

## Atomic-absorption Analyses of a Few Trace Metals in Arabian Sea Waters

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Analyses of Cu, Fe, Zn, Co, Ni and Mn in dissolved and particulate forms from the Arabian Sea are reported. Average concentrations ( $\mu\text{g/litre}$ ) in dissolved form for all the samples are: Cu  $4.9 \pm 0.3$ ; Fe  $20 \pm 2.3$ ; Zn  $19.2 \pm 1.8$ ; Co  $2.2 \pm 0.3$  and Ni  $3.2 \pm 0.3$ . Averages for particulate forms in  $\mu\text{g/g}$  dry weight are: Cu  $250 \pm 43$ ; Fe  $12007 \pm 3048$ ; Zn  $29745 \pm 9959$  and Mn  $431 \pm 128$ . Dissolved manganese can not be analysed by the method used while particulate forms of cobalt and nickel are below the detection limit. Higher concentrations at a few stations nearshore indicate possible addition from land. An attempt has been made to discuss the marine chemistry of all these metals in the light of observed values.

**M**OST of the heavy metals are present in sea water in trace concentrations (ppb). They exhibit an enormous range of chemical reactions and are closely connected with the biogeochemical cycle in the marine environment. Transition group of metals, especially those with half-filled d-shells, have a tendency to attach to donor atoms to undergo bioaccumulation.

Metals in certain concentration are desirable for the growth of marine organisms but their over-accumulation is hazardous. It has been observed that metals, belonging to the transition group, complex more easily with chelate-forming constituents of biomaterial than with synthetic chelating chemicals<sup>1,2</sup>. Near the coast and river mouths the chelating character of humus material can render many of these metals easily assimilable to marine organisms<sup>3</sup>.

As part of an ongoing project on Protection of Marine Environment and Monitoring of Pollutants in India we have initiated observations on toxic and non-toxic heavy metals and metalloids in soluble and in organic forms. In the present paper data are given, relating to dissolved and particulate concentrations of Cu, Fe, Zn, Co, Ni and Mn.

### Materials and Methods

Collection and preservation of water samples for the study of trace metals must be performed in such a way as to exclude contamination as far as possible. During the 16th cruise of *RV Gaveshani* same set of 'aged' two 10 litre all-PVC Van Dorn water samplers with rubber-sealed end caps was used to collect the samples. The first sample was always collected at a depth of 10 m. In order to avoid contamination from the 3.5 m deep metal hull of the ship no smaller depth was sampled. The network of observation stations is given in Fig. 1.

About 2 l of water were used to rinse an acid-washed high-density jerry can which was then filled and immediately transferred to a vacuum

filtration unit. The sea water was filtered through 0.45  $\mu\text{m}$  membrane filter (Millipore HA), in a completely closed system to minimize contamination from the atmosphere of the ship's laboratory. Filtered samples were then transferred to similarly treated jerry cans and the pH was adjusted to between 3 and 4 with 1N HCl. It was observed<sup>4</sup> that at this pH the samples can be preserved for

