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BASELINE LEVELS OF CADMIUM, CHROMIUM, COPPER, LEAD AND ZINC IN SEAWATER FROM THE GULF OF THAILAND

MANUWADI HUNGSPREUGS

Department of Marine Science, Faculty of Science, Chulalongkorn University, Phya Thai Rd., Bangkok Thailand.

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Abstract

A realistic baseline levels of cadmium, chromium, copper, lead and zinc in the seawater from the Gulf of Thailand were obtained. Two cruises were made in the Upper Gulf, one on September 26–29, 1981, when the river run-off was high, and another on February 1–4, 1982, during the low run-off period. For the Lower Gulf, one cruise was made during 12–26 August, 1982. The results show the concentration ranges for dissolved cadmium, chromium, copper, lead and zinc to be 0.01 to 0.11, 0.20 to 0.29, 0.50 to 2.00, 0.01 to 1.16 and 4.0 to 21.0 $\mu g l^{-1}$ *respectively. These are much lower than previous reports by other authors. Possible explanations are given.*

Introduction

The International Council for Exploration of the Sea conducted six Intercomparison Exercises on the analyses of trace metals in marine organisms and also seawater. The Intergovernmental Oceanographic Commission also conducted one Intercalibration Exercise on Seawater Analysis in 1981[1]. For the Gulf of Thailand, the monitoring work on trace elements in the seawater and sediments has been regularly carried out by the Department of Mineral Resources[2]. The high concentration of major cations, especially sodium, in seawater creates a big interference in most analytical methods for trace metals. This often results in erroneously high reported values of these metals in seawater[3]. It can be seen that in the past few years, reported concentrations of trace metals in seawater have been progressively reduced as analytical sensitivity and collection procedure continue to improve[4]. Polprasert and coworkers[5] at the Asian Institute of Technology however reported extremely high values of some heavy metals in seawater from the Upper Gulf of Thailand.

Older methods for seawater analysis, such as extraction with MIBK* followed by spraying of the organic solvent extract into the air-acetylene flame of an atomic absorption spectrophotometer with no deuterium background correction, were unreliable

for many metals like cadmium and lead, of which the contents are just around the detection limit. With the availability of superior detection methods, we now report the baseline levels of cadmium, chromium, copper and lead in seawater from the Gulf of Thailand.

Methods and Materials

Collection of samples

For the Upper Gulf of Thailand, water sampling was made on board the Fisheries Research Vessel No. 1 during 26-29 September 1981, to represent the high run-off season and February 1-4, 1982, to represent the low run-off. For the Lower Gulf, the water collection was made during 12-26 August 1982 on board the R.V. Suk. Water at 0.5 m depth was pumped through clean plastic tubing into a 5l-plastic bottle, avoiding contact with metallic part, 1.2 ml. of 10% HNO_3 was added to each litre of seawater to bring the pH to 3, in order to prevent adsorption of metallic ions to the container walls and to stabilize the water until analysis.

Reagents

Reagents were prepared as follows : purified APDC*, B.D.H., 2g APDC in 100 ml quartz double-distilled water, cobalt chloride L.R. B.D.H., 0.425 g in 500 ml quartz double-distilled water. Nitric acid A.R. (BDH) was redistilled before use. BDH standard metal solutions were used as standards.

Instrumentation

Beckman refrigerated centrifuge with 500 ml polycarbonate tubes with screw tops; Pye Unicam SP-2900 atomic absorption spectrophotometer with deuterium background correction, and graphite furnace; laminar flow cabinets or 'Clean bench'.

Procedure

Since it is possible[6] that major proportions of cadmium, copper and lead are associated with organic and inorganic colloidal species, whenever filtration was needed, acid-washed Whatman No. 1 filter paper were used, to allow as much colloid species as possible to pass through, while only the comparatively large suspended solid was retained on the filter. For the September samples a set of analysis was made with unfiltered sample too, giving the total content of the metals in seawater.

