

Studies on the Sediments of Vembanad Lake, Kerala State: Part IV-Distribution of Trace Elements

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Distribution patterns of Fe, Mn, Ti, Ni, Co and Cu in sediments of Vembanad Lake and adjoining river systems have revealed that (1) elemental concentrations follow closely the texture of the sediments, (2) river sands contain very low concentrations of all elements, (3) in the lake sediments the elemental concentrations increase with decrease in grain size, (4) even among the fine-grained sediments, the sediments in the estuarine region are impoverished in their Mn and Co contents and enriched in their Ni and Cu contents as compared to fine-grained sediments in other parts of the lake and (5) Fe, Mn, Ni, Cu and Co bear significant relationship with organic matter of the sediments. Distribution patterns of elements in the non-estuarine region of the lake (between Arakutti and Alleppey) where sediments are mostly deposited in a fresh water environment are controlled largely by grain size, textural characteristics and mineralogy of sediments. On the other hand, differential behaviour of elements in the estuarine region has been attributed to several factors. The impoverishment of Mn and Co can be due to (i) desorption of these elements from the river borne detritus on coming into contact with saline waters, (ii) dredging operations which may lead to the release of these elements into the waters and (iii) mixing with marine sediments containing low concentrations of Mn and Co. The enrichment of Ni and Cu can be due to their association with (i) organic matter of the sediments, (ii) ferric and manganese hydroxides through adsorption and (iii) mixing with marine sediments which contain relatively higher concentrations of these elements.

On a global basis, estuaries and lagoons are very important for the supply of dissolved and solid material to oceans. Garrels and Mackenzie¹ have estimated that 250×10^{14} g year⁻¹ of material enters the oceans from the continents of which 210×10^{14} g year⁻¹ material is transported via rivers and estuaries. It means almost about 85 % of all soluble and particulate weathering products pass through the estuarine environment before entering coastal waters. Therefore, the estuaries and lagoons which form the transition zones between fluvial and marine environments constitute an important stage in the transport of sediments from continents to oceans. Further, they also serve as traps for a portion of the solid continental weathering products. They represent a situation in which sedimentary detritus during its transport to oceans, and the sedimentary deposits can undergo modifications through several processes operating in these systems resulting in enrichment or impoverishment of various trace elements in the bottom sediments. With a view to understanding the concentration levels of trace metals in sediments and their geochemical behaviour from fluvial to estuarine environments, bottom sediments of Vembanad Lake and adjoining river systems have been investigated for trace metals.

Regional setting of Vembanad Lake, its hydrographic features, distribution patterns of different sediment units and depositional processes operating in different parts of the lake are reported²⁻⁶.

Methods

Sediment samples (about 250) were collected from different parts of the lake as well as from the Muvattipuzha and Ittupuzha rivers using a Van Veen grab during Nov.-Dec. 1969 (Fig. 1). Based on the distribution patterns of the different sediment units and their organic matter content⁵, about 55 samples which represented the broadest possible variations in these parameters were selected for detailed analyses of trace metals from different parts of the lake. The samples were digested with hydrofluoric and perchloric acids following the method of Chester and Hughes⁷. Concentrations of Fe, Mn, Ti, Ni, Co and Cu were determined against standard solutions with a SP 500 Unicam Spectrophotometer. Fe and Mn were estimated by the methods of Sandell⁸. Ti was determined by the method of Riley⁹, and Ni, Co and Cu were estimated using the procedures of Chester and Hughes⁷. Determinations of Fe, Mn, Ti and Co were also carried out in silt-clay fractions of samples in order to understand variations in concentrations of elements in relation to grain size of sediments.

