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MANGANESE, ZINC, COPPER, NICKEL AND COBALT CONTENTS IN SEA WATER AND SEAWEEDS FROM SAURASHTRA COAST

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ABSTRACT

Mn, Zn, Cu, Ni and Co have been analysed in sea water and 24 species of green, brown and red seaweeds collected from Diu, Porbandar and Okha reefs of the Saurashtra coast. The ranges of Mn, Zn, Cu, Ni and Co contents are found to vary from 8.83-10.41, 10.54-11.89, 5.73-8.00, 2.63-3.05, 0.78-0.83 $\mu g \ 1^{-1}$ in sea water; 8.09-120.13, 13.78-35.89, 5.82-32.37, 0.61-4.56, 0.31-2.97 $\mu g \ g^{-1}$ in green seaweeds; 28.93-125.00, 15.61-54.72, 5.75-18.55, 1.43-4.10, 0.50-1.28 $\mu g \ g^{-1}$ in brown seaweeds and 13.01-160.78, 7.31-33.25, 5.08-28.54, 1.23-6.94 and 0.36-3.70 $\mu g \ g^{-1}$ in red seaweeds respectively. The metal content of the investigated seaweeds is in the decreasing order, Mn > Zn > Cu > Ni > Co. The concentration factor (c.f) of the trace metals in seaweeds are in the decreasing order, Mn (9.20×10^2 — 1.54×10^4) > Zn (6.10×10^2 — 4.61×10^3), Cu (8.80×10^2 — 4.05×10^3) > Co (3.97×10^2 — 4.57×10^3) > Ni (2.32×10^2 — 2.28×10^3)
In general, shorter the residence time, more is the c.f. of elements in seaweeds.

Key-words : Trace metals, Sea water, Seaweeds, Saurashtra coast.

The physiological significance of certain elements in seaweeds, as in all other living organisms is well known (Chapman, 1979). Though these elements are required only in minute quantities, seaweeds concentrate and accumulate certain elements more than their normal biochemical budget; however, the function of these surprisingly large extent of accumulated elements is unknown. The trace element contents and their distribution in most of the Indian coastal and offshore waters are well documented. (Sen Gupta, Singbal and Sanzgiri, 1978; Patel, Bangera, Patel and Balani, 1985) and in seaweeds (Pillai, 1956; Zingde, Singbal, Moraes and Reddy, 1976; Agadi, Bhosle and Untawale, 1978; Patel, Pawar, Balani and Patel, 1980). Except the report of Rao and Tipnis (1967) there is no information on the trace elements content in the seaweeds from the Saurashtra coast. In the present attempt Mn, Zn, Cu, Ni and Co have been analysed in sea water and seaweeds from this coast.

Sea water and seaweed samples were collected from Diu (lat. 20° 43' N; long. 71° 02' E), Porbandar (lat. 21° 38' N; long. 69° 37' E) and Okha (lat. 22° 28' N; long 69° 05' E) situated along the Saurashtra coast. There is no freshwater inflow at these places and the tide pattern is semidiurnal. In fact southwest

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region off Arabian Sea experiences biannual reversion of water movements due to the prevailing monsoons. The hydrography of the completely open reef of Diu, partially protected by the artificial construction at Porbandar site and the open reef of Okha on the Gulf mouth of Kutch is not accounted in the present study. The study site at Porbandar is completely separated from the harbour, sewage and other effluent entering sites.

Sea water samples collected in buckets were immediately filtered through ordinary filter paper into acid cleaned 10 litre capacity polythene cans. In the laboratory, sea water was filtered through Whatman GF|C filter paper. From the filtered samples known amount (1-3 1) of water, after adjusting to suitable pH, was preconcentrated by passing through chelax-100 ion exchange resin (50-100 mesh : mixed with pyrex glass powder in the ratio 1 : 1) and eluted with mineral acids. Eluted sample was evaporated to a small volume and dissolvedin 0 1 N HNO_3 and made up to known volume with deionised water. These samples were used for Atomic Absorption Spectrometry (AAS) analyses (Riley and Taylor 1968).