All procedure was conducted in the laminar flow hood. 250 ml of seawater sample, maintained at pH3 for at least 48 hours, was placed in a 500 ml polycarbonate

*MIBK : Methyl isobutyl ketone

APDC : Ammuonum pyrrolidine dithiocarbamate

centrifuge bottle with screw top. 2 ml of cobalt chloride solution was added and mixed, followed by 2 ml of APDC solution. After gentle shaking, the solution was left for 30 minutes. Trace metal-APDC will coprecipitate with cobalt-APDC. After centrifugation at 5000 r.p.m., 20°C, for 30 minutes, the supernatant liquid was gently poured out. 100 ml of double-distilled water was used to wash the precipitate and adhering seawater, and the mixture recentrifuged for 5 minutes. The aqueous layer was poured off and the precipitate dissolved in 1 ml redistilled nitric acid. The clear solution was quantitatively transferred to a 5 ml graduated flask, the volume made up to the mark and quickly transferred to a clean plastic bottle, 20 microlitre was pipetted into the graphite furnace. Standard addition method was used for calibration. This is a simplified version of Huizenga Method of the Rhode Island School of Oceanography[7], suggested by Professor D.R. Kester. This method was found to be very convenient and gave reproducible results. New reagent blank was made on each day.

Results

The 19 sampling stations, from the Upper Gulf and 7 Stations from the Lower Gulf are shown in Fig. 1. The September samples were much more turbid than the February ones especially for the river mouth samples.

The results for the September–February cruises are shown in Tables 1 & 2

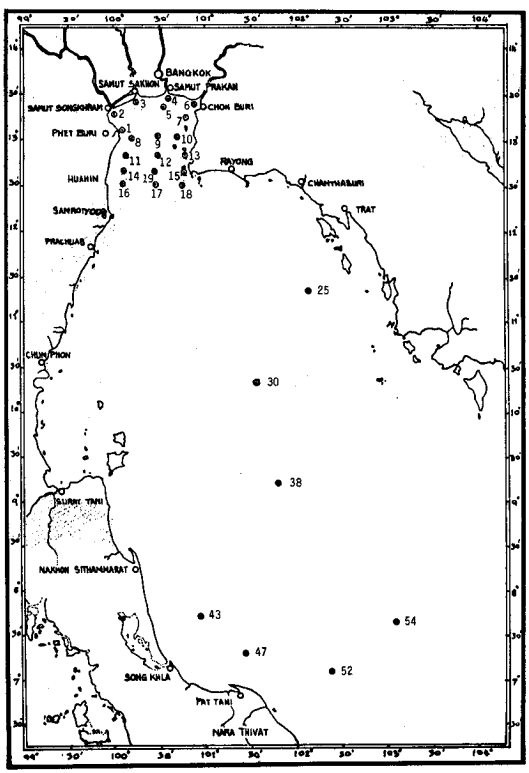

Figure 1.

TABLE 1. CONCENTRATIONS OF CADMIUM, COPPER, LEAD AND ZINC IN SEAWATER ($\mu g.l^{-1}$) FROM UPPER GULF OF THAILAND, SEPTEMBER 26-29, 1981

		Total				Dissolved			
Station	Salinity p.p.t.	Cd	Cu	Pb	Zn	Cd	Cu	Pb	Zn
1	30.13	0.08	2.0	4.4	16.1	0.04	1.77	1.0	12.6
2	30.46	0.16	3.4	3.0	16.2	-	1.02	0.40	12.4
3	29.86	0.07	2.3	3.2	24.4	-	1.10	0.33	17.0
4	30.72	0.26	4.4	4.2	39.9	0.11	2.00	0.20	13.2
5	29.61	0.07	2.4	2.7	19.5	0.09	1.02	0.88	10.4
6	29.99	0.17	1.3	3.3	15.2	0.08	0.50	0.47	-
7	29.91	0.03	2.0	2.8	17.6	-	1.77	1.13	-
8	30.14	0.08	2.1	4.6	15.7	0.03	1.20	0.26	14.0
9	29.99	0.13	1.4	2.4	15.2	0.09	1.02	0.42	13.4
10	29.85	0.07	1.8	3.2	15.9	-	-	-	-
11	30.16	0.05	1.2	2.0	25.5	0.05	0.50	0.16	14.6
12	29.77	0.12	1.5	1.9	19.1	0.02	0.56	0.33	13.2
13	29.72	0.10	1.4	2.3	16.2	0.04	1.13	0.29	11.0
14	29.52	0.06	-	2.7	14.2	-	-	-	-
15	29.59	0.20	1,2	2.1	14.8	0.01	0.66	0.30	12.0
19	29.68	-	-	-	-	-	0.56	0.6	10.8
Mean	29.95	0.11	2.03	3.0	18.4	0.06	1.06	0.44	12.9
Range	29.52-30.72	0.03-0.26	1.2-4.4	1.9-4.6	14.2-39.9	0.01-0.11	0.50-2.00	0.20-1.13	10.8-17.0

