DETERMINATION OF SOME HEAVY METALS IN SEDIMENT FROM MARINE AND RIVER MOUTH

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I. INTRODUCTION

The determination of metals in environmental samples provides a good idea about the presence of non-biodegradable compounds. The industrial wastes, geochemical structure and mining of metals create a potential source of heavy metal pollation in the aquatic environment. It is important to evaluate the heavy metal content in sediments because under certain environmental condition, sediments can act either as a sink or as a source of metals [1, 4, 5]. Sediments can reflect water quality and record the effects of anthropogenetic emission. Moreover, the amount of a given metal that can be released from a contaminated sediment chemically disturbed depends critically on the metal species present.

In Vietnam, the accumulation of metals has been well documented in fresh water. But, the information of contents of heavy metals in sediment is still limited. The present study was carried out to determine the levels of some heavy metals (Cu, Zn, Cd, As) in sediment from marine and river mouth.

II. EXPERIMENT

1. Materials and methods

1.1. Apparatus and analytical procedure

The contents of As, Cu, Zn, Cd in sediments were determined by atomic absorption spectrometry (AAS). The Shimadzu model 680 AAS with a standard hydride generation was used for the determination of As. The absorption wavelenghs were as follows: 193.7; 324.8; 213.9; 228.8 nm for As, Cu, Zn, Cd respectively.

Linear calibration graphs were obtained over the concentration ranges of 0 - 20 ppb for As (III); 0 - 10 ppm for Cu and Zn; 0 - 2 ppm for Cd. The solution of 20% KI was used for reduce As (V) to As (III).

1.2. Chemicals

Deionised water (16 MΩ cm) was obtained with a Mili-Q water system (Millipore Japan) was used for the preparation of reagents and standards. All chemicals including standards and solutions (hydrochloric, perchloric, nitric and sulfuric acid) were ultrapure quality. Working solutions for calibration were

prepared from commercially available 1000mg/l solutions for atomic absorption spectrometry (Wako Pure Chemical Industries Ltd. Japan). As reference materials, DORM-1, DORM-2 (Dogfish muscle - Canada National Research Council) and NIES-CRM-02 (Pond Sediment - National Institute of Environmental Studies Japan) were employed.

All glassware was treated with 10% v/v HNO_3 for 24h, and then rinsed three times with Mili-Q water before use.

2. Sample collection

Sediment samples of marine and river mouths were collected in August 2000. Sediments of river mouths were collected at depths of 0-10 cm, 25-35 cm, 105-140 cm to provide an indication of the rate of contamination. All samples were packed into plastic bags and kept frozen until analysis. The samples were dried at 30°C to constant weight and then were ground and passed through a sieve. The sediment was stored in clean acid-soaked polyethylene packets.

3. Digestion of sample

The sample of 0.5g was weighed into conical beaker and was digested with 10ml of acid mixture (HNO_3-$HClO_4$-H_2SO_4). The sample was heated on the hot plate with a glass cover at 220°C for about 8h. After the colour of solution is ligh yellow or white, cool it. Wash the glass cover with 2ml of HNO_3. Then, evaporate a solution at 220°C up to dry (like sirup).

The residue was dissolved in 25ml of 0.5N HNO_3. Filter the suspended solution with Toyo filter paper No 5C. Wash the beaker and filter paper for three times with 0.5N HNO_3. At last, weigh all the sample solution.

III. RESULTS AND DISCUSSION

1. Study of digestion of sample

Two methods of digestion were studied:

The first method: Put 0.5g of sediment into a conical beaker and digest it with 10ml of acid mixture (concentrated HNO_3, concentrated $HClO_4$, concentrated H_2SO_4 with proportion 10 : 4 : 1). Heat the beaker on hot plate at 160° until the colour of mixture in beaker becomes white or ligh yellow.

The second method: Digest 0.5g of sediment into a teflon beaker. Add 9ml of concentrated HNO_3 and 0.25ml of 1.2M HCl. Leave it at room temperature overnigh. Add 2ml of concentrated $HClO_4$, 2ml of concentrated HNO_3 and 10ml of concentrated HF. Heat it on a hot-plate at 160°C until the colour of mixture in beaker becomes white or ligh yellow.

The analytical dates for two digestion methods are showed in Table 1.

