

MINOR AND TRACE ELEMENTS IN THE MARINE ENVIRONMENT OF THE WEST COAST OF INDIA*

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INTRODUCTION

THERE is a close inter-relationship between the chemical composition of marine organisms and sediments on the one hand and that of sea water on the other. The accumulation of minor and trace elements by plants, animals and sediments, and its significance in the disposal of radioactive wastes have been subjects of extensive study (NAS-NRC Publ. 551).

While the chemical-oceanographic features of the Atlantic and Pacific Oceans are known in considerable detail (Hood, 1963), active work on corresponding aspects in the Indian Ocean is of comparatively recent origin and has taken the form of international cooperation like the International Indian Ocean Expedition (IIOE), 1962-65. As part of a programme of work in collaboration with International Atomic Energy Agency, studies were initiated on the chemistry and radioactivity in the shelf waters off the West Coast of India. Five stations (Bombay, 18° 55' N., 72° 50' E.; Veraval, 20° 54' N., 70° 22' E.; Ratnagiri, 17° 00' N., 73° 15' E.; Mangalore, 12° 51' N., 74° 50' E.; Cochin, 09° 58' N., 76° 16' E.) were selected for work in the coastal region and analyses were carried out on sea water and biological samples collected from these stations. Simultaneously opportunities were also availed of which were offered by IIOE Cruises (of I.N.S. 'Kistna' and R.V. ANTON BRUNN) for representative sampling in the open sea between Latitudes 02° S. and 25° N. and Longitudes 60° E. and 77° E. In the present paper data are reported on the concentration of elements like calcium, potassium, phosphorus and strontium and also trace elements like copper, iron, rubidium, caesium, uranium and radium in the marine environment. Concentration Factors (CF) are discussed with reference to Maximum Permissible Concentrations (MPC) of radionuclides in sea water.

ANALYTICAL METHODS

Sea water samples were filtered through Whatman No. 1 Paper prior to analysis. Biological samples were oven-dried at 100-110°C. before being dry-ashed in an electric muffle furnace at 550°C.; chemical analyses for the elements (except phosphorus and zinc) were done on the dry ash. Sediment samples were oven-dried at 100-110°C. and then refluxed with a (3 : 1, v/v) mixture of concentrated nitric acid and 60% perchloric acid (sp. gr. 1.53) the acid extracts were used for chemical analyses.

For the estimation of calcium, copper and iron in sea water the methods described by Barnes (1959) were followed. Potassium was determined gravimetri-

cally in the form of its tetra phenyl boron complex (Sporek, 1956). Strontium was coprecipitated with calcium as carbonate, dissolved in acid and estimated flame photometrically (Willard, Merritt and Dean, 1958). Total phosphorus was determined according to Hansen and Robinson (1953). Uranium was estimated after coprecipitation with aluminium phosphate as given by Sandell (1959). Zinc was determined spectrophotometrically in a carbon tetrachloride extract of its dithionite complex (Fonselius and Koroleff, 1961).

For the estimation of copper, iron, uranium and zinc in biomaterial and copper and iron in sediment extracts the methods described by Sandell (1959) were followed. Calcium was isolated as the oxalate and determined titrimetrically using EDTA reagent (Henley and Saunders, 1958). Potassium was precipitated by sodium cobaltinitrite and the colour reaction of the cobaltinitrite complex with choline chloride and potassium ferrocyanide was used for its spectrophotometric determination (Allport and Keyser, 1957). The estimation of phosphorus was done on the dry material by the molybdenum blue method according to Kirsten and Carlsson (1960) and Viswanathan (1958). Radium was coprecipitated with barium sulphate and the alpha activity of the precipitate was determined in a ZnS scintillation counter (Goldin, 1961). Rubidium and caesium were determined by neutron activation analysis (Yamagata, Twashima and Tajima, 1962).

RESULTS AND DISCUSSION

The results of the analyses are given in Tables 1-6. Except when otherwise stated, the concentrations of the elements are expressed in parts per million parts (ppm) of water or wet weight of biological material or dry weight of sediment. From Table 1, it is seen that the calcium content of surface sea water in the coastal region varied from 413 to 511 ppm during the period November 1961 to May 1962. Higher calcium values (1030 and 915 ppm respectively) were observed at two stations (Lat. 16° 35'N., Long. 71° 45'E. and Lat. 16°25'N., Long. 72° 08'E.) in the vicinity of the coralline Angria Bank than at stations (in the region Lat. 16° 25'N.-18° 30'N., Long. 71° 45'E.-73° 28'E.) away from the Bank where the mean calcium content was 455 ppm (Vijaykrishnan Nair *et al*, 1965). In offshore water the calcium concentration increased progressively from south to north during the months September-December 1962 (Table 2).