Results

Data (Tables 1-3) reveal the following distinct trends in regard to the distribution patterns of elements studied:

(1) Concentrations of various elements follow closely the texture of sediments. Invariably, the river sands which are apparently devoid of silt and clay size

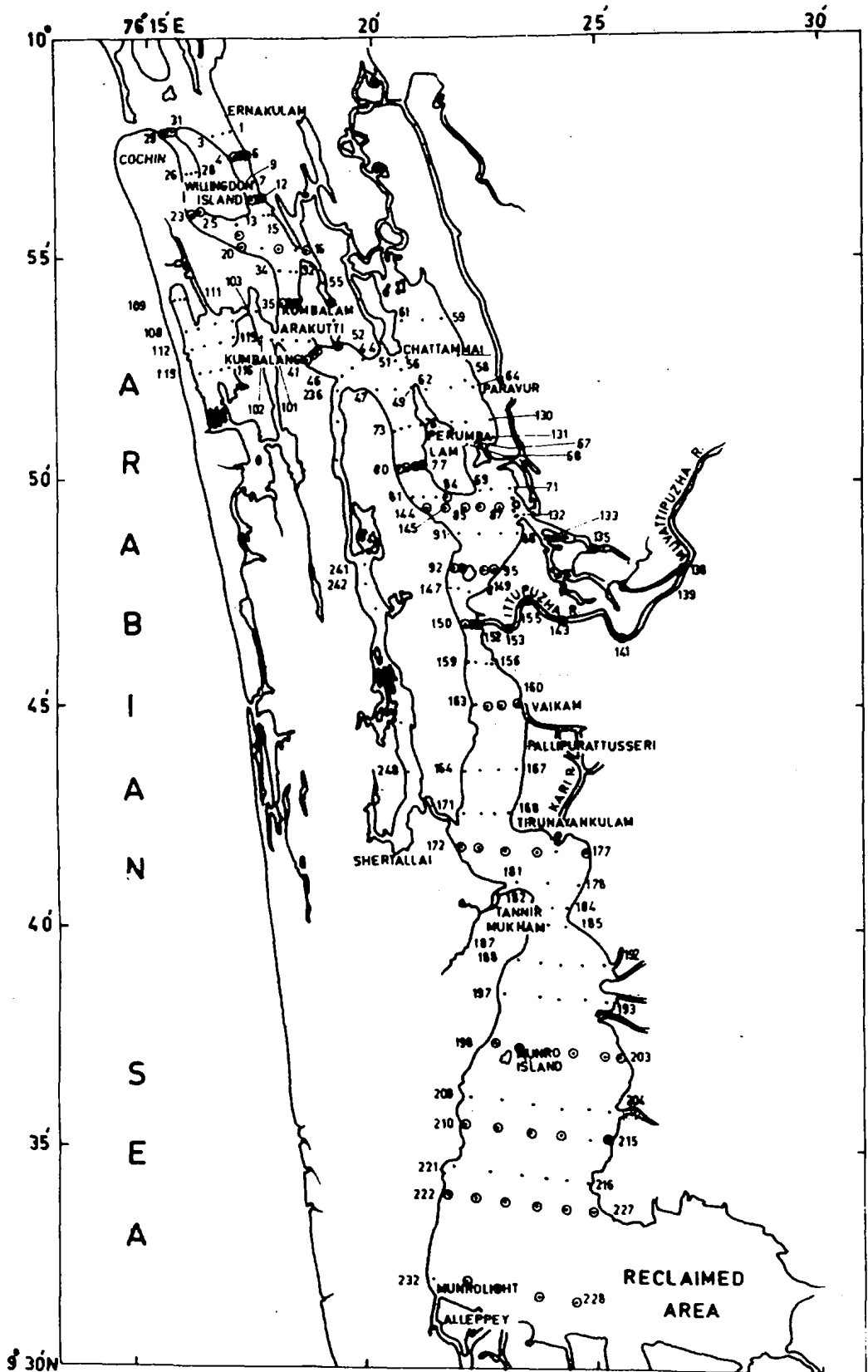


Fig. 1—Location of samples (+) collected [o samples selected for geochemical analysis]

MURTY & VEERAYYA: SEDIMENTS OF VEMBANAD LAKE

Table 1—Elemental Concentrations in Bulk Samples along with Sampling Depth and Textural Data

