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RESEARCH ARTICLES

HISTORY OF HEAVY METAL CONTAMINATION IN BANG PAKONG RIVER ESTUARY, THAILAND

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ABSTRACT

Sediment cores were taken from the Bang Pakong River estuary. Trace metal concentrations were determined using atomic absorption spectrophotometer for Cu, Pb, Zn, Cd, Cr and Ni. Enriched concentrations of Cu, Pb and Zn were observed at the top portions of sediment cores. On applying the sedimentation rates found by the Pb-210 method, these layers were found to correspond to the past 30 years. Slight variation with depth in the sedimentary column were found for Cd, Cr and Ni. The anthropogenic fluxes of heavy metals to the Bang Pakong River sediments appear to be similar to the US offshore sediments.

INTRODUCTION

Over several decades heavy metal profiles in sediments have been employed as indicators of the history of metal pollution in many areas[1,2,3]. By using dated sediment cores several investigators have shown that records of anthropogenic and natural fluxes of elements may be found in sediments which accumulate fast enough that annual strata can be distinguished through radiometric dating techniques[1,4,5,6]. Natural fluxes of elements can be determined from the deeper sections of the sedimentary column and the addition of anthropogenic inputs to the natural ones is reflected in the composition of recently accumulated sediments. Thus dated sediment core may provide a reasonable estimate of the natural level and changes in input over an extended period of time.

Bang Pakong River is one of the most important rivers in the eastern coast of Thailand. It flows through a flood plain of paddy fields, spawning grounds and fish producing areas and serve as a source of water for irrigation of the area[7]. In the last few decades due to the rapid industrial development, the area is surrounded by industrial centers which are believed to be the major sources of metal contamination in the area. The aim of this study is to assess the enrichments of heavy metals and their depositional histories in the Bang Pakong River sediments with a view to undertaking a more detailed study of the metal fluxes into the Bang Pakong River estuary.

