Environmental geochemistry of the Pichavaram mangrove ecosystem (tropical), southeast coast of India

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Abstract Spatial and temporal geochemical variations of various parameters in the water and sediment of a relatively small mangrove situated on the southeast coast of India were examined in detail for the first time. The water quality generally reflects the impact of seawater and the Vellar estuary (mixing effect) aided by evaporation and in situ biological productivity. The depletion and fluctuation of dissolved silica are controlled by biological processes. Nitrate and phosphate are contributed by fertilizer input from adjoining agriculture fields. Total suspended matter (TSM) shows an erratic range and trend due to deforestation and resuspension processes. Sand and silt constitute 70–90% of the sediments. Statistical analysis of the sediments shows the prevalence of a moderately high-energy environment with very effective winnowing activity. Organic matter content is higher in the mangrove sediments in comparison to adjacent estuaries. Water and sediment show fluctuations in their chemical concentration, but no specific trends could be identified. Heavy metals are also enriched in the mangrove sediments, indicating their unique chemical behavior and the existence of trapping mechanisms. Factor analysis and correlation analysis of water and sediments show the complexity of the system and the multitude of contributing sources. The core sediment chemistry suggests the depletion of metal input due to the damming of the detrital inputs. The Pichavaram mangrove seems to be relatively unpolluted, since the anthropogenic signal observed is small and acts as a sink for heavy metals contributed from a multitude of sources without an adverse effect.

Key words Mangrove · Geochemistry · Biological productivity · Anthropogenic impacts · Heavy metal sink

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Introduction

The mangrove ecosystem holds and stabilizes the environment from erosion and acts as a buffer zone between land and sea. Mangroves grow in an intertidal zone in tropical and subtropical regions. The mangrove environment in the sheltered slack water conditions allows the deposition of fine particles normally enriched with metals, high in organic matter and minerals. This ecosystem offers an ideal site to study a number of processes that are important in understanding hydrogeochemical processes such as mixing, dissolution, evaporation and chemical exchange between water and sediments.

In India, mangrove forests cover 360×10^3 ha of coastal tracts (3% of the world's mangrove forest) (Badarudeen and others 1996; Mastallar 1996). Pichavaram mangrove is surrounded by at least ten fishing villages, agricultural land and prawn culture ponds besides regularly attracting a large number of tourists (it has a tourist resort and boating club). The mangrove system undergoes physiochemical changes owing to the input of rivers Coleroon and Vellar and seawater, along with an increasing population, fishing activity and other anthropogenic activities. Pichavaram mangrove has been studied in detail for its plant communities and bacterial abundance (Blasco and others 1975; Vishnu Mittene and Sharma 1975; Govindasamy and Kannan 1991; Jagtap and others 1993; Dious and Kasinathan 1994; Kathiresan and others 1994). The adjoining Coleroon and Vellar estuarine systems have received much attention with regard to their geochemistry (Seralathan and Seetharamasamy 1987; Ramanathan and others 1988; Subramanian and others 1989; Purvaja and Ramesh 1998). There is practically no detailed information on the environmental geochemistry of the Pichavaram mangroves; hence, the present work studies in detail the variation in the water chemistry and sediment (surface and suspended) characteristics and chemistry and the possible anthropogenic impact over the entire Pichavaram mangrove ecosystem.

Study area

The Pichavaram mangrove is situated about 250 km south of Chennai (Madras) on the southeast coast of India (Fig. 1). The mangrove has 51 islets of varying size with an area of 1200 ha, of which 40% is occupied by urban waterways (for fishing), 50% by mangrove forests and the rest by mud and sand flats. The sprawling mangrove is crisscrossed by numerous channels and creeks linking other water bodies in this region. The tides are semi-diurnal with a range of 0.5–1.0 m. The geology of the area is dominated by Quaternary sediments. Wind velocity fluctuates between 5 and 15 kmph. There are 28 mangrove species (mainly *Rhizoporaceae* and *Avicenia officianalis*), a large variety of fish, crabs and shrimps (intense fishing activity) and a s good number of various avian populations (Kathiresan and others 1994). The climate of the region is semi-arid dominated by a northeast monsoon (October–January). Areas surrounding the mangrove are under extensive agricultural use.

Materials and methods

The sampling strategy was to study seasonal and spatial variability in a number of parameters. Accordingly, systematic sampling was carried out in the entire Pichavaram mangrove environment during January 1995 (monsoon), July 1995 (summer) and February (post monsoon) to better understand the various processes operating in this tropical ecosystem. Twenty-five water samples end surface sediments, four suspended sediments and one core sample were collected in order to examine the natural and anthropogenic influences (Fig. 1); 1 l of mangrove