St No.	Depth (m)	Sand Silt Clay			Texture of sediments	Phi median diam.	Conc. of element ppm (Fe in %)					
		%					Fe	Mn	Ti	Ni	Co	Cu
4	2.2	17	31	52	Silty clay	8.2	1.34	225	11830	28	37	21
5	10.4	22	37	42	Sand-silt-clay	7.4	4.69	318	9649	41	44	48
6	3.1	15	31	54	Silty clay	8.2	7.37	318	15715	49	61	100
10	4.9	29	24	47	Sand-silt-clay	7.8	4.47	386	11020	60	50	64
11	7.9	10	42	48	Silty clay		4.47	183		45	41	
12	0.9	66	16	18	Clayey sand	3.35	3.68	214	9194	39	35	28
16	0.9	81	13	6	Sand	2.98	1.56	233	6000	30	46	38
20	0.9	79	12	9	do	2.5	2.01	142	6736	30	71	51
21	4.3	21	36	43	Silty clay	7.3	6.36	380	8375	55	57	39
23	4	Nil	56	44	Clayey silt	7.6	5.92	333	9649	53	74	60
24	6.7	Nil	45	55	Silty clay	8.3	5.25	332	9649	56	48	60
25	3.7				do		5.69	287	8557	34	75	33
29	3.4	48	21	30	Sand-silt-clay	4.7	5.47	488	7685	45	47	36
30	10	36	28	35	do	4.9	9.61	283	10030	46	52	71
31	4	Nil	60	40	Clayey silt	6	6.36	402	10920	46	82	98
35	4.6	3	50	47	do	7.8	2.79	481	12200	39	50	59
36	6.4	5	39	56	Silty clay	8.35	5.36	374	11500	40	50	86
42	9.5	Nil	53	47	Clayey silt			601	10070	51	46	60
43	1.5	79	10	11	Sand	2.38	1.56	191	5735	31	42	14
52	3.4	92	3	4	do	3.12	0.67	136	4971	21	41	16
54	3.1	80	9	11	do	3.08	1.34	185	6682	28	49	23
78		62	29	9	Silty sand	3.52		226	11050	35	69	29
79	3.1	57	25	17	do	3.85	5.58	587	8375	34	62	37
80	4.3	75	11	14	Sand	2.4	0.67	177	8103	34	62	21
144	5.8	23	40	37	Sand-silt-clay	7	5.85	615	14258	54	59	63
145	1.5	97	3	Nil	Sand	2.68	0.67	141	10550	11	30	16
84	1.5	97	2	1	do	2.45	0.22	129	22070	16	31	3
86	2.5	100	Nil	Nil	do	1.98		120	4880	10	35	4
87	0.9	100	do	do	do	1.85		283	10200	23	35	25
92	4.3	55	35	10	Silty sand	3.95	0.22	161	6610	13	50	24
94	2.8	88	9	4	Sand	2.65	1.56	301	7773	25	52	10
95	1.2	99	1	Nil	do	2.2	0.67	415	10410	33	59	46
151	9.2	99	1	do	do	1.75	0.45	30	4823	8	27	Nil
152	1.2	93	5	2	do	1.9	1.12	191	6281	19	39	14
135 R	4.6	96	4	Nil	Sand	0.9	0.89	117	3678	15	37	16
138 R	1.8	93	4	3	do	0.98	0.33	205	7228	17	33	10
141 R	2.5	97	3	Nil	do	1.2	1.45	178	3495	14	37	4
143 R	2.8	98	2	do	do	1.2	1.11	86	2312	13	17	14
153 R	3.1	98	2	do	do	1.55	0.67	96	3040	14	26	Nil
155 R	3.1	96	4	do	do	0.85	0.78	64	2549	11	26	2
160	1.5	55	34	11	Silty sand	3.95	3.35	395	10740	26	49	32
161	4				do		4.91	738	11650	7	59	37
162	3.7				do		4.47	481	8557	8	52	14
172	1.5	85	10	4	Sand	2.3	0.89	149	6974	8	38	8
173	3.7	42	46	13	Sandy silt	4.1	4.24	743	9504	15	62	44
174	5.5	42	41	17	Silty sand	4.55	0.89	552	9685	19	82	43
175	4.9	49	35	16	do	4.1	3.79	587	10510	31	54	43
177	2.8	61	29	10	do	3.6	2.23	396	10252	29	52	20
198	1.2	85	12	3	Sand	1.7	1.67	290	11690	27	56	20
199	4.6	62	24	14	Silty sand	3.25		757	7246	31	66	24
200	2.2	47	39	14	do	3.8	3.57	570	9948	41	66	28
202	1.8	26	67	7	Sandy silt	4.75		665	11690	31	41	58
203	1.2	82	13	6	Sand	3.05	1.23	347	4678	21	39	7
211	1.5	77	16	7	do	2.1	1.56	276	7137	22	39	30
212	1.8	80	14	6	do	2.6	7.82	301	4337	31	49	53
213	2.5	23	55	22	Sand-silt-clay	5.7	5.14	828	10050	11	59	48
222	1.2	57	34	9	Silty sand	4.5	2.9	383	7683	26	59	20
223	1.8	50	42	8	do	4.15	5.47	771	13050	74	79	35
224	2.2	7	44	49	Silty clay	7.98	7.82	898	7046	14	48	54
226	1.8	21	60	19	Sandy silt	4.8		622	6226	18	69	23
227	1.5	20	63	17	do	5.9	5.47	870	6682	17	59	45
229	1.5	5	66	29	Clayey silt	5.9	4.6	570	7173	37	79	53
230	1.5	4	49	47	do	7.6	8.26	683	6790	12	57	63
231	1.8	19	53	27	do	6	7.59	631	7046	13	48	42

