DISTRIBUTION OF NICKEL IN THE MARINE SEDIMENTS OFF THE WEST COAST OF INDIA

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THE distribution of trace elements and the possible factors influencing them in the shelf sediments off the west coast of India have been the subject of study for some time. In continuation of the results pertaining to phosphates, Murty et al.,[1] and Manganese, (Murty et al.[2]) estimations of nickel were carried out and the present paper gives an account of its distribution, and the relationship it bears to other important elements in these sediments.

The location of Stations from where the samples were collected are given in Fig. 1. The marine sediments fringing the west coast of India exhibit texturally, chemically and mineralogically certain well-defined distribution patterns. The inner shelf (upto 20 fms.) is covered by silty clays or clayey silts with very low carbonate content and this is followed seaward by a zone of silty or clayey sands on the rest of the shelf and slope regions characterised by a high carbonate content.[3] This is particularly so between Cochin and Karwar while off Bombay the shelf is covered for a greater part by fine-grained sediments. Studies on the organic matter (in the bulk sediments) have shown that the sediments in the inner shelf and the slope regions are characterised by a higher organic content than those in the region in between.[4] Manganese content shows a distinct trend in that it decreases in a direction seaward and away from land and also from north to south.[2] Clay minerals also exhibit regional variations. (i) The sediments off Bombay and Karwar are characterised by the presence of predominantly mixed layers of montmorillonite and illite with subordinate amounts of kaolinite group of minerals ; (ii) the sediments off Mangalore by the presence of approximately equal proportions of mixed layers of montmorillonite and illite and kaolinite group of minerals ; and (iii) the sediments off Kerala coast having predominantly kaolinite group of minerals with subordinate amounts of montmorillonite.

The estimations of nickel were carried out by the method described in Sandel[5] while iron and organic carbon were carried out respectively by the methods given by Snell and Snell[6]

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and ElWakeel and Riley.[7] All the analyses were carried out only on the silt and clay fractions and not on the bulk sample. All the colorimetric determinations were made on 'UNICAM' spectrophotometer SP 500.

Table I gives the contents of nickel, organic carbon, iron, manganese and calcium carbonate

TABLE I

Stn. No.	Depth	Concentration of				
		Nickel in ppm	Organic carbon in %	Calcium carbonate in %	Manganese in %	Iron in %
638	13	40	1·59	2·5	0·077	3·65
639	17	36	1·48	41·5	0·072	2·5
640	19	24	1·14	39·0	0·064	2·3
641	19	33	1·41	22·5	0·055	4·50
642	26	45	1·86	20·0	0·037	1·55
643	38	29	2·48	32·0	0·028	1·60
645	250	34	6·24	30·0	0·009	2·15
656	10	53	2·24	0·0	0·055	3·55
654	25	30	1·21	0·0	0·058	2·20
653	32	25	1·25	0·0	0·046	1·90
652	42	19	2·00	42·0	0·029	0·20
651	55	20	2·20	0·0	0·017	0·40
650	110	27	2·57	50·1	0·027	0·30
657	10	27	2·83	4·0	0·045	3·65
658	17	31	2·73	7·0	0·037	3·65
659	23	16	2·38	24·0	0·032	1·95
660	43	28	2·17	..	0·033	1·75
661	105	22	2·93	28·5	0·039	2·75
671	13	38	3·90	0·0	0·031	5·10
670	14	34	2·98	0·0	0·028	4·25
669	17	33	2·62	17·0	0·030	4·30
668	23	38	2·76	12·0	0·020	4·85
667	32	12	2·45	15·0	0·020	3·9
666	46	33	3·73	3·8	0·014	3·60

Note : Values of manganese and calcium carbonate are borrowed from Murty *et al.*[2] and Nair *et al.*[3] respectively.