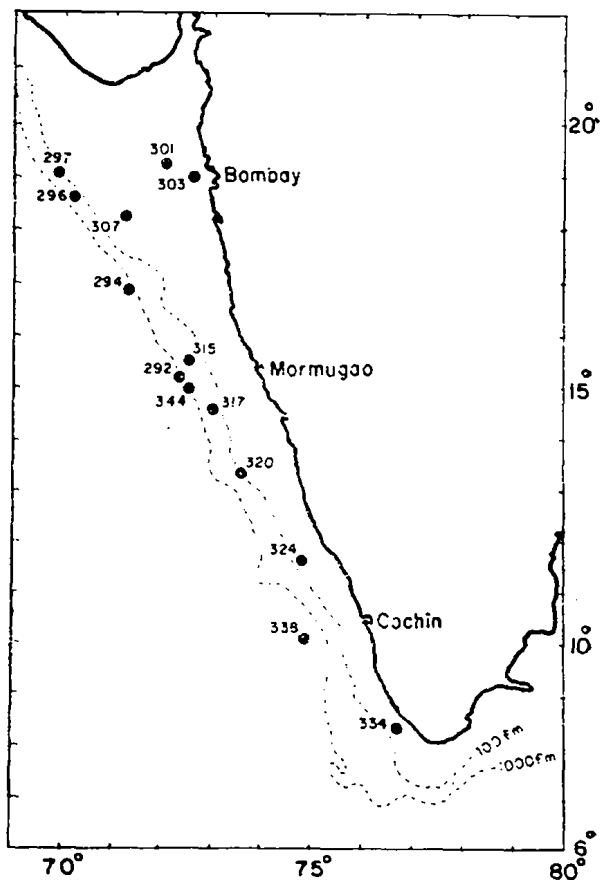


Fig. 1 — Location of stations

2-3 months, provided the jerry cans remain tightly sealed.

The reagents and chemicals used were either redistilled or dissolved in metal-free distilled water. In the atomic absorption spectrophotometry (AAS) for trace metal analysis the prior solvent extraction concentration step<sup>5</sup> was used. Briefly, the method used was a standard addition method of analysis in which 400 ml aliquots of sample were spiked with 0, 1, 2 and 3  $\mu\text{g}$  of each element. 10 ml of a 2% solution of ammonium pyrrolidine dithiocarbamate (APDC) was added to each aliquot and the chelated metals were extracted into 15 ml methyl isobutyl ketone (MIBK) which was aspirated into an air-acetylene flame in a Hilger-Watts Atomspek model H 1550. Re-extraction of each

sample, adding 5 ml APDC and 10 ml MIBK to each aliquot, established a blank. The 4 aliquots were used as repeats for calculating the accuracies of the analyses. The precision of the analyses, determined from repeats of several samples (2-3 runs for almost every sample) and reported as coefficient of variation is 11, 13, 8, 14 and 13% respectively for Cu, Fe, Zn, Co and Ni. Spencer and Brewer<sup>6</sup> obtained accuracies of 11, 8 and 8% for Cu, Zn and Ni respectively in their estimations in the Sargasso Sea and the Gulf of Maine. Sen Gupta<sup>7</sup> could obtain accuracies of 13, 9, 6, 11 and 11% respectively for Cu, Fe, Zn, Co and Ni in his analyses of Baltic Sea water. Considering that the analytical method applied in all the 3 studies was the same, but the models of the atomic absorption

TABLE 1 — CONCENTRATION OF METALS IN DISSOLVED (D;  $\mu\text{g l}^{-1}$ ) AND PARTICULATE (P;  $\mu\text{g g}^{-1}$ ) FORMS

St. No.	Total depth (m)	Sampling depth (m)	Cu		Fe		Zn		Co*	Ni*	Mn†
			D	P	D	P	D	P	D	D	P
292	1700	10	6.8	65	—	260	—	5734	1	4.4	148
		500	2.8	36.2	—	2420	—	1804	0.5	4.4	58
294	1700	10	—	174	—	2720	—	3329	—	—	43
		100	—	427	—	2393	—	1692	—	—	26
		500	5	127	11	746	5.7	944	2	4	22
		1000	7.9	201	13.3	1846	6.3	1114	0.8	2.1	40
296	350	10	6.6	53	10	522	5.5	258	1	3.9	528
		100	6.7	135	18.2	935	7.5	1619	3.3	4	600
		280	4.6	139	14.1	350	5.8	723	4.9	1	15
297	180	10	5	131	11.7	1619	25.4	4450	3.3	1.5	69
		100	3.5	196	10.4	2186	31.5	2505	4.1	2.5	41
		150	6	91	13.1	4591	16	5366	1.6	2	161
301	49	10	4.8	126	25.9	1880	29.4	4526	ND	2	74
		45	7.3	234	12.8	1430	16.1	1591	ND	1.5	117
303	22	10	2.5	33	10.4	22187	18.3	1464	ND	1.5	675
		20	6.3	59	16.8	25207	14.2	1089	ND	2.5	882
307	86	10	3.1	170	16.2	4236	8	5264	ND	1	19
		75	1.7	147	8	6819	7.6	11787	0.8	3	213
315	900	10	3.8	99	19.7	3423	16.1	10845	0.8	5	14
		500	5.2	183	14.1	515	23.3	13014	6.6	4.5	84
		800	3.1	414	25	5397	16.5	13759	3.3	11.5	34
317	240	10	7.7	301	28.4	1913	37.6	4495	0.8	4	19
		200	4.5	71	11.9	1388	8.8	3976	2.4	2	12
320	70	10	5	355	66.9	2605	42.4	7342	ND	3.5	92
		65	4.5	39	34.4	8407	27.2	3506	3.3	4.5	86
324	87	10	4.4	524	35.7	3405	16.9	7690	3.3	ND	42
		80	2.5	232	11.6	7488	29	305	2.4	2	134
334	44	10	4.4	250	14.3	70500	16	204750	ND	2.5	3333
		40	5.8	1417	21.9	69583	23.1	162583	ND	1.5	917
338	1700	10	4.2	400	49.5	32500	15.1	88800	0.8	3	3200
		100	7.7	700	19.2	13900	19.6	68900	2.4	2	800
		500	4.2	450	23	25750	31.2	69650	ND	4.5	450
		1000	3.4	500	20.1	48000	18	154700	0.8	4	500
344	1400	10	3.3	176	29.8	14176	19.5	83235	0.8	1	823
		100	5.8	111	07.2	24333	37.9	88389	0.8	4	778