R = river sample

material are characterised by lowest concentrations of the elements. In the lake sediments, broadly the concentrations increase with decrease in grain size (Table 1).

(2) With a few exceptions, higher concentrations of elements are associated with the silt-clay fractions of sediments than with the bulk samples. This is particularly true of Fe, Mn, and Co. In the case of Ti, generally higher concentrations are associated with the bulk samples than with the silt-clay fraction. However, it could be seen that major portion of Ti is carried in the silt-clay fraction of sediments (Tables 1 and 2).

Table 2—Elemental Concentrations in Silt-Clay Fraction (< 0.062 mm) of Sediment Samples

St No.	Fe%	Mn ppm	Ti ppm	Co ppm
4	6.7	604	6291	57
5	5.36	456	6100	77
6	5.36	456	5973	41
10	5.81	385	5736	46
11	5.58	308	6375	49
12	6.03	462	6009	62
16	5.36	475	6064	70
18	5.58	360	5609	51
20	6.48	475	5827	60
23	5.14	450	5699	56
24	5.81	507	6064	67
25	5.81	629	5882	48
29	5.36	674	5827	47
30	5.14	546	6155	113
35	4.36	442	6373	90
36	5.58	418	6282	67
37	6.48	591	6337	85
41	6.03	270	6464	63
42	6.7	655	6501	74
43	5.81	321	6510	82
77	6.48	340	7193	96
78	6.03	649	7612	103
79	6.93	861	6793	58
80	6.26	418	6464	83
85	5.81	1266	6282	113
87	6.7	810	7557	77
92	5.81	944	2877	61
93	6.48	1176	6956	70
94	6.26	938	6792	77
198	4.36	1221	7157	82
200	6.26	1214	7521	125
201	6.93	1317	7794	99
202	6.48	861	9105	87
210	5.14	803	7157	81
211	4.24	1060	7157	109
213	5.36	1002	7703	119
223	4.97	996	6009	93
224	6.03	835	6701	77
225	6.26	886	7193	83
226	4.97	861	7557	94
227	6.48	713	7703	100
228	5.36	681	7521	74
229	4.36	595	6920	88
231	4.98	687	7157	66

