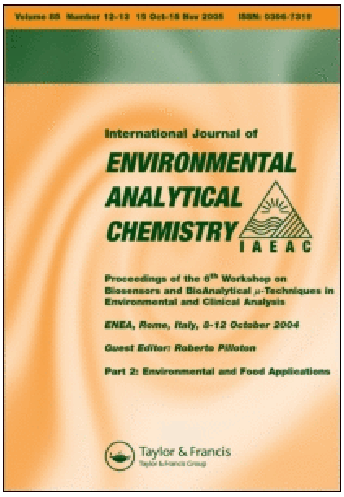

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Recovery of Heavy Metals from Acid Digestion of an Estuarine Sediment and Concentration Profiles of Sediment Cores from Hebe Haven and NGAU MEI HOI, Hong Kong

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RECOVERY OF HEAVY METALS FROM ACID DIGESTION OF AN ESTUARINE SEDIMENT AND CONCENTRATION PROFILES OF SEDIMENT CORES FROM HEBE HAVEN AND NGAU MEI HOI, HONG KONG

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The recovery efficiencies of Cd, Cr, Cu, Fe, Ni, Pb and Zn during acid digestion by different acid mixtures and by block heater and microwave heating were determined for an estuarine sediment sample. For block heater heating, the aqua regia mixture was found the most powerful digestion agent, giving a high yield of 112% for Fe and a poorer yield of 83% for Pb. Compared to block heater heating, HNO_3 digestion by a domestic microwave oven gave a lower yield for Cr, Cu, Fe and Ni. The digestion time of 3–6 min was possibly not sufficient to cause a complete release of the heavy metals. The recoveries for a heating time of 3.8 min and under 'High Heat' were determined as follows: Cd, 99%; Cr, 55%; Cu, 95%; Fe, 87%; Ni, 76%; Pb, 75%; Zn, 88%. Microwave digestion using HNO_3 was used to determine the concentration of the above metals in two sediment cores from Hebe Haven and Ngau Mei Hoi, Hong Kong. Hebe Haven, which is close to a suburban area with some dyeing factories, has its surficial sediment enriched in Cd, Cr, Cu, Pb and Zn, with mean surficial concentrations of 0.259, 65.0, 30.3, 52.4 and 115 mg kg^{-1}, respectively. The corresponding enrichment factors (EFs) were calculated as 3.6, 2.0, 3.0, 1.4 and 1.6. Ngau Mei Hoi is further away from the urbanized coast and only Cd, Cu and Pb are slightly enriched in the surficial sediment, with EFs of 1.1, 1.3 and 1.4, respectively.

KEY WORDS: Heavy metals, acid digestion, recovery, microwave, concentration profile, sediment core.

INTRODUCTION

Several recent reports[1,2,3,4] have indicated that microwave-assisted acid digestion of sediment and soil samples is valuable because of the speed and completeness of digestion. There is also less contamination. In terms of recovery percentages, Table 1 summarizes the performance of acid digestion of sediment and soil samples by hot plate and microwave heating. Compared with hot plate heating, it is shown that microwave heating always gives an equivalent or better extraction efficiency. The enhancement is especially significant in the extraction of Cr. However, a scientific

Table 1 Recovery of heavy metals (%) from acid digestion of sediment and soil samples.

Ref.	*Sample and acid used*		*Heating*	*Cd*	*Cr*	*Cu*	*Fe*	*Ni*	*Pb*	*Zn*
1	CLP soil sample; 10 ml/g;	5 min	Microwave	94	81	91	74	71	90	84
	70% HNO_3; 6 samples/oven	15 min	Microwave	106	100	93	92	92	94	96
	Same as above,	5 min	Microwave	96	85	93	84	76	90	92
	But 12 samples/oven	15 min	Microwave	91	104	97	102	98	94	105
2	NRCC MESS-1 marine sediment; 7 ml/0.2 g; $HNO_3/HF/HClO_4$ [3:3:1]		Microwave	107	83	109	99	89	92	97
3	NIST SRM 1645b river sediment; 20 ml/g; 1:1 $HNO_3:H_2O$		Microwave	100	—	111	—	107	102	100
4	NRCC PAC-1 marine sediment;		Hot plate	—	65	101	—	107	100	98
	20 ml/g; 1:1 $HNO_3:H_2O$		Microwave	—	73	100	—	109	99	97
	As above, but use $HNO_3/HCl/HF$		Microwave	—	92	105	—	120	102	103
	NIST SRM 2704 river sediment; 20 ml/g; 1:1 $HNO_3:H_2O$		Microwave	—	100	103	—	120	111	98
	NIST SRM 4355 soil sample; 20 ml/g; 1:1 $HNO_3:H_2O$		Microwave	—	—	94	—	160	143	105
5	Sediment sample; 5 M HNO_3		Hot plate	80	65	46	79	—	57	94
	15 ml/3–5 g; 5:1 $HNO_3/HClO_4$		Hot plate	82	66	49	75	—	57	88

microwave heating system is very expensive. It is therefore worthwhile to investigate the feasibility and performance of using a domestic microwave oven to do the acid digestion.