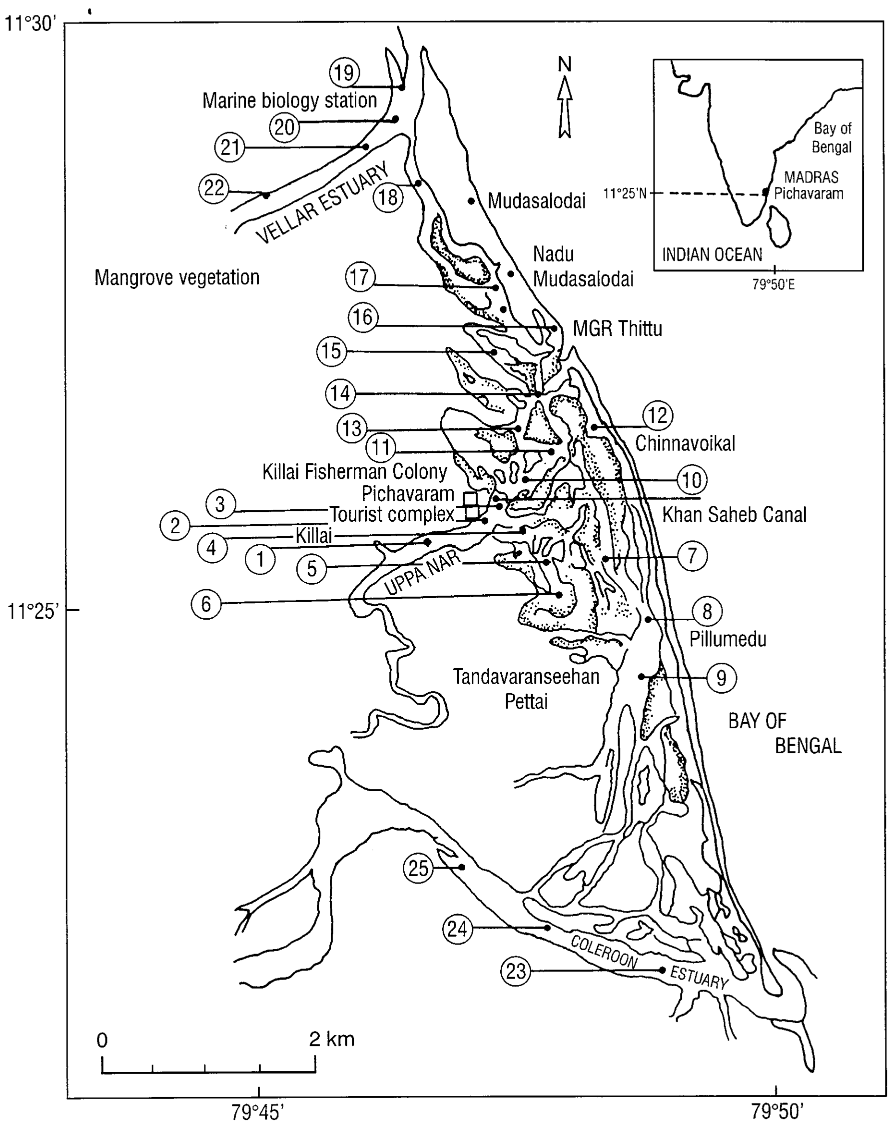

Fig. 1
Location map of the study area, with sampling stations

water was collected in polyethylene bottles at the surface from the middle of channels, along with a 5-l water sample for suspended sediments. Alkalinity and pH were measured in the field using and micropipette titration a portable pH meter, respectively. Surface sediments were collected from the dry part of the mangrove channel near (in contact) to the water body. The sampling site was cleared of vegetation and foreign matter using a scraper. To collect a representative sample, the top layer (between 10 and 15 cm) was removed by scraping and the sample was collected in polyethylene bags. The core sediment was collected by inserting a 1-m-long PVC pipe and pushing manually as far as possible (Ramanathan and others 1996). The core sediment sample was cut into segments of 0-5 cm for analytical work.

The water samples were filtered through 0.45-μm cellulose acetate membranes (Millipore Corporation); suspended and surface sediments were preserved at 4 °C in a cold room within a week of sampling. Sediments were separated by size fractions (>37 μ) using standard sieving. Fractions of <37 μ were separated by the Attenburg cylinder method based on Stokes' law (Griffiths 1967). Slides of sediments were prepared by a 'drop-on-slide' technique (Gibbs 1967) and then glycolated. Mineral compositions were determined using X-ray diffraction (Philips Electronics) with CU-Kα radiation utilizing an Ni filter. Mineral identification and estimation of abundances were carried out following the method of Carrol (1970).

Standard analytical procedures (AAS – cations; colorimetry – anions and silica; pH – ion analyser for pH, Cl^- and F^-) were adopted for water chemistry. For cation analysis, the analytical precession was better than 4–5%; for anions it was 10%. SiO_2 and Al_2O_3 in suspended and surface sediments were analysed by the solution 'A' method of Shapiro and Burnock (1962). Other cations in sediments were determined by AAS after complete digestion (Teflon bomb digestion) using the manufacturer's recommendations and background correction. Standards used were the USGS MAG-1, SCO-1 and G-2. The authors' values for various metals were within 5–10% of the reported values for these reference materials.

Table 1
Chemical composition of surface water [in mg l^{-1}, except for EC ($\mu s\ cm^{-2}$) and pH]

Variables	Pichavaram mangrove ($n=17$)						Vellar estuary ($n=5$)						Coleroon estuary ($n=3$)					
	Monsoon		Summer		Post monsoon		Monsoon		Summer		Post monsoon		Monsoon		Summer		Post monsoon	
	Range	Avg.	Range	Avg.	Range	Avg.	Range	Avg.	Range	Avg.	Range	Avg.	Range	Avg.	Range	Avg.	Range	Avg.
pH	7.4–8.3	7.81	7.4–8.3	7.82	7.51–7.81	7.71	7.55–7.83	7.73	7.5–7.8	7.6	7.7–7.8	7.75	7.62–8.1	7.9	7.72–8.5	8.1	7.9–8.2	8.04
EC	17 500–43 600	37 312	134 000–53 000	44 076	28 000–47 000	41 278	4000–53 600	46 820	45 000–51 000	48 000	32 000–46 000	41 260	17 800–25 000	20 677	18 000–45 000	27 333	15 000–22 000	18 467
Cl	6200–20 100	14 603	11 769–18 505	15 307	9572–16 307	14 058	17 250–19 000	18 100	15 598 17 016	16 420	10980–15 953	14 266	3800–20 000	9267	3100–15 599	7296	4000–10 200	6267
HCO_3	100–220	161	134–195	155.9	122–189	154	115–165	150	134–171	1554	110–134	126.5	135–204	179	164–234	194	180–214	195
SO_4	1400–11 000	5171	2209–9419	3342	2830–3600	3244	8250–10 900	9538	1508–3746	3183	3360–3460	3422.5	225–10 125	3597	120–3362	1346	800–6000	2533
F	0.2–0.45	0.333	0.2–0.5	0.34	0.12–0.6	0.36	0.29–0.34	0.324	0.16–0.4	0.26	0.19–0.33	0.265	0.18–0.33	0.23	0.14–0.38	0.24	0.31–0.34	0.33
PO_4	0.05–2.35	0.28	0.06–1.12	0.23	0.05–1.18	0.39	0.15–0.31	0.23	0.18–0.38	0.26	0.15–0.32	0.23	0.18–0.41	0.3	0.19–0.27	0.23	0.12–0.24	0.2
NO_3	0.35–40.7	5.9	–	–	–	–	0.82–8.37	5.33	–	–	–	–	0.82–1.21	0.6	–	–	–	–
H_2SiO_4	0.11–14.3	5.5	0.4–16.2	6.3	1.2–11.0	11.7	0.5–9.7	5.53	1.2–11.4	6.42	1.3–7.1	3.88	10.25–29	22	21–29	24.6	11.2–14.7	13.16
K	340–560	4.50	205–391	296	156–284	241	440–530	474	264–323	297	176–264	225	180–530	320	150–165	158	120–160	140
Na	1350–12 200	5200	5747–5059	7998	2677–7707	6715	4850–7500	6030	7702–8851	8285.6	5221–7532	6750.8	7200 1082	3187	810–5433	2401	1208–5000	3071
Ca	107–466	208	209–345	292	168–313	273	395–687	550	301–341	327	184–313	258.5	132–275	182	110–329	190	170–400	322
Mg	170–1460	715	905–1347	1162	783–1396	1153	340–860	612	1107–1236	1182	963–1343	1215	160–860	400	135–871	382	230–966	675
TDS	9453–40 693	27 558	22 332–32 872	28 852	16 477–29 702	25 799	32 218–39 172	35 481	28 633–30 666	29 856	21 126–28 901	26 269	39 137–5813	17 236	4775 25 966	11 992	6756–22 914	13 218

