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Geochemical fractionation of heavy metals in Chilka Lake (east coast of India)—a tropical coastal lagoon

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Abstract Chilka lake, the largest coastal lagoon of Asia is one of the most dynamic ecosystems along the Indian coast. Historically the lagoon has undergone a considerable reduction in surface area due, in part, to input from natural processes but mostly due to human activities. The purpose of this investigation is to document the heavy metals' affinity for specific geochemical phases in the recently deposited sediments in the lagoon. Thirty-three samples were collected and analyzed for different geochemical phases of Fe, Mn, Cu, Cr, Ni, Pb, and Zn utilizing a sequential extraction scheme. In the nonlithogenous fraction, the exchangeable fraction was not geochemically significant, having <2% of the total metal concentration for all the elements. However, the carbonate fraction contained the following percentages of the total concentration: <1% Fe, 13% Mn, 6% Cu, 4% Cr, 8% Ni, 13% Pb, and 12% Zn, suggesting the detrital origin of the sediments. Reducible and organic matter-bound fractions were the significant phases in the nonlithogenous fraction, containing 9% Fe, 16% Mn, 15% Cu, 16% Cr, 16% Ni, 14% Pb, and 14% Zn in the former and 4% Fe, 3% Mn, 17% Cu, 3% Cr, 14% Ni, 15% Pb, and 14% Zn in the latter. The phenomenon has been attributed to the scavenging affinity of Fe–Mn oxides and affinity for sorption into organic matter of the lagoon sediments. The lithogenous, residual fraction generally considered as a guide for natural background values was determined to contain 87% Fe, 67% Mn, 61% Cu, 77% Cr, 61.3% Ni, 56% Pb, and 60% Zn of the total concentrations.

Key words Coastal lagoon · Chilka Lake · Sediment · Heavy metals · Chemical fractionation

Introduction

The bottom sediment of aquatic systems can be a major trap for metals. The processes that contribute to the accumulation of these elements in the bottom sediments include adsorption to surfaces of organic particles, clays, and silts; particles settling from the overlying water; and bioaccumulation by benthic organisms (Salomons and Forstner 1984; Elder 1988, 1994; Horowitz 1991; Farrah and Pickering 1993). Thus, in aquatic systems sediments may be both carrier and potential sources of pollutants (Forstner and Muller 1974). Furthermore, pollutants are not necessarily fixed permanently to sediment, but may be recycled via biological and chemical agents within both the sedimentary column and the water column (Forstner 1985). Within the sedimentary column, metals are commonly partitioned into mineral structures, hydrates, sulfides, amorphous hydrous oxides, and organic particles (Forstner 1990). In addition, each element has specific partitioning tendencies with respect to these forms (Tessier and others 1979, 1980). The association of metals with sediments is complicated by the likelihood of their enrichment on particles of smaller grain sizes (Horowitz and Elrick 1987; Elder 1988, 1994; Horowitz 1991).

Heavy metals, in contrast with most pollutants, are not biodegradable and undergo a global ecobiological cycle in which natural waters are the main pathways (Nurnberg 1984). Various remobilization mechanisms of bed sediments including physical resuspension (Bengtsson and others 1990), geochemical remobilization from organic matter (Breteler and Saska 1985); dissolution of hydrous oxides of iron and manganese (Jenne 1968; Horowitz 1991); biomethylation (D'Itri 1990; Winfrey and Rudd 1990), and other biological processes (Elder and Collins 1991) can cause release of these elements to the water column. Additionally, these categories have different behaviors with respect to remobilization under changing environmental conditions (Forstner 1985). Therefore, knowledge of the total content of heavy metals in a sediment does not give a complete picture of the environmental

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situation. Thus, it is vital to perform partitioning studies with the sediment to assess accurately the ecotoxic potential.

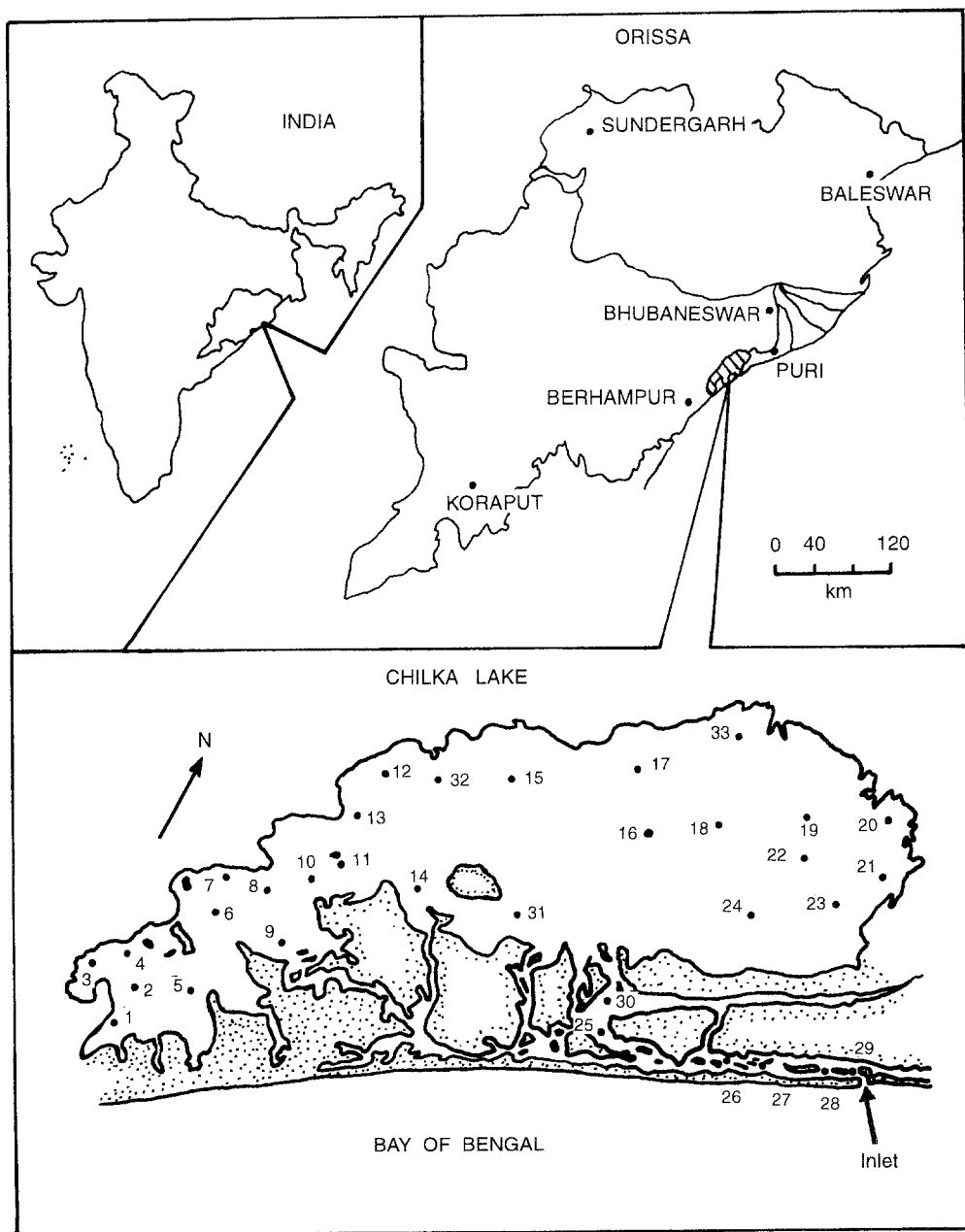
Several studies have been performed on the distribution of heavy metals in coastal lagoon sediments (Harbridge and others 1976; Mallik and Suchindan 1984; Paez-Osuna and others 1986; Nadeau and Hall 1988; Nair and others 1990; Nair and Balchand 1993; Fernandes and others 1991, 1994, Haung and others 1994, Zonta and others 1994). However, most of these studies have reported only the bulk sediment concentration with only a few chemical fractionation studies. The current paper reports for the first time the results of a study undertaken on chemical fractionation of heavy metals in the recently deposited sediments collected from Chilka lagoon and also evaluates

the magnitude of the different types of metals in the sediment.