Table 3—Correlation Coefficient Values between Various Elements

Between elements	r value
Fe and Mn	0.6
Fe and Ni	0.41
Fe and Co	0.44
Fe and Cu	0.73
Mn and Co	0.54
Co and Cu	0.56
Mn and Cu	0.43
Ni and Co	0.44
Ni and Cu	0.54
Between Organic matter and elements	
OM and Fe	0.7
OM and Mn	0.39
OM and Ni	0.66
OM and Co	0.56
OM and Cu	0.83

(3) Although the fine-grained sediments of the lake show relatively higher concentrations of the elements, certain distinct differences in the elemental concentrations exist between sediments of the estuarine region (between Cochin harbour entrance and Arakutti) and the rest of the lake. Both on bulk sample basis as well as on corresponding silt-clay fractions, sediments in the estuarine region are impoverished conspicuously in their manganese content and to some extent of Co also relative to the fine-grained sediments in other parts of the lake. There is not much of difference between the concentrations of Fe associated with fine-grained sediments of the southern region and estuarine region. Relatively high concentrations of Ti are associated with the estuarine sediments than with the fine-grained sediments of the southern region on bulk sample basis while the opposite is the case in the silt-clay fractions of sediments.

(4) Significant correlation is seen (Table 3) between any 2 elements except in case of Fe and Ti, Mn and Ti and Mn and Ni.

(5) Data also show strong correlation between elemental values and organic matter content in sediments (Table 3).

Discussion

Vembanad Lake is an open system. It has a permanent connection with the sea at Cochin and 3 major rivers—Pamba, Manimala and Achankoil join it at its southern end (not shown in Fig. 1). A 4th major river Muvattipuzha with its branch Ittupuzha joins the lake midway between Alleppey and Cochin. All these rivers which flow through the Precambrian formations in their upper reaches and Recent alluvium in the lower reaches supply the dissolved and solid material to the lake during the monsoon months, the latter by way of bed load as well as suspended load. Gopinathan and

Qasim¹⁰ have shown that silting in the estuarine portion occurs during pre and post monsoon while flushing of the finer material takes place during the monsoon period. Further, the bottom sediments of the estuarine region comprise the sediment load brought from the rivers as well as material transported from the sea into the estuary during pre and post monsoon through tidal currents. The fact that material from inshore region finds its way into the estuary is also confirmed by the radioactive tracer studies¹¹.

Detailed investigations¹² carried out on the mineralogy of the sands of Pamba river from source to mouth have revealed the presence of the following heavy mineral assemblage: opaques, ilmenite, rutile, monazite, zircon, pyroxenes, amphiboles, biotite, etc. The clay mineral assemblage consists of predominantly kaolinite group of minerals with subordinate amounts of montmorillonite and illite. Although no information is available on the mineralogy of the sediments from other rivers, their gross mineralogy may be considered to be the same as the mineralogy of Pamba river sediments in view of the fact that they also flow through the same rock formations. However, minor differences in the relative abundances of the various minerals cannot be precluded. In the lake region between Arakutti and Alleppey (Fig. 1) which is (i) under the fresh water regime for major part of the year, (ii) under the direct influence of the rivers that debouch into the lake and (iii) characterised by the presence of sediments deposited as rolling and suspension population, it is possible that major portions of the concentrations of the elements are incorporated into the sediments in a solid phase in association with the various detrital minerals and clay minerals. Apart from this mode of incorporation, it is also possible that these elements are incorporated into the sediments to a certain extent in the adsorbed form in association with the finer fractions of sediments and also with organic matter. Further, these sediments which are supplied by the rivers and are deposited in a fresh water environment are unlikely to undergo any marked changes in their chemistry during their deposition. Hence, variations found in the concentrations of the elements on the bulk sample basis could be related to (i) wide variations in the grain size and textural characteristics of the sediments and (ii) differences in the mineralogical content of the sediments. The fact that differences exist in the mineralogical content of the sediments is also borne out by the variations encountered in the silt-clay fractions.