Results and discussion

Table 1 summarizes the composition of the surface water within this network for the Pichavaram ecosystem and adjacent water bodies (Fig. 1). Figure 2 shows the spatial variation in the average values of the chemical parameters of the surface waters. Pichavaram mangrove water is alkaline in nature without any systematic spatial variation irrespective of seasons (Mook and Koene 1975). The higher pH values are due to the mixing of seawater with estuarine waters and by the mangrove photosynthetic activity, which utilized CO_2, thereby shifting the equilibrium towards highly alkaline (Ruttner 1953). Electrical conductivity (EC) is minimal during the monsoon and maximal during non-monsoon. Thus, the influence of atmospheric precipitation on EC and total dissolved solids (TDS) is more pronounced in the mangrove during the monsoon period. The increase in the ionic strength of the mangrove water during the non-monsoon periods may be due to less riverwater input via estuaries due to the construction of dams, aided by evaporation due to an elevated temperature and friction due to high-speed wind activity in the region.

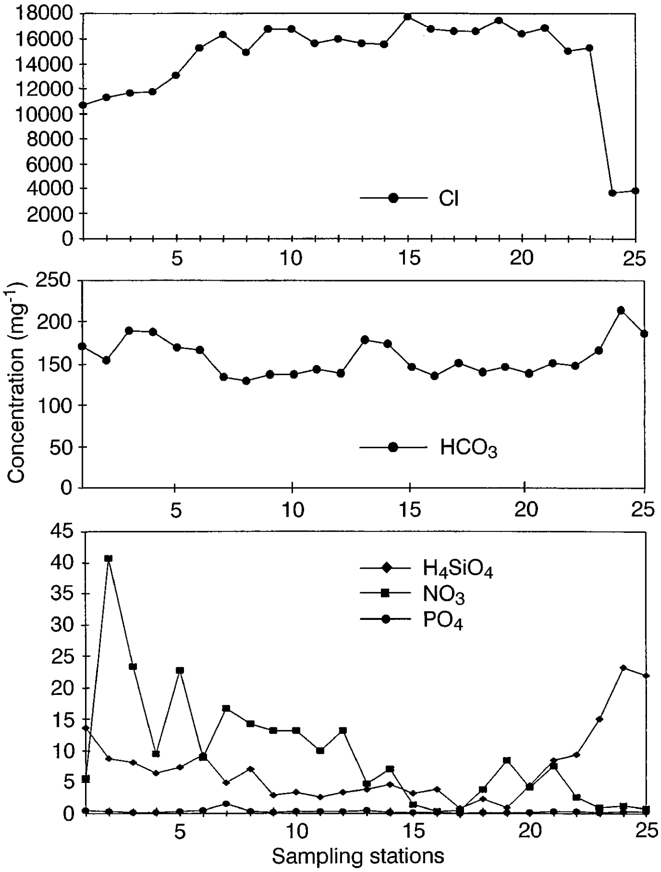

Fig. 2
Profile of concentration of a few dissolved constituents in Estuaries and mangrove

TDS increase from about 9 to 28‰ in the summer and in the interior channels. Chloride and sulphate contribute 70% of the total ions in the mangrove water. EC shows good positive correlation with TDS (0.83), Cl (0.82), SO_4 (0.60) and Na (0.87). The Vellar estuary and seawater inputs during the tides seem to be the primary sources controlling these ions, aided by evaporation processes (Table 1; Fig. 2). The saline soils and saline groundwater in the drainage areas might have also contributed to the higher chloride concentration (Das and Singh 1996). Sulphate concentrations vary from 1400 to 11 000 mg l^{-1} and are excessive during the monsoon. Seawater input along with resuspension mixing (turbidity and mixing) of decayed organic matter and oxidation of buried biogenic materials result in enhanced sulphate levels in mangrove waters (Ramanathan and others 1993). Bicarbonate shows a minor fluctuation within the mangroves and ranges from 100 to 200 mg l^{-1}. The lower concentration is due to the dilution of estuarine waters by seawater and also by the processes of reverse weathering (clay formation) which decreases the alkalinity (Von Damm and Edmond 1984). Moreover, less vegetation (sparingly) in certain fishing channels leads to high evaporation plus low organic matter decay and less root respiration which lowers or masks the bicarbonate concentration.