Study area

Chilka Lake, the largest coastal lagoon of Asia, with an average water surface area of 1054 km², is located along the east coast of India (lat. 19°28'–19°54'N and long. 85°05'–85°35'E). It is one of the first two wetlands placed by India under the Ramsar Convention (IUCN 1987) on Wetland of International Importance. Oriented parallel to the coast between the Eastern Ghats (mountain ranges flanking the east coast of India) and the Bay of Bengal.

Fig. 1 Map of Chilka lake and sample locations



The lagoon connects the Bay of Bengal through a long, narrow channel and is separated by a 60-km-long narrow spit. The Daya and Bhargavi, distributaries of Mahanadi River, enter the lagoon from the north, and many small streams occur along its western margin. Rocky hills composed of hard metamorphosed Precambrian rocks (garnet-sillimanite gneisses, quartzites, and charnockites) project as promontories in the lagoon. The lagoon is shallow, with an average depth of 1.5 m. The tidal range is about 80 cm in the sea inlet area and a few centimeters (not more than 10 cm) in the innermost reaches. A salinity gradient is observed from north to south, increasing exponentially from the innermost reaches of the sea inlet. Water circulation is mainly wind driven. Panda (1993) classified the lagoon based on the geomorphological classification of Kjerfve and Magill (1989) as a choked lagoon.

Methodology

Sampling

Surface sediments were collected during June 1988 using a Peterson Grab sampler at 33 locations in the lagoon (Fig. 1) and placed in acid-rinsed plastic containers. Precautions were taken to prevent contamination during sample collection and handling.

Choice of method and chemical fractionation experiments

Several chemical extraction schemes have been proposed (Chester and Hughes 1967; Gibbs 1977; Tessier and others 1979; Shuman 1982, 1985; Archer and Hodgson 1987; Campbell and Tessier 1987) that utilizes a series of extractants in order of increasing strength, so that each speciation category is sequentially released from the sediment. However, most of the sequential extraction methods exhibit uncertainties (Rendell and others 1980; Tipping and others 1985; Rapin and others 1986; Kheboian and Bauer 1987; Bermond and Sommer 1989; Sholkovitz 1989). The major problems are related to the pretreatment of the samples (drying and storage), the reagents used in the sequential extraction, and readsorption of elements onto solid phase after each chemical attack. It has also been noted that the efficiency of an individual sequential extraction method depends upon sample composition (granulometry and mineralogy), chemical reagents used, and the intensity (temperature, pH, liquid-to-solid ratio) in each attack. Therefore, it is very difficult to choose and compare the results between different selective extraction methods. With regard to complexity of natural elements associated with solid phases, sequential extraction presently may be the best approach in describing the geochemical association of elements, as this procedure develops a direct estimate of mobility and bioavailability of elements in the natural environment. Based on this, the method of Tessier and others (1979) was used in this study, since

it is relevant to the chemical properties of Chilka lagoon sediments (high pH, low organic carbon and carbonate) (Panda 1993).

The chemical fractions and reagents used in the sequential experiments are summarized below, as details are given in Tessier and others (1979):

- | | |
|-------------------------------|---|
| a) Exchangeable fraction (F1) | 1 M MgCl ₂ , pH 7.0 |
| b) Carbonate fraction (F2) | 1 M NaOAc adjusted to pH 5.0 with HOAc |
| c) Reducible fraction (F3) | 0.04 M NH ₂ OH · HCl in 25% (v/v) HOAc |
| d) Organic fraction (F4) | 30% H ₂ O ₂ at pH 2.0 adjusted with conc. HNO ₃ followed by addition of 3.2M NH ₄ OAc in 20% (v/v) HNO ₃ |
| e) Residual fraction (F5) | Mixture of HF, HNO ₃ and HClO ₄ acid |

For total concentration, sediments were digested in Teflon bombs with a mixture of aqua regia and HF. Solutions were analyzed using an atomic absorption spectrophotometer (GBC-902 model), according to manufacturer's conditions, including background correction. Standard reference samples (USGS rock standards MAG-1, SCO-1 and SGR-1) were analyzed along with the sediment samples.

The concentrations of Fe, Mn, Cu, Cr, Ni, Pb, and Zn in each of the leachates were determined by atomic absorption spectrophotometry. Triplicates of each leachate were analyzed. The results are within a 5% limit. Blank values were negligible for all elements under consideration, which indicated the rather high purity of the reagents used. For matrix effects, four equal aliquots of the sample (Ni) were taken, and varying amounts of standards were added to three of the aliquots, up to the same final volume and analyzed. Results were plotted on an absorbance vs concentration curve that extends the concentration axis to the left of zero as well. The resultant curve was used as the calibration curve for the other elements.

Results and discussion

Heavy metal affinity for geochemical phases

The range, mean, standard deviation, and coefficient of variation in total and in different chemical fractions of the metals Fe, Mn, Cu, Cr, Ni, Pb, and Zn for Chilka lagoon sediments are given in Table 1.

Exchangeable fraction

Heavy metals in exchangeable positions are authigenic as well as contributed from natural source. Metals in this

Table 1 Metal contents (in ppm, Fe in %) in geochemical phases of sediments^a

Geochemical phases	Fe	Mn	Cu	Cr	Ni	Pb	Zn
Exchangeable	bdl ^a	<1.0–5.0 ^b	0.06–1.37	bdl–0.62	bdl–1.92	0.28–1.48	0.03–0.17
		(2.0)	0.43	0.16	0.56	0.67	0.08
		[1.0]	0.28	0.13	0.41	0.28	0.04
		{50}	66	82	73	41	50
Carbonate	0.01–0.08	17–67	0.6–7.6	0.1–3.6	2.9–16.5	3.5–8.3	2.25–7.97
	0.03	38	3.1	1.3	7.8	5.3	4.93
	0.02	14	1.95	0.73	2.8	1.28	1.39
	66	37	63	57	35	22	28
Reducible	0.11–0.77	13–119	1.13–17.26	0.49–13.17	5.35–39.4	3.38–12.21	2.46–11.91
	0.38	52	7.88	6.14	17.7	6.02	6.10
	0.17	23	5.04	3.50	6.9	2.29	2.73
	44	45	63	57	39	38	44
Organics	0.07–0.28	2–23	1.75–15.78	0.2–2.89	6.84–29.43	3.86–9.33	2.85–9.47
	0.17	11	8.48	1.20	15.20	6.07	5.88
	0.06	6	4.89	0.71	4.74	1.55	6.61
	39	53	57	58	31	25	26
Residual	1.47–5.87	78–405	6.5–61.3	3.3–58.1	35.3–116.5	14.9–32.4	13.2–36.5
	3.6	210	30.47	28	64	23	25
	1.0	85	17.26	13.98	16.2	4.9	6.6
	27	40	56	50	25	21	26
Total	1.66–5.87	114–595	10–101	4–74	52–143	28–59	21–63
	4.2	314	50	37	106	41	42
	1.2	125	29	19	29	9	12
	28	39	57	49	27	28	28

^a bdl—below detectable limits

^b Value are range, () mean, [] standard deviation, { } % coefficient of variation

phase are readily available and relatively mobile for biological uptake, a process facilitated by the lowered pH of the digestive systems of many bottom-dwelling organisms (Copeland and Ayers 1972). Concentrations determined for exchangeable Fe, Cu, Cr, Ni, and Zn are lower than their respective detection limits; low concentrations of Pb (<1.0–1.5 ppm) and Mn (5 ppm) are also noted. The low concentration of the exchangeable fraction suggests poor elemental availability to the bottom-dwelling organisms in this environment and can be attributed to the high pH (8.0–9.0) (Panda, 1993) of the sediments as an alkaline condition induces a decrease of available trace elements. Sediment pH has a direct relationship to the availability of metals, as it effects their solubility (high pH decrease solubility of most metals) and capacity to form chelates in the sediment (Forstner and Wittmann 1981). Experimental studies by many researchers reported by Forstner and Wittmann (1981) noted that heavy metals sorbed onto solid particles carried by river water and other freshwater systems are desorbed to various extents when these solutions are mixed with naturally occurring high pH water. Thus, it may be stated that the exchangeable fraction is the least geochemically significant fraction in Chilka lagoon sediments.