TABLE 2. CONCENTRATION OF CADMIUM, CHROMIUM, COPPER, LEAD AND ZINC IN SEAWATER ($\mu g l^{-1}$) FROM UPPER GULF OF THAILAND, FEBRUARY 1-4, 1982.

Station	Salinity p.p.t.	Cd	Cr	Cu	Pb	Zn
1	31.43	0.04	0.22	0.52	0.94	13.0
2	30.82	0.05	0.26	0.83	1.05	13.0
4	26.72	0.02, 0.03, 0.29	0.29	0.66, 0.68, 0.72	0.28, 0.36, 0.31	12.6, 12.0, 12.5
8	26.65	0.02	-	0.89	0.54	14.6
9	26.83	0.08	0.27	1.29	1.16	11.4
11	31.62	0.03	-	0.73	0.70	11.2
12	27.25	0.04	0.24	0.46	0.65	12.8
13	27.18	0.05	-	0.48	0.42	11.0
15	27.46	0.03	-	0.56	0.90	13.0
16	27.58	0.05	-	0.81	0.56	11.2
17	27.31	0.06	0.20	1.35	0.68	15.6
18	27.40	0.05	0.24	0.52	0.47	12.0
19	27.23	0.02	0.20	0.53- 0.64	0.20- 0.16	18.0- 21.0- 15.0
Mean	28.11	0.04	0.24	0.75	0.66	13.0
Range	26.65-31.62	0.02-0.08	0.20-0.29	0.52-1.35	0.16-1.16	11.0-21.0

TABLE 3. CONCENTRATION OF DISSOLVED CADMIUM, COPPER, LEAD AND ZINC IN SEAWATER ($\mu g l^{-1}$) FROM THE LOWER GULF OF THAILAND. 12-26 AUGUST, 1982.

Station	Salinity p.p.t.	Cd	Cu	Pb	Zn
25	32.76	0.05	1.2	0.06	6.4
30	30.36	0.02	0.7	0.03	9.8
38	32.14	0.02	1.2	0.02	6.8
43	33.33	0.03	1.0	0.03	4.0
47	32.58	0.04	1.9	0.06	12.0
52	32.57	0.03	2.1	0.01	5.6
54	32.89	0.06	1.7	0.06	4.9
Mean	32.28	0.04	1.4	.04	7.1
Range	30.36-33.33	0.02-.06	0.7-2.1	0.01-0.06	4.0-12.0

TABLE 4. COMPARISON OF THE CONCENTRATIONS OF CADMIUM, CHROMIUM, COPPER, LEAD AND ZINC FOR THE UPPER GULF OF THAILAND.

Element	Present work September 1981		February 1982	Idthikasem *et al*[2]	Polprasert *et al*[5]
	Total	Dissolved	Dissolved		
Cd mean	0.11	0.06	0.04		78.4
range	0.03-0.26	0.01-0.11	0.02-0.16	0.1-3.4	70.2-89.3
Cr mean			0.24		112.0-365.0
range			0.20-0.29		
Cu mean	2.03	1.06	0.75		64.0
range	1.2-4.4	0.50-2.00	0.52-1.35	1.0-20.0	60.0-70.0
Pb mean	3.0	0.44	0.66		484.7
range	1.9-4.4	0.06-1.13	0.06-1.16	2.0-38.0	430.7-560.2
Zn mean	18.4	12.9	13.0		89.7
range	14.2-39.9	10.8-17.0	11.0-21.0	1.6-49.0	58.0-124.2

TABLE 5. CONCENTRATIONS OF Cd, Cu, Pb AND Zn FROM VARIOUS COASTAL AREAS AND OPEN OCEAN (IN $\mu g\ l^{-1}$).

