

Distribution of Zn, Cu, Mn & Fe in Bombay Harbour Bay

VASANTI M MATKAR, S GANAPATHY & K C PILLAI

Environmental Studies Section, Health Physics Division, Bhabha Atomic Research Centre, Bombay 400 085

Received 21 October 1980

Concentrations of biologically significant trace elements—Zn, Cu, Mn and Fe in sea waters, sediments and some organisms (fish, prawn and crab) of Bombay Harbour bay were studied by spectrophotometric methods. All the reagents used in the estimation were subjected to analysis of these metals and the contamination of samples was minimised by purifying the reagents wherever necessary. Accumulation of these metals in flesh of the 3 species was also estimated. Distribution coefficients (K_d) in suspended silt and bottom sediments were higher than in organisms by order of magnitude and were in the order $Zn < Cu < Mn < Fe$ and the average values were in the ratio of 1:3:20:600. While Zn and Fe showed preferential accumulation in finer fractions of sediments higher concentrations of Cu and Mn were indicated in coarser fractions of sediments.

Information on the distribution and concentration of trace elements in the aquatic environment is required to assess accumulation of toxic elements in the organisms and possible transfer to man through food chain. The measurements of trace elements in the marine environment leads to better understanding of their behaviour in the aquatic environment and the identification of the indicator species which serve as indicators of ambient levels of radioisotopes of these elements. The measurement of stable counterparts of some of the radionuclide in the marine environment is also necessary in arriving at acceptable specific activity levels in the environment.

Of the elements known to be essential for the growth of plants and organisms Zn, Cu, Mn and Fe are significant¹⁻⁴. Studies on these elements in the coastal environment assume more significance because of the possible higher biological production, exchange of elements between sediments and water and also in view of the larger human utilization of such areas.

Data on concentration of Zn, Cu, Mn and Fe are scarce especially from Indian coastal waters^{5,6}. Though extensive studies have been made⁷ on the distribution of radionuclides in Bombay harbour bay, no systematic studies of these elements except a few random measurements have been undertaken in the bay environment. The pattern of distribution of these elements with respect to location, suspended silt load and size fraction has not been investigated. The present communication forms a part of the studies carried out on the distribution and behaviour of biologically significant trace elements in the Bombay harbour bay.

Materials and Methods

The presence of wide variety of elements in marine waters imposes stringent requirements on the method

of estimation of these trace elements. Of the different methods available for estimation of these trace metals⁸ like optical methods, polarographic methods and neutron activation, the colorimetric method, adopted without preconcentration, is simple and adequate since the detection limits are very much lower than the concentrations normally reported in sea waters. However in order to get reliable data it is necessary to take adequate precautions to avoid contamination arising from reagents and apparatus used.

Samples of surface sea water were collected in polythene bottles. Suspended silts were separated from sea water by filtration through Whatman No. 42 filter paper. The bottom sediments collected from different locations in the bay were grab samples and were collected in polythene bags. In the case of organisms, they were collected from the bay area. Station locations are marked in Fig. 1.

Sea water—The filtered sea water was directly used for estimation of trace metals.

Sediments—Suspended silt (obtained after filtration of sea water) and sediments were once washed with double distilled water to remove sea water and dried at 105°C to constant weight. The dried solids were powdered fine using an agate mortar and mixed thoroughly. A known amount (~1 g) of the sample was weighed and transferred to a platinum dish. The samples were oxidised using nitric acid, perchloric acid and hydrofluoric acid⁹ and the residue dissolved in dilute hydrochloric acid and made up to 100 ml.

Organisms—Fish, prawn and crab samples were cleaned thoroughly and only the edible portion (flesh) of the organisms was taken for estimation. The dried samples were wet ashed with nitric acid at low temperature and the residue dissolved in dilute hydrochloric acid and made up to 100 ml.