Carbonate-bound fraction

Heavy metals in the carbonate fraction of sediments may be either detrital or authigenic because many metals have

carbonate species that are stable at natural pH and Eh conditions (Stumm and Morgan 1970). The carbonate fraction accounts for a relatively small amount of the total elemental concentrations in this environment. The concentration determined for Fe in this fraction is lower than the detection limit; the levels of Ni, Cu, and Cr, although detectable, remain low (<8%) and comparable to the total concentration (Table 1). For Mn, Pb, and Zn, however, the observed concentrations represent an appreciable proportion to the total metal: 9.1–19.7% Mn, 10.0–14.3% Zn, and 10.3–15.0% Pb. The absolute concentrations follow the order Pb > Mn > Zn > Ni > Cu > Cr > Fe for each sediment. The calcium carbonate concentration content of the sediments of Chilka lagoon varies between 1.5 and 8.0% with the average being 4.2% (Panda 1993), characterizing a very low CaCO₃ content. The results of Paropkari and others (1980) show that even in sediments having 75–90% CaCO₃, the carbonate phase is not a significant contributing factor to the trace metal content of the sediments. Thus, the low carbonate content of the lagoon sediment precludes the possibility of this phase making any significant contribution to the amount associated with the carbonate phase of sediments. However, the relatively higher percentage of carbonate fraction for Pb, Mn, and Zn are most likely the result of similarity in their ionic radii to that of calcium, which allows them to substitute Ca in the carbonate phase (Pederson and Price 1982; Zhang and others 1988). Therefore, this fraction reflects the distribution of detrital calcite and dolomite as well as biogenic decomposition in the lagoon.

Reducible fraction

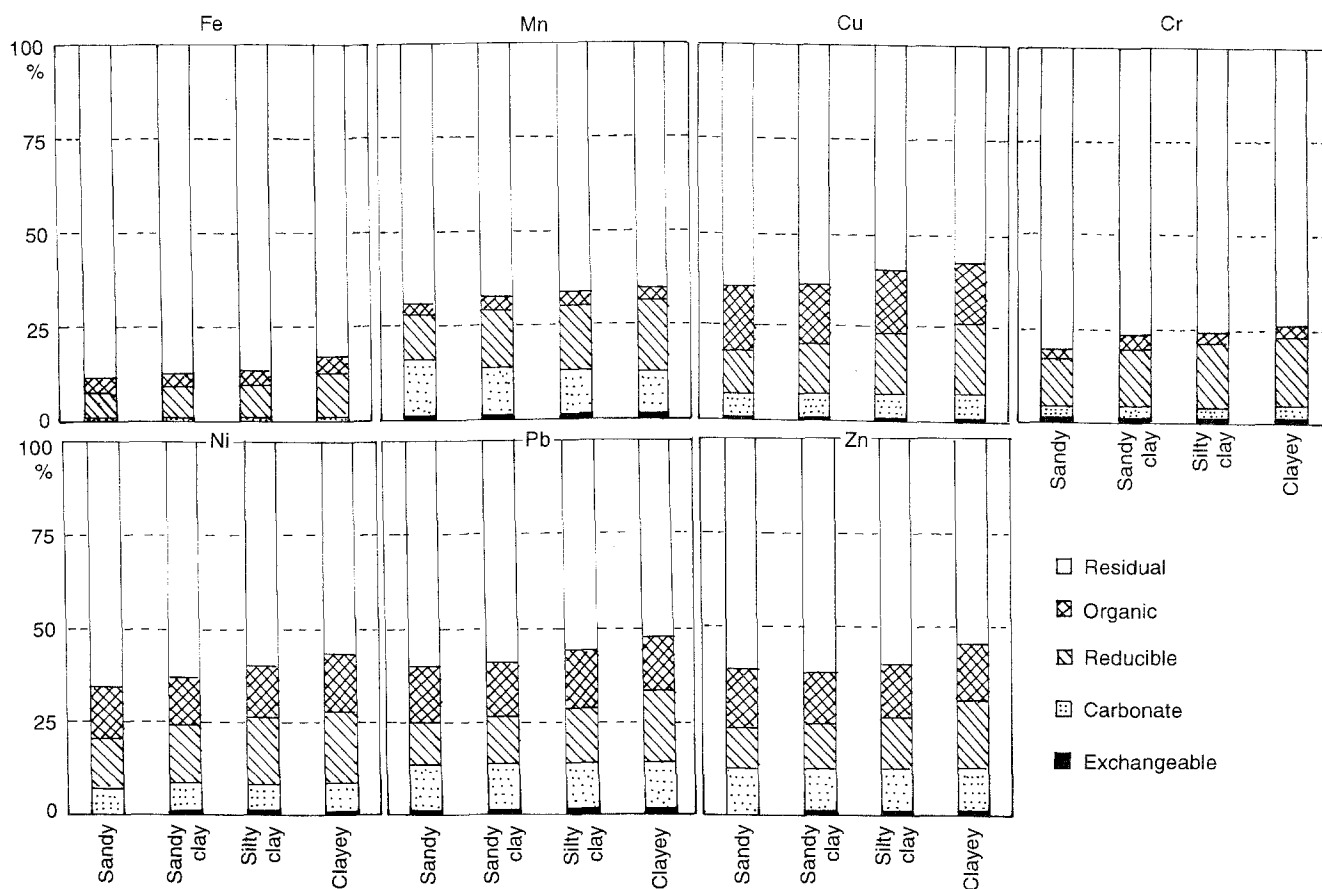
Heavy metals are bound to reducible phases associated with hydrous Fe–Mn oxides either by coprecipitation or by sorption onto preexisting coatings. These processes are very sensitive to change in redox potential, and minor station-to-station variations may greatly effect the relative amounts within this fraction. It is the most important among the labile fractions (F1–F4) and ranges from 6–13.6% for Fe, 11–20.1% for Mn, 10.8–20.1% for Cr, 10.1–19.2% for Cu, 10.3–19.4% for Ni, 10–20% for Zn, and 10.3–19.7% for Pb. The absolute concentrations in this fraction follow the order Ni > Mn > Cr > Cu > Pb > Zn > Fe for each sediment in the environment. Relatively higher concentrations of Fe and Mn in this phase are attributed to the flocculations of colloids of Fe and Mn transported to the lagoon via rivers and ephemeral streams. On the basis of laboratory experiments corroborated by field measurements, Singh and Subramanian (1984) explained that colloids of Fe–Mn oxides act as efficient scavengers for many of the heavy metals (Fe, Mn, Cu, Ni, Zn, etc.). Furthermore, it may be explained that the relatively higher concentrations of other elements such as Cu, Cr, Ni, Pb, Zn, etc., associated with this fraction are caused by the adsorption of these elements by the colloids

of Fe and Mn (Jenne 1968). It is also reasonable to suppose that the relationship existing between Fe and Mn hydroxides and other elements should be good, but in reality this is not so in case of Mn ($r^2 = 0.23$). Thus, it is believed that a single Fe phase could reveal important information about the heavy metal content in the sediment that would not appear in the combined Fe–Mn phase. However, no data are available for chemical forms of trace elements in single Fe fractions to substantiate this premise.