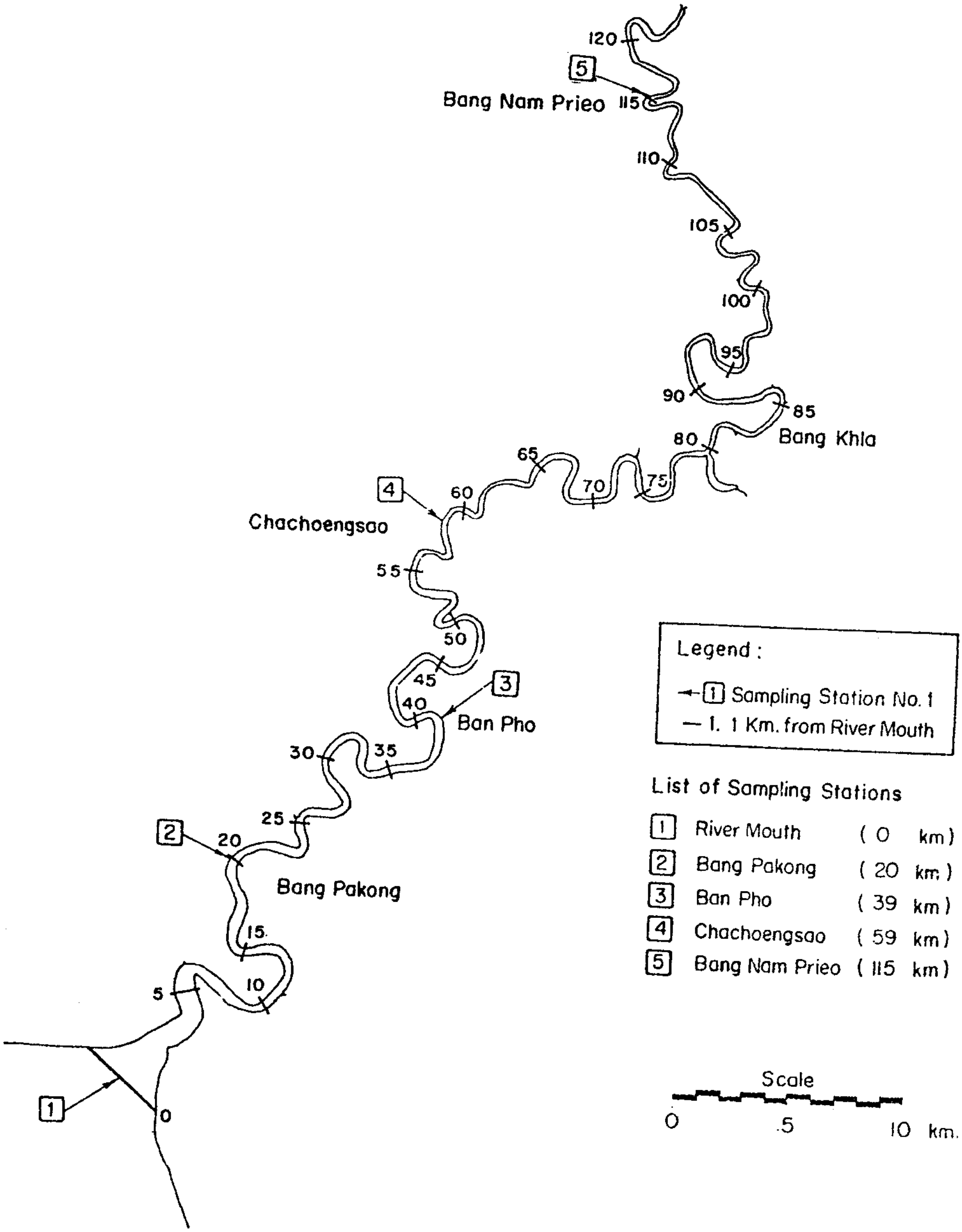

Fig.1. Sampling Station along the Bang Pakong River.

MATERIALS AND METHODS

Core sampling

The sampling location for sediment core samples is shown in Fig.1 and Table1. Station 1,2,3,4 and 5 represent the estuarine, industrial, agricultural, urban and reference area respectively. Core samples were taken by put through the sediment with PVC tubes. The tubes serve as containers which are immediately sealed with plastic sheets. The cores were sectioned under nitrogen atmosphere at every 3 cm intervals up to a depth of 10 cm, and then every 5 cm below that depth. The sediment subsamples were dried overnight at 110 degree celcius, ground and homogenized in an agate mortar, and sieved through a nylon sieved (2 mm mesh size) to eliminate coarse fragments.

TABLE 1. Sampling location

station	N	E
1	13 27' 34"	109 58' 02"
2	13 32 49	101 00 17
3	13 35 49	101 04 56
4	13 40 53	101 04 44
5	13 51 05	101 09 23

Metal analysis

The sediment samples (0.3 g) were then digested in Teflon digestion vessels with 12 ml mixture of $HF+HClO_4$ (5V+V) at 100-150 degree celcius to near dryness. Finally 2 ml of $HClO_4$ was added and evaporated until the appearance of white fumes. The residue was dissolved in concentrated HNO_3 (2 ml) and diluted to 25 ml. The resulting solution was then analyzed by atomic absorption spectrophotometer (Hitachi model 180-30) for trace metals. All the vessels and materials used for metal determinations were cleaned with acid and dried in laminar flow hood before use. A reference material for trace metals (MESS-1) from the National Research Council, Canada was used to check the analytical procedure. The results are given in Table 2.

TABLE 2. Analysis of reference material (MESS-1). All units in ppm.

Element	Certified value	This study(n=6)	% recovery	C.V.*
Cu	25.1±3.8	21.4±1.5	85.3	7.08
Pb	34.0±6.1	28.9±2.9	84.6	10.01
Zn	191.0±17.0	201.6±13.0	105.5	6.31
Cd	0.59±0.1	0.40±0.04	74.6	10.13
Cr	71.0±11.0	59.6±4.0	83.9	6.38
Ni	29.5±2.7	25.1±1.7	85.1	3.76

*C.V. = Coefficient of variation.

Dating techniques

The chemical procedures described by Farmer[8], Nittrouer *et al.*[9], and Carpenter *et al.*[10] were used in the Pb-210 radiometric dating of sediments. Pb-210 activity was determined by alpha spectrophotometry of its granddaughter Po-210 by assuming that Pb-210 and Po-210 are at secular equilibrium. Under the assumption of constant Pb-210 deposition rate and with no postdepositional migration, the net Pb-210 activity from atmospheric deposition in the sediment cores should decrease with depth after correction for the supported lead from local Ra-226. If these conditions are met, then the excess Pb-210 activity (A_z), at depth Z from the sediment-water interface is given by

$$A(z) = A_{(o)}e^{(-xz/S)}$$

where $A_{(o)}$ is the excess Pb-210 activity at the interface, x is the radioactive decay constant of Pb-210 and S is the sedimentation rate in cm/yr.