along with the depths from where the samples were collected. In order to understand the nature of relationship existing between nickel and other parameters analysed, correlation coefficients have been calculated. The values obtained between nickel and organic carbon, calcium carbonate, iron and manganese are 0·1680, − 0·2182, 0·3349 and 0·3703 respectively. The values of correlation coefficients obtained in respect of nickel and iron in relation to depth along each section are given in Table II. A careful examination of the data permits the following generalizations :

(i) The fine-grained sediments in the inner shelf and the sediments in the slope region

TABLE II

Name of the section	r-value for nickel	r-value for iron
Off Bombay ..	−0·19	−0·65
Off Karwar ..	−0·46	−0·52
On Mangalore ..	−0·26	−0·72
Off Cochin ..	−0·39	−0·38

r for manganese has not been calculated as it is clearly evident from the data that it decreases with depth.

contain relatively a higher amount of nickel than the sediments in the outer shelf. Even among the fine-grained sediments, the sediments off Bombay. Karwar and Cochin have relatively a higher concentration of nickel than the sediments off Mangalore.

(*ii*) Nickel co-varies with both manganese and iron. Relatively, it has a stronger correlation with manganese than with iron. It does not show any relationship with organic carbon.

(*iii*) A negative relationship exists between nickel and both calcium carbonate and depth of sampling.

Kraus-kopf[8] made an extensive study of the factors controlling the concentration of several trace elements in sea-water including nickel. He investigated in detail four processes for the removal of these elements namely (*i*) precipitation of insoluble compounds with ions normally present in sea-water, (*ii*) precipitation by sulphide ion in local regions of low oxidation potentials, (*iii*) adsorption by materials such as ferrous sulphide, hydrated ferric oxide, hydrated manganese dioxide and clay and (*iv*) removal by metabolic action of organisms. His results have shown that adsorption is the most important process for the removal of minor and trace elements from the sea-water and their deposition in marine sediments. Nicholls and Loring[9] and Hirst[10] suggested that there is a correlation between nickel and organic carbon content of the sediments and they consider that the latter acts as an adsorbant. Hogdahl[11] has shown that nickel is enriched in marine organisms relative to sea-water to a greater extent. According to Chester[12] nickel may be probably removed permanently from sea-water under conditions of low redox potential when organic rich sulphide-bearing sediments are formed.

In the present case it is possible that precipitation of nickel as insoluble compound does not take place as the sea-water is greatly under-saturated with regard to this element. Also, precipitation of nickel by sulphide is unlikely in the areas under study, in view of the fact that considerable mixing takes place in the shelf waters. pH measurements carried

