

DISTRIBUTION OF COPPER IN THE AQUATIC ENVIRONMENT OF THE BOMBAY HARBOUR BAY*

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ABSTRACT

Copper is an essential constituent of living matter. Because of its biological significance it is necessary to obtain information on the distribution of copper in the aquatic environment. Even though estimation of copper in the off-shore waters in the Arabian Sea have been reported, no detailed studies on the copper content in the different matrices of an estuarine environment have been made.

The paper reports concentration of copper obtained in sea water, marine organisms and sediments collected from different locations in Bombay Harbour Bay. The estimation of copper was carried out using sodium diethyl dithiocarbamate as a complexing agent. Contamination arising from reagent chemicals used were also investigated.

It was observed that copper concentration in sea water in the bay varies from 2.6-7.34 $\mu\text{g/l}$. Of the organisms studied barnacles and crab showed high concentration factors for copper. Bottom sediments in the bay had copper concentrations ranging from 162-276 $\mu\text{g/g}$. There was no correlation between organic matter and copper content in the sediment. Other parameters which influence the distribution of copper in sediments like particle size distribution are being investigated.

SEA WATER is known to contain many elements most of which are present only in trace quantities. Though present in trace concentration in sea water, as a result of physico-chemical and biological interactions many of these trace elements get accumulated in organisms and sediments. Copper is one of the essential trace elements for the growth and normal development of micro organisms, plants and animals. Its biochemical role as an enzyme activator and as a constituent of respiratory pigment of many marine invertebrates are well known (Brooks and Rumsby, 1965). Copper compounds are used as fungicides and herbicides and they are potential sources of aquatic pollution. The study of distribution of copper in different matrices of the environment thus assumes significance.

Copper occurs in sea water principally in the ionic form and the concentration ranges between 1-20 $\mu\text{g/l}$ although considerable seasonal and geographical variations can occur (Riley and Skirpow, 1965). Copper values are reported to range from 2.7-16.8 $\mu\text{g/l}$ in the Arabian Sea coastal waters and 3.9-16.2 $\mu\text{g/l}$ in the open ocean (Sreekumaran *et al.*, 1966). The Tarapur coastal waters have copper values ranging from 13.35-45.12 $\mu\text{g/l}$ (Sarma *et al.*, 1967). No detailed studies on the distribution pattern of copper in the coastal waters, sediments and organisms have been made.

METHOD

The paper presents the results of a study conducted to obtain the distribution of copper in sea water, sediments and organisms of the Bombay Harbour Bay. Surface sea water samples were collected on polythene containers. The bottom

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sediment samples collected from different locations in the bay were grab samples and were contained in polythene bags. In the case of organisms only the flesh was examined for copper content. However in the case of barnacles which were collected from the pillars of the jetties projecting into the bay the whole organisms including the shells were taken up for analysis.

Riley and Skirrow (1965) have reviewed the analytical methods used for the estimation of trace elements in sea water. Good and sensitive analytical techniques and elimination of contamination from apparatus and reagents are essential in obtaining reliable values of trace elements in sea water.

Of the different methods used for estimation of copper using dithizone, sodium diethyl dithiocarbamate, diquinolyl and atomic absorption spectrophotometry, the spectrophotometric method using sodium diethyl dithiocarbamate (DEDTC) is one of the simple and sensitive methods. This method was made use of in the estimation of copper.

Sea water is treated with sodium diethyl dithiocarbamate (DEDTC) and the yellow copper complex extracted by carbon tetrachloride (Strickland and Parsons, 1965). The absorbance of the coloured extract is measured at 435 m μ using a Beckman DU spectrophotometer. Copper cannot be estimated directly in marine samples due to interference from Ca, Mg, Fe, Mn, Bi, etc. The method used for the chemical analysis of soils (Black *et al.*, 1965) was used for estimation. A mixture of Citrate-EDTA at pH 8.5 chelates the interfering elements without preventing the formation of the complex between copper and DEDTC.