RESULTS AND DISCUSSION

Pb-210 radiometric dating

The sedimentation rates were determined by Pb-210 method[8,9,10]. The Pb-210 supported by Ra-226 was substracted from the total Pb-210 activity to give an excess Pb-210 values by utilizing the average Pb-210 activities (0.45 dpm/g) in the deeper sections of the core where the total Pb-210 activity appears to be constant. The excess Pb-210 depth profiles of the station 1,3 and 5 are shown in Fig.2. All profiles showed exponential decreases in the excess Pb-210 activity from the surface to the deeper strata with no indication of a surface "mixed zone". This may be due to loss of surficial sediments when lowering the corer into clay-rich sediments. As the corer penetrated the sediment, the upper mixed zone was probably pushed aside, with the corer retaining only the more consolidated sediments below. The sedimentation rates for station 1-5 were found to be 0.72, 0.68, 0.57, 0.49, and 0.47 cm/yr respectively. Similar sedimentation rate of about 0.54 cm/yr for the Bang Pakong River mouth was reported by Windom *et al.*[11].

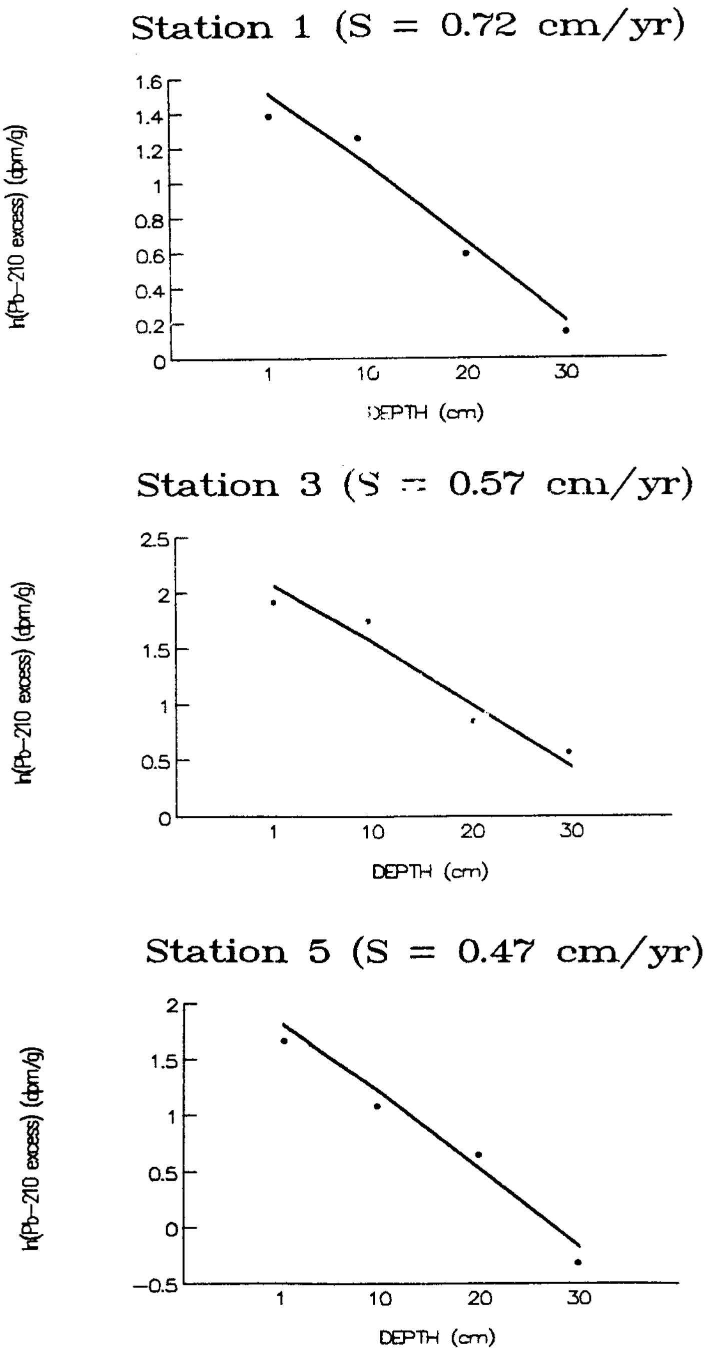

Fig.2. Excess Pb-210 activities as a function of depth in sedimentary column from the Bang Pakong River estuary.