ND = not detectable

\*Not detectable in particulate form

†Estimated only in particulate form

spectrophotometer were different, that the accuracies, we could obtain with the reagents and chemicals available, may lie within the acceptable limit.

Filters containing particulate matter were stored in plastic boxes under refrigeration. After reaching shore they were transferred to a desiccator. When completely dry, these were removed and weighed. Blank filter papers were similarly treated. Each filter paper was transferred to a conical flask containing 1 ml perchloric acid. After evaporation the residue was digested with concentrated HNO<sub>3</sub>. The dried residue was then treated with a drop of concentrated HCl and dissolved in 0.1N HCl making up the volume to 10 ml in each case. Blanks and standards were also similarly treated and run into the AAS.

All the samples were analysed by the same personnel using the same technique so that errors due to personal bias could be almost the same throughout the whole series of measurements.

Dissolved Mn was not found to be extracted with APDC-MIBK combination at the pH at which the samples were analysed. Therefore, the metal was estimated only in particulate form.

### Results and Discussion

Most of the trace metals in sea water have been observed to occur as hydrated ions or weakly bound complexes. Since the metals were extracted by chelating with APDC using MIBK as the solvent, the dissolved metal content can be expected to give a measure of the hydrated metal ions as well as their weakly bound complexes. For, in the latter case, the metal atom should be able to detach itself from the natural chelating agent to complex with the stronger synthetic chelating agent.

No particular trend of depthwise variations could be noted for almost all the metals in their dissolved state. Average concentration of Cu was  $4.7 \pm 0.4 \mu\text{g l}^{-1}$  at 10 m and the values at most of the stations were found to lie around the average. The highest value observed was  $7.7 \mu\text{g l}^{-1}$  at station 317, about 40 naut. mile off the coast of Goa. Higher values of Cu at depths than at the surface at shallow stations indicate higher accumulations of the metal in sediments. Spencer and Brewer<sup>6</sup> recorded a range of  $0.1-4.8 \mu\text{g l}^{-1}$  (mean  $2.1 \pm 0.2$ ) of the metal from Sargasso Sea. In the present study a range of  $1.7-7.9 \mu\text{g l}^{-1}$  (Table 1) and a mean of  $4.9 \pm 0.3$  (Table 2) were observed. It has been observed<sup>7</sup> that some of the organisms in the sea can concentrate Cu. Present data when combined with the measurements of Kureishy and George<sup>8</sup> (Table 3), indicated this at selected localities. Solubility of Cu complexes is very much dependent on the redox conditions in water<sup>9</sup>. At shallow stations, quite frequently higher Cu values were encountered near the bottom indicating that the fraction of this metal concentrated at the surface has been released by the process of decomposition. In deeper stations, however, lower values were obtained for dissolved Cu at mid-depths while the particulate fractions were considerable. Deeper down, however, there was an increase in the dissolved fraction. In the Arabian Sea oxygen con-