The estuarine region, on the other hand, presents a different situation: (i) stable marine conditions prevail for major part of the year while in the monsoon period fresh to brackish water conditions exist at the surface

and marine conditions continue to prevail at the bottom, (ii) it is devoid of coarser sediments due to the presence of a salt wedge all through the year extending up to the southern end of Kumbalam Island (Fig. 1) which acts as a barrier for the transportation of coarser material into the estuary from the south, (iii) by and large, it consists of finer sediments only which are deposited through flocculation of suspended load and (iv) elements particularly Mn, Co, Cu and Ni exhibit a differential behaviour in that the first 2 elements are impoverished to a certain extent while the other 2 are enriched in these sediments relative to the fine-grained sediments in other parts of the lake.

Among the various factors that may be responsible for the differential behaviour of the elements observed in the estuarine region, the most important ones are (1) biological productivity, (2) exchange of trace elements between pre-existing solids and solution, (3) formation of colloids of ferric and manganese hydroxides and their flocculation, (4) diagenesis of sedimentary deposits and (5) mixing with marine sediments. The role of each of these factors is evaluated below with the available data.

Biological productivity---Estuaries are environments of generally high biological productivity. Aquatic organisms are well known for their ability to take up trace elements from solution and particulates¹³⁻¹⁵. Productivity studies in the estuarine part have indicated that phytoplankton production far exceeds the zooplankton production¹⁶. Correspondingly, the underlying sediments are rich in organic matter content⁵. It is therefore possible that the elements are incorporated into the sediments in association with organic matter to a certain extent. While this is broadly so, Ni and Cu seem to have stronger relationship with organic matter in these sediments than Mn and Co (Table 3).

Exchange of trace elements between pre-existing solids and solution---It is well established that adsorption of trace elements from solution on to mineral matter and organic solids takes place in natural waters. In an estuarine situation, the suspended solids capable of providing adsorption sites are subjected to important physico-chemical changes which result from the mixing of river and sea waters. These changes which effect pH, pE and ionic strength influence the adsorption-desorption behaviour of suspended matter. Thus estuaries represent a situation in which solid-solution exchange of trace elements might lead to the enrichment or depletion of trace element content of suspended matter and in turn of bottom sediments.

The ability of pre-existing solids to adsorb trace elements from solution under both fresh water and marine conditions has been well established^{17, 18}. On

the other hand, the desorption of trace elements from river borne particulate matter during laboratory experiments intended to simulate estuarine mixing has been reported by Kharkar *et al*¹⁹. According to them, clay mineral analogs of a river suspended matter were capable of adsorbing certain trace metals in fresh water and partially desorbing them upon contact with sea water. Field evidence for trace element desorption in estuaries has been given by Turekian²⁰ and Evans and Cutshall²¹.

In order to understand the behaviour of the elements, concentrations of the elements have been plotted against percentages of < 16 μm size material of the sediments. The scatter plots (Fig. 2) indicate that very conspicuously manganese and to a lesser extent cobalt undergo desorption in the estuarine region while others do not. Desorption of manganese and cobalt in the estuarine regions has been reported by several workers²²⁻²⁶.

Formation of colloids of ferric and manganese hydroxides and their flocculation—The hydrogenous

precipitation of hydrated oxides of iron and manganese from sea water has important consequences for trace element solid-solution exchange. These hydroxides are very effective in the removal of trace elements from solution in natural waters by lattice substitution and surface adsorption processes. The formation of these oxides is dependent on the hydrolysis of dissolved Fe and Mn ions which is a function of pH of the solution. Estuaries are a transition zone between river water pH 6-7 and that of sea water, 8.1. Thus it is within the estuaries that formation of these solid phases might be expected. The formation of these solid phases in the fresh water environment cannot be precluded if the pH conditions are satisfied.