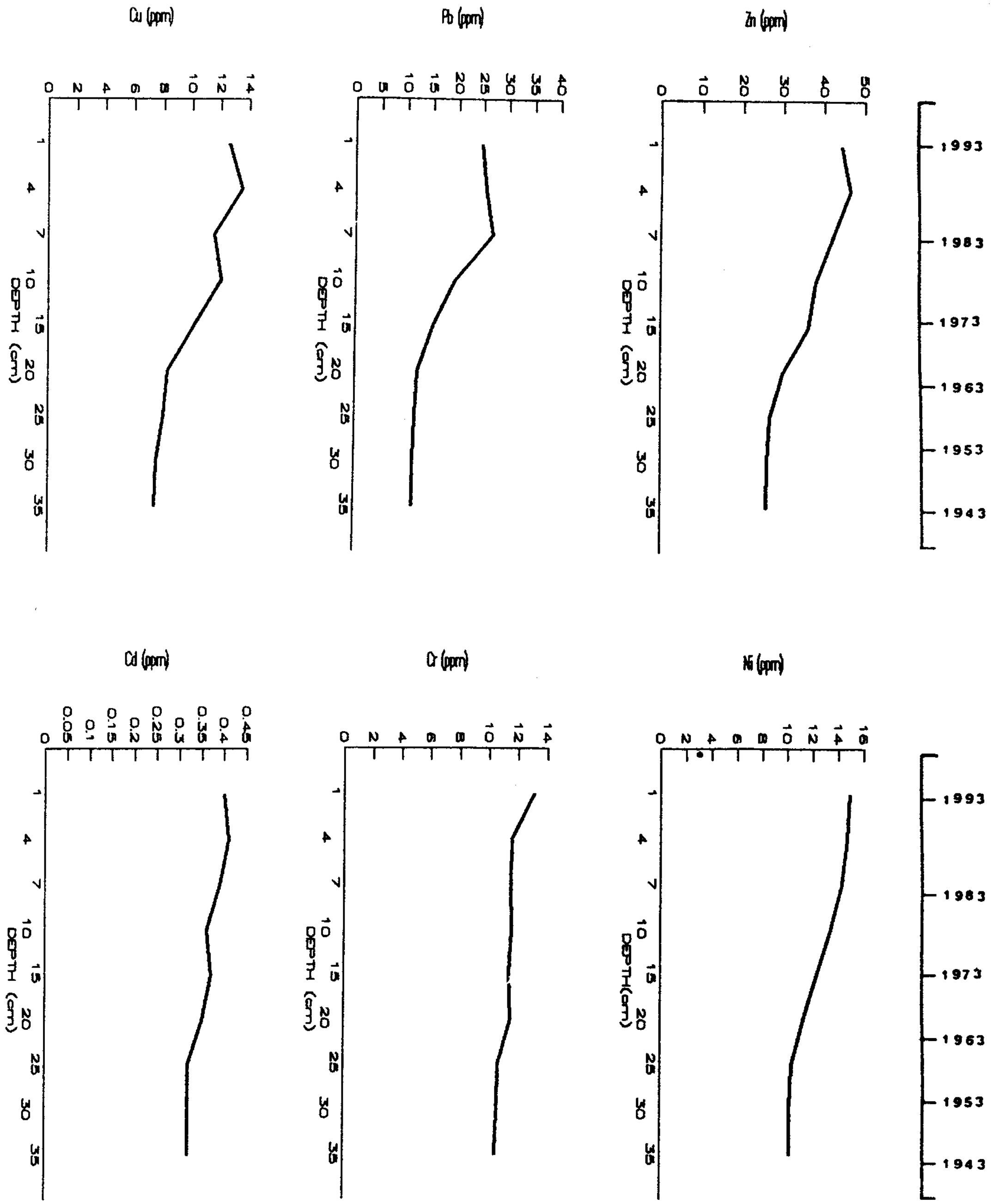

Fig.3. Metal depth profiles of Cu, Pb, Zn, Cd, Cr, and Ni in station 1.

