

## Evaluation of toxic trace metals Cd and Pb in Arabian Sea waters

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**Abstract** - An attempt has been made to present a picture of the distribution of toxic trace elements Cd and Pb in the Northern Arabian Sea by applying an improved analytical technique for the detection of dissolved forms of the metals at nanogram levels.

Depthwise profiles of both the metals have been examined and attempt has been made to correlate these with the general nutrient profiles of the region.

Dissolved Pb is higher at surface and decreases deeper down while dissolved Cd shows elevated intermediate or bottom water concentrations at most of the stations.

Depth profiles of Cd show similarity with the PO<sub>4</sub>-P profiles of the region and to a certain extent to the NO<sub>3</sub>-N profiles too.  $\Delta \text{Cd} : \Delta \text{N} : \Delta \text{P}$  atomic ratio is as  $6 \times 10^{-4} : 12.5 : 1$ .

### INTRODUCTION

Considerable data on trace metals in the marine environment have been and are being collected by several workers in different parts of the world. BREWER(1975) has compiled results of studies done till 1972. Significant advances are made continuously in the determinations of trace metals with the development of sophisticated instruments. Some of the noted investigations are by BOYLE and EDMOND (1975), SCLATER *et al* (1976), BOYLE *et al* (1976,1977), BRULAND *et al* (1978), HYDES (1979), BRULAND (1980), LANDING and BRULAND (1980), MARTIN and KNAUER (1982), HYDES (1983), BRULAND and FRANKS (1983), YEATS and CAMPBELL (1983) and KREMLING (1985). Most of the data published are from the Pacific and the Atlantic Oceans.

Increased awareness of the risks of pollution has resulted in increased use of protective measures to prevent contamination during sampling, storage and analysis of trace metals. PATTERSON and SETTLE (1976) have done extensive work on lead and have stressed that proper measures can reduce lead values by orders of magnitude. We, at N.I.O. have been working on trace metals for many years. Wide range of differences have been observed between our earlier data and those of other investigators in other oceans. Over the years we have been updating facilities for contamination free sampling and storage. On board *ORV Sagar Kanya*, we could collect contamination free samples using PVC coated winch wire and further could finish the initial preconcentration step on board the vessel in a dust free environment. DANIELSSON (1980) carried out studies on a few trace metals in the Indian Ocean.

The present work was initiated to complement the presently available data on cadmium and lead and to obtain some reliable depth profiles.

The results presented here are based on observations at 18 stations in the Northern Arabian Sea. The station positions are shown in Fig.1. Quality of the data have been checked by repeated participation in national and international intercalibration exercises and against such standards obtained from the designated agencies.

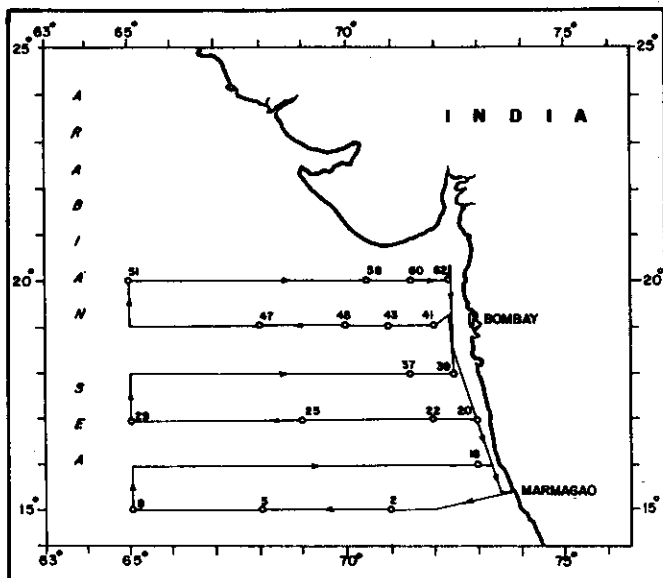


Fig. 1. Station positions.