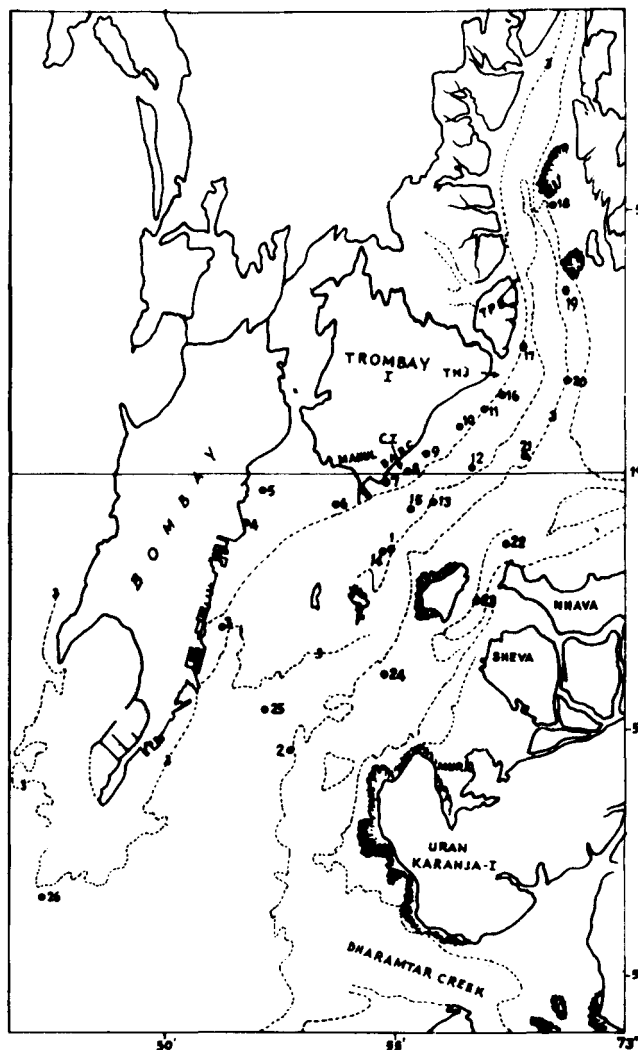


Fig. 1—Station locations from where samples were collected (TPB, Trombay-Panvel Bridge; CJ, Cirus Jetty; TNJ, Trombay-Naval Jetty)

Determination of trace elements—

Spectrophotometric methods were used in all cases. All glassware used were thoroughly washed in 1:1 hydrochloric acid and kept with chromic acid whenever not in use. Then washed profusely with water, followed by double distilled water. In case of Zn estimation, the glassware were also washed with dithizone reagent.

Zinc: Dithizone (diphenyl thiocarbazone) was used for extraction and determination of zinc¹⁰. The dithizone reagent was purified by the method given by Sandell¹⁰ and 0.01% and 0.002% solutions were freshly prepared in distilled CCl₄. Buffer solution and 5% ammonium citrate solution were purified by extraction with 0.01% dithizone solution. Vapours of liquor ammonia were bubbled through double distilled water and the ammonia solution obtained was used for all experiments.

The method was checked and standardised by

establishing calibration curves in both distilled water and sea water. The O.D. of the coloured complex was measured at 530 nm using a Beckman DU spectrophotometer.

Filtered sea water sample aliquots (30 ml) were used for Zn estimations. In the case of sediment and the organism solution, the method of direct extraction with dithizone could not be used due to interference from other metals. Therefore aliquots of sample solutions were first extracted with 5 ml of 0.01% dithizone solution in presence of 5% ammonium citrate in alkaline medium (pH 8.5). The dithizone layer was collected in another separating funnel. The aqueous layer was shaken 2 to 3 times with distilled CCl₄ till no more colour of dithizone was obtained in CCl₄ layer. The combined dithizone fraction was washed once with double distilled water. The dithizone solution thus obtained was reextracted with 0.02 N HCl solution and 2 phases were allowed to separate. The aqueous layer of 0.02 N HCl was then extracted with 0.002% dithizone in presence of buffer solution as in the case of standardization of zinc. The absorption spectra (460-580 nm) of the dithizone extract of the sediment samples and that of sea water are identical with that of pure zinc in distilled water. The absorption spectra of reagent blank showed negligible contribution from the same.

Copper: The spectrophotometric method using sodium diethyl dithiocarbamate (DEDTC) has been used¹¹. Distilled CCl₄ was used. The citrate-EDTA reagent was purified by extraction with DEDTC. The absorbance of the color was measured at 435 nm.

Filtered 750 ml sea water were treated with 5 ml DEDTC and yellow copper complex formed was extracted twice with 10 ml CCl₄. The absorbance of the color was measured at 435 nm using Beckman DU spectrophotometer. Cu could not be estimated directly in sediments and organism solutions due to interferences from other metals. Therefore the method used for chemical analysis of silts¹² was used. A mixture of citrate and EDTA at pH 8.5 chelates the interfering elements without preventing the formation of the complex between Cu and DEDTC.