Table 1. Contents of heavy metal in sediment with different digestion (ppm)

Sample and method	As	Cd	Cu	Zn
E_1				
Method 1	5.68	1.05	277.1	67.09
Method 2	5.25	0.89	260.7	64.21
E_2				
Method 1	17.54	1.44	25.27	122.55
Method 2	15.45	1.38	23.94	112.70
E_3				
Method 1	89.95	2.21	29.18	62,45
Method 2	80.71	2.02	27.24	63,14
Standard sample				
Certified	12.00	0.82	210.00	343.00
Method 1	10.56	0.72	197.4	315.5
	88%	87.8%	94%	92.0%
Method 2	9.24	0.67	189.2	308.2
	77%	81.7%	90.1%	89.8%

The yield of digestion of the method 1 is higher than one of the method 2. So, the first method of digestion has been used in the experiment. The study of influence of temperature on digestion shows that, at the range of 160° - 220°C the yield of digestion increased with increase of temperature. At 220°C the yields of digestion for As, Cd, Cu and Zn were 92%, 93%, 96% and 95% respectively. In general, good recoveries were found for all these metals. Some other authors [2, 6] have shown that on the method 2, the sample is suitably (conveniently) heated up in microwave.

2. Concentrations of As, Cd, Cu, Zn in sediment from river mouth

At one sampling site, we have colected two samples with different depths (one at the surface layer and other at the depth of 105 - 140 cm). We have digested and analysed 17 samples of sediment from Balat river mouth by using above method. The contents of As, Cu, Zn, Cd in sediment are presented in Table 2.

Table 2. The concentrations of heavy metal in sediment from river mouth (ppm)

Sample	Depth (cm)	As	Cu	Zn	Cd
N1	3-5	21.46	70.50	151.24	1.80
N2	26-28	17.03	89.34	78.27	1.10
N3	10-12	21.12	15.62	144.64	1.72
N4	138-140	15.63	52.01	119.46	1.45
N5	9-12	16.05	85.25	137.41	2.01
N6	127-130	9.92	244.62	111.24	1.26
N7	7-9	19.17	38.81	140.07	1.66
N8	136-138	9.45	89.95	98.38	2.67
N9	2-4	16.30	97.29	140.89	2.16
N10	110-112	10.36	138.94	109.38	2.07
N11	4-6	16.92	101.44	113.90	1.90
N12	111-113	19.80	26.62	122.55	1.64
N13	4-5	14.88	145.81	110.67	1.87
N14	105-107	6.45	294.79	70.63	1.15
N15	2-4	22.13	96.26	157.50	1.73
N16	130-131	18.16	103.84	121.94	1.82
N17	32-35	6.84	209.68	95.26	1.24

Note: every couple of sample were collected at the same latitude and longitudle.le.

The concentration of heavy metals were 6.45 – 22.13 ppm for As; 1.1 – 2..6.67 ppm for Cd; 52.01 – 294.79 ppm for Cu and 70.63 – 157.50 ppm for Zn. Trace metalalals can be accumulated in sediment by two main processes: local geochemical proceesess and sorption process. Feiyue Wang [3] show that trace metal concentration i i in relatively uncontaminated toxic sediments may be predominately controlled by tlthe local geochemical background rather than by other active sorbent such as iron aand manganese oxides and organic matter. The importance of the later factors nmmay increase when the aquatic systems are contaminated by metals. Copper, Zinc in wasisaste water can form insoluble sulfur and be accumulated in sediment of river mouth.

The concentrations of As, Cd were normal. According to Neff [2], the meeear shore marine and estuarine sediments contain total Arsenic from about 5 to abooout 15 μg/g of dry weight were considered as uncontaminated sediments. However, / A As in the samples of N_1, N_3, N_{15} were rather high (about 21.00 – 22.00 ppm).

The data in Table 2 also show that the concentrations of these metals s in sediment varried with the depth of sampling site. Arsenic concentrations in surfaaace sediment are higher than those in layer of 110 – 140 cm depth from 1.5 to 2.0 tiimeenes.

In general, the deeper (more) depth of the assembled sediment, the lower (less) content of heavy metals (except Cu). The high contents of As in surface sediment may be due to the pollution during phosphorite processing and using As-rich pesticides....

3. The concentration of As, Cd, Cu and Zn in marine sediment (ppm)

We determined the concentrations of As, Cd, Cu and Zn in 10 samples of marine sediments (near-shore). The results were given in Table 3.