out by Rao and Madhavan[13] have shown that the environment is not the reducing type. Reports of heavy mortality of bottom animals[14] during certain seasons and consequent anoxic conditions are perhaps a transient or passing feature and not long enough to maintain low redox potentials and hence reducing conditions. It may be relevant to mention here that no sulphide odour is noticed in any of the samples collected.
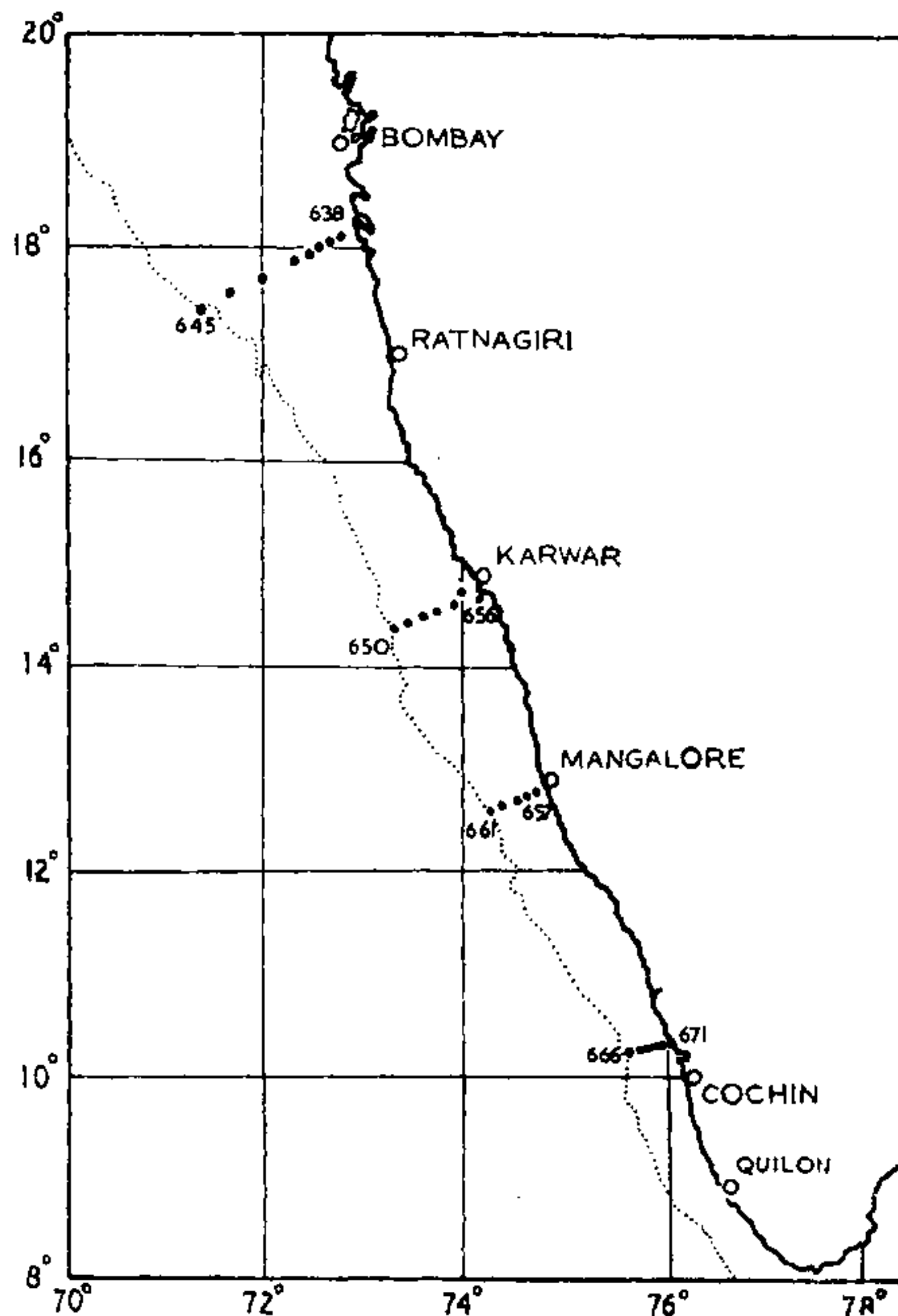

FIG. 1. Map showing the station locations.

Organic carbon in the silt and clay fraction follows the same trend as in the bulk samples. The distribution pattern observed in the sediments of (*a*) the inner shelf, (*b*) outer shelf and (*c*) slope regions has been attributed by Murty *et al.* (*loc. cit.*) respectively to (*i*) the highly productive nature of the coastal waters as a consequence of seasonal upwelling and the presence of fine-grained sediments in the inner shelf, (*ii*) the coarse-grained nature of the sediments in the outer shelf and the presence of oxygenated waters which destroy much of the organic matter and (*iii*) the preservation of organic matter in the slope sediments under oxygen poor waters. The organic carbon does not show any relationship with nickel in the present studies which indicates that it is not bound to organic carbon. The factors that

favour organic carbon to act as an effective adsorbant are (i) the presence of high percentage of organic carbon in the sediments, (ii) absence of agitated and well-ventilated waters, (iii) slow rate of deposition and (iv) the presence of a reducing environment. Considering these factors and comparing the conditions obtaining in the different parts of the shelf, it could be seen that the organic carbon in the sediments of the outer shelf cannot act as an effective adsorbant. The inshore sediments, no doubt, contain a high percentage of organic carbon but the rapid rate of sedimentation taking place in this region prevents it from acting as an adsorbant as it will not be in effective contact with the overlying waters for a considerable period.