Preliminary experiments carried out indicated high concentration of Cu in the ammonium citrate and EDTA. So different volumes of ammonium citrate-EDTA mixture were treated as samples and extracted as given in the case of standardisation and absorption spectra of the organic extract. The spectra clearly showed significant contamination of Cu from these reagents. So the reagent was purified and used. The sediment solution to which were added different volumes of citrate-EDTA mixture showed same values for Cu indicating the volume of citrate-EDTA reagent added was adequate to chelate the interfering

elements and the mixtures do not interfere with the complexing of copper with DEDTC.

Iron: The method consists of treating the sea water with hydrochloric acid and reacting it with O-phenanthroline in acetate buffer in presence of hydroxylamine hydrochloride and measuring the extinction of the ferrous complex formed at 510 nm using a Beckman DU spectrophotometer⁹. The same method was used for sediments and organisms.

Manganese: Mn in sea water was estimated on the basis of Mn catalysed oxidation of leuco base of triphenyl methane dye malachite green by periodate¹¹. The amount of dye produced is proportional to the amount of Mn present and was measured at 620 nm. The method is sensitive for determination of Mn in sea water. The amount of dye formed depends on pH, temperature and salinity of sea water. However this method could not be used for estimation of Mn in organisms and sediments due to interference from Fe¹⁰.

Oxidation of Mn to permanganate by periodate and subsequent measurement at 530 nm was followed. Interference from chlorides and iron was eliminated by the addition of sulphuric acid and phosphoric acid respectively.

Phosphoric acid was found to contribute maximum Mn concentration in the reagent blank (Table 1). This contribution was minimised using dilute phosphoric acid (1:4). Experiments were carried out to show the adequacy of the phosphoric acid added, thereby improving the blank values.

Estimation of contamination from reagents—The most important requirement in any trace element

work, to obtain reliable results, is the estimation of contamination from reagents and the apparatus used. All the reagents used in this study were subjected to analysis, by the same method indicated earlier.

In the present work, contamination levels were reduced to a minimum by purifying the reagents whenever necessary. Dithizone, malachite green, ammonia, etc. were purified as indicated earlier. In the case of Mn estimation in sediments/organisms, the contribution of Mn in blank values was reduced to a minimum by reducing the amount of phosphoric acid used.

In all estimations, chemical blanks were prepared the same way as that of the samples and elemental concentrations were determined. Respective blank corrections were made for all samples in calculating the elemental concentrations. For bottom sediments the contribution from reagent blanks was 1 and 1.3% of the sample values for maximum and minimum values respectively.

Separation of sediments into finer and coarser fractions—The finer (< 3 µm) and coarser (> 50 µm) fractions of sediments were isolated by the sedimentation method¹³. Trace metal contents in each fraction were estimated.

Results and Discussion

Concentrations of Zn, Cu, Fe and Mn in various reagents used in this study are given in Table 1. Some reagents showed higher orders of magnitude of concentrations of metals compared to the rest of the reagents used in the procedure. Maximum contamination of Zn was found in ammonia, Cu in

Table 1—Trace Metal Concentrations in Reagents

Reagent	Manufacturer	Grade	Conc. µg/ml or g			
			Zn	Cu	Mn	Fe
Nitric acid	Polypharm	AR	0.033	0.009	0.038	0.54
Hydrochloric acid	do	GR	0.089	0.009	0.06	0.68
Perchloric acid	May & Baker	AR	0.036	0.027	0.062	2.1
Hydrofluoric acid	E. Merck		0.064	0.028	0.15	4.48
Acetic acid	BDH	Analar	0.02	—	0.04	—
Phosphoric acid	Merck	GR	—	—	0.695	—
Ammonia	BDH	Analar	3.97	0.02	0.05	0.23
Acetone	do	AR	ND	0.001	ND	0.032
Sodium acetate	do	do	do	—	—	0.33
Amm. acetate	do	do	—	—	—	0.04
Sodium thiosulphate	do	do	ND	—	—	—
Amm. citrate	E. Merck	AR	1.47	0.47	—	—
Hydrogen peroxide	Sarabhai Chemicals	GR	—	—	0.073	1.01
EDTA	Hungary	Analar	—	0.43	—	—
Filter paper (42)	Whatman		1.11	1.43	2.45	5.7
Tissue paper	Daxine		4.26	15.8	3.8	12.1

ND = Not detected; — = not analysed

ammonium citrate, Mn in phosphoric acid and Fe in hydrofluoric acid. Filter paper and tissue papers showed high concentration of all metals.

