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Migration and contamination of major and trace elements in groundwater of Madras City, India

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Abstract Groundwater samples collected from both open and bore wells in an area of about 270 km^2 from Madras City, India, have been analyzed for major ions (HCO_3, Cl, Si, Na, Ca, and Mg) and trace elements (As, Se, B, V, Cr, Fe, Co, Pb, Cu, Zn, Cd, Mn, Ni, Mo, and Ba). The study reveals that the quality of potable water has deteriorated to a large extent. Seawater intrusion into the aquifer has been observed in nearly 50 percent of the study area. The toxic elements (As and Se) have already exceeded the maximum permissible limits of drinking water in almost the entire city. A positive correlation of As and Se with other toxic metals such as V, Cr, Fe, B, etc., indicates that all these elements are anthropogenic in origin. Applying multivariate analysis, the source for trace elements in groundwater has been grouped into two major factors: pollution and mobilization factors. The groundwater in the study area is largely contaminated by organic effluents and reflects the intensity of pollution caused by the overlying soil sediment and rapid infiltration of the pollutants.

Key words Groundwater pollution · Madras · Trace element contamination · Factor analysis

Introduction

Madras, a port city on the east coast of India, is one of the four major cities. The metropolitan population has grown from 0.8 to 5.4 million in an area of 1167 km^2. Most of the population is concentrated within the city, which encompasses an area of about 172 km^2. There are four major water ways in Madras: the Adyar and Cooum rivers, the Buckingham Canal and the Otteri Nullah (Fig. 1), which have confluence with the Bay of Bengal. These water ways serve the important function of carrying away storm water during the monsoon season. Earlier studies (Appasamy and Lundqvist 1993; Somasundaram and others 1993) reveal that these waterways contain high concentrations of ammonia, phosphate, fecal coliforms, and organic matter, relative to seawater.

The primary source of water supply for Madras City consists of three rainfed reservoirs in the northwest, which are linked together. Together they provide around 200 Million liters per day (Mld) (Appasamy and Lundqvist 1993). This source was supplemented with groundwater (160 Mld) in aquifers in the northern and southern boundaries of Madras city.

Due to rapid industrialization and overexploitation of the groundwater resources, an anomalous distribution of major and trace elements has taken place in the Madras urban environment. The possible pathways of the major and trace elements in the hydrological system have been identified and quantified in the present study. Depending on the environmental parameters, each element moves at a different rate and, due to the changing environment, the trace metals and associated elements may form complexes and precipitate or become concentrated at several places. In the present study, an attempt has been made to evaluate the spatial changes in the chemical quality of the Madras City groundwater.

Geology

Physiographically, the study area is a low, flat, slightly undulating terrain with a general slope of 3–5° in an E–ENE direction. It receives an average annual precipitation of 1200 mm (both southwest monsoons and intense northeast monsoons) and the average monthly temperature ranges between 25 and 40°C (Achyuthan 1994). The elevation of the study area generally ranges between 30 m in the west and the sea level in the east. Four cycles of erosion in this area gave rise to a complex assemblage of

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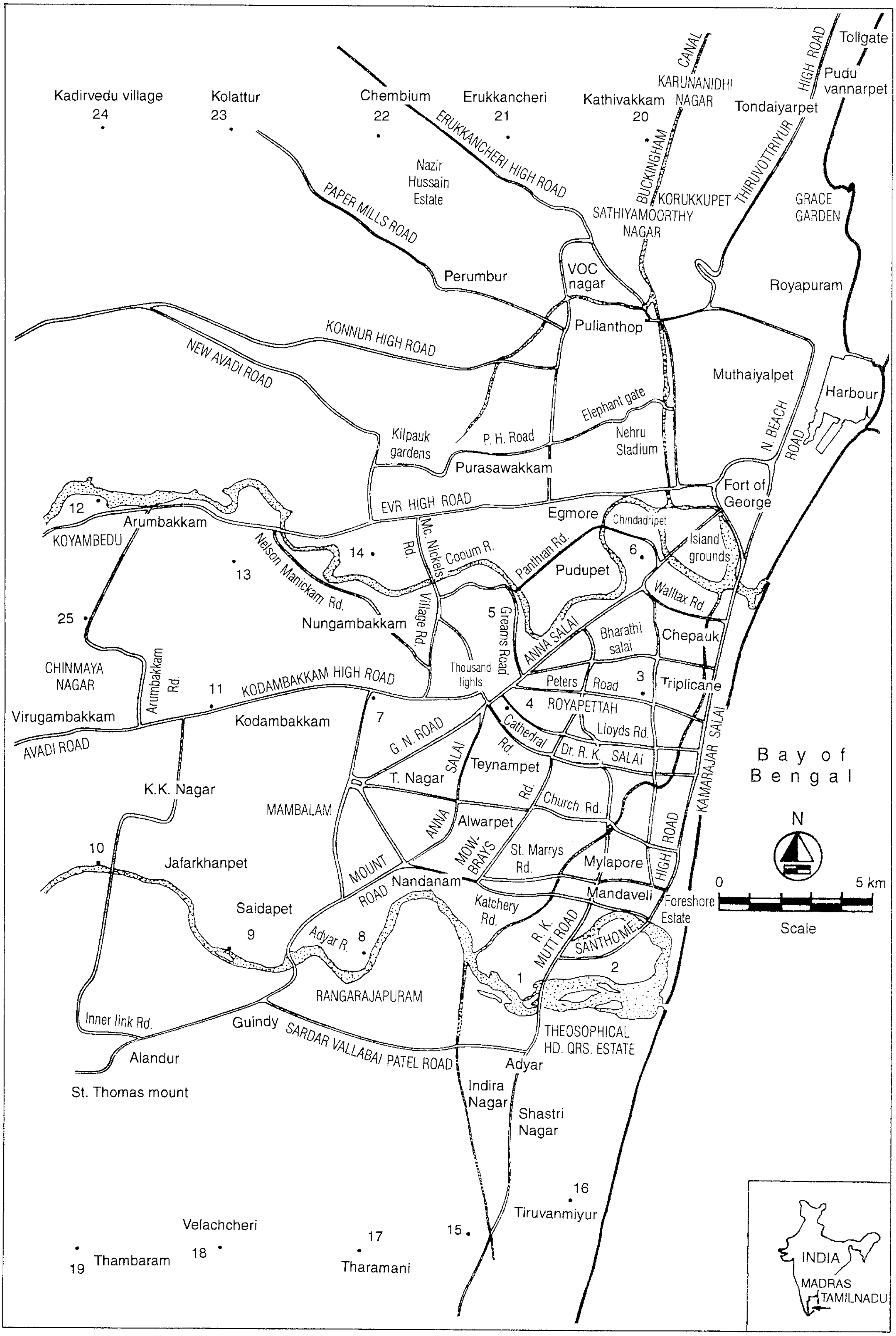