METHODS AND PROCEDURES

NBS 1646 estuarine sediment and a composite marine sediment sample collected from Junk Bay, Honk Kong were used to study for the optimal digestion of sediments for Cd, Cr, Cu, Fe, Ni, Pb and Zn. One gram of 103°C-dried sediment was digested by 18 ml of acid. Three types of acids were tested. They were: Acid 1, 65% HNO_3; Acid 2 (Aqua Regia), 65% HNO_3 + 30% HCl [1:3]; and Acid 3, 65% HNO_3 + 70% $HClO_4$ [3:1]. The sediment was digested in a long tube placed in a block heater for 24 h. The tube is 30 cm in height and 2.3 cm in diameter. Air cooling was used during digestion and usually only a small amount of liquid was lost as vapour during digestion. Alternatively it was digested by a domestic microwave oven in a thick teflon vessel for 3 to 6 minutes, depending on the microwave power selected. The vessel, made especially for microwave digestion by CEM Co., has a volume of 120 ml and a pressure release device. A Sharp R-9H10 microwave oven with a power of 750 W was used. The vessel was capped by an ordinary wrench and placed inside an air-tight plastic bottle that protected the oven from direct attack of the acid fumes. The effect of the length of digestion time, ranging from 8 to 60 hours, was also studied for HNO_3 digestion by block heater heating. All acids used were AR grade. These acids contained negligible amounts of heavy metals as compared to the metal concentrations in the final sediment extract. No boiling stone was used. This was aimed to reduce contamination.

The digested sediment was cooled, filtered and finally diluted to 25 ml. Flame atomic absorption spectrophotometry (AAS) of Cr, Cu, Fe, Ni, Pb and Zn was conducted using the Perkin Elmer 3030 AAS. Cd was determined by graphite furnace AAS using the Perkin Elmer HGA-400 furnace and AS-40 autoinjector and sampler. The GFAAS temperature programming for Cd analysis was: 80°C, 10 sec; 120°C, 25 sec; 400°C, 30 sec; 1600°C (atomization), 3 sec; 2600°C, 3 sec. Maximum power heating and stop flow (Argon) were used during the atomization stage. GFAAS was also used to measure trace amounts of other metals in the blanks. Standard addition calibration was used. Background absorption was corrected by a deuterium lamp for Cd, Ni, Pb and Zn. Detection limits of the analyses in mg kg^{-1} for the use of 1 g of sediment and a final dilution volume of 25 ml were as follows: Cd, 0.020; Cr, 4.0; Cu, 2.8; Fe, 445; Ni, 5.6; Pb, 7.0; and Zn, 0.63.

Sediment cores were taken by a 7.6 cm diameter gravity corer having a tube length of 76 cm. Core H2 was sampled from Hebe Haven on 8/9/1987 and Core S8 from Ngau Mei Hoi on 14/3/1988. Figure 1 shows their location. Hebe Haven is close to a suburban area with several dyeing factories. Ngau Mei Hoi is further away from the urban area and thus acts like a background. The sediment core was cut into thin sections, weighed and dried at 103°C. It was then powdered and stored in air-tight plastic bags at room temperature and in darkness until chemical analysis. The

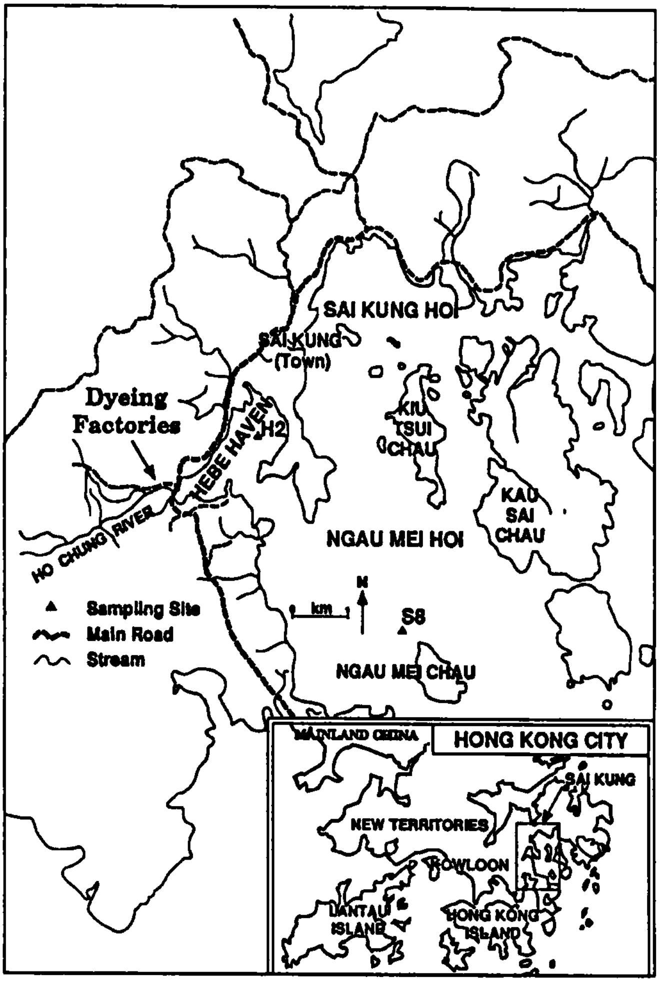

Figure 1 Map of sampling sites.

sediment was digested by 65% nitric acid under 'High Heat' in the microwave oven for a period of 3.8 min.