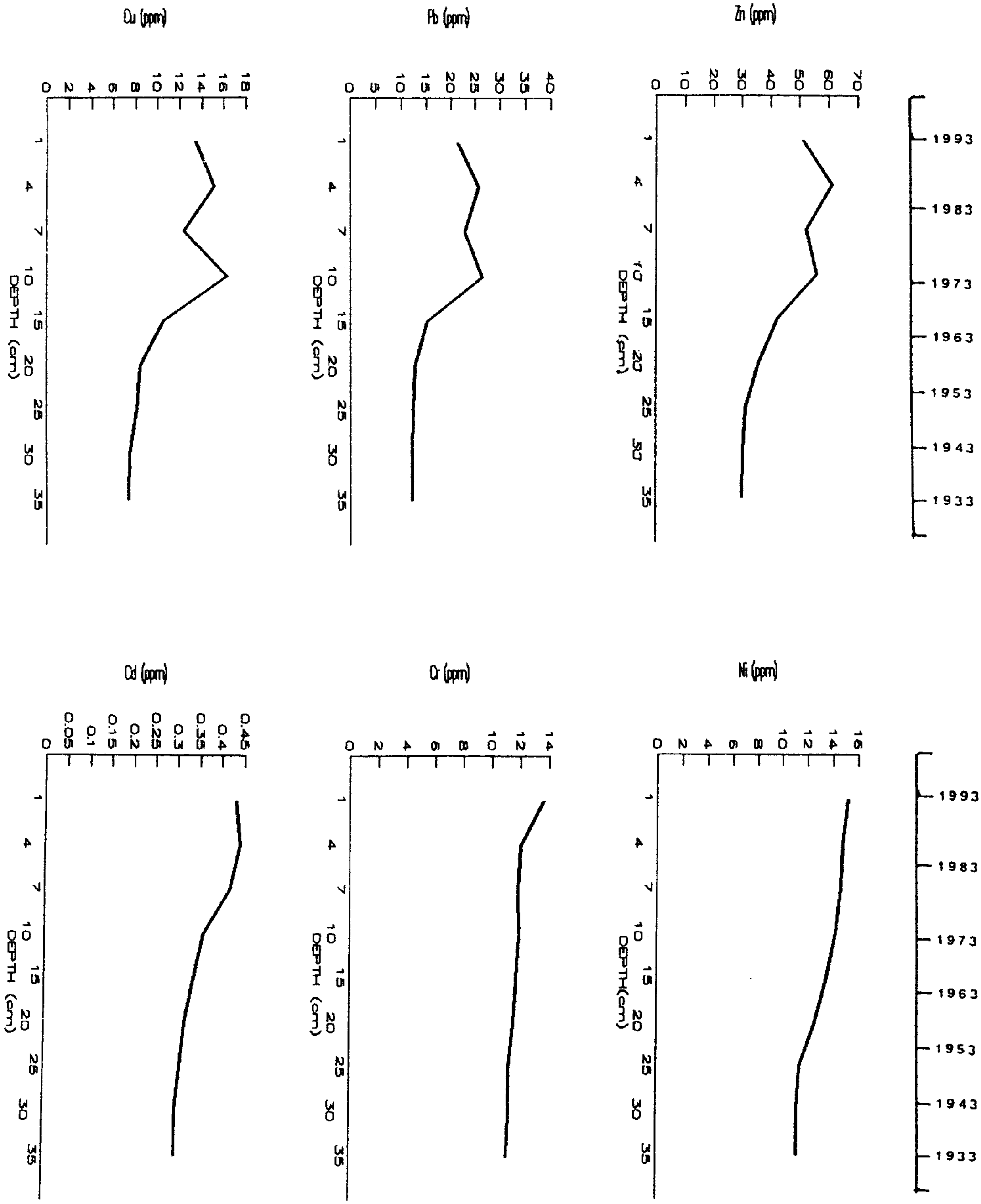

Fig.4. Metal depth profiles of Cu, Pb, Zn, Cd, Cr and Ni in station 3.