Seaweed samples were collected from different parts of the intertidal regions during the lowest low neap tide periods. After handpicking from their natural habitat these seaweeds were cleaned by sea water, tap water, followed by distilled water, air dried, powdered, sieved through muslin cloth and used for metal analyses by AAS after acid digestion under reflux.

The trace metal contents, average of 3 analyses of sea water and seaweeds viz., green, brown and red algae are depicted in Table I. Coefficient of variation as a percentage of standard deviation between the triplicates calculated in sea water is 8-13% for Mn, Zn and Cu and 10-15% for Ni and Co, and in seaweeds 7-20% for Mn, Zn, Cu and Ni and 10-22% for Co. Concentration factor (c.f) is calculated for each metal in seaweeds by the ratio of metal content in seaweed, $\mu g\ g^{-1}$ dry weight, to that in sea water $\mu g\ l^{-1}$ and shown in Table I.

Sea Water :

The ranges of Mn, Zn, Cu, Ni and Co contents were found to

Sea Water The ranges of Mn, Zn, Cu, Ni and Co contents were found to vary from 8.83 — 10.41, 10.54 — 11.89, 5.73 — 8.00, 2.63 — 3.05, 0.78 — 0.83 ug l^{-1} respectively in sea water. Cu was found to be remarkably more in the shoreline water of Diu than those from Okha and Porbandar. Mn, Zn, Ni and Co were relatively more in Porbandar and Okha waters than in that of Diu.

The observed values of Cu in the present study were comparable with the data for the coastal waters of Arabian Sea of the West coast of India (Sen Gupta, Singbal and Sanzgiri, 1978) but less than that of Bombay Harbour Bay waters (Patel, Bangera, Patel and Balani, 1985). Mn content is less than that of coastal water of Coa (Zingde, Singbal, Moraes and Reddy, 1976: Sen Gupta, Singbal and Sanzgiri, 1978, while it is found to be more in the Saurashtra shoreline waters than that of Bombay Harbour Bay. Zn is more in waters of Bombay Harbour Bay, Arabian Sea waters than the recorded values of the present study. Ni content is more or less comparable with Arabian Sea water data and less than Bombay Harbour Bay waters. Co content is less than Arabian Sea waters and more than Bombay Harbour Bay waters. The concentration of Mn, Zn, Cu, Ni and Co observed in shoreline waters in the present study are higher than the reported values of oceanic waters of Arabian Sea and Indian Ocean (Topping, 1969).

Even though the trace metal distribution in the coastal environment is to a great extent influenced by fresh water inflow (Riley and Chester, 1971), the three areas of the current investigation do not show this effect. However *in situ scavanging* and recycling and the tidal currents encountered in the coasts affect the trace metal pattern (Mart, Rutzel, Klahre, Sipos, Platzek, Valenta and Nurnberg, 1982). In this process, after total decomposition of the organic particulates and dead phytoplantkton cells, the trace metals are distributed into surrounding medium. Their shoreward transportation especially in the shallow coastal environments may be responsible for the high trace metal content in shore waters.

SEAWEEDS

Concentration factor (c.f.) of Zn, Cu, Ni and Co was found to vary to a magnitude of 1 to 3 in all the three classes of seaweeds except the c.f. of Zn for brown seaweeds which was found to be 3 order of magnitude. In the case of Mn the c.f. of brown and red seaweeds varied between 3 to 4 orders of magnitude, while for green seaweeds it was between 2 to 4 orders of magnitude. Mn and Ni are found to be minimum in *Ulva fasciata* (Diu) and maximum in *Chondria armata* (Porbandar). Zn and Cu were minimum in *Amphiroa anceps* (Porbandar) & maximum in *Padina tetrastromatica* (Porbandar) and *Valoniopsis pachynema* (Diu) respectively. Co recorded was minimum in *Enteromorpha* sp. (Diu) and maximum in *Amphiroa anceps* (Okha). The metal content in all the seaweeds was in the decreasing order of Mn > Zn > Cu > Ni > Co, with the exceptions of few green seaweeds and a calcified red alga *Amphiroa anceps*. The green seaweeds, *Enteromorpha* sp., *Valoniopsis pachynema* and *Bryopsis plumosa* from Diu concentrated more Cu than Zn. In *Ulva fasciata* collected from Diu the order of accumulation was Zn > Cu > Mn > Ni > Co whereas from Porbandar and Okha it was Zn > Mn > Cu > Ni > Co. *Bryopsis plumosa* and *Amphiroa anceps* concentrate more Co than Ni and their metal contents were in the decreasing order : Mn > Cu > Zn > Co > Ni and Mn > Zn > Cu > Co > Ni respectively. Mn, Zn, Ni and Co were more in brown and red seaweeds whereas Cu was marginally more in green seaweeds (Table I).