RESULTS AND DISCUSSION

Analytical aspects

The analytical precision of the AAS for different metals is affected by the magnitude of the measuring concentration. A concentration close to the detection limit will inevitably be less precisely determined. The typical coefficients of variance (CV in %: standard deviation/mean) for Fe and Zn is low, i.e. 2–5%, because the concentration in the sediment extract is high. Dilution was needed and gave an aqueous sample with lesser salt content that might reduce interferences caused by NaCl in marine sediments. Cu and Cr have a slightly higher CV of around 5%. Pb and Ni have typical CVs of around 5–8%. For graphite furnace AAS analysis of Cd, background absorption was a major factor affecting the determination. The HNO_3/HCl and $HNO_3/HClO_4$ sediment extracts in this study produced extensive background absorption (Figure 2) and to some extent affected the quality of the data. The HCl matrix was previously reported unsuitable for GFASS analysis of Cd and Pb[6]. Typical CV of Cd is 5–10% for 3 replicate injections. In average, four replicates were digested and analyzed per sample. With respect to overall chemical analysis, the average CV is better than 6% for Zn, Fe, Cr and Cu and better than 10% for Cd, Pb and Ni. Finally, the blanks from block heater heating were found to have higher metal content than those from microwave heating.

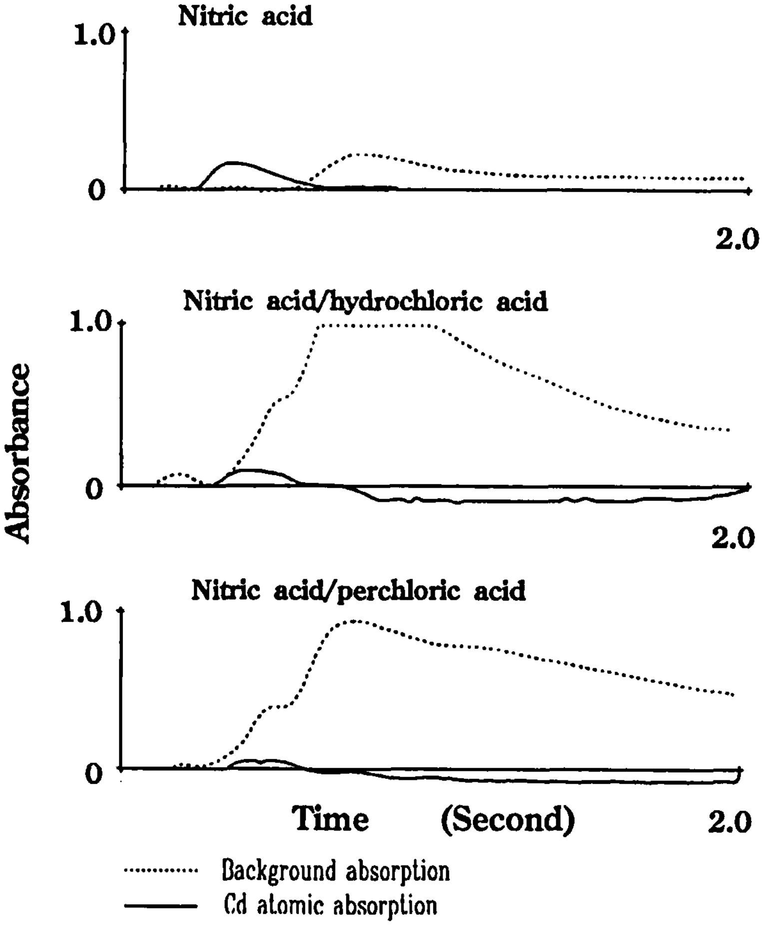

Figure 2 Graphs showing the background and atomic absorption of Cd in a sediment sample digested by three different acids.

Effect of length of digestion time for HNO_3 digestion by block heater

The results are shown in Table 2. Three different composite sediment samples were tested. The concentrations obtained for different digestion times were averaged and the CVs calculated. The CV is an immediate indicator of the extent of variance. Subsequent t-tests can then be conducted for specific pairs of data.

The CVs obtained for Cd, Fe and Zn are small (Cd: 5%; Fe: 2–5%; Zn: 3%) and imply no significance when compared with the CVs of the overall chemical and analytical procedures as reported above. The effect of different digestion times on recovery is therefore considered insignificant.

For Cu, Ni and Pb, the CVs range from 3 to 7%. The sediment used in Test Two has higher Cu, Ni and Pb contents and should provide greater reliability because a smaller instrumental error is expected. For Cu, only the 111 mg l^{-1} (46/61 h) data is

Table 2 Extracted metal concentrations for sediment samples digested by nitric acid for different periods of time.