Elimination of contamination from apparatus and reagents used

All glasswares used were washed with 1:1 HCl. In order to obtain the contribution of copper from the various reagents used in this work, aliquots of the reagents were processed and copper estimated in them. The results obtained are given in Table 1. Ammonium citrate and EDTA have significant contamination of copper. These reagents were purified as given below and used.

TABLE 1. *Copper in reagents*

Manufacturer	Grade	Reagent	Copper
Polypharm	A.R.	Hydrochloric acid	0.0085 μ g/ml
"	A.R.	Nitric acid	0.0085 "
J. T. Baker	'Baker	Perchloric acid	0.027 "
Chemical Co., U.S.A.	'analysed'		
E. Merk	G.R.	Hydrofluoric acid	0.0283 "
B.D.H.	Analar	Ammonia	0.0201 "
B.D.H.	L.R.	Acetone	0.0007 "
E. Merk	A.R.	Ammonium citrate	0.473 μ g/g
"REANAL", Hungary		EDTA	0.4304 "
Whatman		Filter paper	1.427 "
Dexina		Tissue paper	15.8 "

Reagents

- i. Standard copper solution: 0.393 g of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (AR) was dissolved in 100 ml double distilled water. The double distilled water was obtained by redistilling water in a glass flask.

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- ii. DEDTC reagent: 1 g of sodium diethyl dithiocarbamate was dissolved in 100 ml of distilled water to which was added 0.1 g anhydrous Na_2CO_3 .
- iii. Carbon tetrachloride: Distilled.
- iv. Citrate-EDTA Reagent: Dissolved 12.5 of EDTA in water and to this added 50 g of ammonium citrate. The solution was diluted to about 225 ml, the pH was adjusted to 8.5 using ammonia and solution made upto 250 ml. The solution was purified by taking 100 ml aliquots of this reagent and treating with 5 ml of DEDTC and extracting with 25 ml of CCl_4 . The reagent was freed of traces of DEDTC by further extraction with CCl_4 .

TABLE 2. *Copper in sea water samples from Trombay Bay*

Location	Date of collection	Copper ($\mu\text{g/l}$)
Trombay Naval Jetty	6-2-1970	7.03
Trombay Panvel Bridge		7.34
CIRUS Jetty	16-2-1970	5.74
"	8-4-1970	5.70
Trombay Naval Jetty	"	7.13
Station No. 1*	17-4-1970	6.70
" No. 2	"	7.20
" No. 8	20-4-1970	5.80
" No. 9	"	2.60
" No. 10	"	5.20
" No. 11	"	3.80
" No. 12	"	3.00
" No. 13	"	4.20

*Locations are indicated in Fig. 4.

Standardisation of the method

25 ml each of filtered (Whatman 42) sea water was transferred to 5 different 60 ml separatory funnels. Added 2 ml of DEDTC reagent to one of the separatory funnels and mixed thoroughly. Then added 2.5 ml of carbon tetrachloride and extracted the copper-DEDTC complex formed by vigorously shaking for a minute. After allowing the layers to separate the organic layer is runoff through a Whatman filter paper into a 10 ml standard flask. The extraction was repeated using another 2.5 ml of CCl_4 . After mixing the extracts, it was transferred to an absorption cell and absorbance measured against CCl_4 blank at 435 $\text{m}\mu$ using a Beckman DU spectrophotometer. Known amounts of copper ranging from 1 to 5 μg were added to different flasks and the absorbance of the various extracts measured. Fig. 1 gives the calibration curve obtained for copper in sea water.

ESTIMATION OF COPPER

Sea water: 750 ml of the filtered sample was used for the estimation. Experiments were conducted to determine the optimum time and the volume of CCl_4 required for the complete extraction of copper from sea water. It was found that by using 10 ml CCl_4 each time with two extractions of 10 minutes shaking it is possible to extract the copper quantitatively from this volume of sea water.

Preparation of sample solution of sediment, barnacles and fish flesh

Sediments: The samples after thorough mixing were centrifuged, washed once with distilled water to remove the adhering sea water and oven dried at 105°C to constant weight. The dried sample was powdered fine and 1 g of the dried sample was used for solubilising by repeated treatment with HNO₃, HClO₄ and HF (Jackson 1958). The residue was dissolved in a small volume of 1:1 HCl and made up to 100 ml.