Nutrients

Dissolved silica concentration ranges from 0.11 to 16.2 mg l^{-1} and its concentration is moderately higher in summer (Table 1; Fig. 2), with fluctuation in the interior channels. Silica is mainly derived from silicate weathering. Estuarine input and resuspensions seem to be the major sources controlled by the complex physicochemical process operating here. The extent to which rapid removal and addition are capable of influencing the silica budget in the mangrove region is generally difficult to assess, but the depletion and fluctuation of silica seem to be controlled by biological processes (silica secreting and consuming organisms). Phosphate values are higher and are contributed mainly from weathering of phosphatic nodules present in the drainage area (Coleroon) and fertilizer [di-ammonium phosphate (DAP) and N:P:K] application on the adjoining agricultural fields (Tandon 1987; Vaidhyanathan and others 1989). Nitrate concentration varies from 0.35 to 40.7 mg l^{-1} and is excessively contributed from biological activity and fertilizer application. Figure 2 shows the greater influence of the Vellar estuary over the mangrove nutrient distribution (except H_4SiO_4). Figure 2 also shows the higher concentration of nitrate followed by silica and phosphate in mangroves. Thus, the in situ biological productivity and fertilizer input from adjoining agricultural fields influence the nutrient budget in the mangrove.

Cations

All the major cations show a wide variation within the mangroves and are higher in the non-monsoon periods.

Table 2
Chemical composition of surface and suspended sediments in Pichavaram mangrove [in $\mu g\ g^{-1}$ except for Si, Al and OM (%)]

Surface sediments, Locations	Si	Na	K	Ca	Mg	Cd	P	Ni	Mn	Fe	Cl	Cu	Zn	Pb	Al	OM
1	36.69	26 800	7980	9647	4272	6	292	80	385	29 100	89	24	50	8	18.16	5.80
2	30.33	31 200	10 120	10 640	5100	7	301	64	645	26 100	122	26	63	10	17.18	4.80
3	31.11	30 100	9942	9762	4900	9	361	44	860	35 400	110	24	80	7	18.00	8.90
4	40.03	40 100	11 642	12 640	5200	8	120	38	987	33 800	160	27	120	11	19.78	10.30
5	34.23	24 800	7173	8922	4164	7	353	85	1248	41 000	175	47	130	12	18.00	7.30
6	30.97	29 800	10 643	9562	4865	6	283	80	1120	39 100	182	49	80	15	15.30	13.40
7	33.23	23 600	6943	8840	4092	8	353	71	934	35 000	156	35	95	11	17.38	6.90
8	30.00	29 800	7692	9800	5200	7	301	57	708	29 300	131	20	81	10	18.78	5.50
9	32.34	29 600	6021	10 062	4092	5	284	58	909	36 800	120	36	110	17	16.11	8.00
10	41.50	21 100	5622	8642	4927	4	353	51	1200	33 100	123	33	85	16	16.32	9.50
11	28.54	31 200	9600	9800	4082	3	361	50	1080	24 700	162	29	85	15	22.10	2.50
12	38.24	26 100	6600	9100	4337	2	215	49	917	27 600	173	28	88	13	16.10	6.90
13	33.45	29 800	8660	9022	4547	10	301	51	687	29 300	186	64	66	11	17.12	3.50
14	29.66	29 100	9600	9421	5200	9	224	59	866	23 400	141	69	120	14	14.78	7.50
15	36.80	24 200	8700	9022	4117	6	335	82	1900	36 400	162	71	110	8	19.16	6.90
16	41.50	42 100	9600	9421	5100	7	378	84	860	25 200	129	76	96	7	20.10	4.50
17	31.00	30 100	5900	10 642	5227	8	350	86	697	46 900	110	81	112	6	15.48	10.00
18	33.90	23 200	7560	8740	4061	7	387	15	119	20 300	43	4	81	5	14.21	1.00
19	46.38	51 200	9720	14 670	5672	8	103	17	121	26 400	42	7	71	4	23.78	3.00
20	37.13	27 800	8640	9200	5112	8	163	26	92	25 400	36	11	102	6	20.10	3.10
21	25.65	22 000	8630	7621	3892	9	181	31	86	24 600	28	16	111	7	14.10	1.40
22	27.21	23 900	7640	8061	3941	4	206	18	130	31 000	39	20	122	8	13.10	2.20
23	35.23	26 400	7860	18 946	8003	7	370	19	166	26 500	61	3	52	7	18.12	1.00
24	58.10	57 800	6900	16 760	6607	9	241	21	182	16 200	42	3	59	4	25.62	0.56
25	32.57	21 000	5100	18 662	8167	10	344	32	630	25 900	46	7	68	3	14.01	0.32
Suspended sediments																
2	51.20	34 500	7800	13 570	17 580	13	1900	97	1495	44 510	–	93	127	6	21.5	11
5	49.60	56 000	6400	3763	2428	32	1600	210	735	17 535	–	47	18	2	27.6	14
12	52.20	47 860	7200	13 470	14 160	8	1500	22	739	15 369	–	33	17	3	11.7	13
17	44.60	36 200	7800	10 220	9275	16	960	26	456	14 746	–	23	18	4	10.4	15