Time of digestion (h)	*Mean recovered concentration of:*						
	Cd $(mg\,kg^{-1})$	*Cr* $(mg\,kg^{-1})$	*Cu* $(mg\,kg^{-1})$	*Fe* $(mg\,kg^{-1})$	*Ni* $(mg\,kg^{-1})$	*Pb* $(mg\,kg^{-1})$	*Zn* $(mg\,kg^{-1})$
				Test One			
8	0.126	21.4	11.8	27.1	8.45	29.4	—
16	0.116	19.0	11.6	25.7	7.96	28.9	—
23	0.120	20.1	11.7	28.5	9.19	27.8	—
39	0.110	26.1	12.4	28.7	9.53	26.9	—
47	0.115	25.1	11.8	29.1	9.17	29.7	—
68	0.118	25.9	12.3	29.0	9.31	28.8	—
Mean Conc.	0.117	22.9	11.9	28.0	8.94	28.6	—
CV	5%	14%	3%	5%	7%	4%	
				Test Two			
8	—	55.9	101	37.1	23.1	162	1160
16	—	60.3	107	38.2	24.5	161	1130
24	—	61.4	103	38.2	22.6	158	1110
46	—	72.2	111	38.9	26.8	179	1140
61	—	70.5	111	39.1	23.2	173	1190
Mean Conc.	—	64.1	107	38.3	24.0	166	1146
CV	—	11%	4%	2%	7%	5%	3%
				Test Three			
8	—	24.5	8.68	20.3	10.7	21.9	—
26	—	28.8	9.28	22.2	11.1	24.6	—
46	—	31.1	8.86	22.1	11.5	25.0	—
61	—	31.5	9.49	22.9	11.7	24.4	—
Mean Conc.	—	29.0	9.08	21.9	11.0	24.0	—
CV	—	11%	4%	5%	4%	6%	
Mean recovery around 24 h [%][a]	96.0	84.5	94.9	97.7	92.1	93.3	93.0
RSD	—	5.9%	2.2%	0.4%	5.4%	4.1%	—
CV	—	9%	3%	0%	7%	5%	—

[a] Mean recovery calculated by using the highest concentration obtained as 100% recovery.

significantly different from the rest. The 46-h recoveries of Ni and Pb are also significantly higher than those from other trials of shorter duration. There is also a tendency that some loss of Pb recovery occurred when digestion was extended to 60 h. This is shown in all the three tests.

Cr is the only metal showing significant difference of recovery for different digestion times. The CVs range from 11 to 14% and are much higher than the CV of chemical analysis. A longer extraction time is shown (Table 2) to promote release of Cr from the sediment. It is probably because nitric acid is not effective for its extraction (Tables 1 and 3) and a longer digestion time will then help. A concentration cut point is noted for Cr in the interval of 23–47 h in all three tests. The pairs of data are significantly different (Test One: 20.1 and 26.1 mg kg^{-1}; Test Two: 61.4 and 72.2 mg kg^{-1}; Test Three: 28.8 and 31.1 mg kg^{-1}). Test One shows that some time between 23 and 39 h is required to attain maximum release of Cr from nitric acid digestion.

Different acids and heating methods

The results are shown in Table 3. A time of 24 h was used for block heater heating. For microwave oven heating, the time used could not go beyond 6 min for the 'Medium High Heat' and 3.8 min for 'High Heat' operation without having excessive evaporation of the acid. Excessive leaking out of volatile acids must be avoided in the use of domestic microwave oven because there is no special venting device, otherwise damage could occur. Capping by an ordinary wrench might not be the best sealing method. It is suspected to be the main cause for the leakage of acid from the vessel prior to sufficiently acting upon the sediment particles. Tighter and more repeatable capping might be made possible by using the special capping station provided by the manufacturer for use with the pressure release type teflon vessel. Insufficient digestion time has reduced the recovery of certain metals as indicated later.

Cadmium Only the Cd result shows complete to over-complete recovery. There are two possible causes leading to this apparent complete Cd extraction. Firstly, Cd is expected to be overestimated because background absorption correction with the deuterium lamp is not adequate to correct the background absorption caused by NaCl, which is rich in estuarine and marine sediment samples. Secondly, as Cd in the sediment is mostly anthropogenic in source and mainly associates with the portion of fine particles that are readily digestible, the recovery is therefore more complete.

The result of NBS sediment analysis should be more reliable because the Cd concentration is much higher than that of the Composite Junk Bay sediment. A 10-fold dilution was made before GFAAS analysis. This tremendously cut down the background absorption, which was found especially serious in extracts containing HCl or $HClO_4$ (Figure 2) as stated previously. Analysis of low levels of Cd was therefore more susceptible to this interference, which could lead to a less precise determination.

The NBS sediment has a large standard deviation (0.36 ± 0.07 mg kg^{-1}), corresponding to a CV of 19%. The grand mean for all NBS sediment analyses is

Table 3 Recovery of heavy metals from sediment samples by different acid mixtures and by different heating [Acid 1: HNO_3; Acid 2; HNO_3/HCl; Acid 3: $HNO_3/HClO_4$; percentage of recovery based on NBS reference value; BH: Block heater heating; MIC: Microwave oven heating].