Fig. 1 Sampling sites in the Madras urban area

fluvial, estuarine, and marine deposits. Geomorphic evolution and morphostructural analyses suggest neotectonic activity during the quaternary period resulted in marine regression (Achyuthan 1994) and large-scale changes in migration of river courses (Subramanian 1979). The quaternary deposits are the only lithological units spread over most of this area. These consist of boulder beds, laterites and alluvium deposits. The thickness of the alluvium increases towards the east and ranges between 30 and 50 m.

The aquifers of this region are recharged by precipitation, irrigation return, flow from riverbeds and surface waterbodies. Of these sources, precipitation recharge is predominant. Groundwater is abstracted for domestic use to augment the city water supply. In most places, local requirements are met only by shallow dug and open wells. The hydrogeochemical studies performed here involve collection and analysis of water from the dug and open wells surrounding the major water ways of Madras.

There has been a tremendous increase in demand for groundwater and hence determining its quality becomes necessary to assess the utility of this resource. In Madras City, the groundwater has been largely contaminated by organic pollutants and reflects the intensity of pollution caused by the overlying soil sediment and rapid infiltration of the pollutants through seepage.

Hydrogeochemistry

Groundwater contains some chemical substances. This concentration in groundwater is a function of initial composition of water, rainfall, land use, type of surrounding rocks (such as charnockites, granites, upper Gondwana sandstone and shales, recent alluvium and estuarine and marine deposits) (Achyuthan 1994), volume of water movement and its velocity and recharge mechanisms. Hence, the correlation of water chemistry with hydrologic and geologic environments will provide valuable information on the aquifer system. In recent times, much attention has been focused on the increasing ionic concentrations in groundwater, which have been attributed to human interference, proliferation of industries, and recent agricultural practices. In irrigated areas, where irrigated return flow recharges the aquifer, constituents such as salts, leached from soil or applied agrochemicals, may move into the aquifer systems, thus degrading the water quality. It has thus become necessary to assess, quantify, and monitor the quality variations in groundwater, caused by point and nonpoint source pollution in the urban environment of Madras.

Methodology

Representative groundwater samples (Fig. 1) were collected from various locations covering the major sections of the Madras urban area during the months of May–June (summer) 1993. New 1-l polythene bottles were used for sample collection and preservation. Water samples were collected from both bore and open dug wells. Samples were collected from wells near the Adyar and Cooum rivers and away from the river terraces (Fig. 1). pH, temperature, and depth of the wells were measured on site while collecting the sample. The samples were divided into two portions and kept air-tight. One part of the sample was acidified with 0.1 N HCl on site, so as to prevent adsorption onto the walls of the container. The other portion was used to determine major ions such as HCO_3, Cl, Si, Ca, Mg, and Na using standard procedures (Ramesh 1985).

All trace elements, which include As, Se, B, V, Fe, Co, Pb, Cu, Zn, Cd, Mn, Ni, Mo, and Ba, were analyzed using the highly sensitive inductively coupled plasma–mass spectrometer (ICP-MS). While performing the analysis, two sets of internal standards were run, one at the begining (NBS-120b) and the other in between the analyses, to have a check on the accuracy and precision of the results (Balaram 1992). For most of the elements, the detection limits are around 1 ppb.

Analytical data were processed with various computer programs for statistical evaluation. Elemental contour diagrams for all the major and trace elements are presented (Figs. 2–8 below). The impacts of natural and anthropogenic sources on the elemental concentration, distribution, migration pattern, and the total area affected by each element have been deciphered using these maps.

Results and discussion

The results of the major and trace element concentrations of the groundwater samples of Madras City are presented in Table 1. Major ions such as Cl, HCO_3, Si, Na, Ca, and Mg and trace elements such as As, Se, B, V, Cr, Fe, Co, Pb, Cu, Zn, Cd, Mn, Ni, Mo, and Ba have been analyzed and the results are discussed below.

Major ion chemistry

The goundwater of this region is generally colorless and odor-free, and the pH ranges from 7.5 to 8.8. An anomalously high concentration (963 ppm) of HCO_3 has been observed in the samples collected adjacent to the Cooum river (Table 1, Fig. 1). HCO_3 is mainly derived from rock weathering and the pollution contribution is minimal—about 2 percent (Meybeck 1979). Most of the HCO_3 must have been derived from soil CO_2. It can be observed from the contour map (Fig. 2) that an approximate area of 5.7 km^2 is above the permissible limit [600 ppm according to Indian Standard Specifications for Drinking Water 1983] for drinking water. Silica concentration varies between 7 and 71 ppm (Table 1). The weathering of silicates and mineral–water reactions are primarily responsible for the observed increase in silica content of groundwater.