The strontium content of the few coastal water samples examined for this element are lower than the average value reported for sea water viz., 8 mg/l (Culkin, 1965).

The concentration of potassium in the coastal water samples ranged from 374 to 528 ppm with a mean value of 428 ppm, during the period 1961-1962. The variations observed are in keeping with the nature of and fluctuations in the coastal environment. In offshore samples (September-December 1962), the potassium content increased progressively from south to north (Table 2).

The total phosphorus content of surface sea water along the coast near Bombay varied from 65 to 173 ug/l ; the variations paralleled those of another non-conservative element, copper. In offshore samples, the total phosphorus at the surface was less, the range being 25.8 to 54.0 ug/l. Zinc concentrations in surface water

TABLE 1

Chemical constituents of coastal surface waters in Arabian Sea

Location	Period	Ca	K	Sr	Total P	Total Fe	Cu	U
		ppm	ppm	ppm	ug/l	ug/l	ug/l	ug/l
Bombay 18° 55'N, 72° 50'E.	July 1961	124	..	4.8	110	2.0	10.0	..
	Nov. 1961	413(2)	528(2)	2.0(2)	114(1)	8.0(2)	16.8(2)	..
	Dec. 1961	438(6)	502(6)	6.8(6)	127(6)	6.0(6)	6.7(6)	..
	Jan. 1962	421(5)	447(5)	4.0(5)	173(5)	2.4(5)	15.8(5)	..
	Feb. 1962	413(3)	440(3)	5.8(3)	68(3)	2.0(3)	11.1(3)	..
	Mar. 1962	437(3)	418(3)	4.6(3)	91(3)	5.3(3)	12.7(3)	3.0(3)
	Apr. 1962	428(4)	374(4)	4.1(4)	77(3)	4.5(4)	12.1(3)	1.7(4)
Veraval 20° 54'N, 70° 22'E.	May 1962	511(9)	377(10)	5.2(9)	65(9)	4.0(9)	6.8(9)	3.0(9)
	Oct. 1963	425(3)	26.6(3)	8.8(3)	2.2(3)
	Dec. 1963	425	23.9	9.9	1.9
Ratnagiri 17° 00'N, 73° 15'E.	Mar. 1964	388(3)	12.2(4)	5.0(4)	3.2(5)
	Feb. 1964	430(2)	11.3(2)	4.3(2)	2.6(2)
Mangalore 12° 51'N, 74° 50'E.	Jan. 1964	426(2)	36.0	5.7	3.1
	Mar. 1964	437(2)	10.2(2)	14.9(2)	3.1(2)
Cochin 09° 58'N, 76° 16'E.	Jan. 1964	420(2)	9.3(2)	2.8(2)	3.2(2)
	Feb. 1964	427(3)	11.2(3)	2.7(3)	3.3(3)

Figures within brackets indicate the number of samples analysed.

TABLE 2

Chemical constituents of offshore surface waters in Arabian Sea

Period	Element	Unit	Latitudes degrees North				
			00-05	05-10	10-15	15-20	20-25
Sep.-Dec. 1962	Calcium	ppm	427(12)	431(25)	441(13)	456(24)	492(6)
	Potassium	ppm	332(12)	365(25)	361(12)	372(12)	397(6)
	Total Phosphorus	ug/l	25.8(8)	40.5(25)	48.0(18)	54.0(29)	45.1(20)
	Total Iron	ug/l	..	12.8(17)	3.7(23)	6.4(31)	7.6(19)
	Copper	ug/l	..	16.2(15)	13.7(23)	8.7(36)	10.6(19)
	Zinc	ug/l	..	25.2(7)	31.3(5)
	Uranium	ug/l	2.5(14)	2.2(26)	3.7(18)	2.7(36)	2.4(14)
Jan.-Mar. 1963	Calcium	ppm	438(8)	419(5)	416(4)	413(1)	..
	Potassium	ppm	398(9)	494(3)	499(4)
	Total Iron	ug/l	6.1(12)	1.8(6)	5.9(2)
	Copper	ug/l	11.6(10)	12.5(5)	3.9(4)
	Zinc	ug/l	21.1(12)	25.9(8)	16.3(6)
	Uranium	ug/l	2.3(11)	2.1(9)	1.5(4)
	July-Sep. 1963	Total Iron	ug/l	21.1(9)	25.0(12)	32.8(23)	36.1(13)
Copper		ug/l	6.5(10)	7.6(16)	11.3(27)	12.0(18)	11.3(5)
Zinc		ug/l	45.0(2)	33.7(9)	43.4(22)	51.1(3)	..