Sea water—Concentrations of trace metals in filtered sea water from different locations are given in Table 2.

Samples taken on the same day from different locations showed variations in Zn values possibly due to variations in silt content in the bay waters. Large variations in Zn as in present study have not been observed either in Arabian Sea offshore waters⁵ (16.3-51.1 µg/litre) or in offshore water of Tarapur⁶ (41.8-65 µg/litre). Variations in Cu concentrations were much lower than those observed for Zn in sea water. A wide range of values of Cu have been reported from Arabian Sea⁵ (2.7-45.12 µg/litre). Much wider variations have been reported for Fe concentrations, in sea water from offshore waters of the west coast of India⁵ (1.8-36.1 µg/litre). Mn concentration is within the range of values reported for Arabian Sea waters (1.5 to 11 µg/litre).

Bay organisms—Concentrations of trace elements in flesh of fish, prawn and crab are given in Table 3. Even in the same species variations in concentrations could be observed possibly due to age, etc. of the organisms. No attempts were made to study these aspects. The concentrations were very similar to those obtained in organisms, from other areas in the west coast of India^{5,6}. From the average values of these elements in sea water (Table 2), the concentration factors (accumulation factor) for these elements in flesh of the organisms were calculated (Table 4). The accumulation factors for Zn, Cu, Fe and Mn in flesh of these organisms were of the same order, though the zinc values were higher followed by Cu, Fe and Mn.

Suspended silt—In order to obtain the actual distribution of these trace metals between sea water and suspended silt, sea water samples collected during the nonmonsoon period were separately studied (Table 5). The nonmonsoon sampling was preferred since during monsoon there is much more resuspension of sediments in bay waters due to turbulence and run off from shore in addition to dilution of the suspended material by mixing of the fresh silt from run off.

Of the total amount of Zn, 10.9-91.8% was found in the dissolved form while of Cu 8.5-78.4% was found. In the case of Mn an average of about 1% was only in the soluble fraction even though it is reported that Mn is found in soluble form. For Fe, the soluble fraction was <1%. In case of Zn, the concentration of soluble fraction appears to be related to the silt load. However in the case of Mn and Fe, there was no influence of suspended silt load on the natural concentration of the soluble fraction of these metals in bay waters.

Table 2—Concentration of Trace Elements in the Sea Water

Date of collection (1970)	Location*	Conc. (µg/litre)			
		Zn	Cu	Mn	Fe
Feb.					
6	Trombay	7.02	7.03		
	Naval Jetty				
6	Panvel	10.66	7.34		
6	Cirus Jetty	2.65	5.74		
16	do	16.22	5.7	0.84	17.7
April					
8	Trombay	7.67	7.13	4	
	Naval Jetty				
8	Trombay Panvel Bridge	12.25		4.08	
11	St 1	15	6.7		11.4
17	St 2	21.46	7.2		11.4
17	St 8	11.11	5.8		12.3
30	St 9	8.9	2.6		5
30	St 10	16.94	5.2		
30	St 11	6.56	3.8		11.4
30	St 12	7.66	3		5
30	St 13	22.68	4.2		5
June					
18	Cirus Jetty	20.17	4.8	0.48	
August					
1	do	33.92	4.51	4.51	
Average		14.54	5.5	2.78	9.9

*Given in Fig. 1

Table 3—Concentration of Trace Elements in Fish, Prawn and Crab

[Only flesh is used in analysis]

Conc. µg/g wet wt			
Zn	Cu	Mn	Fe
Fish (<i>Arius</i> sp.)			
9.42	0.88	1.41	11.5
22.17	2.3	1.8	3
30.55	4.35	3.74	—
Prawns (<i>Ascelis indius</i>)			
11.15	11.2	—	15
Crab (<i>Scylla serratta</i>)			
83.5	23.6	4.76	295.5
60.7	34	—	114.2

Bottom sediments—The concentration of Zn, Cu, Fe and Mn in the bottom sediments of the bay are given in Table 6.

Though a clear pattern could not emerge from the concentrations of Zn in bay sediment, it was evident that higher concentration was observed near the shore areas close to the Trombay Naval Jetty, where the tidal currents slow down as a result of the land areas projecting into the bay and causing the higher siltation

rate⁷. The lowest values for Zn were obtained in sediments from the middle stream in the bay.