Though the metal contents of seaweeds were quite variable, the trend of high content of Mn followed by Zn and Cu was observed in seaweeds from inshore waters along East to West coasts of the Indian Subcontinent, a typical tropical zone (Pillai, 1956; Agadi, Bhosle and Untawale, 1978; Patel, Balani and Patel; Rao, 1980 and Tipnis, 1967). The seaweeds from other tropics also acumulate more Mn

Table I. Metal contents of seawater µgl⁻¹ and seaweeds µgl⁻¹ (dry wt.)

Seaweed	Collection Site	Mn	C.F. x 10³	Zn	C.F. x 10³	Cu	C.F. x 10³	Ni	C.F. x 10²	Co	C.F. x 10²
Sea water	D	8.83		10.54		8.00		2.63		0.78	
	P	10.41		11.89		5.73		3.05		0.83	
	O	9.37		11.38		5.91		3.05		0.81	
Chlorophyta	D	27.22	3.08	20.89	1.98	13.79	1.72	1.49	5.66	0.48	6.15
Enteromorpha	P	40.20	3.86	32.30	2.72	8.93	1.56	1.37	4.49	0.60	7.23
intestinalis	O	32.45	3.46	23.75	2.08	5.82	0.98	0.86	2.82	0.35	4.52
(Linn.) Link.											
Enteromorpha sp.	D	25.57	2.89	13.78	1.21	15.92	1.99	0.89	3.38	0.34	3.97
	P	37.73	3.62	28.34	2.38	13.76	2.40	0.94	3.08	0.42	5.06
Ulva fasciata Delile	D	8.09	0.92	22.08	2.05	16.07	2.01	0.61	2.32	0.50	6.41
	P	10.18	0.98	22.05	1.85	6.12	1.07	0.83	2.72	0.67	8.07
	O	12.78	1.36	17.95	1.58	8.53	1.44	1.00	3.28	0.89	10.98
Chaetomorpha	D	21.71	2.46	15.86	1.50	14.22	1.78	1.33	5.06	0.88	11.28
antennina	P	35.42	3.46	26.99	2.27	5.93	1.03	1.20	3.93	0.79	9.52
(Bory) Kuetz.	O	19.98	2.13	19.57	1.72	7.14	1.21	1.43	4.69	0.81	10.00
Cladophora	D	50.78	5.75	20.58	1.95	18.92	2.36	1.49	5.66	0.62	7.95
fascicularis	P	120.13	11.54	35.89	3.02	8.92	1.56	2.60	8.52	1.00	12.05
(Mertens) Kuetz	O	80.35	8.57	27.34	2.40	7.78	1.32	2.98	9.77	0.94	11.60
Bryopsis plumosa	D	84.81	9.60	23.22	2.20	30.49	3.81	2.18	8.29	2.27	29.10
(Huds.) Ag.	P	78.94	7.58	18.98	1.60	20.73	3.61	2.57	8.42	2.97	35.78
	O	45.00	4.80	15.57	1.37	17.89	3.02	1.97	6.46	2.00	24.69
Caulerpa racemosa											
(Forssk.) Weber V.	D	25.38	2.57	20.98	1.99	12.81	1.60	3.44	13.08	0.79	10.12
Bosse.	P	53.03	5.09	19.36	1.63	8.96	1.56	4.56	14.95	1.06	12.77
	O	45.77	4.88	22.93	2.01	5.99	1.01	2.76	9.05	0.69	8.52
Valoniopsis pachynema	D	53.78	6.09	19.97	1.39	32.37	4.05	1.20	4.56	1.40	17.95
(Martens) Boergs.	P	103.33	9.93	27.38	2.30	20.75	3.62	1.71	5.61	1.73	20.84
Phaeophyta	D	50.19	5.68	21.98	2.08	18.55	2.32	4.10	15.59	1.20	15.38
Dictyota dichotoma	P	48.11	4.62	24.22	2.03	13.02	2.27	3.49	11.44	0.93	11.20
(Huds) Lamour.	O	70.53	7.52	27.37	2.40	12.93	2.19	3.77	12.36	1.00	12.34
Padina tetrastromatica	D	57.83	6.55	22.49	2.15	12.07	1.51	1.70	6.46	1.05	13.46
Hauck.	P	97.48	9.36	54.77	4.61	8.80	1.53	2.22	7.28	1.07	12.89
	O	32.18	3.43	22.57	1.98	7.11	1.21	1.46	4.79	0.89	10.99