Organic matter-bound fraction

The organic matter-bound fractions are normally <7% of the total concentration for Fe (1.2–6.7%), Mn (2.5–5.6%), and Cr (2–6%), but in the remaining metals are present in relatively significant proportions of the total metal concentration: 11.5–18.8% Cu, 10.4–20.9% Ni, 12.1–17.2% Pb, and 12.1–18.1% Zn. The absolute concentrations in the organically bound fraction follow the order Cu > Pb > Ni > Zn > Fe > Mn > Cr for each of the sediments. Heavy metals become associated with organic matter through biological uptake and adsorption with subsequent incorporation into resistant organic degradation products, such as humic substances. In Chilka lagoon sediments organics are probably the major source of metal in this fraction because all metals that have high concentrations in this fraction also correlate with organic content. The lower percentage of Fe in this phase probably results

Fig. 2 Partition of heavy metals in different fractions in each of the sediment types present in Chilka lake



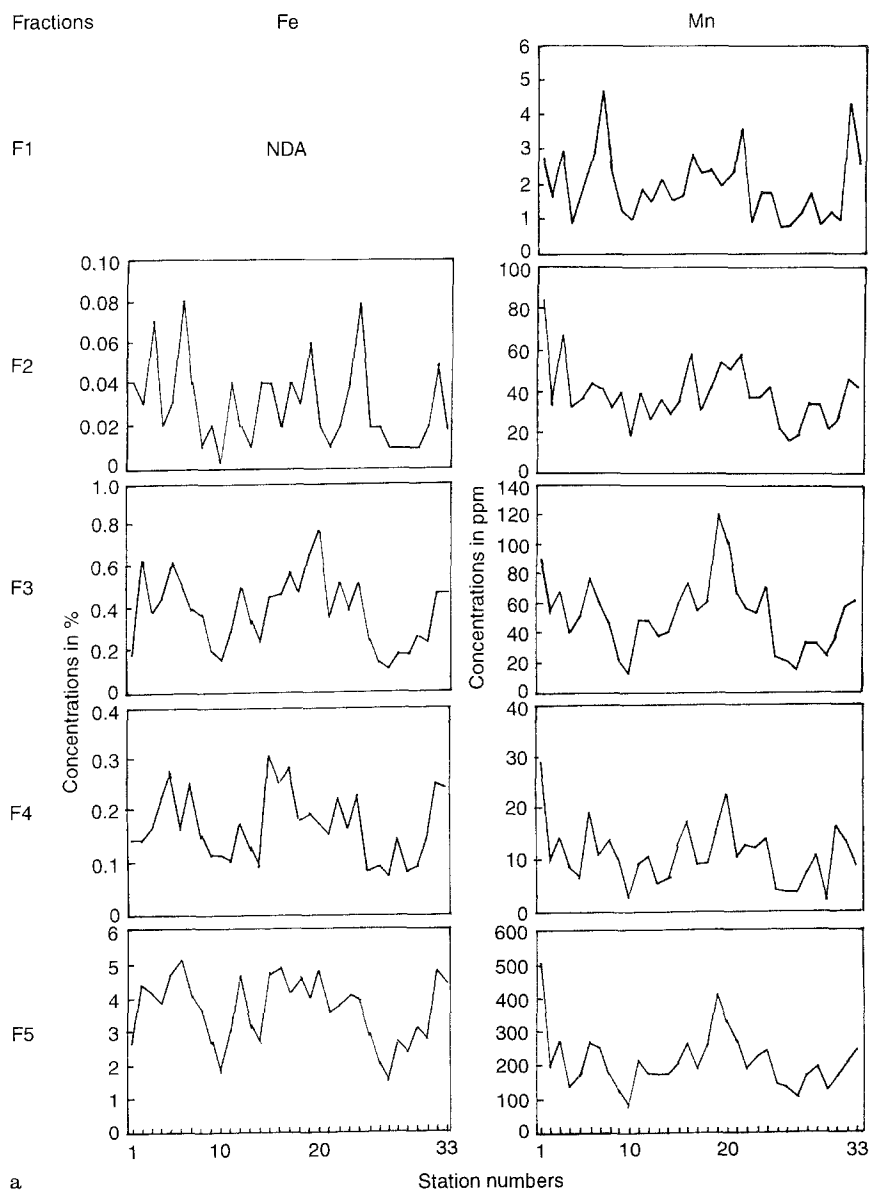
from competition between Fe-organic complex and hydrous Fe oxide forms.

Residual fraction

Trace metal concentrations in the residual or inert fraction are higher than those observed in any of the preceding extractions, representing more than 50% of the total metal concentration: 81.2–89.5% Fe, 62.1–75% Mn, 50–63.2% Pb, 72.1–84.2% Cr, 53.4–70.9% Ni, 50.2–66.3% Zn and 54.4–68.8% Cu. The absolute concentration follows the order Fe > Cr > Mn > Ni > Cu > Zn > Pb for each sediment. It can be seen from Fig. 2 that the grain size of the sediment has no appreciable influence on the distribution of elements associated with different geochemical phases. This is in contrast to the general belief that higher quan-

ties of heavy metals accumulate on finer grain sizes and can be attributed to the large aggregation of particles (Panda 1993), as in conditions where the sediments contain a significant fraction of flocculent-aggregate particles that can have abnormally high adsorptive capacities, some deviation from conventional grain size/concentrations relationship may be expected. Further, Panda (1993) showed that mineralogy and heavy metal concentrations in the lagoon are primarily controlled by source materials (adjoining hinterland, barrier islands, etc.). This feature reflects the predominance of physical weathering, high erosion rates along the drainage basin, and high sedimentation rates in the lagoon. The metals present in the residual fraction can be used as a guide to the degree of contaminant of the system: the greater percentage of metal present in the category, the lower the pollution, because this inert phase corresponds to detrital or lattice bound metals that can not be remobilized (at least under normal

Fig. 3 a The trends of Fe and Mn content in geochemical phases of the sediments (NDA represents nondetectable amount and F1, F2, F3, F4, and F5 represent exchangeable, carbonate, reducible, organic and residual fractions, respectively), b The trends of Cu and Cr content in geochemical phases of the sediments (F1, F2, F3, F4, and F5 represent exchangeable, carbonate, reducible, organic, and residual fractions, respectively), c The trends of Ni and Pb content in geochemical phases of the sediments (F1, F2, F3, F4, and F5 represent exchangeable, carbonate, reducible, organic, and residual fractions, respectively), d The trends of Zn content in geochemical phases of the sediments (F1, F2, F3, F4, and F5 represent exchangeable, carbonate, reducible, organic, and residual fractions respectively)



polluting circumstance); the lower percentage in this category indicates higher pollution. The results show the relative unpolluted nature of the Chilka lagoon environment at the time of sampling. Thus, it can be concluded that the concentration of heavy metals in Chilka lagoon sediments are controlled by mineralogy of the land-derived fragments and the effect of man-made enrichment upon absolute concentration is minimal.

Heavy metal trends in geochemical phases of sediments

Trends occurring in the heavy metal content in geochemical phases of the sediments are shown in Fig. 3. The percentage composition of different geochemical fractions of heavy metals is given in Fig. 4.