Figures within brackets indicate the number of samples analysed.

(offshore) are higher (16.3 to 51.0 ug/l) than those reported for other marine regions (1-23 ug/l) (Hood, 1963).

The uranium content of offshore sea water varied from 1.5 to 2.7 ug/l with a mean value of 2.4 ug/l. Analysis of latitudewise distribution of the element indicated minimum values along 08° 00'N. and maximum values along 12° 00'N. during September-December 1962 (Unni, 1966).

TABLE 3
Elemental composition of biological samples from Bombay Harbour Bay (1961-62)

Sl. No.	Species	Calcium ppm	Potassium ppm	Phosphorus ppm	Iron ppm	Copper ppm
1	<i>Parapenopsis stylifera</i>	877	5325	4351	48.7	3.5
2	<i>Metapenaeus monoceros</i> ..	854	9458	1320	18.6	4.0
3	<i>Harpodon nehereus</i> ..	507	2342	2810	8.3	0.2
4	<i>Solonocera indica</i> ..	805	5710	..	38.3	5.0
5	<i>Metapenaeus affinis</i> ..	750	5290	..	43.7	2.9
6	<i>Hippolysmata ensirostris</i>	932	5593	5146	41.3	3.8
7	<i>Parastromateus niger</i> ..	314	6711	..	18.0	0.3
8	<i>Chirocentrus dorab</i> ..	247	5815	1899	6.4	1.9
9	<i>Pampus sinensis</i> ..	260	6909	11150	12.5	1.3
10	<i>Scoliodon sorrakowah</i>	209	5174	13310	9.2	0.2
11	<i>Eleutheronema tetradactylum</i>	203	5711	10505	8.4	0.3
12	<i>Otolithus</i> sp.	7033	5013	35.4	0.5
13	<i>Katylisia marmorata</i>	1822	11700	..	271.0	1.3
14	<i>Panulirus</i> sp. ..	326	7454	..	5.1	6.0

TABLE 4
Natural radioactive elements in biological samples from Bombay Harbour Bay (1963-64)

Sl. No.	Species	Potassium ppm	Uranium gm/gm wet wt.	Radium ug/gm wet wt.
1	<i>Crassostrea cucullata</i>	1247	9.7×10^{-8}	6.5×10^{-6}
2	<i>Enteromorpha intestinalis</i>	368	1.1×10^{-8}	1.7×10^{-6}
3	<i>Caulerpa taxifolia</i>	102	7.4×10^{-9}	4.5×10^{-6}
4	<i>Scylla serrata</i>	1894	2.6×10^{-8}	6.1×10^{-6}
5	<i>Gracilaria</i> sp.	8810	1.3×10^{-7}	7.0×10^{-6}
6	Sponges (Siliceous)	..	1.3×10^{-8}	3.6×10^{-6}
7	<i>Crassostrea gryphoides</i>	..	1.3×10^{-7}	..
8	<i>Oedogonium</i> sp.	1052	1.8×10^{-8}	3.2×10^{-6}
9	<i>Clibanarius padavensis</i>	2780	5.6×10^{-7}	9.2×10^{-6}
10	<i>Pomadysys hasta</i>	3320	2.7×10^{-9}	3.8×10^{-6}
11	<i>Catenella repens</i>	395	1.9×10^{-8}	4.6×10^{-6}

It is seen from Table 3 that the clam, *Katylisia marmorata*, accumulates calcium, potassium and iron to a higher degree than the other species examined.

Accumulation of natural radioactive elements, potassium, uranium and radium is maximum in the case of the alga, *Gracilaria*, among the species examined (Table 4). Potassium and rubidium were the major contributors to natural beta activity in the organisms investigated by Mauchline and Templeton (1964). *Enteromorpha* sp. is found to be the highest specific concentrator for rubidium and caesium among the algal species examined so far (Table 5).