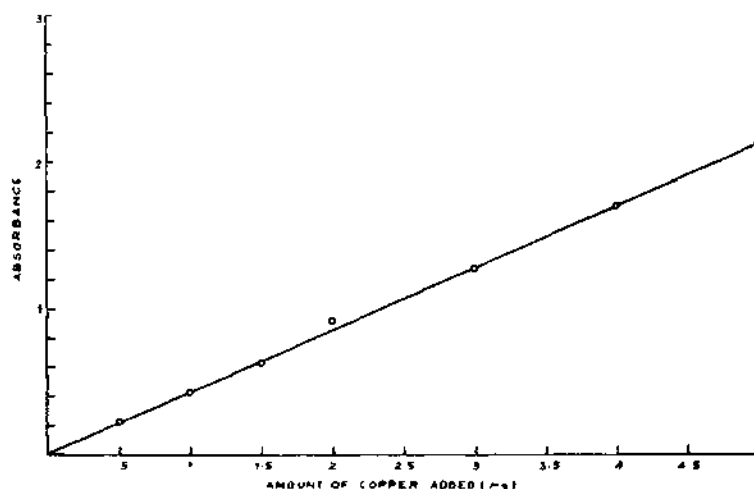


Fig. 1. Calibration curve for copper

Barnacles: The whole organisms (including shells) were taken up for analysis. The dried samples were solubilised in the same way as the sediment.

Fish: The dried flesh was wet ashed with conc. HNO₃. The residue was taken up in 1:1 HCl and made up to 100 ml with distilled water.

Separate reagent blanks were prepared for each group of samples in order to estimate the contribution of copper from the reagents.

Estimation of copper in sample solutions

Transferred 1 ml of the sample solution to a separatory funnel. Added 10 ml of citrate-EDTA reagent and 2 ml of 1 N ammonia and mixed thoroughly. Now 2 ml of DEDTC is added and the copper complex was extracted twice using 2.5 ml of CCl₄ each time. The absorbance of the combined filtered extract was measured at 435 mμ and the copper concentration was estimated.

RESULTS AND DISCUSSION

The blank values obtained for reagent chemicals are given in Table 1. Ammonium citrate and EDTA gave high values for copper. The absorption spectrum of the CCl₄ extract (Fig. 2) shows significant contribution from copper especially when the volume of complexing agent is high. The copper in the citrate-EDTA reagent will inhibit complete extraction of copper from the sample.

The absorption spectrum of the purified reagent shows almost complete elimination of copper (Fig. 3). Moreover the sediment solutions to which were added

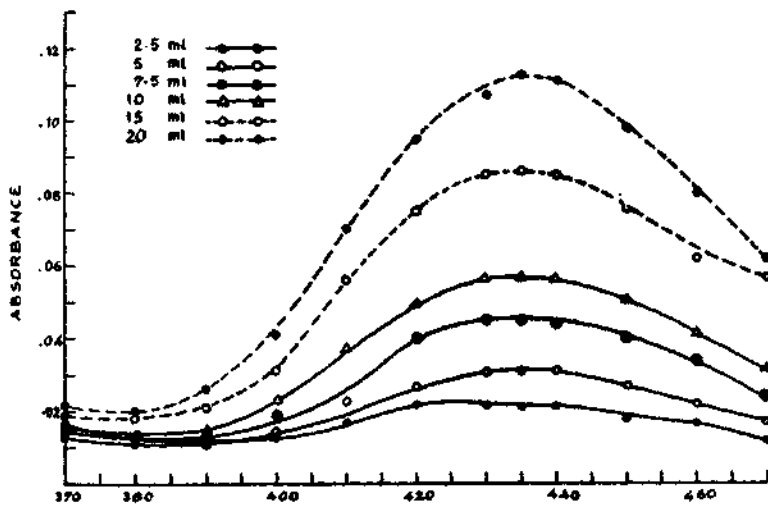


Fig. 2. Absorption spectrum of the CCl_4 extract of unpurified citrate-edta reagent (different volumes) with dedtc.