Based on the mean content of heavy metals in Table 1,

the following metals appear to concentrate in the geochemical phases of the sediments in the following order:

Fe: Residual > Reducible > Organic > Carbonate > Exchangeable

Mn: Residual > Reducible > Carbonate > Organic > Exchangeable

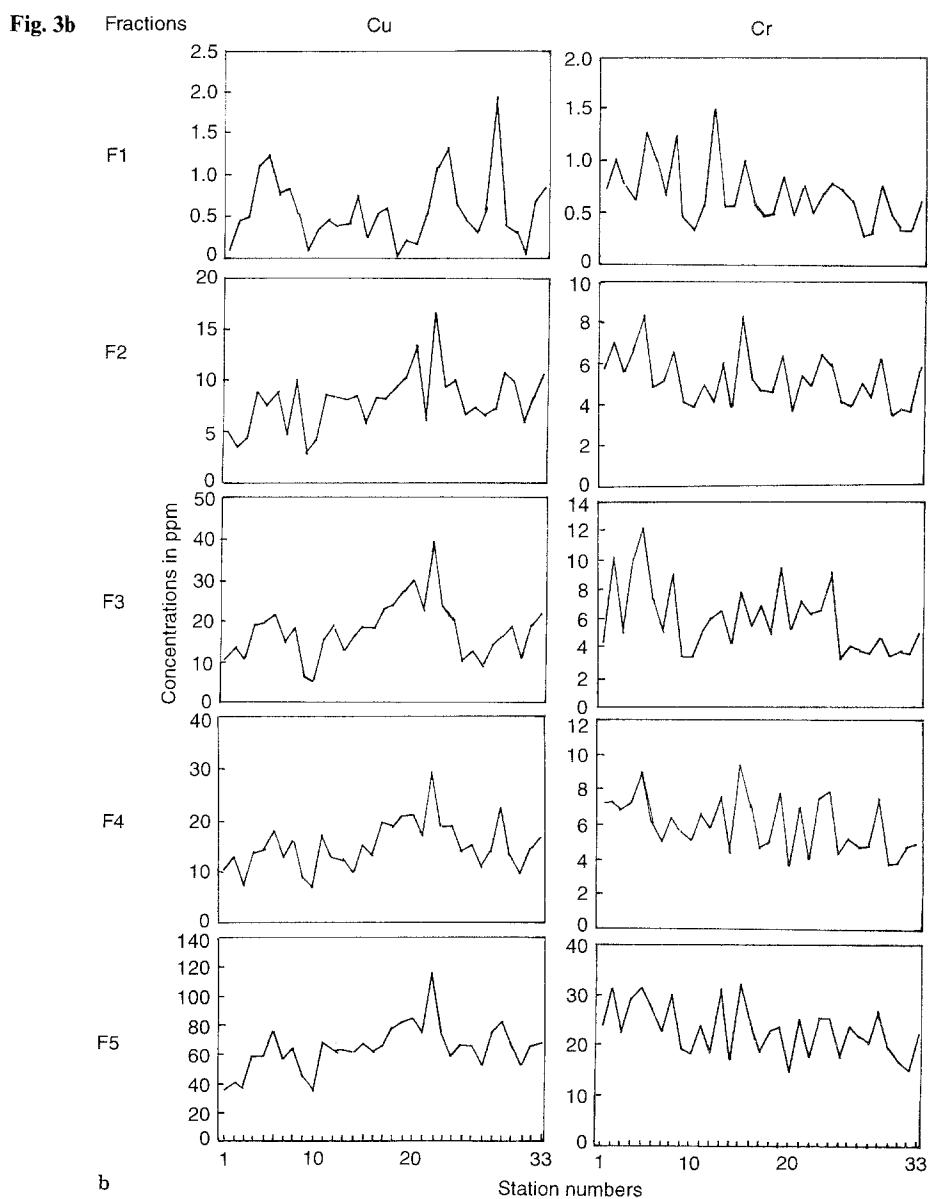
Cu: Residual > Organic > Reducible > Carbonate > Exchangeable

Cr: Residual > Reducible > Carbonate > Organic > Exchangeable

Ni: Residual > Reducible > Organic > Carbonate > Exchangeable

Pb: Residual > Organic > Reducible > Carbonate > Exchangeable

Zn: Residual > Organic > Reducible > Carbonate > Exchangeable



High quantities of certain metals are present in some parts of the lagoon. A statistical method (Rose and others 1979) was used to indicate the sample numbers having anomalous or significant high heavy metal values. Table 2 lists the sample numbers of the heavy metals that have anomalously high values in the geochemical phases. Almost 60% (20 of 33) sites exhibited an anomalous value for at least one metal in one geochemical phase. It is evident that no sample frequently repeated for many of the heavy metals. Hence, it is not possible to unequivocally determine if this is the result of contamination from anthropogenic sources, since there is no point source for these metals. This may be due to localized natural elevated concentrations of metals, without any anthropogenic input in these sites.

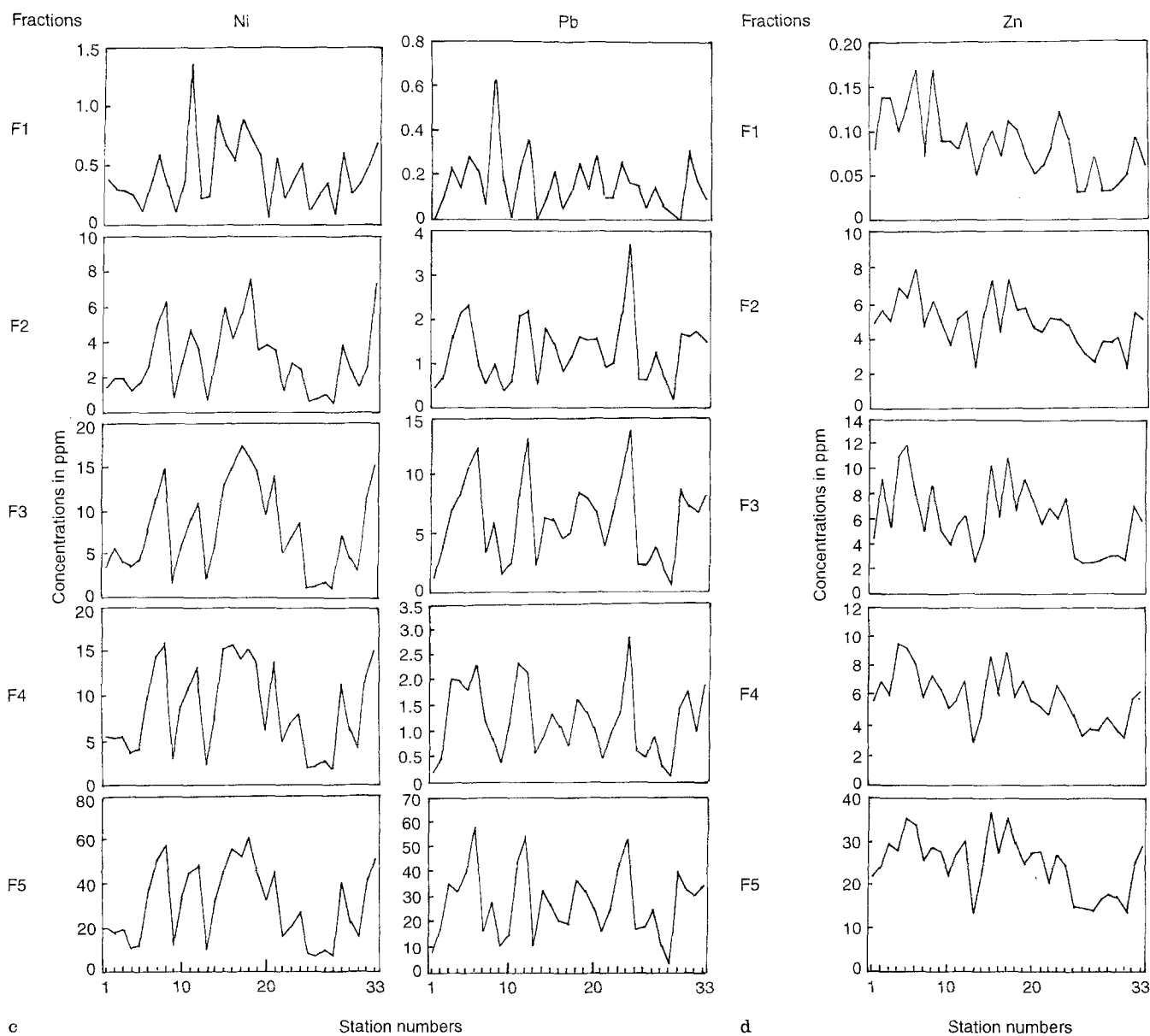
Table 2 Sample numbers with anomalous high metal values in the geochemical phases