Table 3
Correlation coefficient of dissolutions in Pichavaram mangrove

	pH	EC	TDS	TSM	Cl	HCO_3	SO_4	F	PO_4	H_4SiO_4	K	Na	Ca	Mg
pH	1	−0.84	−0.79	−0.07	−0.74	0.59	−0.51	−0.64	−0.72	0.12	−0.75	−0.86	−0.6	−0.83
EC		1	0.83	0.02	0.82	−0.64	0.6	−0.58	−0.03	−0.57	0.8	0.87	0.65	0.78
TDS			1	0.10	0.90	−0.65	0.860	0.67	−0.03	−0.68	0.78	0.81	0.78	0.71
TSM				1	0.04	−0.35	0.11	−0.03	−0.27	0.03	0.08	0.02	−0.02	0.11
Cl					1	−0.59	0.61	0.81	−0.04	−0.67	0.76	0.81	0.78	0.76
HCO_3						1	−0.46	−0.38	−0.06	0.35	−0.6	−0.66	−0.44	−0.67
SO_4							1	0.33	−0.03	−0.5	0.55	0.5	0.82	0.37
F								1	−0.06	0.77	0.67	0.73	0.34	0.71
PO_4									1	0.06	0.12	0.05	−0.01	0.05
H_4SiO_4										1	−0.75	−0.68	−0.44	−0.60
K											1	0.84	0.55	0.78
Na												1	0.67	0.94
Ca													1	0.51
Mg														1

Sodium is the dominant cation (80%) followed by Mg, Ca and K (Tables 1, 2). Na and Cl behave similarly and are increasing or decreasing with respect to the mixing behavior. Potassium remains almost constant and is the less dominant cation. Na is more mobile than K and dominates the natural solutions (Milliot 1970). Mg is higher than Ca in the mangroves, which may be due to the adsorption of Ca onto clay minerals and due to the biological consumption of Ca in the mangrove ecosystems. Ca can also be removed due to the precipitation of carbon-

Table 4
Factor analysis of Pichavaram waters

Variable	Factor				Communality
	1	2	3	4	
pH	−0.79	0.009	−0.25	0.40	0.85
EC	0.76	0.03	0.01	−0.49	0.82
TDS	0.70	0.04	−0.07	−0.68	0.96
TSM	0.09	0.70	−0.52	−0.05	0.77
Cl	0.83	−0.41	−0.09	−0.39	0.84
HCO_3	−0.61	0.57	−0.09	−0.39	0.84
SO_4	0.29	0.06	−0.08	−0.91	−0.91
F	0.88	−0.23	−0.06	−0.04	−0.84
PO_4	0.06	0.03	0.92	0.06	0.86
H_2SiO_4	−0.74	0.18	0.13	0.24	0.67
K	−0.74	0.18	0.13	0.24	0.67
Na	0.83	0.05	0.06	−0.33	0.81
Ca	0.34	0.01	0.03	−0.87	0.86
Mg	0.91	0.15	0.06	−0.15	0.88

ate concretions (Ramanathan and others 1993) and from CO_2 degassing in alkaline waters (Kilham 1990).
The erratic ranges and trends in the total suspended matter (TSM) are primarily due to deforestation of the mangroves resulting in resuspension of the sediments in the ecosystem and redistribution by tidal and wind action. This is also reflected in the higher levels of dissolved silica, most of which are primary silica colloids released by bio-turbulance and mixing effects.
Correlation and factor analysis were employed to delineate the sources controlling/affecting the mangrove water chemistry (Tables 3, 4). Factor analysis is a technique whereby a data set is analyzed by creating one or more factors, each representing a cluster of interrelated variables within the data set. Table 4 indicates the loading of each variable accounted for by chemical analysis, using 14 variables, an average of 84% of the total ionic variability accounted for by four composited factors. Factor 1 essentially consists of data for EC, TDS, Cl, F, Na, Mg and Ca and indicates their contribution by seawater and by mixing effects of fresh/brackish waters. Factor 2 consists of TSM, HCO_3, H_4SiO_4, K and Mg and can be interpreted as the contribution by natural geochemical weathering processes. Factors 3 and 4 are made up of PO_4, H_4SiO_4 and K with negative loading for all other ions, indicating an additional source for these ions such as in situ biological processes (adsorption/desorption) and anthropogenic inputs (fertilizer application, etc.). Correlation coefficient analysis also shows a mixture of very good correlation (0.5–1.0), poor to insignificant correlation (<0.5) and negative correlation. These two statistical analysis show that the above discussed multiple sources were controlling/contributing to the mangrove water chemistry.

Texture and mineralogy

Grain size measurement helps in determining the textural and depositional characteristics of the environment. Sand and silt constitute 70–90% of the mangrove sediments, followed by clay. Mean size varies from 0.13 mm to 0.22 mm (0.27 mm = 1.9 ∅, 0.125 mm = 3.06 ∅) with an average of 0.179 mm = 2.428 ∅ (fine sand) (Table 5). The statistical analysis shows that the sediments are moderately to poorly sorted, coarsely skewed and platy to leptokurtic in nature (Lindholm 1987), indicating the prevalence of a moderately high-energy environment with very effective winnowing activity (Reineck and Singh 1980). Minerological studies show that clay minerals are enriched in the suspended sediments relative to the surface sediments (Table 6). Montmorillonite is the abundant clay mineral present due to the dominance of fine-grained sediments. Quartz and feldspar are the major detrital minerals. Carbonates are also present, derived from carbonate concretions rather than deposition of primary carbonates.

Table 5
Grain size parameters of Pichavaram mangrove sediments (phi grade scale)

Sample no.	Surface sediments			
	Mean size	SD	Skewness	Kurtosis
1	2.86	0.94	0.04	0.75
2	2.65	0.96	0.25	0.80
3	2.28	0.85	0.52	0.62
4	2.93	0.76	0.23	0.52
6	2.70	1.04	0.20	0.58
7	3.06	0.90	0.19	0.85
9	2.25	0.96	0.12	0.55
10	2.51	1.05	0.03	0.52
15	2.26	1.16	0.16	0.96
16	2.23	0.88	0.10	0.83
17	2.25	1.05	0.15	0.54
18	2.53	0.34	0.26	1.28
19	2.31	0.43	0.36	1.28
20	2.61	0.85	0.03	0.94
23	1.96	0.40	0.56	0.89
24	2.0	0.44	0.51	0.97
25	1.9	0.40	0.52	0.98