Padina sp.	P	125.00	12.09	39.17	3.29	9.03	1.58	2.50	8.19	1.18	14.21
Spatoglossum asperum	D	45.37	5.14	19.24	1.62	12.25	1.53	2.16	8.21	1.06	13.58
J.Ag.	P	34.31	3.29	23.81	2.00	6.40	1.1[illegible]	1.58	5.16	0.85	10.24
	O	28.93	3.09	15.61	1.37	8.97	1.52	1.89	6.19	0.90	11.1[illegible]
Cystoseira indica	D	49.47	5.69	24.06	2.28	15.99	2.00	1.43	4.66	0.79	10.13
(Thivy et Doshi) Mairh	P	58.73	5.64	21.79	1.83	9.36	1.63	2.67	8.75	1.13	13.61
	O	34.26	3.66	18.67	1.61	5.75	0.97	1.58	5.18	0.50	6.17
Sargassum johnstonii Setchell and Gardner	O	70.10	7.48	26.83	2.56	10.31	1.74	3.87	12.61	1.20	14.81
S. swartzii (turn.) C.Ag.	P	53.01	5.09	23.55	1.98	8.93	1.56	1.98	6.49	0.80	9.63
	O	78.00	8.32	30.76	2.70	9.78	1.65	4.00	13.11	1.23	15.18
S. tenerrimum J. Ag.	D	41.85	4.74	25.52	2.42	15.26	1.91	2.87	10.9[illegible]	1.07	13.72
	P	64.87	6.23	34.69	2.92	8.53	1.49	3.12	10.23	1.12	13.50
	O	67.37	7.19	28.79	2.53	10.78	1.82	4.00	13.11	1.28	15.80
Rhodophyta											
Gelidiella acerosa	D	30.99	3.51	24.65	2.34	28.54	3.57	2.39	9.09	0.36	4.61
(Forsk.) Feldman	P	39.38	3.78	23.38	1.97	17.93	3.13	2.87	9.41	0.45	5.42
et Hamel	O	34.51	3.68	28.71	2.52	20.75	3.51	3.45	10.55	0.55	6.79
Amphiroa anceps	D	17.38	1.97	10.38	0.93	07.08	0.89	2.76	10.49	2.92	37.43
(Lamk.) Decsne.	P	13.01	1.25	7.31	0.61	5.08	0.86	2.31	7.57	2.73	32.89
	O	15.71	1.08	8.93	0.79	6.58	1.11	3.54	11.61	3.70	45.67
Sarconema filiforme (Sond.) Kylin.	P	85.97	8.26	12.38	1.04	7.86	1.37	3.09	10.13	0.75	9.03
	O	120.25	12.83	13.73	1.20	9.46	1.60	3.43	11.24	0.83	10.25
Hypnea musciformis	D	69.11	7.83	28.53	2.70	17.91	2.24	1.92	7.30	0.75	9.61
(Wulf.) Lomour,	P	61.76	5.93	33.25	2.79	12.47	2.18	3.37	11.05	1.26	15.18
	O	87.97	9.39	25.31	2.22	9.38	1.58	2.93	9.61	1.06	13.08
Gracilaria corticula	D	51.14	5.79	24.71	2.34	10.05	1.26	1.79	6.81	0.67	8.58
(Agadh) J. Ag.	P	137.46	13.20	29.47	2.48	6.74	1.17	2.74	8.93	0.80	9.63
	O	75.38	8.04	27.96	2.46	8.78	1.48	2.27	7.44	0.75	9.25
Acanthophora spicifera	D	26.51	3.00	21.32	2.02	13.78	1.72	2.00	7.60	1.02	13.08
(Vahl.) Boergs.	P	18.00	1.73	16.96	1.43	10.85	1.89	1.23	4.08	0.85	10.24
Chondria armata (Kuetz.) Okamura Var. *plumaris*	P	160.78	15.44	27.67	2.32	15.34	2.68	6.94	22.75	1.26	15.18
Boergs.	O	130.43	13.92	21.92	1.93	11.51	1.95	5.64	18.49	1.07	13.21
Laurencia sp.	D	45.83	5.20	23.34	2.21	15.54	1.94	3.35	12.74	1.00	12.82
	P	102.30	9.88	27.30	2.30	9.46	1.65	3.23	10.59	1.34	16.14
	O	90.58	9.67	25.19	2.21	8.83	1.49	2.18	7.15	1.12	13.82