Geochemical phases	Fe	Mn	Cu	Cr	Ni	Pb	Zn
Exchangeable	—	7, 32	11	8	28	5, 12	6, 8
Carbonate	6, 24	1	18, 33	—	22	5, 15	6
Reducible	20	19, 20	—	12, 24	22	5	5
Organics	—	1, 20	—	24	22	15	4
Residual	—	1, 19	—	6	22	—	—

Comparison of geochemical extraction phases with single extraction

A total extraction quantity for each heavy metal was determined by summing the quantities of the heavy metals within each geochemical phase for each sample location.

Fig. 3c, d



c

d

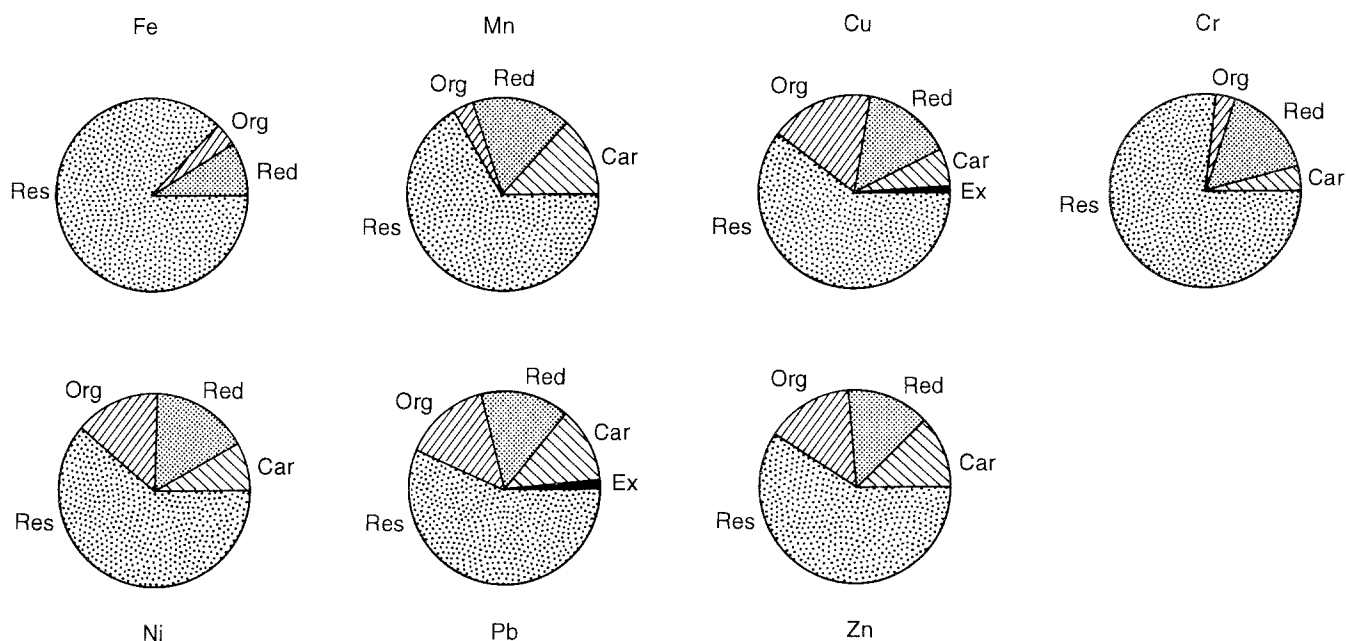


Fig. 4 Average concentration of heavy metals in different geochemical fractions of sediments (Ex, exchangeable; Car, carbonate; Red, reducible; Org, organic; and Res, residual fraction)

This is identified as combined extraction, and the aqua regia + HF digestion method as a single extraction method. The heavy metal concentrations for all metals for both extraction procedures compare favorably and are quite similar (Fig. 5). Figures for individual metals for comparison are provided in Panda (1993) and are available on request, but for the sake of brevity are not included here.

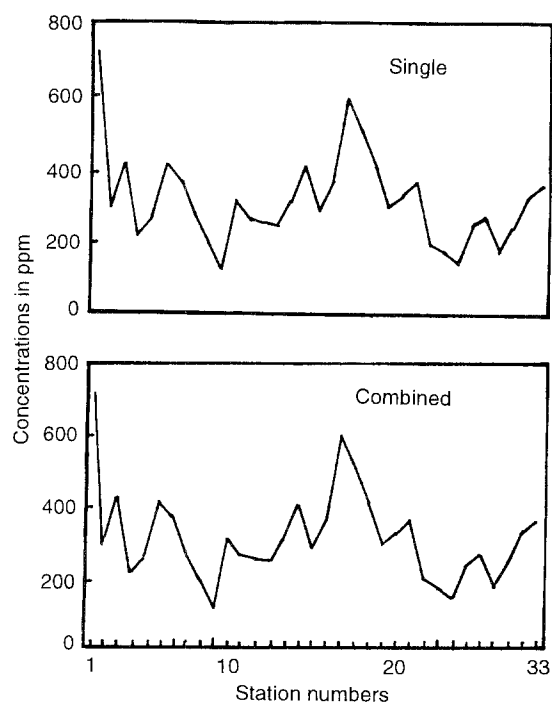


Fig. 5 Comparison of the trends of total Mn content in the combined and single extraction procedure

Table 3 Percentage composition of lithogenous and nonlithogenous fractions of heavy metals in Chilka lagoon sediments

Heavy metals	Lithogenous fraction	Nonlithogenous fraction
Fe	86.5	13.5
Mn	67.2	32.8
Cu	61.0	39.0
Cr	76.8	23.2
Ni	61.3	38.7
Pb	58.4	41.6
Zn	59.6	40.4

are provided in Panda (1993) and are available on request, but for the sake of brevity are not included here.