TABLE 5
Rubidium and Caesium in biomaterial (1963-64)

Sl. No.	Species	Rubidium ppm	Caesium ppm
1	<i>Ulva fasciata</i>	15.7	0.037
2	<i>Padina</i> sp.	18.6	0.040
3	<i>Sargassum</i> sp.	5.2	0.190
4	<i>Enteromorpha intestinalis</i>	332.8	0.190
5	<i>Catenella repens</i>	36.0	0.020
6	<i>Metapenaeus dobsoni</i>	4.7	0.001
7	<i>Arius</i> sp.	8.1	0.001
8	<i>Katylisia opima</i>	1.6	0.004
9	<i>Pseudoscleraena diacanthus</i>	1.2	0.004
10	<i>Metapenaeus monoceros</i>	3.1	N.D.

Samples Nos. 1 to 5 are on dry weight basis and 6 to 10 are on wet weight basis.

TABLE 6
Copper and iron content of marine sediments (1963)

Sl. No.	Location		Copper	Iron
	Lat. °N.	Long. °E.	ug/gm dry sediment	
1	17° 54'	72° 27'	99.5	5250
2	17° 25'	71° 39'	13.3	2250
3	17° 41'	71° 33'	9.5	2200
4	18° 27'	71° 33'	17.3	1875
5	19° 08'	71° 41'	43.0	5888
6	19° 47'	72° 04'	18.5	5375
7	20° 22'	71° 47'	..	6750
8	20° 30'	70° 54'	105.0	5375
9	20° 43'	70° 19'	450.0	5250
10	20° 23'	70° 00'	75.0	5625
11	19° 56'	69° 24'	40.0	3300
12	20° 35'	69° 18'	34.3	4580
13	20° 49'	69° 41'	130.0	6150
14	21° 07'	69° 48'	99.5	5625
15	21° 23'	69° 46'	77.5	5725

In the sediment samples examined (Table 6) the iron contents were fairly constant, the average being 4750 ug/gm. dry weight. The mean copper content was 55 times lower.

The data obtained in the present investigation can be utilized in the calculation of concentration factor (CF) which is defined as the ratio of the concentration of the element in the organism per unit weight to the concentration of the element in sea-water per unit volume. Typical values of CFs are as follows :

(i) Clam, *Katelysia marmorata* :

$$CF_{Ca} = 4.3, CF_K = 26.5, CF_{Pb} = 24,860, CF_P = 102,000.$$

(ii) Alga, *Gracilaria* :

$$CF_K = 20, CF_U = 50, CF_{Ra} = 208.$$

CF values have been used, among others by Pillai *et al* (1966) in the calculation of (MPC)_{water}. Maximum permissible concentrations for radionuclides in sea water, (MPC)_{sea water} can be calculated according to the formula :

$$(MPC)_{sea\ water} = \frac{P}{30\ or\ 100} \times \frac{5}{7} \times \frac{3}{10} \times \frac{1}{W_1 CF \left(\frac{B}{K+B} \right) + W_2 CF_{salt}}$$

where P is the maximum permissible daily intake of radionuclides in uc,

W₁ is the daily intake of marine organism,

CF is the concentration factor for marine organisms eaten,

B and K are the biological and physical decay constants,

W₂ is the daily intake of salt, and

CF_{salt} is the concentration factor for salt.

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SUMMARY

In view of the affinity of marine organisms and sediments for minor and trace elements and their radioisotopes, analyses were carried out on marine environmental samples at five stations on the West Coast of India (Veraval, Bombay, Ratnagiri, Mangalore and Cochin) during the period 1962-65. The following ranges of concentrations were observed in sea water : Potassium, 374-528 ppm ; Calcium, 388-511 ppm ; Strontium, 2.0-16.8 ppm ; Phosphorus, 65-173 ug/l ; Iron, 2-36 ug/l ; Copper, 2.7-16.8 ug/l and Uranium, 1.7-3.3 ug/l. Analyses were carried out on sea water samples collected from the Indian Ocean during the International Indian Ocean Expedition. Results are also given for the calcium, potassium, phosphorus, iron, copper, uranium and radium contents in marine biological samples collected

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from Bombay. Five algal species have been examined for their contents of Rubidium and Caesium. Alga, *Gracilaria* was found to concentrate natural radioactive elements Potassium, Radium and Uranium more than the other species examined. Clam, *Katylisia marmorata* was found to concentrate potassium, iron and phosphorus to a very high degree.

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