Table 1 Major and trace element concentration in groundwater of Madras[a]

	Sample																								
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
pH	8.10	8.20	8.80	8.40	8.40	7.70	8.60	7.50	7.60	8.50	7.90	8.00	7.90	8.00	8.40	7.90	7.90	7.70	7.70	7.70	7.60	8.00	7.70	7.90	7.70
HCO_3	305	414	622	744	451	500	366	219	561	378	152	378	963	256	744	414	402	390	378	244	549	268	366	317	317
Element																									
Cl	3,244	1,013	1,725	2,360	5,357	2,314	931	15,845	410	138	365	319	3,646	2,337	410	455	410	1,816	818	1,090	1,884	795	841	1,566	2,745
Si	21	12	49	19	58	31	43	56	66	69	34	44	35	25	7	34	27	46	71	22	18	32	21	51	29
Ca	36	16	16	14	10	32	16	298	16	12	32	6	24	20	12	36	18	26	20	30	14	12	24	16	18
Mg	110	170	2	138	56	55	21	46	55	2	26	32	24	94	49	31	32	21	39	26	56	45	24	24	33
Na	468	556	562	448	286	394	205	515	225	279	171	259	518	32	452	231	165	106	157	231	198	98	231	356	385
As	421	2,477	313	271	963	515	141	1,724	97	104	122	93	516	56	412	157	74	200	183	122	314	147	150	236	371
Se	18	82	37	40	79	76	30	92	16	14	14	12	42	13	51	23	12	13	14	14	24	15	14	22	20
B	169	1,959	1,185	1,268	845	474	187	253	151	171	140	106	304	98	1,053	190	180	186	101	148	293	128	135	434	222
V	264	2,193	375	282	1,067	560	208	1,460	81	258	135	107	370	56	365	167	79	131	161	107	265	117	125	230	272
Cr	16	88	16	16	33	32	9	59	11	9	9	6	20	5	20	12	6	10	10	7	14	8	9	12	14
Fe	474	264	189	191	202	332	100	417	168	118	137	92	170	91	244	146	124	119	122	151	160	131	117	155	124
Co	4	3	1	1	2	5	2	28	4	1	2	1	2	2	2	1	4	2	2	2	2	2	2	2	2
Pb	4	2	5	3	1	14	4	2	25	10	11		4	15	5	6	7	7	7	7	6	6	5	4	3
Cu	29	530	288	221	521	386	125	559	40	34	36	24	145	32	153	64	25	30	32	26	52	31	27	48	57
Zn	5,443	350	169	373	535	306	81	8,466	109	59	89	46	81	132	271	127	177	1,153	274	84	218	59	298	167	60
Cd	1	3	1	2	2	2	1	3	1	1	1	1	2	1	1	2	1	1	2	1	2	1	2	2	2
Mn	264	316	19	19	19	1140	16	10,187	312	19	46	17	17	131	284	72	153	47	25	91	1,194	57	21	41	1,938
Ni	42	85	30	33	39	39	28	76	36	29	31	28	41	26	41	32	33	40	46	35	39	44	44	43	46
Mo	5	6	17	3	7	10	3	2	2	2	4	5	5	2	4	6	2	2	2	4	3	2	2	2	2
Ba	60.00	25	66	24	26	127	49	144	103	21	178	138	42	195	32	44	196	192	195	59	41	264	66	21	428

[a] HCO_3 through Na: the concentration is given in milligrams per liter; As through Ba: the concentration is given in micrograms per liter. For sample location, see Fig. 1