Mean 2.428 ∅ = 0.179 mm

Table 6
Average mineralogical composition (%) of Pichavaram mangrove sediments

	Quartz	Feldspar	Clay	Carbonate
Pichavaram				
Suspended	40	23	30	7
Bed	50	32	14	4
Coleroon–Vellar estuary				
Suspended	38	45	14	3
Bed	52	40	4	4

Sediment chemistry

The general chemical properties of surface sediments collected in the Pichavaram mangroves are shown in Tables

Table 7
Chemical composition of surface sediments [in $\mu g\ g^{-1}$ except for Si, Al and OM (%)]

Variable	Pichavaram mangrove			Vellar estuary			Coleroon estuary		
	Max.	Min.	Avg.	Max.	Min.	Avg.	Max.	Min.	Avg.
Si	41.5	28.54	34	46.38	25.65	34	58.1	32.67	42
Al	22.10	14.78	17.63	23.78	13.10	17	25.62	14.01	19
Na	42 100	21 100	28 205.8	51 200	22 000	29 620	57 800	21 000	35 061
K	11 642	5622	8246	7560	9720	8448	7860	5100	6287
Ca	12 640	8640	9756	14 670	7621	9658	18 946	16 760	18 123
Mg	5227	4082	4672.5	5672	3892	4536	8167	6607	7592
Fe	46 900	23 400	32 482	31 000	20 300	25 540	26 500	18 200	23 533
P	378	120	305.6	387	103	208	370	241	318
Zn	130	50	93	122	71	97	68	52	60
Pb	17	6	11.2	8	4	6	7	3	4.6
Co	54	19	35.3	36	14	23	18	16	16.6
Cd	10	2	6.6	9	4	7	10	7	8.6
Ni	86	38	62	31	15	21.4	32	19	24
Mn	1248	385	941	130	86	110	630	166	326
Cr	186	89	141.2	43	28	38	61	42	49.6
Cu	81	20	43.4	20	4	11.6	7	3	4.3
OM	13.4	2.5	7.14	14	1.0	4.6	1	0.32	0.616
Average Cl values in mg/l	20 000	6200	14 656	19 000	10 980	16 476	20 000	3100	7610

5–7 and Figs. 3 and 4. Organic matter (OM) concentration varies from 2.5% to 13.4%. OM content is higher in the interior channels. OM contents of the Vellar and Coleroon estuaries are relatively lower than those of the mangrove sediments. The spatial variations of the total Fe, Mn, P, Ni, Cu, Zn and Pb in the mangrove and in the influencing zones of the estuary, especially near Coleroon, were significantly different. The concentration of Fe ranges from 2.34% to 4.69% and averages 3.25%. The average Fe content of the mangrove sediment is slightly higher than that of the Vellar and Coleroon estuaries (Table 7; Ramanathan and others 1993). This observed higher concentration of Fe in the mangrove sediments might be a result of the textural and mineralogical characteristics of the mangrove sediments. In this context, it is important to note that clays and feldspar were the dominant mineral species present in the sand and silt size populations of the sediments (Table 6). Mn is the next abundant heavy metal followed by Cr, Zn and other metals. Fe–Mn complexes seem to have a strong bearing on the dispersal patterns of other metals in this aquatic sedimentary environment mainly due to their geochemical affinity (Forstner and Wittman 1983). Although no specific significant heavy metal trend was identified, the heavy metal concentrations were slightly higher in the in-

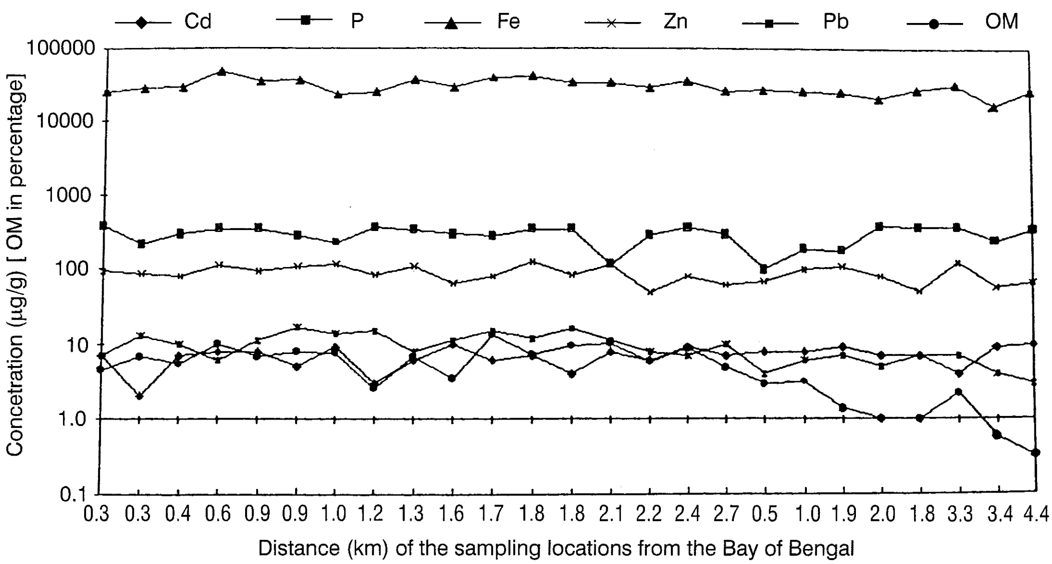

Fig. 3
Variation in some surficial sediment-bound metals (see Fig. 1 for sampling locations)