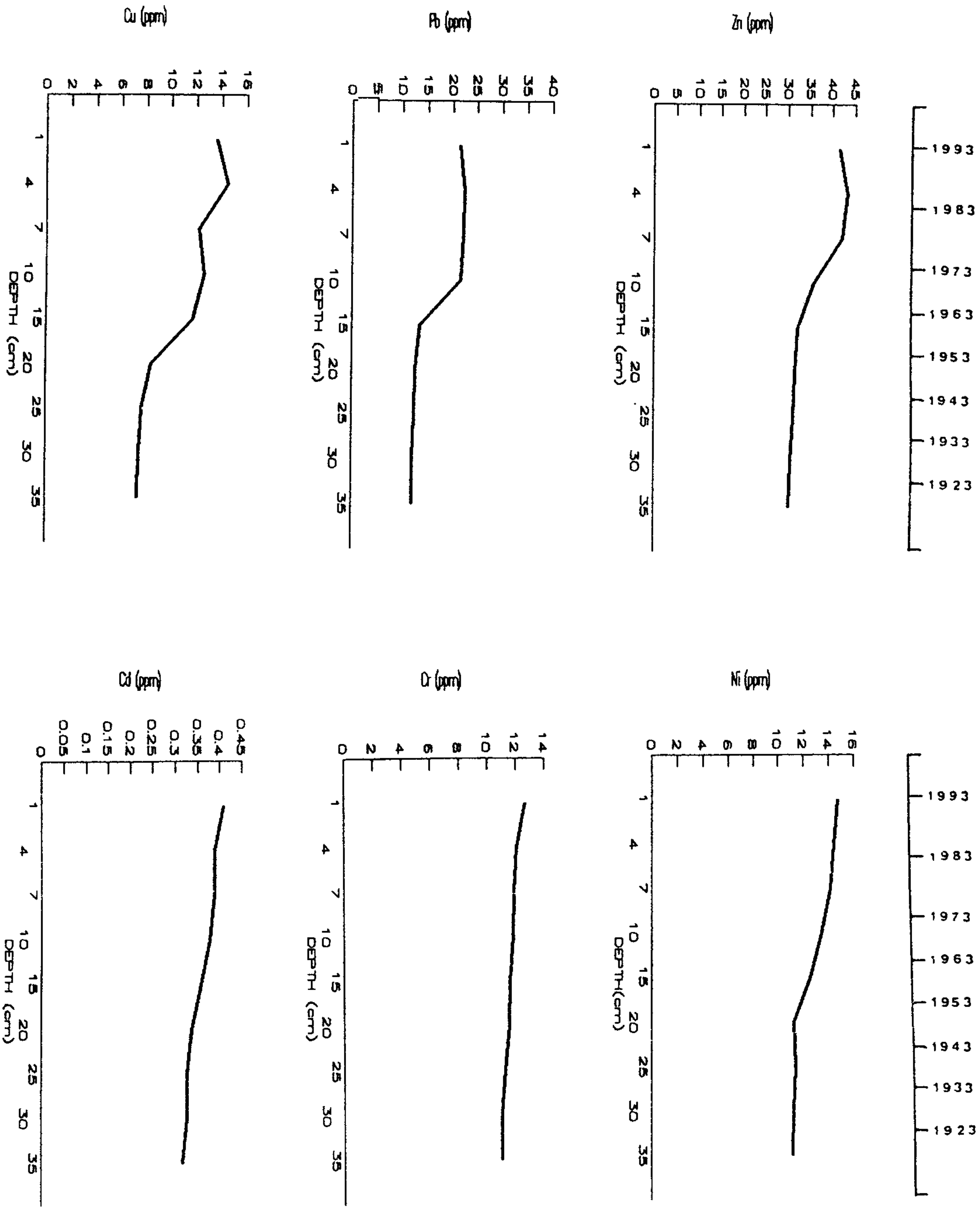

Fig.5. Metal depth profiles of Cu, Pb, Zn, Cd, Cr and Ni in station 5.