It is well known that Kerala region is a zone of intense weathering. It is quite possible that Fe and Mn leached from the rocks during weathering are transported in solution in considerable measure by the river waters. The studies of Sankaranarayanan and Qasim⁴ and the salinity structure in the estuarine

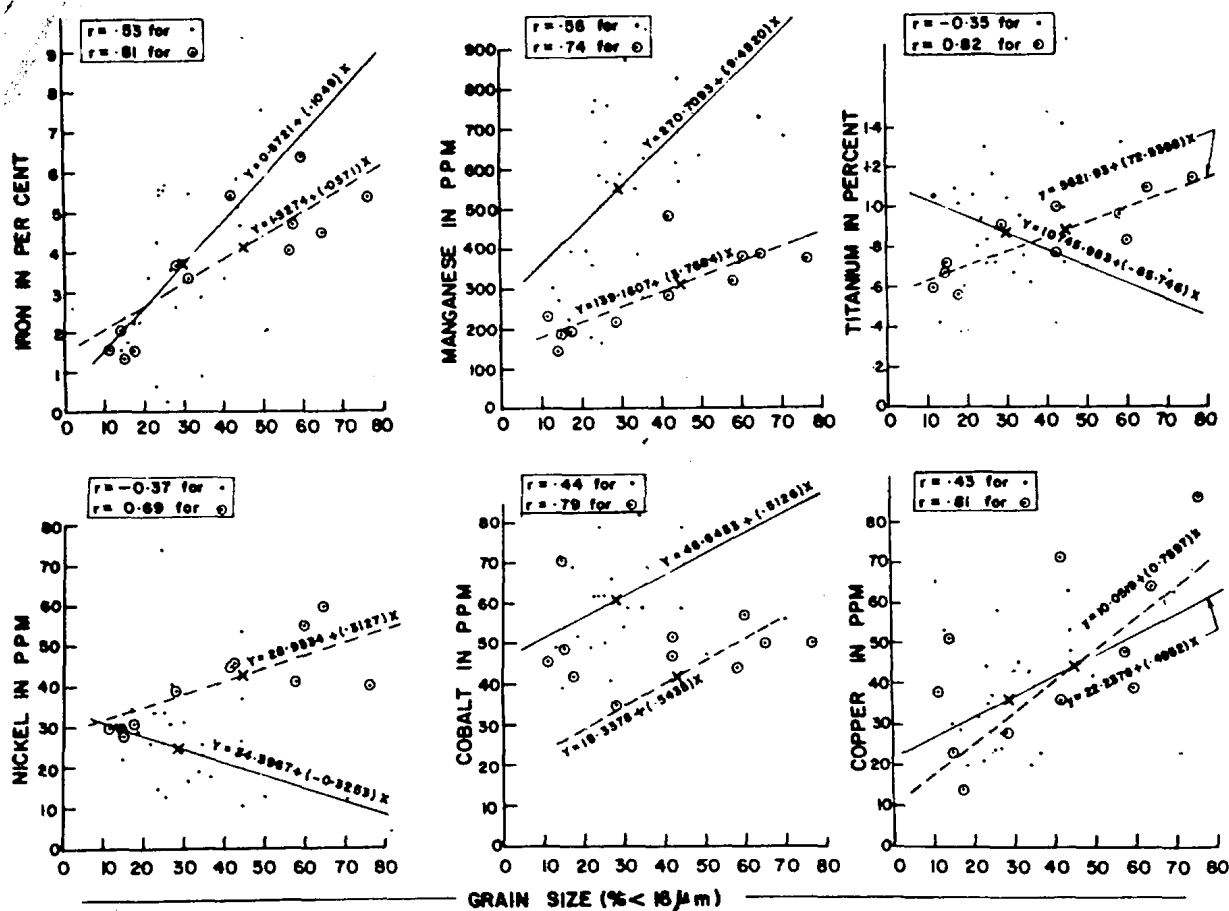


Fig. 2—Relationship between concentration of elements and percentage of < 16 μm size fraction of samples [(+) Samples from the lake between Arakutti and Alleppey; (o) Samples from the estuarine region; —, regression line for lake sediments; and ---, regression line for estuarine sediments. X mark on the regression line indicates centre of gravity of points i.e. X, Y. Values in the regression equation in scatter plot between Titanium and < 16 μm are in ppm