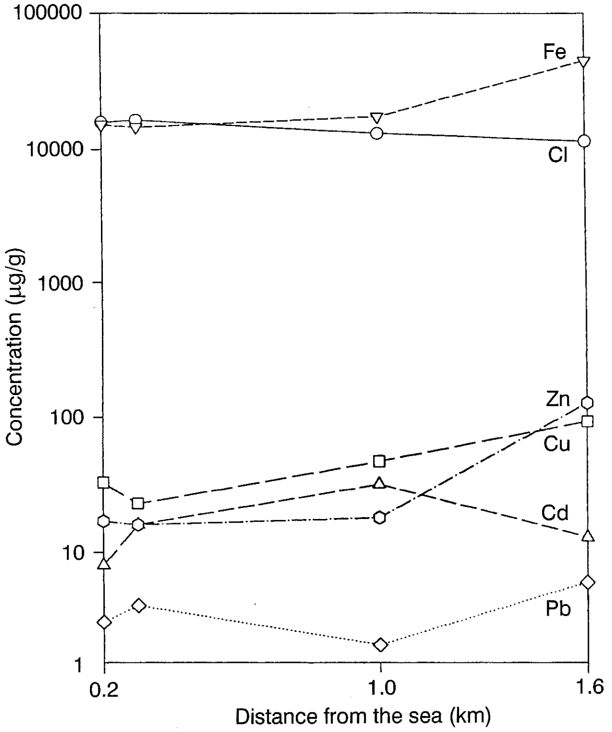

Fig. 4
Variation in particulate-bound metals in mangrove (see Fig. 1 for sampling locations)

terior channels and in frequently used waterways (e.g. 5, 6, 9 and 10). A comparison of these heavy metals with that of the adjacent estuaries (Tables 7 and 8; Ramanathan and others 1993) indicates that these metals are enriched more in the mangrove sediments than in the adjacent estuaries. The observed enrichment of the heavy metals can be explained by the unique chemical behavior of the mangrove sediments. Similar observations were made earlier by Delacerd (1983) and Badarudeen and others (1996). They observed that the mangrove sediments act as a filter for many toxic metals including Zn, Cr, Ni and Cu.

The concentrations of heavy metals in this study were generally below the levels found in polluted and unpolluted estuaries and mangroves (Everaats and Fischer

Table 8
Factor analysis of Pichavaram sediments

Variable	Factor					Communality
	1	2	3	4	5	
Si	−0.88	0.16	−0.12	−0.17	0.09	0.85
Al	−0.92	−0.09	−0.01	0.14	0.03	0.86
Na	−0.88	0.04	0.04	0.32	0.05	0.89
K	−0.06	0.03	−0.03	0.94	−0.01	0.88
Ca	−0.26	0.84	0.19	−0.90	−0.01	0.81
Mg	0.01	0.93	0.23	−0.12	0.05	0.93
Fe	0.21	−0.09	−0.70	−0.15	−0.06	0.56
P	0.24	0.12	−0.41	−0.58	0.02	0.56
Zn	0.05	−0.42	−0.12	−0.01	−0.58	0.52
Pb	0.19	−0.32	−0.40	0.07	−0.72	0.82
Co	0.23	−0.43	−0.32	−0.05	−0.70	0.83
Cd	0.19	0.83	0.08	0.18	0.25	0.88
Ni	0.09	−0.11	−0.95	−0.07	−0.01	0.93
Mn	−0.22	−0.12	−0.77	−0.18	−0.35	0.81
Cr	−0.04	−0.29	−0.74	0.15	−0.47	0.87
Cu	0.04	−0.22	−0.85	0.07	−0.78	0.78

Table 9
Concentration of heavy metals in sediments average shale and soil reported by previous studies (mean values with range given in parentheses, in $\mu g\ g^{-1}$)

Location and type of sediment	Cu	Zn	Pb	Mn	Reference	Comments
1. Pichavaram mangrove, India.	43.4 (20–81)	93 (50–130)	11.2 (6–17)	941 (385–1248)	Present study	Relatively clean and Avicennia covered Tropical mangrove
2. Kumarakam mangrove, India.	48 (19–92)	236 (112–466)	–	452 (305–645)	Badarudeen and others 1996	Relatively clean Tropical mangrove
3. Sai Keng mangrove, Hong kong	12.4 (1–31)	53.3 (17–147)	58.2 (8–241)	97.9 (34–223)	Tam and Wong 1995	Relatively clean
4. Brisbane mangrove, Australia	22.4 (3–30)	97.9 (41–144)	66.8 (20–82)	–	Mac Key and others 1992	Industrial and urban discharge
5. Saudi mangrove, Arabian Gulf	1.8 (0.1–4)	7.3 (2–17)	11.8 (6–19)	28.7 (2–69)	Sadiq and Zaidi 1994	Nil
6. Sepetiba Bay mangrove, Brazil.	12.4	311	17.8	–	Lacerda and others 1993	With Avicinnia covered
7. Mangrove, S. Australia	(30–80)	(142–190)	(85–112)	–	Habinson 1986	Nil
8. Average Shale	45.0	95.0	20.00	850.00	Ravichandran and others 1995	–
9. Average Soil	30.0	90.0	19.00	550.00	Bowen 1979	–

Table 10
Correlation coefficient of Pichavaram sediments

	Si	Al	Na	K	Ca	Mg	Fe	P	Zn	Pb	Co	Cd	Ni	Mn	Cr	Cu
Si	1	0.67	0.71	−0.13	0.34	0.22	−0.25	−0.22	−0.01	−0.27	−0.34	0.03	−0.20	0.07	−0.16	−0.18
Al		1.00	0.81	0.21	0.17	−0.12	−0.20	−0.20	−0.02	−0.15	−0.18	−0.21	−0.06	0.19	0.09	−0.06
Na			1.00	0.32	0.23	−0.01	−0.23	−0.39	−0.09	−0.23	−0.25	−0.05	−0.19	−0.01	−0.01	−0.01
K				1.00	−0.05	−0.07	−0.19	−0.35	−0.02	−0.69	−0.09	0.13	−0.07	0.10	0.18	0.01
Ca					1.00	0.88	−0.17	−0.06	−0.20	−0.33	−0.40	0.57	−0.30	−0.19	−0.36	−0.41
Mg						1.00	−0.26	0.06	−0.25	−0.36	−0.47	0.18	−0.31	−0.31	−0.46	−0.44
Fe							1.00	0.20	0.06	0.34	0.37	−0.17	0.66	0.47	0.47	0.53
P								1.00	−0.30	0.07	0.13	−0.20	0.42	0.32	0.21	0.24
Zn									1.00	−0.01	−0.03	−0.17	0.17	−0.80	0.01	0.04
Pb										1.00	0.83	−0.41	0.45	0.52	0.72	0.37
Co											1.00	−0.45	0.39	0.40	0.37	0.37
Cd												1.00	−0.16	−0.32	−0.42	−0.23
Ni													1.00	0.71	0.71	0.83
Mn														1.00	0.75	0.61
Cr															1.00	0.66
Cu																1.00