D = Diu; P = Porbandar; O = Okha;

than Zn (Sivalingam, 1978; Guimares, Drude de Lacerda and Teixeira, 1982; El Tawil and Baghlaf, 1983) Therefore it seems that the tropical seaweeds tend to accumulate more Mn than Zn as evidenced by the present study also.

It is likely that the sulfate groups of carrageenans of red seaweeds and sulfated heteropolysaccharides of green seaweeds provide numerous anionic sites for the polyvalent cations as do the carboxylate groups is uronic acids of algin. Polysaccharides are known to posses strong affinity towards the polyvalent metal ions (Percival and McDowell, 1967). The decreasing order of affinity of the five elements for algin, and carrageenan respectively is :

Cu > Co > Ni > Zn > Mn (Haug, 1961)
Zn > Co > Mn > Ni > Cu (Paskin-Hurlburt, Tanaka and Skoryna 1976)

However these metals in seaweeds in the present study do not conform to the above sequence. These differences in the metal sequence are probably due to the involvement of complexation of metal ions with the bulk organic ligands such as proteins and lipids, in addition to the one or more polysaccharides as mentioned above, and the cumulative effect of all these factors.

The concentration of particular trace metal at its natural or slightly or moderately more levels in the ambient medium reflects the bio-deposition of the metal in seaweeds (Hagerhall, 1973; Patel, Pawar, Balani and Patel 1980). It can be seen that Cu content in the seaweeds from Diu is more than in the seaweeds from other two places. The abundance of the elements in sea water unless influenced by anthropogenic activities or regional input of these elements, depends upon their reactivity. High reactive elements have short residence time (Goldberg 1963). The bioavailability is also governed by oceanic residence time (T) of the elements. Yamamoto, Otsuka, Okazaki and Okamoto K-I (1979) have reported the accumulation of short T elements such as the transition metals in seaweeds from their ambient medium to several folds that in general, shorter the T more is the c.f. of elements in seaweeds. Present results, though confined to five metals only, the c.f. of these elements in seaweeds follows more or less a similar trend. Mn > Zn > Cu > Co > Ni and is contradictory to the suggestions of Goldberg that the order of the c.f. of the transition metals in marine organisms follow the Irwing-Williams order (Mn < Co < Ni < Cu > Zn) of metal stability constants (Riley and Chester, 1971).

It can be concluded that Mn content of Saurashtra seaweeds of tropical region is more than Zn. Mn content of sea water and seaweeds of Saurashtra is less than the waters and and seaweeds of Goa coast which is highly polluted with this metal (Zingde, Singbal, Moraes and Reddy, 1976). Cu content is more in waters, consequently more Cu is found in seaweeds of Diu coast rather than those from Porbandar and Okha. Mn and Zn contents are more in Porbandar and Okha waters and same is the case in the seaweeds from these two places rather than from the seaweeds of Diu. The c.f. of trace element is primarily governed by the concentration of the metal present in ambient medium and its residence time.

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REFERENCES

Agadi, V.V., N.B. Bhosle and A.G. Untawale, 1978. Metal concentration in some seaweeds of Goa (India). *Botanica Marina.* **21** : 247-250.