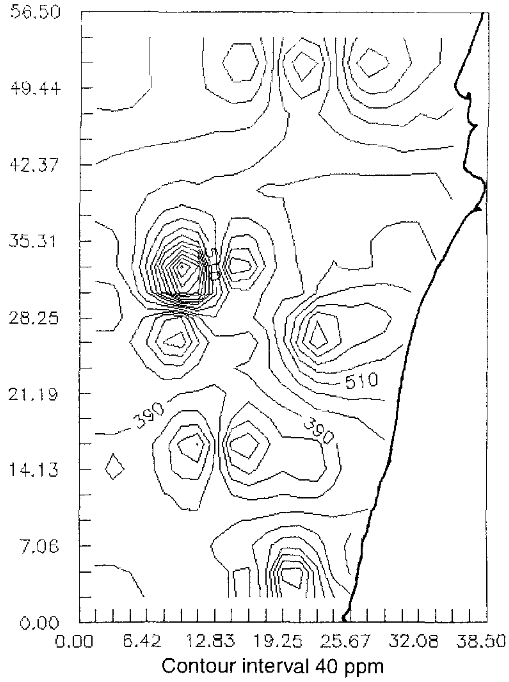

Fig. 2 Concentration contour map of bicarbonate in the groundwater of Madras

In order to estimate the extent of salinity encraochment into the inland basin, the distribution pattern for Cl and Na has been studied. The spatial distribution of Cl in 50 percent of the groundwater samples of Madras City has been found to exceed 1000 ppm (Table 1, Fig. 3a), indicating saline water intrusion. A Cl content of 600 ppm has been considered as the highest acceptable salinity level for human consumption (Rosenthal 1994). In other parts of the basin, the concentration is less than 1000 ppm, indicating marginal mixing behavior, and the situation is likely to be reversed during the monsoon season. Similarly, the maximum concentration of Na is observed along the coastline, which gradually decreases towards the mainland (Fig. 3b). Overdrafting of the groundwater in the adjoining areas of the coastline is a major factor for the migration of saline water, due to the local cone of depression. Other influencing factors are natural agencies such as storms, high tide, and incursion of the estuarine backwaters. Pollution may be another important source for Na and Cl in the groundwater of Madras City. According to Feth (1981), chlorination of the public water supply to purify water, direct sewage discharge, and industrial brines may provide an additional source of Cl and Na. Groundwater flowing through a normal and active hydrological gradient is characterized by Na/Cl ratios in the range of 0.86:1 (Rosenthal 1994). The Na/Cl ratio of the Madras aquifer varies between 0.01:2, indicating the changes in Na/Cl ratio upon mixing between seawater and freshwater.

The contour pattern of Mg resembles that of Na (Fig. 4a). Seawater has a high Mg content and hence anomalous zones are restricted to the coastal areas. The samples taken adjacent to the Adyar river also show a high Mg concentration (Table 1) possibly due to the encroachment of seawater during spring tides, which penetrate into the groundwater system through seepage. The contour pattern for Ca (Fig. 4b) is restricted to one point source (sample 8) showing an anomalous concentration of 300 ppm. Anomalous concentrations of other elements in this sample confirm pollution of the groundwater of this location. Towards the downstream part of the Adyar river (sample 1), a high concentration of Ca is found, indicating that Ca mixes with the groundwater system and follows the course of the groundwater pattern. Thus, the dominant cations

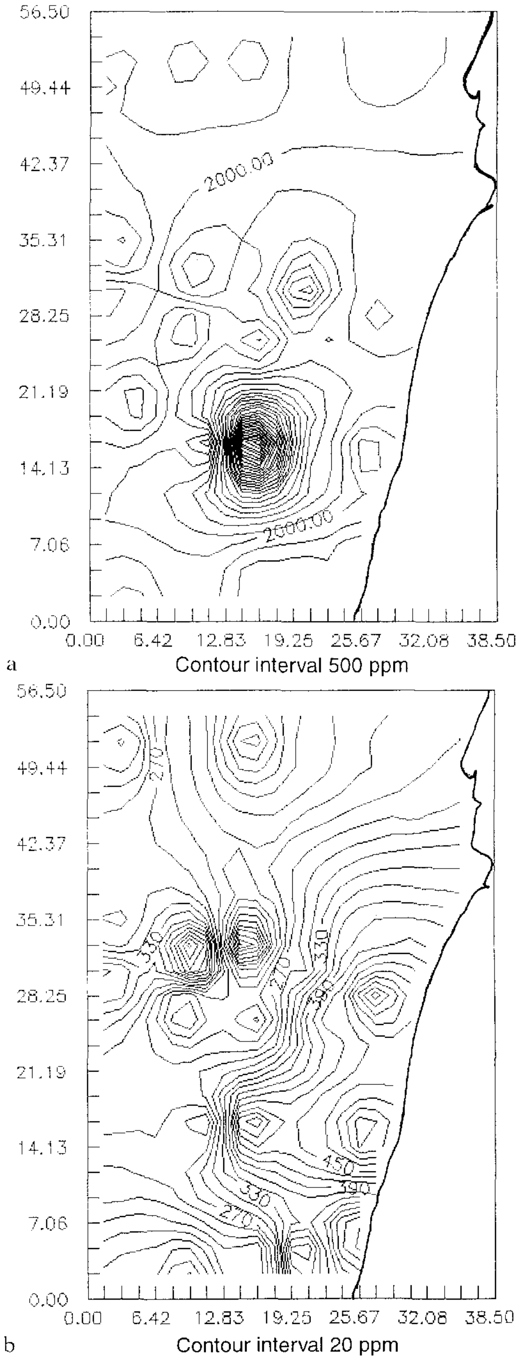

Fig. 3 **a**, Concentration contour map of chloride in the groundwater of Madras. **b**, Concentration contour map of sodium in the groundwater of Madras