Metal profiles

Sediment concentrations of Cu, Pb, Zn, Cd, Cr, and Ni in station 1,3 and 5 are shown in Fig.3-5. These metals exhibit almost similar profiles at all stations. At great depth the concentrations fall to near constant values of 7 ppm of Cu, 12 ppm of Pb, 29 ppm of Zn, 0.3 ppm of Cd and 11 ppm of Cr and Ni which are taken as baseline concentrations (Table 3). Turekian and Wedepohl[12] gives average background concentrations for shales of 45 ppm of Cu, 20 ppm of Pb, 95 ppm of Zn, 0.3 ppm of Cd, 90 ppm of Cr and 68 ppm of Ni and ranges which include the Bang Pakong baseline values for all metals.

It can be clearly seen that there is enrichment of Cu, Pb and Zn in the top portions of sediment cores. While Cd, Cr and Ni appear to be slight variating with depth in the sedimentary column. These findings may be compared with two studies by Erlenkeuser *et al.*[2] who carried out studies on recent sediment cores of the western Baltic Sea, and by Bruland *et al.*[1] who investigated the composition of basin deposits off Southern California. Both groups found enhanced concentrations of Cu,Pb,Zn and unchanged concentrations of Ni in the surface layers compared to those in strata at greater depths which had accumulated earlier. These results are in accord with those in Bang Pakong sediments. Such enrichments of Cu, Pb, and Zn may be attributed to the history of industrial development of the area and by some diagenetic recycling process. The enrichment factors, the ratio of the surface concentrations to that of deeper concentrations indicated that the concentrations of Cu, Pb, and Zn in recent strata have been increased almost double times compared to those deposited several decades ago (Table 3).

By using the sedimentation rates as mentioned above, it is estimated that Bang Pakong estuary has been affected anthropogenically with respect to Cu, Pb, and Zn for the past 30 years, althouh not on a serious scale when compared with other estuaries of the world. Similar observations with respect to Cd and Pb have been observed in the Chao Phraya River estuary by Hungspreugs and Yuangthong[12].

Estimation of metal fluxes into Bang Pakong River sediments

The sedimentary flux of any metal (F in ug/cm2/yr) may be calculated as follows[4]

$$F = R (1 - \phi) DC$$

where R is the sedimentation rate (cm/yr), ϕ is the porosity (0.6-0.8), D is the dry density of the sediment (2.08 g/cm3), and C is the metal concentration (ppm). A natural flux is calculated from the baseline concentrations, while the present day and maximum anthropogenic fluxes calculated by substracting the baseline concentrations from the surface and maximum concentrations respectively. the results of these calculations for both natural and anthropogenic fluxes are presented in Table 4.

The results of metal fluxes clearly indicated that the present day and maximum anthropogenic inputs were found highest in station 2 for all metals. This observation can be attributed that station 2 environments contain much higher industrial activities compared to other stations. As a consequence, those metals of industry whose forms in this estuarine waters are subject to precipitation or accumulation in solid phases, are enriched in recent sediments from station 2. In contrast, the lowest anthropogenic inputs were found in station 4 and 5 which are located in the upstream and believed to be least contaminated. The anthropogenic fluxes of heavy metals to the Bang Pakong River estuary compared with those studies by Bruland et al1 and Goldberg et al3 appear to be similar to those for the Santa Barbara Basin off Southern California but are two orders of magnitude lower than those for the Narragansett Bay in Rhode Island (Table 5). This indicated that the rate of anthropogenic inputs of heavy metals into the Bang Pakong River estuary are comparable to the US offshore sediments but are well below than those intense industrial areas.

CONCLUSION

Radiometric dating studies and metal analysis of sediments have been applied to core samples from the Bang Pakong River estuary in an attempt to assess the enrichments of heavy metals and their depositional histories. Radiometric dating techniques using Pb-210 activity have disclosed sedimentation rates ranging from 0.47 cm/yr in the upstream to 0.72 cm/yr in the river mouth. Metal profiles clearly indicated that there is enrichment of Cu, Pb and Zn inthetop portions of sediment cores and slight variation in concentrations of Cd,Cr and Ni in the sedimentary column. It is estimated that Bang Pakong estuary has been affected anthropogenically with respect to Cu, Pb and Zn for the past 30 years. The results of flux calculations showed that station 2, a site of intense industrial activities contains highest anthropogenic inputs of heavy metals to the area.

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TABLE 3. Comparison between maximum, baseline values of each stations and average shales value (All units in ppm).