## MATERIAL AND METHODS

Water samples were collected on board *ORV Sagar Kanya* using a special self lubricating winch bearing PVC coated hydrowire moving between teflon rollers. Samples were collected in teflon lined Goflo samplers. Disposable plastic hand gloves were used during the collection of samples in pretreated polyethylene bottles. Soon after collection, the water samples were filtered through 0.45  $\mu\text{m}$  pore size membrane filters. Prior to use the filters were stored in dilute acid and washed with metal free water obtained from a MQ apparatus. pH of the filtered samples was adjusted to  $\sim 3$  using 1M nitric acid diluted from ultrapure, Merck product. The analytical procedure followed was that published by DANIELSSON *et al* (1978). The method consists of a two stage preconcentration technique. In the first stage the metals are complexed using APDC (Ammonium pyrolidine dithiocarbamate) and extracted in MIBK (Methyl Isobutyl Ketone). In the second stage, the organic extract is washed with milliQ water so as to avoid salt and is backextracted into acidic medium by using concentrated nitric acid (ultrapure, Merck). The final extract is then made to a known volume with milliQ water. All such extracts were stored in high density polyethylene vials with screw caps and refrigerated for later analysis in the shore laboratory.

Determinations of Cd and Pb were performed on a GBC 902 atomic absorption spectrophotometer equipped with GF2000 Graphite furnace.

Standards were similarly extracted using open ocean surface water previously extracted and then spiked with standards. Blanks were determined with each batch of samples.

All plasticware and glassware used were previously soaked in acid for about a month and washed thoroughly with milliQ water and dried prior to use.

Table 1. Concentrations ( $\mu\text{g/L}$ ) of dissolved Cd and Pb in Arabian Sea waters.

Station No.	Position	Depth (m)	Cd	Pb
2	15°N 71°E	25	0.26	0.31
		50	0.27	0.31
		100	0.26	0.07
		200	0.13	0.61
		300	0.52	0.63
		1000	0.25	0.61
		2000	0.32	0.48
		2500	0.19	0.41
		2550	0.49	0.32
		2600	0.04	0.35
5	15°N 68°E	25	0.41*	0.35
		50	0.18*	0.25
		100	0.28	0.31
		200	1.50*	0.37
		500	0.53	0.27
		900	0.16	0.45
		1900	0.12	0.37
		2900	0.19	0.26
8	15°N 65°E	25	0.04	0.95
		50	0.08	0.40
		100	0.14	0.34
		175	0.10	0.28
		500	0.18	0.33
		1000	0.15	0.40
		2000	0.15	0.59
		3000	0.13	0.40
18	16°N 73°E	20	0.12	0.65
		50	0.00	0.78
		73	0.00	0.56
20	17°N 73°E	15	0.30	0.61
		30	0.11	0.41
22	17°N 72°E	20	0.04	0.66
		50	0.06	0.65
		100	0.63	0.95
		200	1.42*	2.08*
25	17°N 69°E	25	0.62*	0.20
		50	0.01	0.10
		100	0.03	0.24
		250	0.06	0.20
		500	0.05	0.62
		1000	0.16	0.32
		2000	0.07	0.34
		2400	0.15	0.22
		2450	0.16	0.30
		2500	0.64*	0.28
29	17°N 65°E	25	0.10	0.27
		50	0.00	0.08
		100	0.12	0.13
		400	0.20	0.08
		900	0.16	0.04
		1900	0.24	0.20
		2900	0.01	0.50
37	18°N 69°E	15	0.01	1.09
		50	0.09	0.42
		80	0.09	0.29

Contd.