		Cd	Cu	Pb	Zn
Ligurian Sea, Italy (8)		0.1-0.8	0.2-3.9	-	-
Var River Estuary, France (9)		-	-	-	10.3-12.6[a]
Los Angeles, U.S.A. (4)		-	-	0.150	
Baltic Sea (10)		0.11	1.0	-	4.1
English Seas (11)		0.27-1.13	1.45-2.07	-	-
Oslo Fjord, Norway (12)		0.42-0.26	0.52-1.42	0.36-0.91	-
Upper Gulf of Thailand	September 1981				
(Dissolved)	Mean	0.06	1.06	0.44	12.9
	Range	0.01-0.11	0.50-2.00	0.06-1.13	10.8-17.0
(Total metal)	Mean	0.11	2.03	3.0	18.4
	Range	0.03-0.26	1.2-4.4	1.9-4.6	14.2-39.9
February 1-4, 1982					
(Dissolved)	Mean	0.04	0.75	0.66	13.0
	Range	0.02-0.08	0.52-1.35	0.16-1.16	11.0-21.0
Lower Gulf of Thailand					
Dissolved)	Mean	0.04	1.4	0.04	7.1
	Range	0.01-0.06	0.7-1.9	0.01-0.07	4.0-14.0
Open Oceans (1)		0.059	0.33	0.45	5.68
(14)		0.02-0.06	0.10	-	0.03-0.08
(13)		0.04-0.12	0.10-2.6	-	0.4-3.0
(15)		0.002	0.11	0.11	-

[a]Probably refer to ionic forms only

Discussion

Since the Upper Gulf of Thailand is a semi-enclosed sea area with large influence from the coast, comparison will be made with similar coastal areas. From Table 5, it can be seen that the metal values are comparable in various areas of the world. The Upper Gulf is no more polluted than other gulfs with respect to the heavy metal content. Generally the oceanic water centains much less trace metals as the metal sources are mostly from the rivers. We shall normally find decreasing concentration of anthropogenic metals further away from the river mouths. In our case we did find the lower Gulf to contain lower amount of metals than the Upper Gulf.

Cadmium

The total cadmium content of seawater from the Upper Gulf collected during September is in the range 0.03-0.26 $\mu g\ l^{-1}$ and in the range 0.01-0.1 $\mu g\ l^{-1}$ for the dissolved form. For the February collection the range for dissolved cadmium is 0.02-0.08 $\mu g\ l^{-1}$. The Lower Gulf contained dissolved cadmium in the range 0.01-0.06 $\mu g\ l^{-1}$. These are lower than the Oslo Fjord (12) and not higher than the Baltic Sea (10) or the Ligurian Sea (8)

Upon comparison with results from other Thai workers in Table 4, Idthikasem's values[2] were higher than ours by an order of magnitude, using the APDC/MIBK extraction followed by Flame Atomic Absorption. However, Polprasert *et al*[5] found extremely high concentration of cadmium in the Upper Gulf although they considered their stations nearer to the coastline. Hungspreugs and Siriruttanachai[16] found value of cadmium content at a very near coast oyster farming area of Ang Sila, Cholburi of only around 0.55 $\mu g\ l^{-1}$. Even this latter value is likely to be too high due to the method available to them at that time, i.e. ordinary flame atomic absorption with out background correction. The results of Polprasert *et al*[5] seemed most improbable as they reportedly used 500 ml seawater, evaporated it down to 10 ml then subjected the concentrated brine solution, about 15 g NaCl in 10 ml of water, into the flame. There would be extremely high interference from the sodium and other cations even if it were possible to spray that brine through a fine tube into the flame without clogging it. The standard solution used were in pure water, not saline water. The only known attempt of direct measurement of trace element, namely, copper, in seawater, was done by Ediger[17] by using the flameless graphite furnace, after getting rid of NaCl by the addition of excess NH_4NO_3 to convert NaCl ion into $NaNO_3$ of low boiling point and decomposes at 380°C during ashing cycle. The Lower Gulf water contained the dissolved cadmium in the range 0.01-0.06 $\mu g\ l^{-1}$

Chromium

Dissolved chromium was determined in the February cruise samples and found to be in the range 0.20 to 0.29 $\mu g\ l^{-1}$ which Polprasert *et al*[5] found the range of 112 to 365 $\mu g\ l^{-1}$.