TABLE 2 — CONCENTRATION OF METALS IN DISSOLVED ( $\mu\text{g/LITRE}$ ) AND PARTICULATE ( $\mu\text{g/DRY WT}$ ) FORMS IN DIFFERENT DEPTH RANGES

[Values are average  $\pm$  SE]

	Depth, m												All samples			
	10		20-80		100-500		800-1000		P		D		P		D	
Copper	4.7 $\pm$ 0.4	204 $\pm$ 37	4.7 $\pm$ 0.8	355 $\pm$ 196	5.1 $\pm$ 0.4	222 $\pm$ 0.4	4.8 $\pm$ 1.3	371 $\pm$ 72	4.9 $\pm$ 0.3	250 $\pm$ 43						
Iron	26.5 $\pm$ 4.8	1169 $\pm$ 5006	17.6 $\pm$ 3.5	1982 $\pm$ 9567	14.2 $\pm$ 1.4	7012 $\pm$ 2535	19.5 $\pm$ 2.8	18414 $\pm$ 12107	20.0 $\pm$ 2.3	12007 $\pm$ 3048						
Zinc	20.8 $\pm$ 3	30870 $\pm$ 14941	19.5 $\pm$ 3.1	22608 $\pm$ 14425	18.7 $\pm$ 3.6	21548 $\pm$ 9007	13.6 $\pm$ 3	56524 $\pm$ 40191	19.2 $\pm$ 1.8	29745 $\pm$ 9959						
Cobalt	1.5 $\pm$ 0.4	ND	2.2 $\pm$ 0.6	ND	2.9 $\pm$ 0.6	ND	1.6 $\pm$ 0.7	ND	2.2 $\pm$ 0.3	ND						
Nickel	2.8 $\pm$ 0.4	ND	2.5 $\pm$ 0.4	ND	3.2 $\pm$ 0.4	ND	5.9 $\pm$ 2.3	ND	3.2 $\pm$ 0.3	ND						
Manganese	—	649 $\pm$ 308	—	391 $\pm$ 147	—	254 $\pm$ 86	—	191 $\pm$ 85	—	431 $\pm$ 128						

D = dissolved; P = particulate; ND = not detectable

TABLE 3 — CONCENTRATION OF METALS IN ZOOPLANKTON\* AND IN PARTICULATE MATTER AT 10 m

(All values are in  $\mu\text{g/g}$  dry weight)

St. No.	Cu		Fe		Zn		Co† Plankton	Ni† Plankton
	Plankton	Particulate	Plankton	Particulate	Plankton	Particulate		
315	72	99	1010	3423	1382	10845	ND	ND
320	111	355	762	2605	942	7342	23	17
334	10	250	1923	70500	9274	204750	ND	ND
338	79	400	2984	32500	22494	88800	34	ND
Concentration factor	2060		6487		31370		2989	

\*From Kureishy and George<sup>8</sup>

†Not detectable in particulate matter

ND = not detectable

centrations were very low<sup>10</sup> (between 100 and 800 m). This indicates that conditions at mid-depths were not sufficient to dissolve the Cu accumulated by organisms at the surface.

Average concentration of Fe at 10 m was  $26.5 \pm 4.8 \mu\text{g l}^{-1}$ . The highest value observed was  $66.9 \mu\text{g l}^{-1}$  at station 320 about 70 naut. mile off the coast. Off Bombay the values were intermediate in the range. Fairly high concentrations of Fe are normally attributed to the presence of large quantities of soluble organic matter in the sea<sup>11</sup>. Observed concentrations of Fe give a measure of truly soluble complexes of  $\text{Fe}^{3+}$  ion and colloidal ferric hydroxide. Ferric ion present as  $\text{Fe}(\text{OH})^{2+}$  cannot exceed concentration of the order of  $1 \mu\text{g Fe/litre}^{12}$ . Hence most of Fe concentrations in the present data can be attributable to soluble complexes and colloidal  $\text{Fe}^{3+}$  compounds.