Station No.	Position	Depth (m)	Cd	Pb
39	18° 29.61N 72°-38.47E	15	0.07	0.30
		40	0.04	0.57
41	19°N 72°E	20	0.27	0.18
		60	0.09	0.02
43	19°N 71°E	15	0.52	0.09
		50	0.05	0.02
		75	0.04	0.00
45	19°N 70°E	20	0.03	0.30
		50	0.06	0.42
		100	0.08	0.31
		190	0.16	0.30
47	19°N 68°E	20	0.04	0.18
		50	0.12	0.31
		100	0.07	0.24
		500	0.18	0.29
		1000	0.11	0.21
		1900	0.17	0.33
		2900	0.11	0.20
51	20°N 65°E	20	0.05	0.48*
		50	0.04	0.22
		100	0.04	0.25
		500	0.09	0.17
		1000	0.11	0.27
		2000	0.15	0.42
58	20°N 70°-30'E	20	0.05	1.00
		50	0.10	0.74
		85	0.07	0.55
60	20°N 71°-30'E	15	0.05	0.16
		30	0.05	0.35
62	20°N 72°-30'E	15	0.09	0.22

\* Values not included for mean calculations

## RESULTS AND DISCUSSION

Table 1 shows the concentrations of dissolved Cd and Pb found at different stations at different depths.

In all 18 stations were sampled out of which 7 were deep and 11 were shallow. Near bottom samples were collected. No surface sample was collected to avoid ship's contamination. The first sampling depth was 15-20m for shallow stations and 25m for the deep ones. Concentrations at these depths have been used as nearsurface concentrations.

### Cadmium

Seven profiles have been prepared for 7 deep stations. A typical Cd profile is shown in Fig.2 together with the corresponding phosphate and nitrate profiles for that region. It can be seen that Cd profile resembles the phosphate profile and to some extent the nitrate one too. This shows that Cd is a nutrient type trace element. Rightly it has been used in paleo-oceanographic studies as a proxy for phosphate. Removal

of the element from surface waters possibly by plankton or biological particulates is obvious from the profiles.

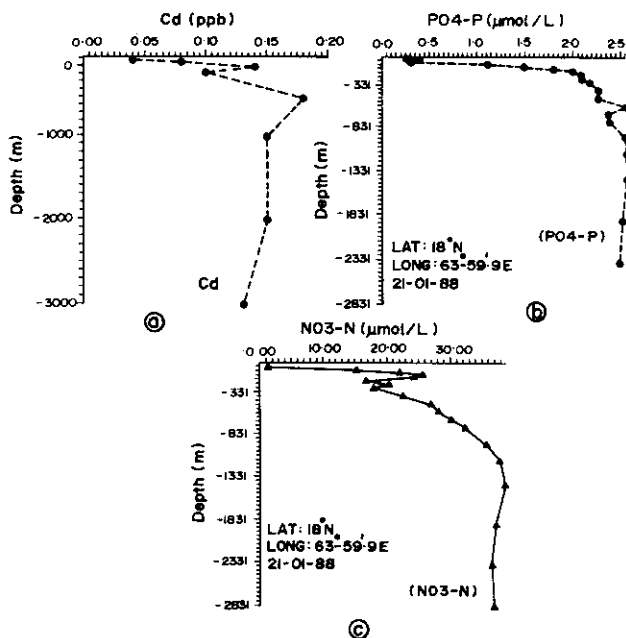


Fig. 2. Depthwise variation of dissolved Cadmium (Cd), Phosphate (PO<sub>4</sub>) and Nitrate (NO<sub>3</sub>).

Table 2. Cd concentrations in different Oceanic areas.