Description of digestion acid and type of heating	*Digestion time*	*Cd*	*Cr*	*Cu*	*Fe*	*Ni*	*Pb*	*Zn*
					(Mean Recoveries in %)			
NBS 1646 Estuarine Sediment								
Reference Value (mg kg^{-1} except Fe in g kg^{-1})		0.36	76	18	33.5	32	28.2	138
Coefficient of variance [CV]		19%	4%	17%	3%	9%	6%	4%
Acid 1 (BH)	24 h	108	66	101	97	78	65	86
Acid 1 (MIC) Medium High Heat	4 min	107	49	89	82	65	71	84
Acid 1 (MIC) High Heat	3 min	109	48	86	79	63	70	80
Acid 1 (MIC) High Heat	3.8 min	99	55	95	87	76	75	88
Acid 1 (MIC) Heat Heat	4 + 4.2 min	107	50	91	83	71	73	89
Acid 2 (BH)	24 h	97	91	102	112	91	83	87
Acid 2 (MIC) Medium High Heat	5 min	93	71	99	111	80	70	93
Acid 2 (MIC) High Heat	3.2 min	102	74	94	112	82	68	88
Acid 3 (BH)	24 h	96	72	107	100	98	63	87
Grand Mean Concentration (mg kg^{-1}; Fe in g kg^{-1})		0.367	48.6	17.3	32.1	25.0	20.0	120
Grand Mean Recovery [%]		102	64	96	96	78	71	87
CV		6%	23%	7%	14%	15%	8%	4%
Junk Bay Composite Sediment Sample				mg kg^{-1} except Fe in g kg^{-1}				
Acid 1 (BH)	24 h	0.109	23.2	15.9	24.9	9.8	33.2	91.2
Acid 1 (MIC) Medium High Heat	3 min	0.094	14.6	14.2	22.3	8.0	37.2	84.2
Acid 1 (MIC) High Heat	3 min	0.083	16.4	14.7	22.8	7.9	33.6	84.2
Acid 1 (MIC) medium High Heat	6 min	0.097	18.9	16.6	23.6	8.7	36.8	88.1
Acid 1 (MIC) High Heat	3 min	0.096	19.2	16.4	23.4	8.2	35.2	90.3
Acid 2 (BH)	24 h	0.084	37.5	16.9	29.6	12.8	42.7	93.7
Acid 2 (MIC) Medium High Heat	6 min	0.087	29.3	16.3	28.7	11.7	37.0	102
Acid 2 (MIC) High Heat	3 min	0.089	28.0	15.4	26.9	11.5	37.2	93.1
Acid 3 (BH)	24 h	0.094	26.5	13.6	23.9	10.0	31.9	89.9
Grand Mean Concentration of Junk Bay Sediment		0.093	23.7	15.6	25.1	9.85	36.1	90.8
CV		9%	31%	7%	11%	18%	9%	6%

0.367 mg kg^{-1} with a CV of 6%. This figure is very close to the reference value. The mean for the Composite Junk Bay sediment is 0.093 mg kg^{-1} and the CV is 8%. Low CVs probably indicate that all digestion procedures are equivalent and extracting the same amount of Cd from the sediment. Fiszman et al.[5] obtained recoveries of 80% and 82% for 5 M HNO_3 and [5:1] $HNO_3/HClO_4$, respectively. The poorer recoveries as compared with the present values may be due to the use of only 15 ml of the acids per 3–5 g of sediment, which should likely be insufficient to digest the sediment. Poorer recoveries were also found for other heavy metals in that study.

For microwave digestion with HNO_3, the mean yield is 106% which is very similar to values obtained in other studies (91–107%)[1,2,3].

Chromium Cr shows poor recovery. Aqua Regia is the most powerful acid mixture for its extraction and has a maximum recovery of 91% with block heater heating. Acid 3 ($HNO_3/HClO_4$) ranks second (72%). This pattern is realized in both the NBS and Composite Junk Bay sediment. Fiszman et al.[5] obtained recoveries of 65% for HNO_3 and 66% for $HNO_3/HClO_3$. The lower recoveries, as explained, may be due to insufficient amount of acids used.

Microwave heating yielded less Cr in this study. It was also found to be less effective in other studies (73–104%; Table 1). The maximum recovery attainable in this study for the NBS sediment is only 74% with the use of Aqua Regia. A short digestion time[1] is considered the main cause for incomplete extraction.

Copper Similar to Cd, the grand mean Cu concentration (17.3 mg kg^{-1}) determined for the NBS sediment is very close to the reference value. The CV is 7%. All acids are considered good for Cu extraction by block heater heating (HNO_3: 101%; HNO_3/HCl: 102%; $HNO_3/HClO_4$: 107%). The use of $HNO_3/HClO_4$ for the Junk Bay sediment is shown to yield less Cu. However, this may be due to experimental deviation because the data point has a high CV of 9%.

Although it may not be significant statistically, Table 3 shows that microwave digestion yielded less Cu in this study. The Aqua Regia digestion has recoveries of 94% and 99%. With nitric acid, the yield is also lower (86–95%), but the range is sufficiently close to the Hillman et al. results (91–93%)[1] for a soil sample. The Junk Bay sediment shows a similar pattern.

Iron For both the NBS and Junk Bay sediment, Fe is more effectively extracted by Aqua Regia (Block heater recovery: 112%), and there is no decrease of yield with the use of domestic microwave heating. Acid 3 ($HNO_3/HClO_4$) also gives a good recovery (100%). The yield of HNO_3 digestion is smaller (97%) and the use of microwave heating further reduces the recovery to 79–87%. However, the result again agrees with the Hillman et al. recovery of 74–84%[1]. Short-time microwave digestion reduces the yield.