A negative relationship exists between nickel and carbonate content. This indicates that there is no enrichment of nickel in these sediments by the organisms in their tests.

Nickel co-varies with manganese and iron. Relatively, it has a stronger correlation with manganese. A comparison of the distribution patterns of manganese and nickel shows that they are closely similar in that (i) both show a negative trend with depth, (ii) in general both are enriched in the nearshore and slope sediments relatively to the sediments in the outer shelf, and (iii) both show a decreasing trend from north to south except in the case of the Cochin section where though manganese content is less, the nickel content is high. This similarity in distribution might suggest that they are both closely related in these sediments. Adsorption by clay minerals on their surfaces is considered to be more effective in nearshore areas owing to the higher concentration of suspended clay particles. Information available on the manganese content in the clay fraction of a few of the samples (Table III)

TABLE III

Name of the section	Station No.	MnO content
Off Bombay ..	638	0·05
	642	0·03
Off Karwar ..	656	0·04
	652	0·03
Off Mangalore ..	657	0·02
	659	0·01
	661	0·02
Off Cochin ..	671	0·02
	669	0·01
	666	0·01

shows that a considerable portion of manganese is concentrated in the clay fraction and that it shows the same trend as in the silt and clay fraction. The hydrographic conditions in the shelf region being similar along the different parts of the west coast of India, this can

perhaps be attributed to (i) the differences in the source rocks present along the different parts along the west coast and (ii) the differences in the adsorption capacities of the different clay minerals present in the different regions. It is quite possible that nickel may also be simultaneously getting fixed up in the sediments by this process. Thus while this process may be operating it is not unlikely that a part of nickel might have entered the basin of deposition structurally combined with the sediment and from the present studies it is not possible to determine what proportion of nickel is derived from the sea-water and what proportion is detrital in origin.

Along the Cochin section, the nickel content is high in spite of the fact that the manganese content is low. This may perhaps be due to (i) the presence of the basic rocks along this coast which contain a relatively higher content of nickel and (ii) the high content of iron in these sediments which may be scavenging the nickel from the waters. The relatively stronger correlation observed with iron than with manganese in the sediments of this section supports this surmise.

1. Murty, P. S. N., Reddy, C. V. G. and Varadachari, V. V. R., *Proc. Nat. Inst. Sci. India*, 1968, **34.**

2. —, Rao, Ch. M. and Reddy, C. V. G., *Curr. Sci.*, 1968, **37.**

3. Nair, R. R. and Abraham Pylee, *Bull. Nat. Inst. Sci. India*, 1968, **38.**

4. Murty, P. S. N., Reddy, C. V. G. and Varadachari, V. V. R., *Proc. Nat. Inst. Sci. India* (in press).

5. Sandell, E. B., *Colorimetric Determination of Traces of Metals*, Interscience, New York, 1950.

6. Snell, E. D. and Snell, C. T., *Colorimetric Method of Analysis*, I, 3rd ed., D. Van Nostrand Co., New York, 1949.

7. ElWakeel, S. K. and Riley, J. P., *J. Cons. Perm. Int. Explor. Mer.*, 1957, **22.**

8. Kraus-kopf, K. B., *Geochim. et Cosmoch. Acta*, 1956, **9.**

9. Nicholls, G. D. and Loving, D. H., *Ibid.*, 1962, **26.**

10. Hirst, D. M., *Ibid.*, 1962 b, **26.**

11. Hogdahl, O. T., *Trace Elements in the Ocean*, The Central Institute for Industrial Research, Oslo, 1963.

12. Chester, R., *Chemical Oceanography*, eds. J. P. Riley and G. Skirro, Academic Press, London and New York, Vol. **2.**

13. Rao, D. S. and Madhavan, N., *J. Mar. biol. Ass. India*, 1964, **2.**

14. Seshappa, G., *Nature, Lond.*, 1953, **171.**