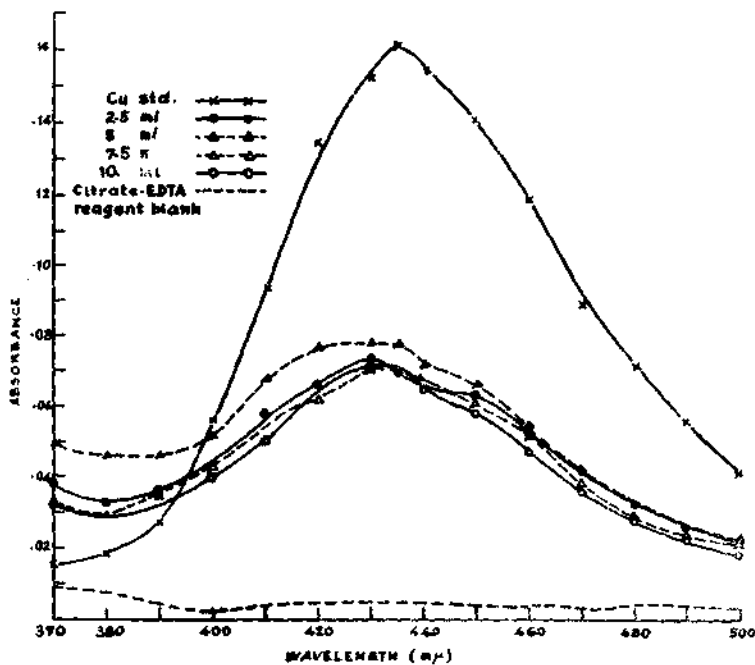


Fig. 3. Absorption spectrum of cu-dedtc complex from a sediment sample with purified citrate-edta reagent (different volumes)

different volumes of citrate-EDTA mixture showed same values for copper indicating that the value of citrate-EDTA reagent added is enough to chelate the interfering elements and the mixture do not interfere with the complexing of copper with DEDTC.

TABLE 3. *Copper in biological samples*

Sample	Location	Date of collection	Copper ($\mu\text{g/g}$) of wet flesh	Concentration Factors *
Fish	Trombay	2-1-1970	0.88	160
Prawns	Naval Jetty	"	11.20	2036
Fish	"	6-2-1970	2.30	418.1
Barnacle	CIRUS Jetty	6-6-1969	79.50	14450
"	"	26-12-1969	42.40	7709
"	Trombay	6-2-1970	76.30	13870
Crab (<i>Scylla serrata</i>)	Naval Jetty	"	"	"
	Trombay bay	5-6-1970	118.2**	21500**
	"	19-9-1970	169.8**	30870**
Cat fish (<i>Arius</i> sp.)	"	"	4.48	814.5
Fish	"	"	4.35	791
Catfish (<i>Arius</i> sp.)	"	30-9-1970	2.81	501.9
Bombay-duck (<i>Harpodon nehereus</i>)	"	31-8-1970	1.89	343.7

*Concentration factors are based on the average value of 5.5 $\mu\text{g/l}$ in sea water.

** $\mu\text{g/g}$ of dry flesh. Concentration factors calculated on the basis of dry weight.

TABLE 4. *Copper in bottom sediments*

Location	Date of collection	Ignition loss (%)	Copper ($\mu\text{g/g}$)
Station No. 1	17-4-1970	14.26	212.2
2	"	11.21	163.2
4	"	12.63	210.3
8	"	10.66	252.6
9	"	10.81	165.5
10	"	10.52	208.3
11	"	11.37	264.3
12	"	12.03	183.1
13	"	11.10	268.7
15	20-4-1970	10.01	178.9
16	"	11.10	276.3
17	"	10.01	262.0
18	"	10.80	162.1
19	"	10.10	178.9
20	"	10.10	226.5
21	"	9.72	273.5
22	"	10.15	183.0
23	"	11.16	217.6
24	"	11.21	182.1
25	"	8.46	230.5
26	"	8.80	163.4
27	"	8.60	176.0

Copper concentrations in sea waters (Table 2) varies from 2.6-7.34 $\mu\text{g/l}$ and the average value of 5.5 $\mu\text{g/l}$ is obtained for sea waters of the bay. High pick up of copper by sediments may explain the low values for copper in sea water.