Pollution status

The low concentration of the nonlithogenous fraction (Table 3) suggests the poor element availability to the biota in this environment. When attempting to determine the extent of pollution of heavy metals in the sediments in this environment, it is of primary importance to establish the natural level of these substances, i.e., precivilization

Table 4 Geoaccumulation indices in Chilka lagoon

I_{geo} class	I_{geo}	Elements
>5	6	Ni, Pb Fe, Mn, Cu, Cr, Zn
4-5	5	
3-4	4	
2-3	3	
1-2	2	
0-1	1	
<0	0	

Table 5 Distribution of metal species from different geographical locations (in ppm)^a

Fractions	Fe							Mn							Cu							Pb							Cr							Ni							Zn							
	1	2	3	4	5	6	7	1	2	3	4	5	6	7	1	2	3	4	5	6	7	1	2	3	4	5	6	7	1	2	3	4	5	6	7	1	2	3	4	5	6	7	1	2	3	4	5	6	7	
Exchange	bdl	bdl	—	bdl	2.7	bdl	18.40	49.56	5.00	6.17	70	20	0.74	0.43	bdl	0.67	0.03	0.34	—	0.16	0.16	0.12	94.86	—	0.84	bdl	0.67	14.00	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	
Carbonate	<0.01	—	294	106	606	300	87.73	84.00	18.63	603	38	3.40	3.10	1.7	5.30	0.32	—	3.53	1.94	2.2	1.30	1.47	2.61	36	7.80	0.40	—	55.88	7.80	7.80	7.80	7.80	7.80	7.80	7.80	7.80	7.80	7.80	7.80	7.80	7.80	7.80	7.80	7.80	7.80	7.80	7.80	7.80	7.80	
Reducible	0.01	0.05	4117	93	1082	3800	22.64	186.56	18.00	6.33	47	52	2.40	7.88	2.3	6.02	0.32	<3.38	9.41	0.78	1.3	6.14	5.00	1.35	13	17.70	1.20	322.35	29.41	17.70	17.70	17.70	17.70	17.70	17.70	17.70	17.70	17.70	17.70	17.70	17.70	17.70	17.70	17.70	17.70	17.70	17.70	17.70	17.70	17.70
Organics	0.10	<0.02	588	144	137	1700	48.11	23.32	5.00	13.26	35	11	0.24	8.48	bdl	6.07	6.08	20.28	4.71	5.75	2.7	1.20	1.18	2.50	42	15.20	9.60	73.68	20.59	15.20	15.20	15.20	15.20	15.20	15.20	15.20	15.20	15.20	15.20	15.20	15.20	15.20	15.20	15.20	15.20	15.20	15.20	15.20	15.20	15.20
Residual	0.91	1.08	4117	3241	—	36000	76.41	99.11	21.00	19.70	—	210	—	30.47	—	23.00	18.24	23.66	27.07	20.77	—	28.00	10.29	11.27	—	64.00	20.40	119.73	14.71	64.00	64.00	64.00	64.00	64.00	64.00	64.00	64.00	64.00	64.00	64.00	64.00	64.00	64.00	64.00	64.00	64.00	64.00	64.00	64.00	64.00

^a Yellow river (Hong and Forstner 1984); 2, Rhine river (Hong and Forstner 1984); 3, Bate De Nice river (Rapin 1984); 4, Cochin estuary/lagoon (Nair and Balchand 1993); 5, Arabian Gulf (Abayachi and Douabul 1986); 6, this study—Chilka lagoon; 7, Weser estuary (Calmano and Forstner 1983). bdl: below detection limit; —: not cited in the literature; Exchange: exchangeable

level. Fossil argillaceous sediments (average shale) is a worldwide standard in general use and satisfies the basic requirement of being uncontaminated and based, for most elements, on a large number of sediment samples. In this study also average shale is used as a reference to trace metal enrichment in Chilka lagoon sediments. A quantitative measure of the extent of pollution in Chilka lagoon was calculated from the heavy metal concentration in the sediment using the method of Muller (1979), which is known as an index of geoaccumulation (I_{geo}). This is defined as $I_{geo} = \log_2 C_n/1.5B_n$, where C_n is the measured concentration of heavy metal n in the sediments or size fraction and B_n represents the geochemical background concentration of metal in n , either found in the literature or measured directly in texturally equivalent uncontaminated sediments or size fraction. The factor of 1.5 is introduced to account for variations of background values, which can be attributed to mineralogical variations in the sediments. The index of geoaccumulation consists of seven grades (0–6) whereby the highest grade (6) reflects 100-fold enrichment above background values. The index values for Chilka lagoon are given in Table 4. The index values remain in class 0 (background concentration) for Fe, Mn, Cu, Cr, and Zn, suggesting that there is no pollution with respect to these metals. Ni and Pb metals have a geoaccumulation rating of 1 (double the background values).

In general our results show that natural processes control the levels of heavy metals in the sediment. The results of this study can be compared with similar data from other geographical locations, employing identical extraction procedures (Table 5). The table is helpful in deciding the status of the tropical coastal lagoon with respect to the chemical fractionation of these elements.

References

- Abayachi JK and Douabul AZ (1986) Trace element geochemical associations in the Arabian Gulf. *Mar Pollut Bull* 17(8): 353–356
- Archer FC and Hodgson IH (1987) Total and extractable trace element contents of soils in England and Wales. *J Soil Sci* 38: 421–431
- Bengtsson L, Hellstrom T, and Rakoczi L (1990) Redistribution of sediments in three Swedish Lakes. *Hydrobiologia* 129: 167–181
- Bermond A and Sommer G (1989) Simulation of heavy metal extraction in soil samples compared with the experimental results. *Environ Technol Lett* 10: 989–994
- Breteler RJ and Saska FI (1985) The role of sediment organic matter on sorption-desorption reactions and bioavailability of mercury and cadmium in an intertidal ecosystem. In: Cardwell RD, Purdy R, and Bahner RC (Eds), *Aquatic toxicology and hazard assessment. Proceedings Seventh Symposium*. Philadelphia: American Society for Testing and Materials, STP 854, pp 454–885
- Calmano W and Forstner U (1983) Chemical extraction of heavy metals in polluted river sediments in Central Europe. *Sci Total Environ* 28: 77–90
- Campbell PGC and Tessier A (1987) Current status of metal speciation studies. In: Patterson JW and Passino R (Eds), *Metals speciation, separation and recovery*. Michigan: Chelsea Lewis Publishers. p 201