Area	Depth (m)	Mean (µg/L)	Reference
Pacific Ocean	0-100	0.026	BOYLE, SCLATER & EDMOND (1976)
North Atlantic	*	0.06	do
do	*	0.06	EATON (1974)
Indian Ocean	surface	0.07	KREMLING & PETERSON (1977)
do	0-100	0.015	CHESTER & STONER (1974)
do	>100	0.064	DANIELSSON (1980)
Arabian Sea	<100	0.067	do
65°E Long.	>100	0.137	This work
do	>100	0.137	This work

At all the deep stations Cd increases gradually with depth, generally between 200-500m. The enrichment factor varies between 2-4. DANIELSSON(1980) has reported an enrichment factor of about 4 for the Indian Ocean. Most of his observations were from the south of the equator. Comparison of our values with those of earlier workers has been represented in Table 2. Our average values are higher than those reported by others but since we have confirmed the validity of our results by analysing standard

reference materials for comparison, we do not expect significant contamination errors. Our values of such standard materials in comparison to the existing concentrations, have been shown in Table 3.

Table 3. Results of the analysis of aqueous standard material obtained from National Research Council, Canada.

Std. material code	Cd conc.		% error	Pb conc.		% error
	exist.	found		exist.	found	
NASS	0.029	0.035	22	0.251	0.229	-8.7
CASS	0.026	0.032	25	0.251	0.202	-19.5

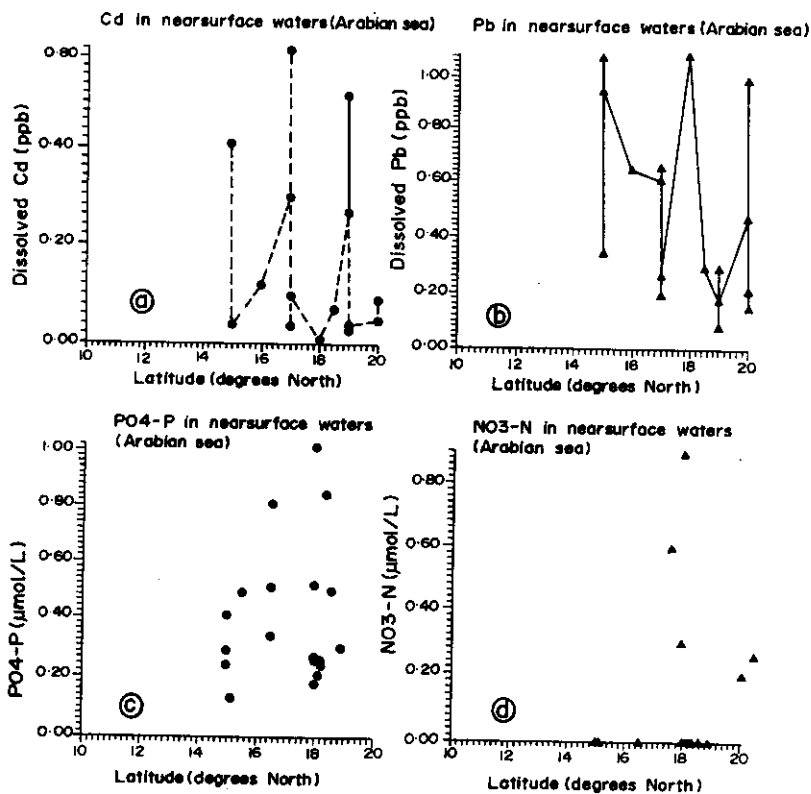


Fig. 3. Latitudinal variations of dissolved metals (Cd & Pb) and dissolved nutrients ( $PO_4$  &  $NO_3$ ) in nearsurface waters.

The nearsurface Cd concentrations vary between 0.04-0.26  $\mu\text{g/L}$  with an overall average of 0.15 $\mu\text{g/L}$ . The average of intermediate and deep Cd enriched waters was about 0.34 $\mu\text{g/L}$ .