Table 3. The concentration of As, Cd, Cu, Zn in marine sediments

Samples	Location	As (ppm)	Cu (ppm)	Zn (ppm)	Cd (ppm)
M_1	Vungtau	6.43	59.39	56.42	1.50
M_2	Cochien	9.46	16.52	76.09	1.70
M_3	Hamluong	13.80	15.40	90.26	2.00
M_4	Hamluong	10.59	26.98	68.59	2.07
M_5	Hamluong	11.75	40.17	88.5	1.48
M_6	Cuadai	8.54	20.45	65.28	1.95
M_7	Cuatieu	9.06	18.01	68.45	1.64
M_8	Cuatieu	8.52	36.12	73.06	2.09
M_9	Soairap	10.34	30.65	68.63	1.22
M_{10}	Soairap	10.10	29.76	84.75	1.79

The concentrations of As were 6.43 to 13.8 ppm. There values were not high and lower the contaminated levels. Dao Manh Tien in the paper [8] of sediment Quangninh reported that the content of heavy metals is as follows: 0.95 – 1.18 ppm for As, 0.88 – 1.25 ppm for Cd, 7.33 – 18.50 ppm for Cu and 62.44 – 99.2 ppm for Zn. It can be concluded that the concentrations of heavy metals in studied sediment are hgher than in the samples obtained from marine of Quangninh (except Zn). In addition, the levels of four metals in marine sediment are lower than those in sediment of river mouth. However, the arsenic concentration is higher than in some marine sediments in the wold [7] (As in sediment of Biscaye Bay is 5.1 ppm).

IV. CONCLUSIONS

1. The method of digestion of sediment was studied. The digestion with concentrated acid mixture (HNO_3-$HClO_4$-H_2SO_4) at 220°C has good recovery: 92% for As, 93% for Cd, 96% for Cu and 95% for Zn.

2. The concentrations of As, Cd, Cu, Zn in sediment of Balat river mouth werereere determined. Their range of concentration are: As (6.45 – 22.13 ppm), Cd (1.1 – 2.66667.67 ppm), Cu (52.01 – 294.79 ppm), Zn (70.63 – 157.50 ppm). The concentration of theseseese metals in some samples is high. The more depths of assembled sediment, the loweereiver concentration of heavy metal (except Cu).

3. The concentration of As, Cd, Cu, Zn in marine sediment from some locaticororion in South of Vietnam was studied. The contents of these metals are as follows: AA: As (6.43 – 13.8 ppm), Cd (1.22 – 2.09 ppm), Cu (15.40 – 59.39 ppm), Zn (56.42 – 90.26)).).3).

Although, there is no very high levels of heavy metals in sediment froomrom marine and river mouth, a potential danger may occur in the future depending coior on the agricultural and industrial development in these regions.

Acknowledgements. Our experiments were carried out at the Center ffofo for Marine Environmental Studies, Ehime University, Japan. I expreeseseess acknowledgement to professor Tanabe Shinsuke for his support. I shall bring mainnany thanks also to Doctor Kunito Takashi for his comments and suggestions.

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TẠP CHÍ KHOA HỌC ĐHQGHN, KHTN & CN, t XIX, $N_0$1, 2003

XÁC ĐỊNH MỘT SỐ KIM LOẠI NẶNG TRONG TRẦM TÍCH BIỂN VÀ TRẦM TÍCH CỬA SÔNG

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Việc xác định nồng độ kim loại (đặc biệt là kim loại có độ độc cao) trong các mẫu trầm tích có thể cung cấp những thông tin về mức độ ô nhiễm môi trường, quá trình địa hóa hoặc chu trình vận chuyển các chất độc trong môi trường.... Vì vậy, trong bài báo này, chúng tôi giới thiệu phương pháp phá hủy mẫu trầm tích bằng hỗn hợp axit đặc (HNO_3, $HClO_4$, H_2SO_4 với tỷ lệ 10: 4: 1 ở nhiệt độ 220°C). Bằng phương pháp này, hiệu suất chuyển các kim loại As, Cd, Cu, Zn từ mẫu vào dung dịch có thể đạt 92%, 93%, 96%, 95% tương ứng. Nồng độ của As, Cd, Cu, Zn trong 17 mẫu trầm tích cửa sông đã được xác định với giá trị: As (6,45 -22,13 ppm); Cd (1,1 - 2,67 ppm); Cu (52,01 - 294,79 ppm); Zn (70,63 – 157,5 ppm). Nồng độ của As, Cd, Cu, Zn trong 10 mẫu trầm tích biển thấp hơn so với trầm tích cửa sông và có giá trị như sau: As (6,43 - 13,8 ppm); Cd (1,22 - 2,09 ppm); Cu (15,40 - 59,39 ppm); Zn (56,42 - 90,26 ppm).