- Chester R and Hughes MJ (1967) A chemical technique for the separation of ferro-manganese minerals, carbonate minerals and adsorbed trace elements from pelagic sediments. *Chem Geol* 2:249–262
- Copeland RA and Ayers JC (1972) Trace element distribution in water, sediment, phytoplankton, zooplankton and benthos of Lake Michigan: A baseline study with calculation of concern-factors and build up of radioisotopes in the food web. Ann Arbor, Michigan: Environmental Research Group. 271 pp
- D'Itri FM (1990) The biomythylation and cycling of selected Metals and Metalloids in aquatic sediments. In: Baudo R, Giesy JP, and Mantau H (Eds), *Sediment—chemistry and toxicity of in-place pollutants*. Chelsea, Michigan: Lewis Publishers. pp 163–214
- Elder JF (1988) *Metal Biogeochemistry in surface-water systems: A review principles and Concepts*. Denver, Colorado: US Geological Survey, Circular 1013. 43 pp
- Elder JF (1994) Distribution and grain-size partitioning of metals in bottom sediments of an experimentally acidified Wisconsin lake. *Water Res Bull* 30:251–259
- Elder JF and Collins JJ (1991) Freshwater molluscs as indicators of bioavailability and toxicity of metals in surface water systems. *Rev Environ Contam Toxicol* 122: 37–79
- Farrah H and Pickering WF (1993) Factors influencing the potential mobility and bioavailability of metals in dried lake sediments. *Chem Speciat Bioavail* 5:81–96
- Fernandes HM, Oliveira AE, Patchineelam SR, Cardosok K, and Holanda L (1991) Evaluation of the metal dynamics in sediments of a tropical coastal lagoon by means of radiotracers and sequential extractions. In: Kershaw PJ and Woodhead DS (Eds), *Proceedings International Symposium on radionuclides in the study of marine process*, Norwich. London: Elsevier p 383
- Fernandes HM, Bidone ED, Veiga LHS, and Patchineelam SR (1994) Heavy metal pollution assessment in the coastal lagoon of Jacarepagna, Rio de Janeiro, Brazil. *Environ Geol* 85:259–264
- Forstner U (1985) Chemical forms and reactivities of metals in sediments. In: Leschber R, Davis RD, and L'Hermite P (Eds), *Chemical methods for assessing bioavailable metals in sludges and soils*. London: Elsevier. pp 1–30
- Forstner U (1990) Inorganic sediment chemistry and elemental speciation. In: Baudo R, Giesy JP, and Mantau H (Eds), *Sediment—chemistry and toxicity of in-place pollutants*. Chelsea, Michigan: Lewis Publishers pp 61–105
- Forstner U and Muller G (1974) *Schwermetalle in Flüssen und See*. Berlin: Springer. 255 p
- Forstner U and Salomons W (1980) Trace metal analysis on polluted sediments. Part I: Assessment of sources and intensities. *Environ Technol Lett* 1:494–505
- Forstner U and Wittmann GTW (1981) *Metal pollution in the aquatic environment*, 2nd ed. New York: Springer-Verlag. 481 pp
- Gibbs RJ (1977) Transport phases of transition metals in the Amazon and Yukon Rivers. *Geol Soc Am Bull* 88:829–843
- Harbridge W, Pilkey OH, Whaling P, and Swetland P (1976) Sedimentation in lake of Tunis: A lagoon strongly influenced by man. *Environ Geol* 1:215–225
- Haug W, Campedon R, Abrao JJ, Bernat M, and Latouche C (1994) Variation of heavy metals in recent sediments from Piratininga lagoon (Brazil): interpretation of geochemical data with the aid of multivariate analysis. *Environ Geol* 23:241–247
- Hong YT and Forstner U (1984) Speciation of heavy metals in Yellow River sediments. *Proceedings, symposium on heavy metals in the environment*. Heidelberg. pp 872–875
- Horowitz AJ (1991) *A primer on sediment-trace element chemistry*, 2nd ed. Chelsea, Michigan: Lewis Publisher. 136 pp
- Horowitz AJ and Elrick KA (1987) The relation of stream sediment surface area grainsize and composition of trace element chemistry. *Appl Geochem* 2:437–451
- IUCN (1987) *India*. In: *A Directory of Asian wetlands*. Gland, Switzerland: International Union for Conservation of Nature (IUCN). pp 367–505
- Jenne FA (1968) Controls on Mn, Fe, Co, Ni, Cu and Zn concentrations in soils and water: The significance of hydrous Mn and Fe oxides. In: Gould RF (Ed), *Trace inorganics in waters*. *Advances in Chemistry Series* 73. Washington, DC: American Chemistry Society. pp 337–387
- Kheboian C and Bauer CF (1987) Accuracy of selective extraction procedures for metal speciation in model aquatic sediments. *Anal Chem* 59:1417–1423
- Kjerfve B and Magill KE (1989) Geographic and hydrodynamic characteristics of shallow coastal lagoons. *Mar Geol* 88:187–199
- Mallik TK and Suchindan GK (1984) Some sedimentological aspects of Vembanad Lake, Kerala, west coast of India. *Indian J Mar Sci* 13:159–163
- Muller G (1979) *Schwermetalle in den sedimenten des Rheins: Veränderungem seit 1971*. *Umschau* 79:778–783
- Nadeau JE and Hall MJ (1988) Distribution pattern of metals in sediments of the Great Sound Complex, New Jersey. *Mar Geol* 82:113–122
- Nair SM and Balchand AN (1993) Speciation of trace metals in sediments of a tropical estuary. *Environ Geol* 21:96–102
- Nair SM, Balchand AN, and Nambisan PNK (1990) Metal concentration in recently deposited sediments of Cochin backwaters, India. *Sci Total Environ* 97/98:507–524
- Nurnberg HW (1984) The voltametric approach in trace metal chemistry of natural waters and atmospheric precipitation. *Anal Chim Acta* 164:1–21
- Oakley SM, Nelson PO, and Williamson KJ (1981) Model of trace metal partitioning in marine sediments. *Environ Sci Technol* 15:475–480
- Paez-Osuna F, Botello AV, and Villanueva S (1986) Heavy metals in Coatzacoalcos estuary and Ostion lagoon, Mexico. *Mar Pollut Bull* 17:516–519
- Panda D (1993) *Texture, mineralogy and chemical composition of Chilka lake Sediments*. PhD thesis (unpublished). Berhampur, India: Berhampur University. 222 pp
- Paropkari AZ, Topgi RS, Rao CM, and Murthy PSN (1980) Distribution of Fe, Mn, Ni, CO, Cu and Zn in non-lithogenous fractions of sediments of Gulf of Kutch. *Indian J Mar Sci* 9:54–56
- Pederson TF and Price NB (1982) The geochemistry of manganese carbonate in Panama Basin sediments. *Geochim Cosmochim Acta* 46:59–68
- Rapin F (1984) Speciation of heavy metals in a sediment core from Baie de Nice (Mediterranean Sea). *Proceedings, symposium on heavy metals in the environment*. Heidelberg. pp 1005–1008
- Rapin F, Tessier A, Campbell, PGC, and Carigan PR (1986) Potential artifacts in the determination of metal partitioning in sediments by a sequential procedure. *Environ Sci Technol* 20:836–840. Am. Chem. Soc. Publishers
- Rendell PS, Batley GE, and Cameron AJ (1980) Adsorption as a control of metal concentrations in sediment extracts. *Environ Sci Technol* 14:314–318
- Rose AW, Hawkes HE, and Webb JS (1979) *Geochemistry in mineral exploration*, 2nd ed. New York: Academic Press. 657 pp
- Salomons W and Forstner U (1984) *Metals in the hydrocycle*. New York: Springer-Verlag. 349 pp
- Sholkovitz ER (1989) Artifacts associated with the chemical leaching of sediments for rare-earth elements. *Chem Geol* 77:47–51
- Shuman LM (1982) Separating soil iron- and manganese-oxide fractions for microelement analysis. *Soil Soc Am J* 46:1099–1102
- Shuman LM (1985) Fractionation method for soil microelements. *Soil Sci* 140:11–22
- Stumm W and Morgan JJ (1970) *Aquatic chemistry*. New York: Wiley-Interscience, 583 pp
- Singh SK and Subramanian V (1984) Hydrous Fe and Mn oxides—scavengers of heavy metals in the aquatic environment. *CRC Crit Rev Environ Control* 14(1):33–90
- Tessier A, Campbell PGC, and Bisson M (1979) Sequential extraction procedure for the speciation of particulate trace metals. *Anal Chem* 51:844–851
- Tessier A, Campbell PGC, and Bisson M (1980) Trace metal speciation in the Yamaska and St. Francois Rivers (Quebec). *Can J Earth Sci* 17:90–105
- Tippling E, Hetherington NB, Tilton J, Thompson DW, Bowles E, and Hamilton-Taylor J (1985) Artifacts in the use of selective chemical extraction to determine distributions of metals between oxides of manganese and iron. *Anal Chem* 57:1944–1946

- Winfrey MR and Rudd JW (1990) Environmental factors affecting the formation of methylmercury in low pH lakes. *Environ Toxic Chem* 9: 853–869
- Zhang J, Huang WW, and Martin JM (1988) Trace metal distribution in Huanghe (Yellow River). *Estuarine Coast Shelf Sci* 26: 499–516
- Zonta R, Zaggia L, and Argese E (1994) Heavy metal and grain-size distributions in estuarine shallow water sediments of Cona marsh (Venice lagoon, Italy). *Sci Total Environ* 151: 19–28