 ng l^{-1})
- In Pondicherry region, the seawater - fresh water interface steadily moves inland during summer to maximum extent of about 6000 meters and in monsoon it will travel backwards the seaward side and keeps the toe position at about 3000 meters from the sea.

CONCLUSION

In this study an effort has been taken to identify the pathways and contamination of major and trace elements, nutrients and pesticide residues in the ground water of Pondicherry region, a coastal plain in south India. Overexploitation of groundwater and improper management of natural resources, led to the unequal distribution of major and trace elements in nature. Also it can be seen that the major element concentrations are predominantly influenced by natural agencies than anthropogenic activities. On the other hand the trace metal concentrations, nutrients and pesticide residues in ground water indicate that the polluted over lying environment due to man made activities, is influencing the quality of ground water in Pondicherry region. It is also evident from the numerical analysis that the overexploitation of ground water led to the seawater intrusion in this area.

The problem of pesticides and other agricultural impacts on the ground water and the environment requires a new focus for research and farm management. More integrated farm management and more complete research into integrated farming system is needed, with a focus on efficiency and off- site impacts rather than just maximizing yields. Pesticides and fertilizers will remain as a tool for agricultural production but clearly less toxic compounds can be adopted; greater efficiencies and more judicious use can clearly be employed. To resolve agricultural non point source problems fully, policies for production must be integrated with policies for conservation and environmental protection, if we are to effect a satisfactory balance between efficient and economic agricultural production and protection of our water resources. Thin study suggests that the fresh water resources in this region need to be widened and have to be protected against unwarranted mining and over exploitation of groundwater to meet the ever-increasing demands. If the aquifers e stressed further, the quality of water may deteriorate, making unfit for various needs of the society.

Recommendations

Research

- A close and critical examination of land use change, tidal influence as well as seawater intrusion and the improvements thereof for, increasing production, productivity and returns in agriculture without deteriorating water quality and quantity
- Agriculture and concomitant industrial development systems research on a holistic basis needs to be taken up
- Focus on EIA on a representative basis of ecosystems, technologies, production systems and regions to generate reliable data to understand their interactions
- Mechanisms for surveillance, monitoring and control of agriculture and industrial production systems with environment in focus for pollution indicator parameters.
- Application of remote sensing data in land use planning for agriculture and industries

Information exchange

- Strengthening institutional infrastructure for information exchange
- Use of satellite communication system on a district level
- Preparation of compendium of local / block-level information on important aspects such as regulations, permissible levels of pollutants, legal framework etc.

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