Stations 8,29 and 51 have been considered separately. Cd concentrations in these vary from 0-0.24 $\mu\text{g/L}$  (0-2.1 nmol/L) and agree well with the general range of 1 pmol/Kg-1.1 nmol/Kg for oceanic waters (BRULAND, 1983). The upper limit of concentration is about twice that reported by BRULAND. Considering the quantum of shipping and other activities in this part of the Indian Ocean, we feel that the concentrations of trace elements could be higher than those in other oceans. Comparison of Cd profiles with

those of phosphate shows a close resemblance giving  $\Delta\text{Cd} : \Delta\text{P}$  atomic ratio of about  $6 \times 10^{-4}$  while  $\Delta\text{N} : \Delta\text{P}$  atomic ratio is 11-14 : 1 i.e., about 12.5 : 1. Thus  $\Delta\text{Cd} : \Delta\text{N} : \Delta\text{P}$  is  $6 \times 10^{-4} : 12.5 : 1$  by atoms. BRULAND (1980) calculated  $\Delta\text{Cd} : \Delta\text{N} : \Delta\text{P}$  atomic ratio as  $3.47 \times 10^{-4} : 15.2 : 1$  for the North Pacific. He also suggested the existence of an organic tissue carrier phase produced by phytoplankton within the surface photic layers and decomposed via oxidative processes predominantly within the surface waters and the shallow thermocline. The present results support the observation at the same time confirming that this is true in general for all the oceans irrespective of their geographical location.

For highly productive coastal waters  $\Delta\text{Cd} : \Delta\text{P}$  atomic ratio differs. Probably differences in productivity affects the incorporation of Cd in plankton debris.

Fig.3 shows plots of Cd/Pb and  $\text{PO}_4\text{-P}/\text{NO}_3\text{-N}$  in nearsurface waters w.r.t. latitude. Highest Cd values are observed between 17-18°N latitude coinciding with high  $\text{PO}_4\text{-P}$ .

Examination of Fig.4(b) shows that but for one or two values, highest concentrations of Cd are found in the nearsurface coastal waters. This could suggest a land based source of Cd.

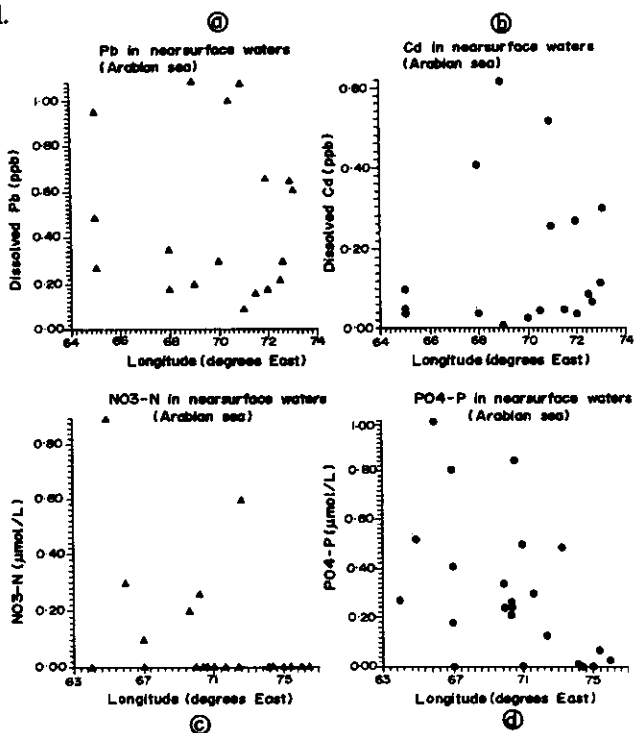


Fig. 4. Longitudinal variations of dissolved metals (Cd & Pb) and dissolved nutrients ( $\text{PO}_4$  &  $\text{NO}_3$ ) in nearsurface waters.

### Lead

Depth profiles have been prepared at all the seven deep stations. Three of the deep station profiles have been shown in Fig.5 (a,b,d). A typical shallow water Pb picture is seen in Fig.5(c). In general Pb shows a nearsurface enrichment which drops down considerably in the thermocline region and a steady increase is observed thereafter with higher values deeper down. For shallow waters, Pb decreases with depth.