Copper

The dissolved copper concentration for the Upper Gulf was found to be in the range 0.50 to 2.00 $\mu g\ l^{-1}$ for September and 0.52 to 1.35 $\mu g\ l^{-1}$ for February while Idthikasem et al[2] found 1.0 to 20.0 $\mu g\ l^{-1}$ and Polprasert *et al*[5] found 60-70 $\mu g\ l^{-1}$

For the Lower Gulf, the dissolved copper was in the range 0.7-1.9 $\mu g\ l^{-1}$

Lead

The dissolved lead content in the Upper Gulf water was in the range 0.20 to 1.13 for September and range 0.16 to 2.60 $\mu g\ l^{-1}$ for February. Polprasert *et al*[5] reported alarmingly high values of 430.7 to 560.2 $\mu g\ l^{-1}$.

The Lower Gulf showed much lower level of lead at 0.01 - 0.07 $\mu g\ l^{-1}$

This metal is reported to be the most difficult element to find in the marine environmental sample, especially seawater. Waldichuk[3] once wrote that "Research and monitoring of lead in the sea has been plagued by a lack of reliable analysis. Various problems of contamination, high background levels and interference in lead analysis have often given highly variable concentrations which were almost always too high." Several Intercalibration Exercises were organized by the International Oceanographic Commission in 1981[1] seemed to be more successful. There are not many recent reports on lead in coastal water to compare our result with.

Zinc

This work found the mean value for zinc in the Upper Gulf to be 10.8 to 17.0 $\mu g\ l^{-1}$ for September and 11.0 to 21.0 $\mu g\ l^{-1}$ for February. For the Lower Gulf the range for zinc was 4.0 to 14.0 $\mu g\ l^{-1}$

This is probably the least difficult among the 4 elements to be measured due to its comparatively high level in seawater compared to the other three. But it is also easy to get contamination as zinc is on of the most common metal in everyday use. This element can be measured in the final sample by graphite furnace or flame atomic absorption.

Conclusion

From these data some conclusion can be drawn about the present baseline values of cadmium chromium, copper, lead and zinc in the Upper Gulf and the Lower Gulf of Thailand. Concentration values for the other metals are being found next. Similar investigation will be carried out for the Andaman Sea, using the same analytical methods. The values found here seem normal for such a marine environment and should cause no alarm as the AIT Report[5].

The lower values for Cd, Cr, Cu, Pb and Zn found in this work were probably attributed to the followings

1. The use of a new, sensitive, and comparatively contamination-free method, under the 'Clean Bench'

2. Purity of the quartz double-distilled water

3. Extreme care in sample collection and manipulation to minimize possible contamination from air, glasswares, etc.

4. Measurement of the trace metal using Flameless Graphite Furnace Techniques.

Work is also in progress on the metal budget of the Gulf by studying the sediment strata. Coupling with dating method, anthropogenic effect of the past few years should become known.

Acknowledgement

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บทคัดย่อ

เพื่อที่จะหาค่าพื้นฐานของโลหะแคดเมี่ยม โครเมี่ยม ทองแดง ตะกั่ว และสังกะสีในน้ำทะเลจากอ่าวไทย จึงได้เริ่มงานนี้ขึ้นในปี พ.ศ. 2524 - 2525 การเก็บตัวอย่างในอ่าวไทยตอนบนกระทำ 2 ครั้ง ครั้งแรกในเดือนกันยายน 2524 ซึ่งเป็นฤดูน้ำมาก และครั้งที่ 2 ในเดือนกุมภาพันธ์ 2525 ซึ่งเป็นฤดูน้ำน้อย ในอ่าวไทยตอนล่างได้มีการเก็บตัวอย่างในเดือนสิงหาคม 2525 ผลการวิเคราะห์พบว่าปริมาณแคดเมี่ยม โครเมี่ยม ทองแดง ตะกั่ว และสังกะสี อยู่ในช่วง 0.01-0.11, 0.20-0.29, 0.50-2.00, 0.01-1.16 และ 4.0-21.0 ไมโครกรัมต่อลิตร ตามลำดับ ซึ่งต่ำกว่ารายงานของผู้วิจัยคนก่อน ๆ มาก ได้เสนอแนะเหตุผลของความแตกต่างนี้ไว้ด้วย