Nickel The block heater recoveries are 78%, 91% and 98% for Acids 1, 2 and 3, respectively. HNO_3 is clearly less effective in the extraction of Ni when compared with other acid mixtures. The Junk Bay sample appears to have less Ni extracted for Acid 3. However, low Ni content in this sample may be the cause of less precise and accurate measurement.

Microwave heating again reduces the recovery of nitric acid (63–76%) and Aqua Regia (80–82%) digestion. The nitric acid recovery also agrees with the Hillman et al. findings of 71–76% for short-time microwave digestion[1].

Lead The recovery of Pb is poor with all acids used. The recoveries are 65%, 83% and 63% for Acids 1, 2 and 3, respectively. Aqua Regia is again a more powerful digestion acid. The same pattern is shown in the digestion of the Junk Bay sediment.

Microwave HNO_3 digestion appears to increase the recovery slightly. The NBS yield is 70–75%, compared to 65% for block heater heating. The enhancement is less obvious in the digestion of the Junk Bay sediment. In the digestion by Aqua Regia, there is a reduction of recovery in both the NBS (68–70%) and Junk Bay sediment.

The Pb recoveries determined in this study are lower than values found in other studies (Table 3). A very low yield of 57% was also obtained by Fiszman et al.[5]; however, insufficient acid has been mentioned as the cause for a generally low recovery in this case.

Zinc Before the results are discussed, attention should be paid to the problem of zinc contamination during the analysis. For instance, while the original HNO_3 was found to have a low level of Zn ($<0.030\ \mathrm{mg\,l^{-1}}$), the HNO_3 blank could be contaminated to a level between 0.090 and 1.50 $\mathrm{mg\,l^{-1}}$. Therefore, some sample replicates could have abnormally high Zn values and were rejected by the Q-test. Compared with microwave heating, the blanks from block heater heating have a significantly higher Zn content. The CVs of the data points are also higher.

In general, Zn recovery is slightly lower than those obtained in other studies (Table 1). The block heater digestion yields are 86%, 87%, and 87% for Acids 1, 2 and 3, respectively. The CVs of the grand mean Zn concentration are 4% for the NBS sediment and 6% for the Junk Bay sediment. Therefore, it is possible that all the procedures, including microwave digestion, have equivalent Zn extraction efficiency. A similar result was obtained in another study[4] as shown in Table 1.

To summarize, the Aqua Regia mixture is the most powerful digestion agent for estuarine and marine sediments, but the extract produces a lot of background absorption during GFAAS analysis of Cd. Longer heating time up to 39–46 h promotes release of Cr, Ni, Pb and Cu during HNO_3 digestion. Microwave-aided digestion by concentrated HNO_3 can be carried out by a domestic type of machine. When compared to heating by laboratory type of microwave digester, the yields are lower, but are reasonably constant when the digestion time is the same and the sediments have similar properties.

Heavy metal concentration profiles of sediment cores

Metal concentrations versus depth are plotted in Figure 3. All concentrations except those of Cd have been corrected for extraction efficiencies as follows: Cr, 55%; Cu, 95%; Fe, 87%; Ni, 76%; Pb, 75% and Zn, 88%.