As in the case of Zn, higher values of Cu were observed in the shore sediments near the Trombay Naval Jetty area and lower values in locations in the middle stream. Distribution pattern of Mn in various bay sediments followed generally that of Zn and Cu.

More or less uniform concentrations in sediments were also evident from the ratio of maximum to minimum values of Fe observed in sediments, 1.15, which is the lowest among all the elements studied. Standard deviation for the mean value was only 3.3% compared to 13.6, 14.5 and 18.6% for Zn, Cu and Mn respectively.

From the average values of Zn, Cu, Fe and Mn in filtered sea water samples (Table 2) distribution coefficient for these elements in bottom sediments were calculated (Table 7). The K_d factors were in the order of $Zn < Cu < Mn < Fe$ and the average values were in the ratio of 1:3:20:600. It is evident that the accumulation factors obtained earlier in organisms for all these elements are of the same order (Table 4). The average accumulation factors (in flesh of organisms) were lower by factor of 10, 20, 300 and 4000 for Zn, Cu, Mn and Fe respectively compared to their K_d factor in sediment. It is evident from these data that the accumulation of these trace metals by organisms will have only negligible influence compared to their

Table 6—Concentration of Trace Elements in Bay Sediments

St No.	Conc. $\mu\text{g/g}$			
	Zn	Cu	Mn	Fe
1	154.7	212.2	851.5	73670
2	174.8	163.2	1002	73500
4	157.5	210.3	1000	69630
8	215.7	252.6	1124	73280
9	169	165.5	1142	71190
10	292.2	208.3	1015	74690
11	189.7	264.3	1196	71810
12	139.5	183.1	746.7	72660
13	226.6	268.7	928	71550
15	186	178.9	814.9	75230
16	224	276.3	1318	72130
17	182.8	262	952.6	72240
18	165	162.1	921.3	74030
19	138.5	178.9	925.5	75710
20	187	226.5	785.2	80350
21	191.8	273.5	772.5	77270
22	172.8	183	1080	74610
23	153	217.6	991.5	75650
24	168.6	182.1	896	72300
25	169.6	230.5	908	72440
26	194.8	163.4	898	70470
27	215.7	176	935.5	69980
Average	180.4 \pm 24.5	210.9 \pm 39.3	963.8 \pm 138.8	73381 \pm 2445

Table 4—Concentration Factors for Trace Elements in Bay Organisms

[Av. value of elements in sea water (Table 2) are used for calculation of concentration factor]

Organism	Concentration factor ($\times 10^3$)			
	Zn	Cu	Mn	Fe
Fish (<i>Arius</i> sp.)	0.65	0.16	0.51	0.31
	1.5	0.42	0.65	1.2
	2.1	0.79	1.3	—
Prawns (<i>Ascelis indius</i>)	0.77	2	—	1.5
Crab (<i>Scylla serratta</i>)	5.7	4.3	1.7	6
	4.2	6.2	—	1.2
Average	2.5	2.3	1.04	2.04

Table 7—Distribution Coefficient (K_d) for Bottom Sediments for Zn, Cu, Mn and Fe

St No.	Zn	Cu	Mn	Fe
	($\times 10^4$)	($\times 10^4$)	($\times 10^5$)	($\times 10^6$)
1	1.03	3.16	3.06	6.46
2	0.815	2.27	3.6	6.45
8	1.94	4.36	4.04	5.96
9	1.9	6.37	4.1	14.2
10	1.13	4.01	3.65	—
11	2.89	6.96	4.3	6.3
12	1.82	6.1	2.68	14.5
13	0.999	6.4	3.33	14.3
Average	1.57	4.95	3.6	9.45

Table 5—Distribution of Zn, Cu, Fe and Mn between Sea Water and Suspended Silt during Nonmonsoon

Location	Suspended silt load mg/litre	Sea water $\mu\text{g/litre}$				Suspended silt $\mu\text{g/g}$ (dry)				% of dissolved form			
		Zn	Cu	Fe	Mn	Zn	Cu	Fe	Mn	Zn	Cu	Fe	Mn
CIRUS	115	16.2	5.7	17.7	0.84	159.5	252.6	74370	1314	46.9	16.4	0.21	0.55
TNJ	280	7.7	7.1	—	4	224.3	276.3	70620	1932	10.9	8.5	—	0.73
TCB (T)	314	12.3	—	5	4.08	224.5	—	71960	1893	14.8	—	0.02	0.68
St 1	8.7	15	6.7	11.4	—	154.7	212.2	73670	—	91.8	78.4	1.51	—
CIRUS	112	33.9	—	—	4.51	224	—	—	1314	43.3	—	—	3.09
Average										41.5	31.3	0.58	1.25