Chapman, A.R.O., 1979. *Biology of seaweeds.* University Park Press. Baltimore, Maryland, U.S.A. 134 pp.

El Tawil, B.A.H. and A.O. Baghlaf, 1980. Trace metals in some marine species. *Pharmazie,* **38** : 200 — 201.

Goldberg, E.D., 1963. The oceans as a chemical system, In : *The Sea,* Vol. 2 (edited by M.N. Hill). John Wiley & Sons, New York. p. 3-25.

Guimaraes, J.R.D., L. Drude de Lacerda and V.L. Teixeira, 1982. Concentrations of heavy metals in benthic algae of Bay of Ribeira Angra dos Reis. and subjected monitor species. *Revista Brasileira de Biologia.* **42** : 553-557.

Hagerhall, B., 1973. Marine botanical-hydrographical trace elements studies in the Ore.und area. *Botanica Marina,* **16** : 53-64.

Haug. A., 1961. The affinity of some divalent metals to different types of alginates. *Acta Chemica Scandinavica* **15**: 1794 — 1795.

Mart, L., H. Rutzel, F. Klahre. L. Sipos, U. Platzek, P. Valenta and H.W. Nurnberg. 1982. Comparative studies on the distribution of heavy hetals in the oceans and coastal waters. *The Science of the Total Environment,* **26**: 1-17.

Paskin-Hurlburt, A.J., Y. Tanaka and S.C. Skoryna, 1976. Carrageenan and the binding of lead. *Botanica Marina.* **19** : 59-60.

Patel, B., S. Pawar, M.C. Balani and S. Patel, 1980. Macro algae as 'sentinel' of trace and heavy metals in the management of coastal environment. In : *Management of environment* (edited by B. Patel). Wiley Eastern Ltd., Publication. New Delhi. P. 371-388.

Patel, B., V.S. Bangera, S. Patel and M.C. Balani, 1985. Heavy metals in the Bombay Harbour Area. *Marine Pollution Bulletin.* **16**: 22-28.

Percival, E. and R. H. McDowell, 1967. *Chemistry and enzymology of Marine algal polysacharides,* Academic Press, London.

Pillai, V.K., 1956. Chemical studies on Indian seaweeds 1. Mineral constituents. *Proceedings of Indian Academy of Sciences:* **44**B : 3-27.

Rao Sitakara, V. and U.K. Tipnis, 1967. Chemical composition of marine algae from Gujarat coast. In : *Proceedings of the Seminar on Sea, Salt and Plants.* (edited by K. Krishnamurthy) Catholic Press, Ranchi, India, P. 277 — 288.

Riley, J.P. and D. Taylor. 1968. Chelating resins for the concentration of trace elements from sea water and their analytical use in conjunction with atomic absorption spectrophotometry. *Analytica Chemica Acta,* **40** : 479-485.

Riley, J.P. and R. Chestar, 1971. *Introduction to Marine Chemistry*. Academic Press, London, 465 pp.

Sen Gupta, R., S.Y.S. Singbal and S. Sanzgiri, 1978. Atomic-absorption analyses of a few trace metals in Arabian Sea waters. *Indian Journal* of *Marine Sciences*. **7** : 295 — 299.

Sivalingam, P.M. 1978. Biodeposited trace metals and mineral content studies of some tropical marine algae. *Botanica Marina,* **21** : 327-330.

Topping, G., 1969. Concentration of Mn, Co, Cu, Fe, and Zn in northern Indian Ocean and Arabian Sea. *Journal* of *Marine Research,* **27** : 318-326.

Yamamoto, T.Y., Otsuka, M. Okazaki and K-I Okamoto, 1979. Distribution of chemical elements in algae. In : *Marine Algae in Pharmaceutical Science,* (edited by H.A. Hoppe. T. Lerving and Y. Tanaka). Walter de Gruyter, Berlin. PP. 569 — 607.

Zingde, M.D.. S.Y.S. Singbal. C.F. Moraes and C.V.G. Reddy, 1976. Arsenic, copper, zinc and manganese in the marine flora and fauna of coastal and estuarine waters around Goa. *Indian Journal of Marine Sciences* **5** : 212 — 217.