Table 4—Average Concentrations of Elements for Different Major Sediment Units in the Study Area and Other Regions

	Conc. of element ppm (Fe in %)					
	Fe	Mn	Ti	Ni	Co	Cu
Present study						
River sands*	0.93	134	4083	15	31	9
Lake sands	1.16	220	8412	23	45	21
Silty sands	4.03	570	9450	28	61	30
Clayey silts	5.94	517	8963	33	65	63
Silty clays	5.44	387	10685	41	49	60
Southwest coast of India						
Nearshore (mud bank) sediments ³⁰						
Bulk samples	5.27	188				
Clay samples				115	20	175
Innershelf sediments ^{27,31,32}						
Off Cochin						
Silty clays	5.58	270	2200	63	59	138
Off Ambalapuzha						
Clayey silts	4.92	250	3400	44	64	64
Clyde Estuary ³⁶						
Muds	1.4	420		53		25
Sandy muds	0.7	355		30		16
Solway Firth ³⁷						
Muds		360		38	16	10
Kaohsiung Harbour ³⁸	2.56	523		59	35	74
Los Angeles Harbour ³⁹						
Silty clays	3.2	414		42.8		152
Sandy silts	2.22	411		31.1		89.9
Silty sands	1.55	319		20.6		45.7
Narragansett Bay ⁴⁰	3.3	410		28	8	190
Chesapeake Bay ⁴¹						
CHSP 1314	3.9	450		46	12	26

* Sediment unit

region suggest that the environmental conditions in the estuary are favourable for the formation of colloids of Fe and Mn oxides and their flocculation. It is therefore considered possible that part of these elements might be incorporated into the sediments in association with these hydroxides through adsorption. In fact Murty *et al.*²⁷ reported the presence of Fe and Mn of non-lithogenous origin in the adjacent inner shelf region which they attributed to the flocculation of colloids of Fe and Mn oxides supplied by the rivers.

Diagenesis of sedimentary deposits—As mentioned earlier, the estuarine region is highly productive and the underlying sediments are correspondingly rich in organic matter content. But the processes of diagenesis and the consequent enrichment of elements like Mn, Cu through the creation of anaerobic conditions in the estuarine sediments at sub-surface levels²⁸ could be ruled out in view of the extensive dredging operations that take place every year in the estuarine region for the maintenance of Cochin Harbour. On the other hand, dredging operations may aid in the release of the elements like Mn and Co from the sediments to waters²⁹. It is therefore possible that the impoverishment of Mn and Co observed in the estuarine sediments could be partly due to these operations.

Mixing with marine sediments—When compared to the adjacent inner shelf sediments^{27,30-32}, the fine-grained sediments of the estuary show similar concentrations of Fe, but higher contents of Mn and Ti and lower concentrations of Ni and Cu. It has been indicated earlier that the estuarine region receives material from the adjacent marine environment. The differences in the behaviour of the various elements in the estuarine region relative to the fine-grained sediments of the other regions of the lake could be partly attributed to the mixing of the innershelf sediments with the estuarine sediments. Such a process has been reported by other workers elsewhere³³⁻³⁵.

In Table 4 are given concentrations of elements reported from some of the unpolluted parts of estuaries from different regions³⁶⁻⁴¹. A perusal of these values with the average values obtained for Vembanad Lake sediments reveals that the sediments of the lake do not indicate any sign of pollution. However, in recent years several developments have taken place, for example, construction of a barrage at Tannermukham to prevent incursion of salt water to the southern part of the lake, establishment of a shipyard at Cochin, development of Cochin harbour, reclamation of land for construction purposes, formation of several new

islands in the midst of the lake and establishment of several industries, etc. All these must be having some impact on the environment of the lake. Taking the data presented here as the base line data, it may be worthwhile to re-survey the area to understand the impact of the recent developmental activities and to what level the area has been polluted.

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