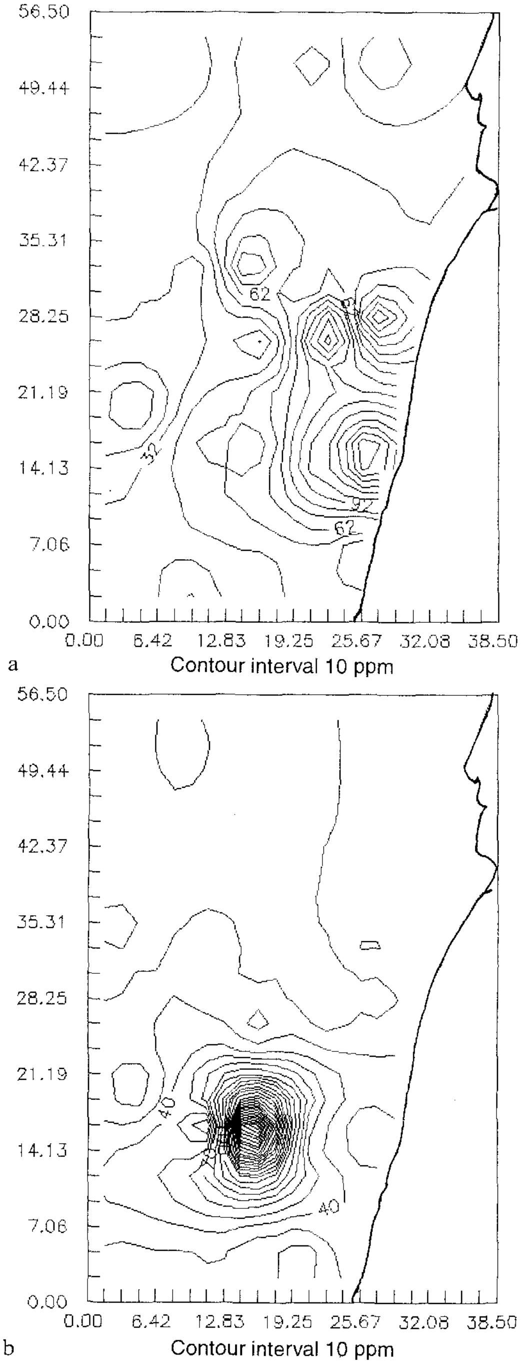

Fig. 4 **a** Concentration contour map of magnesium in the groundwater of Madras. **b** Concentration contour map of calcium in the groundwater of Madras

and anions of the groundwater of the Madras area are in the order of $Cl^- > Na^+ > HCO_3^- > Mg^{2+} > Ca^{2+}$, respectively. It can be noted (from Table 1, Fig. 1) that in the Madras aquifer, major ion concentrations generally increase towards the coastline. This is due to continuous withdrawal of groundwater year after year through bore wells and hand pumps, lowering the groundwater table. In addition to this, the backwaters enter the river channels and the cations would migrate to the groundwater system because all these outlets are already full of industrial and sewage effluent waters. Thus the migration/distribution pattern of these elements in the groundwater of Madras City indicate pollution, coupled with seawater intrusion. This unequal hydrochemical aerial distribution in the groundwater reveals the lack of uniformity in the groundwater flow (Sage and Lloyd 1978).

Trace elements

The range and average concentrations of some of the trace elements of environmental concern in the groundwater of Madras city are shown in Table 2. The average concentration in rivers and oceans and the World Health Organization (WHO) and Minimum National Standards (MINAS) for drinking water are also listed for comparison. All the trace elements show high concentrations (several orders of magnitude) in the groundwater of Madras in comparison to global averages for rivers and seawater.

Arsenic concentration in the groundwater of Madras City is exceedingly high and has reached the supersaturation levels in all the samples (Fig. 5). Arsenic concentration in water is in the form of arsenic compounds. For the first time, an attempt is made to assess the areas severely affected by As pollution in Madras City. The highest concentration of 2477 ppb has been observed in the groundwater and the contour covers the entire geochemical map (Fig. 5), suggesting that the groundwater requires a thorough treatment for As before it is used for domestic purposes. The contour diagram also suggests that the highly anomalous spots are the two places corresponding to the flow channel of the Adyar river and the Buckingham canal, which are the discharge points for industries to dump their effluents and for domestic sewage. The present reconnaissance survey indicates that there is an urgent need to carry out a detailed systematic study to estimate the area affected by As contamination. In our study, the total area of the sampling site is approximately 280 km^2, and the entire area can be provisionally categorized as polluted with As.

The occurrence of As in natural waters is usually associated with sedimentary rocks of marine origin, weathering of volcanic rocks, fossil fuels, mineral deposits, mining wastes, agricultural use, and irrigation practices (Hunt and Howard 1994). Arsenic occurs naturally in the earth's crust at about 1.8 ppm. Numerous minerals, rocks, sediments, and soils contain As partly as a constituent of sulfide minerals. Arsenic is also adsorbed onto clay colloids bound to organic matter to form water-soluble complexes with Al, Fe, Ca, and Mg (Ganje and Rains 1982). Overextraction of groundwater, especially during summer, enhances the liberation 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.

Anthropogenic sources of As are numerous, both in the form of organic metal complexes and inorganic ions. Arsenic compounds are used in paint industries as paint pigments and in textile and tanning industries. Household detergents may also contain about 10–70 ppm of As, as

Table 2 WHO[a] and MINAS drinking water standards and average river and seawater composition[a]

Element	Range		Mean	WHO		MINAS		River[b]	Ocean[b]
	Minimum	Maximum		HDL	MPL	HDL	MPL		
As	56	2477	407	50	150	30	150	2	3
Se	12	92	32	0	10	10	10	0.2	0.1
V	56	2192	377					1	2
Cr	5	88	18	75	200	75	200	1	0.2
Fe	91	474	182	500	1000			40	2
Pb	1	25	7	50			5	1	0.03
Cu	24	559	141	50	1500		1000	7	0.5
Zn	46	8466	765				1000	30	2
Cd	1	3	2	5			10		0.05
Ni	26	85	40				100	2	0.5

[a] WHO: World Health Organization Standards (1984). MINAS: Minimum National Standards (Central Pollution Control Board) Government of India 1993). HDL: highest desirable level. MPL: Maximum permisible level

[b] Turekian (1971)