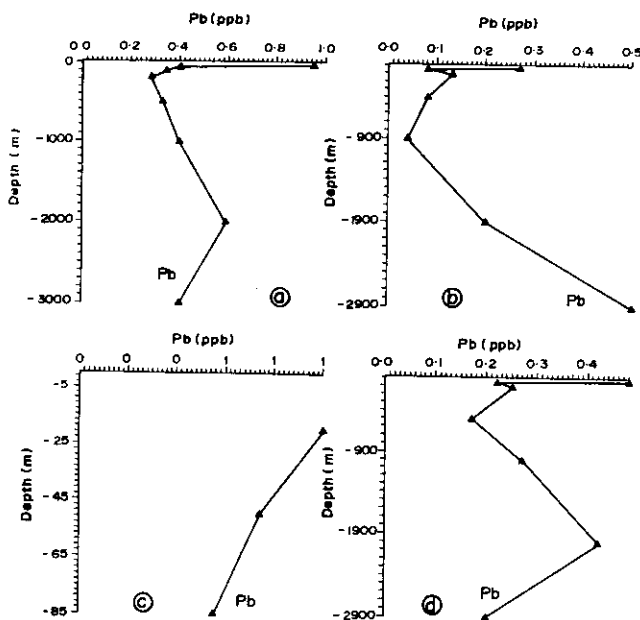


Fig. 5. Depthwise variation of dissolved Lead (Pb) at some stations.

Based on SCHAULE and PATTERSON'S (1981) study on Pb in the North Pacific, the concentrations varied between 25-75 pmol/Kg (5.1- 15.5 ng/Kg). BRULAND (1983) reports 5-175pmol/Kg (1-35ng/Kg) Pb for open ocean waters. However since Pb values in the oceans mainly depend on the aeolian anthropogenic input, a lot depends on the geographical location of the region and the intensity of human activity. Considering stations 8,29 and 51 open ocean type, the range of concentration observed is 0.04-0.5  $\mu\text{g/L}$  (0.1-2.3 nmol/L). DANIELSSON (1980) has reported a range of 0.02-0.16  $\mu\text{g/L}$  for the Indian Ocean (North of equator). Since these values did not compare well with the earlier reported values from other regions, the author declared them to be sample contamination values. During the course of our analysis of these samples we have also analysed standard aqueous material supplied by the National Research Council, Canada. While the existing concentration of Pb was 0.251  $\mu\text{g/L}$ , we have found values such as 0.229 $\mu\text{g/L}$  & 0.202  $\mu\text{g/L}$  which are within  $\pm 20\%$  range. Hence we can confidently assert the validity of our results and stress that Pb values in this part of the Indian Ocean are higher than other open oceanic regions.

Examination of depth profiles of Pb represented in Fig.5 reveals that there is about a 4-fold Pb enrichment in the upper part of the water column relative to the waters below the thermocline. These values support the anthropogenic source of Pb and its short residence time in the water column.

SCHAULE and PATTERSON'S (1983) profiles of Pb for the North Atlantic and the North Pacific show a surface enrichment, then a decrease in concentration followed by a steady deep water concentration between 2000-5000m . Depth profiles in the present study distinctly show a steady rise after the initial fall in Pb values and a deep water high value approximately beyond 2000m.

Pb in nearsurface waters (0-100m) is higher at the coastal stations than in those of oceanic ones. The average concentration for the coastal stations being 0.45  $\mu\text{g/L}$  and that for the oceanic ones being 0.24  $\mu\text{g/L}$ .



## CONCLUSION

The concentrations of Cd found in the open Arabian sea are in a range comparable to that found in other oceans. Pb concentrations show a trend of variation similar to that observed in other oceans but the values are higher than those found elsewhere. The vertical profiles indicate that Cd is a nutrient type trace element and could be transported in association with phytoplankton debris. Pb profiles are similar to those presented by other workers from other oceanic regions. We attribute the high values to the anthropogenic input which could be higher in the Indian Ocean as compared to other oceans.

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