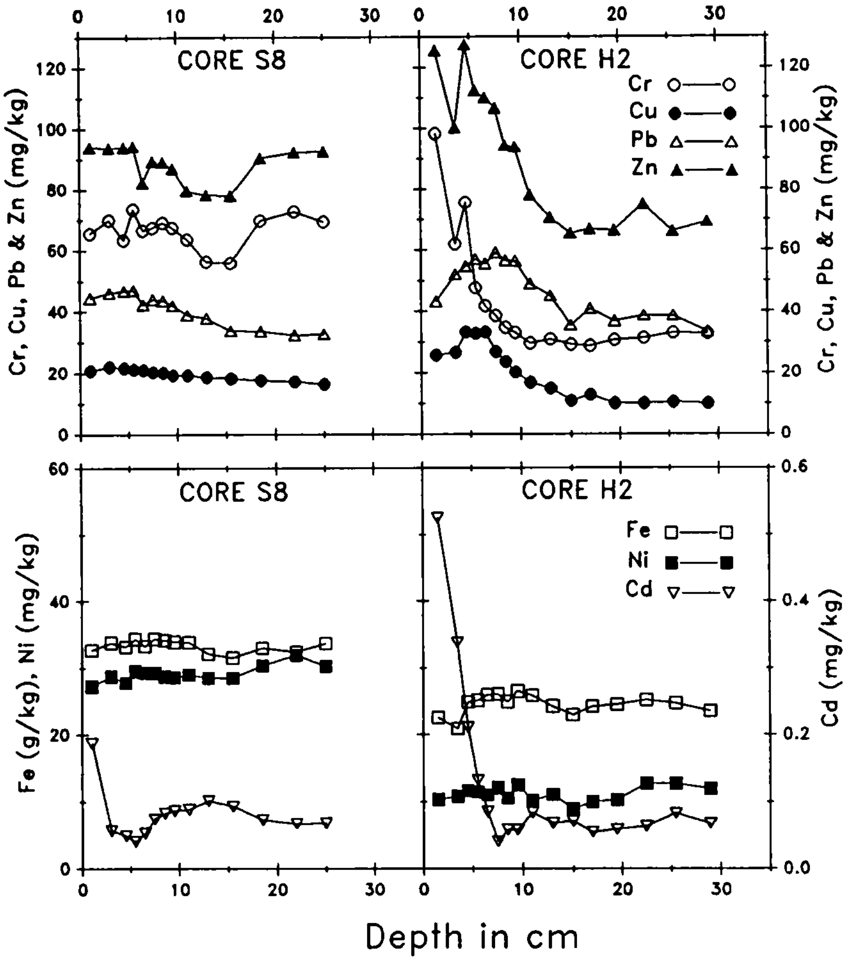

Figure 3 Heavy metal concentration profiles of sediment cores from Hebe Haven and Ngau Mei Hoi, Hong Kong.

Cadmium Cd concentration increases significantly towards the water-sediment interface in the top surface sediment of Core H2. Taking the mean concentration of the bottom *three layers* as the background, and comparing it with the mean of the top 7 cm of sediment, an enrichment factor (EF) of 3.6 was found for Core H2. One possible source of Cd was the dyeing and municipal wastewater discharge through the Ho Chung River.

There is a sharp increase of Cd in the top 1 cm of surficial sediment of Core S8, although the magnitude is smaller than that found in Core H2. Compared with the profiles of Cu and Pb, which show quite a steady increase from the bottom most layers, it is possible that Cd pollution originated more recently. Furthermore, due to the very low Cd concentration in the natural aquatic environment, anthropogenic enrichment is likely to be more easily shown. It does not necessarily mean that Cd is more capable to pollute areas far from the urban coast.

Chromium and zinc The concentration profiles of Cr and Zn are similar. Enrichment is significant in Core H2, but not in Core S8. In Core S8, there is a drop and rise of concentrations between the depth of 10–18 cm, forming a valley-shaped pattern. With the limited number of cores analyzed here, it is difficult to elaborate on the cause. While Zn is a general indicator for urban development, Cr is more or less a specific pollutant providing the necessary evidence of industrial pollution by the dyeing factories in the Ho Chung area. An EF of 2.0 was calculated for Cr and 1.6 for Zn. Untreated dyeing wastewater used to be discharged to Hebe Haven through the Ho Chung River. It is also noted that the background Cr and Zn contents of Ngau Mei Hoi are much higher than those of Hebe Haven. This is also true for Cu, Fe and Ni. The source of the sediments must be from drainage areas having different rock formation.

Copper and lead Both Cu and Pb show enrichment in Hebe Haven and Ngau Mei Hoi, although it is less serious in the latter case. Cu also is a common pollutant in dyeing wastewater[7]. The EF is 3.0 for Core H2 and 1.3 for Core S8. The use of anti-fouling paints on the bottom of ships and boats is suspected to cause Cu pollution in Ngau Mei Hoi. Such paints may contain a very high percentage of copper compounds[8]. As shown in Figure 1, Ngau Mei Hoi is the only exit to the open sea from Hebe Haven and Sai Kung Town. Very busy navigation was observed during sampling.

The use of tetraethyl lead in gasoline has caused Pb to pollute areas far from the coast because of atmospheric transfer of the automobile exhaust. Enriched Pb might also come from fishing and boating activities in this resort area. While the EFs for other metals are very different for Hebe Haven and Ngau Mei Hoi, they are similar for Pb, with values of 1.42 (Hebe Haven) and 1.38 (Ngau Mei Hoi). Pb pollution is thus widespread.

Iron and nickel In comparison with other heavy metals, the Fe concentration in sediment is very high and may well be up to 3.5%. Although Fe is consumed in extremely large quantities in many domestic and industrial activities, enrichment is less noticeable. The very high Fe background is likely to make the anthropogenic flux insignificant. Ni is similar in that anthropogenic flux is unimportant because Ni mainly comes from the erosion of natural crustal rock particles[9]. No significant enrichment is therefore found for these two metals.

To summarize, there is enrichment of Cd, Cr, Cu, Pb and Zn in surficial sediment of a site close to a suburban area with some dyeing factories. Compared to values obtained in some other studies shown in Table 4, the level of Cd and Cu enrichment (EF of 3.6 and 3.0) is significant but not serious. The concentrations of the topmost sediment layer are only 0.526 (Cd) and 25.8 (Cu) mg kg^{-1}, which should cause no great concern. Cr pollution is more serious and substantiates the impact of the discharge from dyeing factories. The EF is 2.0 and the top layer concentration

Table 4 Heavy metal contents in mg kg^{-1} in some estuarine and coastal sediments.