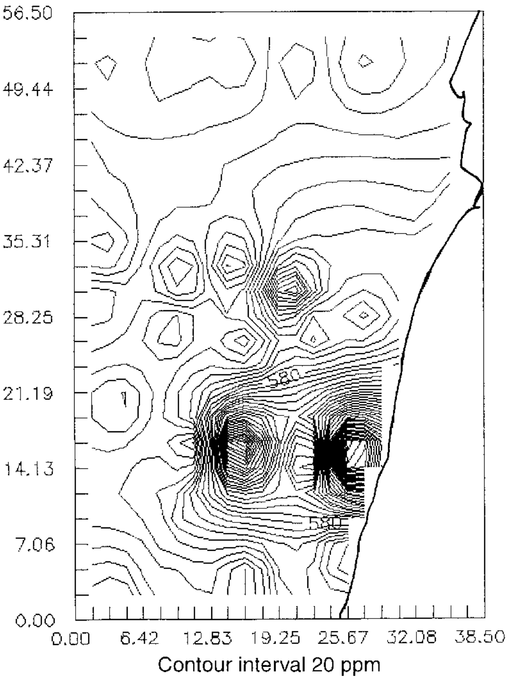

Fig. 5 Concentration contour map of arsenic in the groundwater of Madras

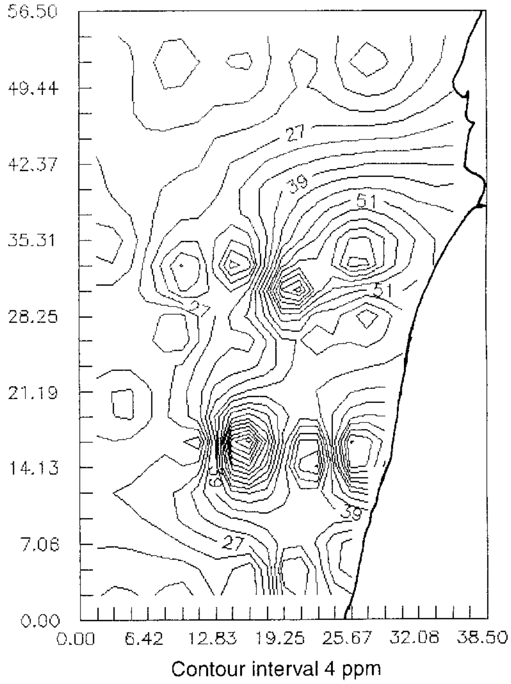

Fig. 6 Concentration contour map of selenium in the groundwater of Madras

is exemplified by the highest concentration along a section of the Adyar river (samples 2 and 8). Prior to 1968, inorganic forms of As were used extensively in agriculture as insecticides, fungicides, herbicides, and desiccants. 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. Further, the organic effluents discharged by the industries can complex with As to form nondegradable metal complexes and enter the groundwater through the river systems.

Arsenic becomes toxic when its concentration reaches 50 ppb in water used for drinking purposes (Table 2). 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 As greater than 100 ppb is consumed. Much higher concentrations (9000–10,000 ppb) of As in drinking waters have resulted in severe gastrointestinal disorders, impairment of bone marrow function, and neurologic abnormalities.

The distribution of selenium in the groundwater of Madras City is shown in Fig. 6. Concentration of this toxic trace metal is observed along the Adyar and Cooum rivers. Although the abundance of Se is not as high as that of As, its uniform distribution in the groundwater is a cause for concern. All the samples are above the permissible limit of 50 ppb (Table 2) indicating slow accumulation of Se in the natural system and rising at alarming rates. A roughly estimated area of 279 km^2 is already categorized as toxic zone. Se also has a low mobilization factor (4.7) and accumulates in soils, plants, and other biota adjoining the effluents and, in turn, would enter into the groundwater system. Se is an essential nutrient for animals and is required at a concentration of 40 ppb in their diets (Adriano 1986). Although Se is one of the essential nutrients for metabolic activity for human and plant life, its excess leads to many disorders, such as total degenerative changes in bones, bone marrow malfunctioning, and congestive heart failure.

The pathways of migration and accumulation of As and Se could be: (1) industries dumping the untreated effluents into the natural hydrologic system, and (2) the industries releasing highly variable pH solutions (mostly water with a low pH of approximately 2), which would react with soils, sediments, and other materials to scavenge the toxic metals into the groundwater. Since they have longer residence times, they need to be monitored and treated before they reach permissible limits.

Iron in the goundwater is mostly in the form of inorganic complexes derived from laterite and other types of soils. Excess Fe would be mostly accumulated and discharged through the industrial effluents. The WHO (1984) standard for Fe in the drinking water is 500 ppb (Table 2). Generally, Fe levels in the area surveyed fall within this limit; there is a uniform increase towards the Adyar and Buckingham Canal area.

V and Cr move together and form inorganic complexes. The industries manufacturing high-speed and high-temperature metals use V and Cr in large quantities as their raw materials. Anomalous zones of V (Fig. 7) and Cr are concentrated along the Adyar river and the coastline (Table 1). In Madras, large quantities of effluents are discharged by 90 tanneries in places such as Pallavaram, Chrompet, and Pammal, increasing the Cr content in the groundwater.