1992; Real and others 1993; Table 9). However, certain sites in the interior undistributed channels (Figs. 3, 4) have higher concentrations of metals. The higher concentrations were patchy and vary from one metal to another. This also supports the unique chemical behavior of the mangrove sediments. In the suspended sediments, metal concentrations behave conservatively with chloride content (Fig. 4; Table 7). This indicates the flocculation of metals attached to the suspended sediments, causing deposition and metal enrichment in the mangrove surface sediments (Ramanathan and others 1993).

Factor analysis of elementar data on mangrove sediments indicates five trends (Table 8) using 16 variables; an average of 80% of the total elemental variability was accounted for by five composited factors. Table 8 also indicates the loading of each variable accounted for in the analysis. The data can be interpreted as: factor 1 shows the contribution from detritals and clays; factor 2 from carbonate concretion; factor 3 from biogenic processes; factors 4 and 5 from fertilizer input and anthropogenic activities. Table 10 also shows that poor to negative correlation exists between almost all the metals. It should be noted that most of the elements are not well represented by these statistical analysis. So, such an interpretation should be used with caution for a complex system like mangroves where there are a multitude of contributing sources. The average metal concentration is comparable to the average values of shale and soil (Table 9). Enrichment factors (metal/Al ratio) are also less when compared to the average values of shale and soil (Ravichandran and others 1995). The observations suggest that the mangrove is relatively unpolluted and may be acting as a sink for heavy metals contributed from a multitude of sources.

The sedimentary core chemistry has also been studied to obtain an insight into the impact of agriculture, urban and other anthropogenic activities in the recent past in this ecosystem. Si, Al, P and Cd show an increasing trend, and Fe, Cu and Pb shows a decreasing trend with depth (Fig. 5). In the middle depth, fluctuation (increase or decrease) in certain metal concentrations is also observed. Though some metal concentrations in the mangrove increase almost by a factor of 1 in comparison to average shale/soil (Table 9), the metal/Al ratio is often

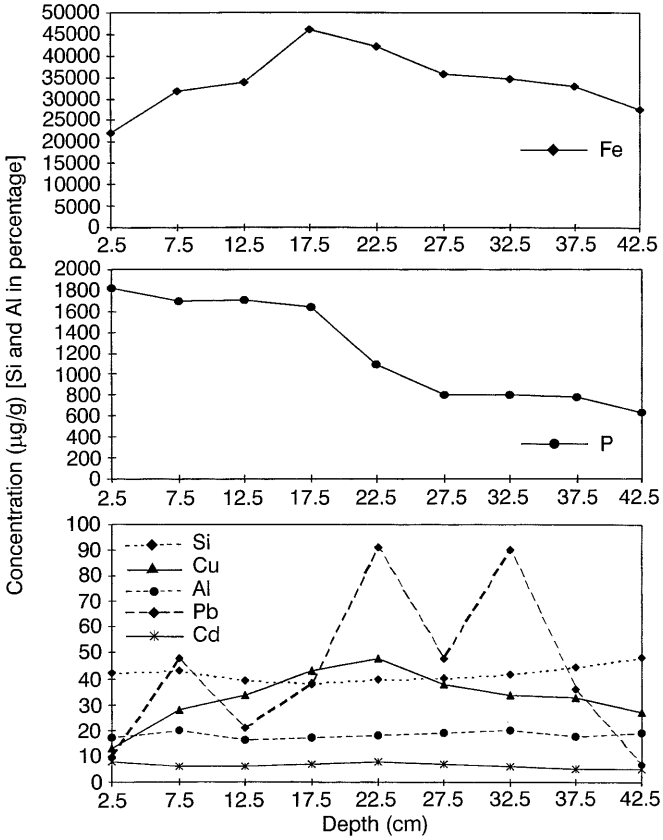

Fig. 5
Vertical profile of certain elements in sediment core (sampling station no. 6)

less than average shale with a few exceptions (Ravichandran and others 1995). The decrease of metal concentrations is due to less input of metal associated with detritals from source rock weathering (due to dam construction). A marginal increase in metals is due to anthropogenic inputs. The fluctuations of metal concentration in certain depths may be attributed to leaching, metal uptake by vegetation and post-depositional remobilization (Ramanathan and others 1996).

Conclusion

1. Higher pH values are due to the mixing effect and photosynthetic activity.
2. TDS increase from about 9‰, to 28‰ in the summer and in the interior channels. Chloride and sulphate contribute 70% of the total ions in the mangrove water.
3. Silica budget in the mangrove seems to be controlled by biological processes. Nitrate and phosphate are contributed from anthropogenic sources. Sodium is the dominant cation (80%) followed by Mg, Ca and K.
4. Statistical analysis confirms the multiple sources controlling mangrove water chemistry.
5. The erratic TSM behavior is primarily due to deforestation, tidal and wind action.
6. Sand and silt constitute 70–90% of the mangrove sediments followed by clay. Sediments are moderately to poorly sorted, coarsely skewed and platy to leptokurtic in nature.
7. Chemical and statistical analysis of the sediments suggest that the mangrove is relatively unpolluted, with unique chemical behavior and a multitude of sources, along with the existence of a trapping mechanism.
8. The core sediment chemistry suggests that the lesser input of metals is associated with detritals due to dam construction.
9. The study reveals the lesser impact of anthropogenic signatures in the Pichavaram mangrove ecosystem.

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