Station	Cu				Pb				Zn				Cd				Cr				Ni			
	M	B	E	S	M	B	E	S	M	B	E	S	M	B	E	S	M	B	E	S	M	B	E	S
1	14	7	2.0	45	27	12	2.3	20	47	26	1.8	95	0.4	0.3	1.3	0.3	13	11	1.2	90	15	10	1.5	68
2	15	8	1.9		39	12	3.3		59	30	2.0		0.5	0.3	1.7		14	11	1.3		16	11	1.5	
3	15	7	2.1		26	12	2.2		61	30	2.0		0.4	0.3	1.3		14	11	1.3		15	11	1.5	
4	14	7	2.0		25	12	2.1		47	30	1.6		0.4	0.3	1.3		13	11	1.2		15	11	1.5	
5	15	7	2.1		22	12	1.8		43	30	1.4		0.4	0.3	1.3		13	11	1.2		15	11	1.5	
average	15	7	2.1		28	12	2.3		51	29	1.8		0.4	0.3	1.3		13	11	1.2		15	11	1.5	

M = Maximum value B = Baseline values

E = Enrichment factors S = Average shales value

TABLE 4. Natural and anthropogenic fluxes of heavy metals (ug/cm2/yr) to Bang Pakong River estuary.

	Cu	Pb	Zn	Cd	Cr	Ni
St1.						
Present-day anthropogenic	1.35	3.40	4.80	0.02	0.67	1.22
Maximum anthropogenic	1.67	4.21	5.61	0.02	0.67	1.23
Natural	3.41	5.30	11.98	0.15	4.84	4.70
St2.						
Present-day anthropogenic	1.84	6.57	7.71	0.04	1.11	1.39
Maximumanthropogenic	2.99	10.64	10.82	0.05	1.11	1.57
Natural	4.51	6.74	16.31	0.18	5.82	6.09
St3.						
Present-day anthropogenic	1.61	2.54	5.58	0.03	0.66	1.05
Maximum anthropogenic	2.70	4.28	8.32	0.04	0.66	1.05
Natural	2.50	4.13	10.18	0.10	3.76	3.79
St4.						
Present-day anthropogenic	1.40	2.51	2.84	0.02	0.28	0.81
Maximum anthropogenic	1.79	2.93	3.71	0.03	0.28	0.81
Natural	2.30	3.84	9.66	0.10	3.58	3.58
St5.						
Present-day anthropogenic	1.32	1.99	2.36	0.02	0.36	0.75
Maximum anthropogenic	1.59	2.28	2.88	0.02	0.36	0.75
Natural	2.32	3.81	9.58	0.10	3.49	3.55

TABLE 5. Fluxes of heavy metals to coastal environments (ug/cm2/yr).

	Santa Barbara[1]	Narragansett Bay[3]	Bang Pakong Estuary St1	Bang Pakong Estuary St2
Pb				
anthropogenic	2.1	124.0	3.4	6.6
natural	1.0	2.6	5.3	6.7
Zn				
anthropogenic	2.2	230.0	4.8	7.7
natural	9.7	14.0	12.0	16.3
Cu				
anthropogenic	1.4	193.0	1.4	1.8
natural	2.6	3.1	3.4	4.5

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บทคัดย่อ

ได้เก็บตัวอย่างตะกอนดินจากชะวากทะเล (estuary) บริเวณแม่น้ำบางประกงแล้วนำมาวิเคราะห์ปริมาณโลหะ ทองแดง ตะกั่ว สังกะสี แคดเมียม โครเมียม และนิเกิล โดยเครื่อง atomic absorption spectrophotometer ได้พบปริมาณโลหะ ทองแดง ตะกั่ว สังกะสี สะสมบริเวณส่วนบนของแท่งตะกอนดิน การศึกษาอัตราการตกตะกอนโดยวิธีตะกั่ว-210 พบว่า การสะสมนี้เกิดขึ้นย้อนหลังไปประมาณ 30 ปีที่แล้ว สำหรับโลหะ แคดเมียม โครเมียม และนิเกิล พบว่ามีปริมาณแปรผันเล็กน้อยตามความลึกของชั้นตะกอนดิน จากการคำนวณหาอัตราการป้อน (flux) ของโลหะหนักอันเนื่องมาจากกิจกรรมมนุษย์ พบว่า มีอัตราใกล้เคียงกับที่พบในตะกอนดินบริเวณนอกชายฝั่งของประเทศสหรัฐอเมริกา