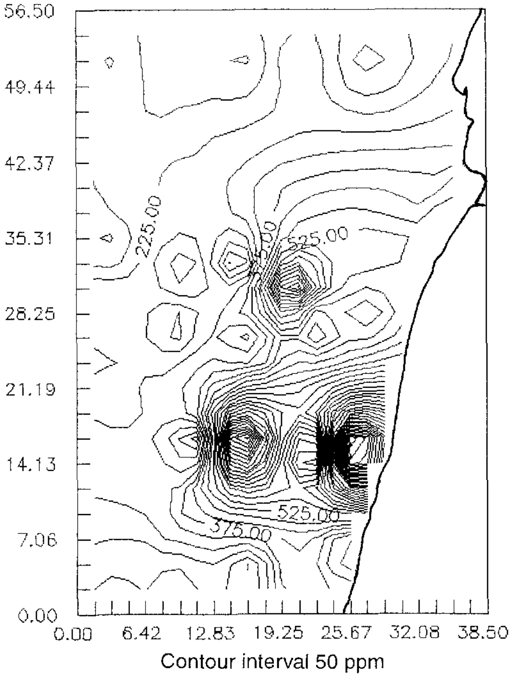

Fig. 7 Concentration contour map of vanadium in the groundwater of Madras

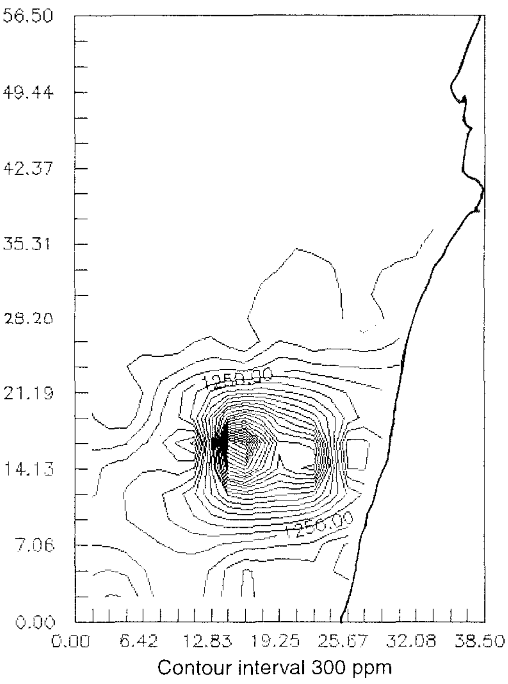

Fig. 8 Concentration contour map of zinc in the groundwater of Madras

Zinc concentration in the groundwater of Madras City is generally within the permissible limits. However, an anomaly is observed at three locations (samples 1, 8, and 18) where their concentration is very high. Figure 8 shows the migration and distribution of Zn in the groundwater. Besides these trace elements, B, Co, Pb, Cu, Cd, Mn, Ni, Mo, and Ba were also analyzed. However, their concentrations are well below the permissible levels for drinking water. There are several sources of trace elements in the Madras urban environment, both natural and man-made: weathering of parent material (rocks), burning of fossil fuels, sewage and industrial effluent discharge, underground disposal of toxic wastes, etc. With the exception of the parent material, all are anthropogenic in nature. In many rivers, lakes, and aquifers around Madras City the human impact is many times greater than the natural input of trace elements, as is evident from the results obtained in this study.

Interelemental correlation

Statistical analysis is a tool that can be applied to measurable variables to identify certain factors, such as *pollution*, for quantification. The correlation coefficient matrix for all the elements is presented in Table 3. Ca shows a strong positive correlation with other trace metals, indicating that clays derived by weathering of feldspar are adsorbing most of the trace elements. A positive correlation of Cu and V with other elements suggests that the pollutants are mostly derived by industrial effluents, which are being delivered into the hydrological system by the industries

Table 3 Interelemental correlation matrix of chemical data for groundwater of Madras

	pH	HCO_3	Cl	Si	Ca	Mg	Na	As	Se	B	V	Cr	Fe	Co	Pb	Cu	Zn	Cd	Mn	Ni	Mo	Ba
pH	1																					
HCO_3	−0.26	1																				
Cl	0.47	0.28	1																			
Si	−0.09	0.84	0.37	1																		
Ca	0.01	0.47	0.59	0.69	1																	
Mg	0.24	0.48	0.64	0.63	0.83	1																
Na	0.43	−0.11	0.64	0.15	0.63	0.62	1															
As	0.01	0.43	0.58	0.64	0.99	0.86	0.67	1														
Se	0.05	0.44	0.61	0.67	0.99	0.85	0.67	0.99	1													
B	0.03	0.54	0.64	0.58	0.56	0.62	0.27	0.52	0.58	1												
V	−0.22	0.98	0.31	0.87	0.52	0.54	−0.07	0.48	0.5	0.59	1											
Cr	−0.06	−0.19	−0.44	−0.31	−0.41	−0.35	0.37	−0.4	−0.34	−0.2	−0.13	1										
Fe	0.15	0.47	0.61	0.61	0.83	0.97	0.66	0.88	0.86	0.56	0.53	−0.35	1									
Co	−0.27	0.86	0.36	0.76	0.45	0.39	−0.09	0.39	0.4	0.78	0.86	−0.26	0.38	1								
Pb	0.09	0.43	0.47	0.71	0.69	0.55	0.32	0.64	0.68	0.37	0.43	−0.46	0.49	0.35	1							
Cu	−0.23	0.96	0.32	0.87	0.5	0.52	−0.07	0.46	0.48	0.53	0.97	−0.2	0.5	0.81	0.49	1						
Zn	−0.11	0.54	0.47	0.79	0.89	0.63	0.42	0.84	0.87	0.52	0.57	−0.4	0.61	0.51	0.82	0.57	1					
Cd	0.33	−0.1	0.53	−0.16	0.17	0.4	0.49	0.23	0.23	0.32	−0.1	−0.11	0.46	−0.06	−0.14	−0.12	−0.07	1				
Mn	−0.41	0.08	−0.35	0.13	−0.18	−0.28	−0.4	−0.23	−0.2	−0.22	0.88	0.15	−0.26	0.01	−0.01	0.18	0.02	−0.29	1			
Ni	0.26	−0.33	0.3	−0.39	0.04	0.15	0.54	0.12	0.04	−0.03	−0.33	−0.31	0.22	−0.21	−0.38	−0.35	−0.24	0.49	−0.43	1		
Mo	0.13	0.51	0.65	0.74	0.98	0.83	0.64	0.95	0.97	0.58	0.55	−0.44	0.82	0.48	0.73	0.54	0.89	0.14	−0.2	0.01	1	
Ba	0.14	0.51	0.66	0.74	0.98	0.83	0.64	0.95	0.97	0.58	0.56	−0.44	0.82	0.48	0.73	0.54	0.89	0.14	−0.21	0.02	0.99	1