*Description**		*Cd*	*Cr*	*Cu*	*Ni*	*Pb*	*Zn*
Surficial Sediment							
From reviews[a]	L	0.01-5	—	—	2-34	2-98	5-135
	U	0.21-9.9	—	—	10.3-63	12.5-280	75-2800
	M	—	2-107	1-231	26.5	—	—
Spencer Gulf,[b]	R	1.5-24	—	—	—	60-967	—
S. Australia	BK	0.15	—	—	—	15	—
Patos Lagoon[c] Estuary, Brazil		0.1-20	8-337	0.8-20	—	8-267	20-214
Core Sediment							
Thailand[d]:	T	1.25	21	8	—	17.5	20
Upper Gulf	B	0.15	16	6.25	—	8	14
Core B	EF	8.3	1.3	1.2	—	2.2	1.4
Italy[15]:	T	—	194	46	161	85	170
N. Tyrrhenian Sea:	B	—	190	36	166	36	113
Core 8	EF	—	1.0	1.3	0.97	2.4	1.5
California[e]:	T	—	NR	NR	—	45	129
Newport Bay	B	—	NR	NR	—	7	41
Core 12	EF	—	2	above 2	—	6.4	3.1
Core 14	T	—	78	40	—	49	160
	B	—	about 78	NR	—	6	80
	EF	—	1.0	elevated	—	8.2	2.0
Washington[f]:	T	—	50	60	50	80	110
Sinclair Inlet	B	—	43	15	28	9	58
Core SIN2	EF	—	1.2	4.0	1.8	8.9	1.9
Krka River[g]	T	—	60	12.5	50	68.8	34
Estuary,	B	—	118	63	53	18.8	49
Yugoslavia	EF	—	0.51	5.0	IR	3.7	IR

U: Upper concentration ranges; L: Lower concentration ranges; M: Mean; T: Topmost layer; B: Bottommost layer; EF: Enrichment factor calculated by T/B; NR: Not reported; IR: Irregular profile; BK: Background; R: Range.

[a] Cd and Pb from Ref. 10; Ni from Ref. 11, Zn from Ref. 12; Cr and Cu from Ref. 6. Very high and low values not included; [b] From Ref. 13; Near a lead smelter plant; [c] From Ref. 14; Receives urban, industrial and harbour effluent; [d] From Ref. 6; Approximate concentrations read from graphs; HNO_3 leached; Authors claimed to find only Cd and Pb enrichment by Al-normalised data. [e] From Ref. 16; Concentrations from both listed data and from graphs. [f] From Ref. 17; Approximate concentrations read from graphs; Top concentrations usually not the maxima; Downward movement of metals suspected. [g] From Ref. 18; Pb and Cu from core data of Station 4; Surface depletion of Cr; Irregular Zn and Ni pattern.

98.2 mg kg^{-1} which should be considered moderately high. Pb pollution has spread off-coast possibly due to atmospheric transfer and its use in fishing and boating activities in the area. The top layer concentration is 43.2 mg kg^{-1} with an EF of 1.4, which is low. Zn enrichment is similar to that of Pb, with an EF of 1.6 and a top layer concentration of 126 mg kg^{-1}.

CONCLUSIONS

1) For HNO_3 digestion, time is a factor affecting the recovery of Cr, Cu, Ni, and Pb. More than 24 hours are required, but a too long a heating time appears to reduce

the yield slightly. Cd, Fe and Zn recoveries are not significantly affected as long as the digestion time is more than 8 h. For a block heater digestion time of 24 h, the recoveries of metals from HNO_3 digestion are as follows: Cd, 108%; Cr, 66%; Cu, 101%; Fe, 97%; Ni, 78%; Pb, 65%; and Zn, 86%.

2) Aqua regia (HNO_3/HCl) is a more powerful digestion agent than HNO_3 and $HNO_3/HClO_4$ for Cr, Ni, Fe, and Pb. The extraction efficiencies of Cd, Cu and Zn are similar for the three acids studied. The recoveries of Aqua Regia digestion by block heater heating for a time of 24 h are as follows: Cd, 97%; Cr, 91%; Cu, 102%; Fe, 112%; Ni, 91%; Pb, 83%, and Zn, 87%.

3) The use of a domestic microwave oven to digest sediment is possible. The use of an air-tight bottle to hold the teflon digestion vessel keeps the leakage of acid fumes to a minimum. Compared with block heater heating using HNO_3, it has equivalent or better recoveries for Cd, Pb and Zn. The yields for Cr, Cu, Fe and Ni are lower. The main cause is insufficient digestion time. A longer digestion time should be made possible by using teflon vessels capped by the capping station supplied by the manufacturer. The recoveries of HNO_3 microwave digestion using a time of 3.8 min under 'High Heat' are as follows: Cd, 99%; Cr, 55%; Cu, 95%; Fe, 87%; Ni, 76%; Pb, 75%; and Zn, 88%.

4) Microwave HNO_3 digestion has been successfully used to determine the heavy metal content in two sediment cores. The concentration profiles indicate a significant anthropogenic flux of Cd, Cr, Cu, Pb and Zn (EFs of 3.6, 2.0, 3.0, 1.42 and 1.6, respectively) to the coastal sediment. Cd, Pb and Cu pollution (EFs of 1.1, 1.3 and 1.38, respectively) is also realized in an area much further away from the urbanized coast. The cause for Pb pollution in this "background" area is suspected to be through atmospheric transfer of automobile exhaust and the use of Pb in fishing and boating activities in the area. Cu most probably comes from the use of copper-containing antifouling paints on bottoms of boats and ships. Finally, background concentrations of Cr, Cu, Fe, Ni and Zn in Ngau Mei Hoi are significantly higher than in Hebe Haven.

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