Examining the data given in Table 1 we can see that at almost all the deep stations there is a minimum in the particulate fraction. The almost reverse relations deeper down indicates the predominance of colloidal and  $\text{Fe}^{3+}$  fractions. Richness of the deep water in both the particulate and soluble fractions of Fe probably indicates that the metal settled as insoluble iron hydroxides or phosphates under conditions of increasing pH at or near the bottom, a phenomenon normally encountered in deep waters of all the oceans. Table 1 also indicates that the metal is not concentrated to any appreciable extent by the organisms at the surface. From Table 3 we can calculate that Fe concentration in zooplankton varies between only 3 and 29% of the total particulates. This is in agreement with earlier observations from the Indian waters that Fe is not a limiting factor for plankton production in the sea<sup>13</sup>. Thus, it can be concluded that in the Arabian Sea Fe is present mostly in suspended and particulate forms.

Average concentration of Zn at 10 m was  $20.8 \pm 3.0 \mu\text{g l}^{-1}$ . Concentrations at stations offshore were lower than the average while nearshore they were higher. Highest concentration of Zn was  $42.4 \mu\text{g l}^{-1}$  at station 320 where the highest

concentration of Fe was also noted. This is obviously due to coastal input. Zn concentrations in pretreated sewage near almost all the big cities show, on long term measurements, regularly occurring high concentrations interspersed with normal values<sup>7</sup>. Concentrations of zinc in the nearshore waters and sewage of Bombay are fairly high (0.4 to 347 and 0.2 to 221  $\mu\text{g/l}$  for water and sewage respectively)<sup>14</sup>. We attribute the addition from land as the cause for high Zn concentrations in some of the present samples.

Present range of  $5.5\text{--}42.4 \mu\text{g l}^{-1}$  (mean  $19.2 \pm 1.8$ ) compares well with the range of  $0.8\text{--}52.6 \mu\text{g l}^{-1}$  (mean  $9.7 \pm 0.5$ ) recorded by Spencer and Brewer<sup>6</sup> from Sargasso Sea and the Gulf of Maine. The difference in the mean values is due to the larger number of samples analysed and higher frequencies of low concentrations encountered in the observations of Spencer and Brewer<sup>6</sup>. They examined 234 samples while presently only 35 were studied. Also oceanographic characteristics in the two areas can be different.

Zn is concentrated by almost all organisms in the sea in varying quantities. Combining present values for particulate and suspended fractions with those for zooplankton (Table 3) it is seen that the latter makes up for a significant fraction at selected localities.

Attempts to measure Co and Ni showed very low concentrations in water and in particulate matter, which were below the sensitivity of the method of analysis. The depthwise variations of these 2 metals are erratic but a trend of decrease can be noted from the data. It has been suggested<sup>7</sup> that organisms might concentrate Ni at the surface which can be released at depths. Present data show that these metals are not present in particulate form (Table 1) and give an indication that they might be selectively absorbed by organisms as a local phenomenon.

Concentration of  $1.5 \mu\text{g l}^{-1}$  was obtained for Ni (excluding the sole high value  $11.5 \mu\text{g l}^{-1}$ ) while Spencer and Brewer<sup>6</sup> obtained  $0.4\text{--}2.5 \mu\text{g l}^{-1}$  from waters of the Sargasso Sea and the Gulf of Maine.

Examining Table 2 closely we find that the concentrations of all the metals should vary both horizontally and vertically. This can be evident from the standard errors (SE) which in almost all cases are higher than the coefficients of variation obtained in the analysis. The only exception is Ni which shows significant SE only at the deepest range. This, probably, lends support to the conclusion stated above. However, SE of all average values lie within the precision of the analytical method indicating the reproducibility of the data. The wide variations in SE of concentrations in particulate form (Table 2) and in metallic fractions in plankton indicate that in the Arabian Sea these are very much dependent on the space and location of samplings.

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