Table 8—Distribution of Elements in Finer and Coarser Fractions of Sediments

[Values are expressed in $\mu\text{g/g}$ dry wt]

St No.	Zn		Cu		Mn		Fe	
	Fine	Coarse	Fine	Coarse	Fine	Coarse	Fine	Coarse
2	183.1	168.8	111.8	158.4	956.8	1500	77450	69340
9	191.4	183.8	148.4	165.4	994	1517	80260	72190
11	208.4	163	153	173.6	1196	1526	81470	76260
12	179	159.7	139.6	151.7	776	1284	77980	75020
13	174.8	171.2	128.6	133.5	870.8	1440	76560	75950
16	249.3	174.6	145.9	156.8	1209	1669	81320	72240
21	214.5	267.1	138.2	159.9	647.3	1312	60220	100800
22			121.2	140.1			80560	97410

accumulation in suspended silt and bottom sediment and subsequently in the transport of these metals from the bay.

Distribution of Zn, Cu, Mn and Fe in finer and coarser fractions of sediments—In the case of Zn and Fe the finer fraction showed relatively higher concentration (Table 8) compared to the coarser fraction. However this was reversed in the case of Cu and Mn. Jafee and Waltus¹⁴ have shown correlation between particle size and Fe content in Humber estuary. Studies on Columbia river sediments¹⁵ have shown that in fractions of sediments with different particle size groups maximum activity was associated with the finer and coarse fractions. Possibly these anomalies are due to the presence of large amount of organic materials attached to the coarser fraction of sediment since both clay minerals and organic matter can influence the distribution of metals.

Acknowledgement

The authors are grateful to Dr A.K. Ganguly, National Fellow, D.S.T. (formerly Director, Chemical Group, BARC, Bombay) for guidance and to Shri S.D. Soman, Head, Health Physics Division, for his keen interest in the work.

References

1 Rowe W R & Gloyna E P, *Tech report 4*, U.S.A. E.C., Contract AT(11-1)-490, 1964.

2 Buckman H O & Brady N C, *The nature and properties of soils* (Eurasia Publishers, New Delhi) 1964.
 3 Black C A, *Soil-plant relationship* (John Wiley, New York) 1968.
 4 Agarwala S C & Sharma C P, *Soil fertility—Theory and practice*, edited by J.S. Kanwar (ICAR, New Delhi) 1976.
 5 Sreekumaran C, Bhatt Y M, Naidu J R, Krishnamoorthy T M, Gogate S S, Rama Rao M, Doshi G R, Sastry V N, Shah S M, Unni C K & Vishwanathan R, AEET/HP/PM-5, 1966.
 6 Sarma T P, Shah S M, Sastry V N, Krishnamoorthy T M, Unni C K, Gogate S S, Doshi G R, Rama Rao M, Neralla V R & Rao S R, *Bull natn Inst Sci*, 38 (1968) 308.
 7 Pillai K C, Dey N N, Mathew E & Kothari B U, *Impacts of nuclear releases into the aquatic environment* (IAEA-198/16, 277, Vienna) 1975.
 8 *Reference methods for marine radioactivity studies*, Technical report series No. 168, IAEA, Vienna, 1970.
 9 Jackson M L, *Soil chemical analysis* (Constable and Co. Ltd, London) 1958.
 10 Sandell E B, *Colorimetric determination of traces of metals*, (Interscience Publishers, New York) 1959.
 11 Strickland J & Parsons T R, *A manual of sea water analysis*, (Fish Res Bd Can Bull) 1965, 125.
 12 Black C A (eds), *Methods of soil analysis*, (American Society of Agronomy Inc., Wisconsin, USA) 1965.
 13 Clyde Orr (Jr) & Dallavalle J M, *Fine particles measurement—Size surface and pore volume*, (The MacMillan Co., New York) 1959, 43.
 14 Jaffe D & Walters J K, *The science of total environment*, Vol. 7, 1977, 1.
 15 Nelson J L, Perkins R W & Nielsen J M, HW-83614, General electric, 1964.