Table 4 Varimax rotated-factor matrix of major and trace elements in groundwater of Madras

Variable	Factors					Communality
	1	2	3	4	5	
HCO_3	0.063	−0.18	0.141	0.934	0.043	0.97
Cl	0.289	0.896	0.074	0.038	−0.067	0.969
Si	−0.105	0.156	−0.023	−0.056	0.03	0.997
Ca	0.241	0.941	−0.035	−0.094	−0.08	0.976
Mg	0.522	−0.048	−0.115	0.042	0.064	0.979
Na	0.494	0.247	0.427	0.451	0.127	0.95
As	0.939	0.279	0.066	−0.041	0.004	0.989
Se	0.747	0.382	0.353	0.194	0.042	0.957
B	0.719	−0.226	0.239	0.312	0.358	0.928
V	0.946	0.235	0.111	−0.055	0.065	0.991
Cr	0.948	0.247	0.124	−0.003	−0.015	0.994
Fe	0.322	0.58	0.427	0.002	−0.089	0.964
Co	0.295	0.939	−0.032	−0.049	−0.07	0.99
Pb	−0.295	−0.136	−0.036	−0.023	−0.147	0.991
Cu	0.769	0.352	0.379	0.107	0.144	0.991
Zn	0.141	0.89	0.052	−0.164	−0.029	0.982
Cd	0.655	0.24	−0.139	0.184	−0.507	0.96
Mn	0.291	0.916	−0.042	−0.028	−0.103	0.971
Ni	0.837	0.329	−0.114	−0.089	−0.235	0.965
Mo	0.155	−0.107	0.913	0.152	0.224	0.955
Ba	−0.163	0.089	−0.109	−0.209	−0.169	0.991
pH	0.069	−0.272	0.251	0.105	0.855	0.981
Eigenvalue	12.17	4.61	2.07	1.25	1.07	
Variance (%)	48.7	18.4	8.3	5	4.3	
Cumulative variance	48.7	67.1	75.4	80.4	84.7	

either directly or indirectly. Moderate correlation of Na with other elements indicates that Na enters the effluent system by seawater encroachment. Na concentration directly depends on the seawater intrusion into the groundwater horizons. Pb shows a poor negative correlation with other trace elements such as Cr, Cd, Mn, and Ni. The spatial distribution of Pb contours to the west of the other elemental distributions, indicating that it is deposited in the soil as soon as it is released by the industries. Its mobilization factor is very high (100) and the soil acts as a sink; hence it shows poor correlation with other trace elements. In general, the correlation matrix shows a strong correlation among trace metals and a poor correlation with other major constituents. This indicates that the analysis of major constituents alone may not reflect the actual status of pollution.

Factor analysis

The most widely used statistical technique in geochemistry is R-mode factor analysis. Klovan (1975), Joreskog and others (1976), and Demooy and others (1988) have provided excellent descriptions of factor analysis applied to geochemical problems. A varimax rotated-factor matrix tested on the groundwater of Madras City is presented in Table 4. All 22 parameters have been shown with loadings for five factors. The higher eigenvalues for the first two factors account for nearly 70 percent of the variance and hence, in the factor matrix, only these two factors have been considered for discussion.

Factor 1

This factor is statistically dominant and accounts for 49 percent of the variance. This factor is characterized by very strong positive loadings on V, Cr, As, Ni, Cu, Se, B, and Cd, indicating that all these elements are of anthropogenic origin. All these trace metals could be associated with only one factor: *migration of pollutants from industrial outlets to groundwater*, and hence it can be categorically stated that factor 1 is only the effluents from industries.

Factor 2

This factor accounts for 18 percent of the variance and shows strong positive loadings on Ca, Co, Mn, Cl, Zn, and Fe. This factor can be termed the *mobilization factor*. In the Madras basin, it is possible that the mobilization factor also controls the distribution of trace elements in the groundwater system. A combination of industrial effluent into the environment (factor 1) and mobilization of heavy metals (factor 2) can explain the trace element scenario.

Conclusions

In this paper we have tried to identify the pathways and contamination of major and trace elements in the groundwater of Madras City, a coastal metropolitan city in India. The anomalous distribution of elements is mostly man-made, as can be determined from our observations. Overexploitation and improper management of natural resources led to the unequal distribution of major and trace elements in nature. Trace element pollution is a new concept with a wider perspective because trace elements control human metabolism and enter into the human system through various ways.

On critical examination of the data, it can be seen that the major and trace metal concentrations in the groundwater increased several-fold, indicating that the polluted overlying water is influencing the quality of groundwater in the Madras urban area. However, in certain locations, the groundwater quality is still unaffected, even though these areas are relatively close to pollution sources. This phenomenon suggests that the contaminants drain only in a fixed direction coinciding to the hydrological gradient, topography, and local geological structures such as joints, porosity, and permeability and the physicochemical processes in the soil. Movement of pollutants such as As, Se, V, and Cr with the groundwater downstream is significant because it increases the possibility of accumulation of pollutants in the biosphere.

Regular monitoring of the quality of groundwater should be undertaken, temporally and spatially, to identify the sources of toxic contaminants and other inhibitory compounds that affect the potability of water. Since development, environment, and public health are interlinked, it is necessary for all concerned to adopt sustainable utilization of the available water resources.

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