Table 3 gives the concentration of copper in different organisms collected from the bay. Barnacles and crab flesh showed high concentration factors for copper.

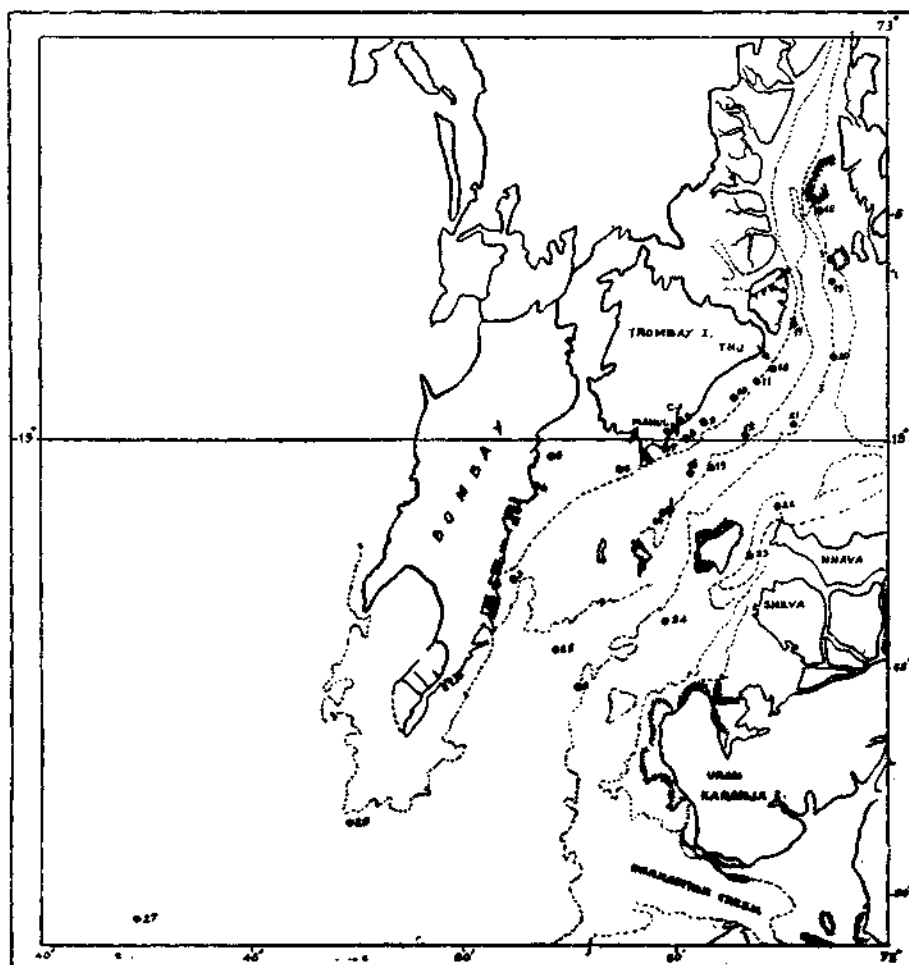


Fig. 4. Sampling locations (Station numbers)

The bottom sediment samples (Table 4) showed wide variations in copper content ranging from 162.1 to 276.3 $\mu\text{g/g}$. One of the sediments when leached with neutral N ammonium acetate solution gave only 1.3 $\mu\text{g Cu/g}$ of dry sediment. The same sediment when leached with ammonium acetate after oxidation with H_2O_2 gave higher values of copper (24 $\mu\text{g/g}$) indicating that copper is bound with organic matter in the sediment. However the loss on ignition and oxidisable carbon (unpublished data) in the different sediments did not show any correlation with the copper content in the sediments. Investigations on the concentration of copper in fine grained fractions of the different sediments are in progress to establish the possible correlation between copper content and particle size distribution in sediments.

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