

# DIGESTION METHODS FOR TOTAL HEAVY METALS IN SEDIMENTS AND SOILS

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(Received 12 May 2000; accepted 12 March 2002)

**Abstract.** The objectives of this study were to analyze the total contents of Cd, Cr, Cu, Ni, Pb, and Zn in the freshwater sediments and the arable and non-arable soils of Taiwan, and to compare the different digestion methods for their determination. Two hundred and thirty-nine freshwater sediments were collected from the Fei-Tsui Reservoir Watershed (FTRW) in northern Taiwan. Forty-two surface (0–15 cm) and subsurface (15–30 cm) soil samples were likewise collected from 21 representative arable soils derived from various parent materials and with varying weathered degrees in different regions of Taiwan. In addition, one hundred and ninety-four non-arable soils were collected from the different forest regions, industrial parks, resident areas, and commercial areas. Several digestion methods including the *aqua regia* and different combinations of concentrated acids (HClO<sub>4</sub>, HNO<sub>3</sub>, H<sub>2</sub>SO<sub>4</sub>, or HF) were compared. All samples were digested both by the *aqua regia* method and the Baker and Amacher method for Cd, Cr, Cu, Ni, Pb, and Zn. The Reisenauer method was used for Cr and the Bureau method for Pb further. The results indicate that the best digestion methods to analyze the total contents of heavy metals in the sediments and soils were recommended as follows: the Baker and Amacher method for Cd, Cr, Cu, Ni, and Zn; the Reisenauer method for Cr, but for simplicity the Baker and Amacher method is also recommended as the flexible method for the total analysis of Cr; the *aqua regia* method for Cu, Ni, and Zn; and the Bureau method for Pb.

**Keywords:** digestion method, heavy metal, sediment, soil, total analysis

## 1. Introduction

The total analysis of heavy metals such as Cd, Cr, Cu, Ni, Pb, and Zn in sediments and soils, is commonly done to evaluate the degree of contamination of aquatic and terrestrial environments. Different digestion methods are used for this purpose including various combinations of concentrated acids such as hydrofluoric acid (HF), hydrochloric acid (HCl), nitric acid (HNO<sub>3</sub>), perchloric acid (HClO<sub>4</sub>), and sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) (Bureau, 1982; Reisenauer, 1982). Different digestion equipment was likewise employed like open beakers heated on hot plates, digestion tubes put in the block digestors, and digestion bombs placed in conventional and microwave ovens



(Burau, 1982; Reisenauer, 1982). Hossner (1996) reported that the advantages of the dissolution of heavy metals in sediments and soils using concentrated inorganic acids are low cost and low salt matrix in final solution for the determination of total heavy metal content. Mendoza *et al.* (1996) used HF-HNO<sub>3</sub> and *aqua regia* to digest the residual fraction following the sequential extraction of exchangeable, reducible, and oxidized fractions of Cd, Co, Cr, and Pb contained in canal and dam sediments in Mexico. Chlopecka *et al.* (1996) used the mixture of HF and HClO<sub>4</sub> to digest the residual fraction following the sequential extraction of exchangeable, carbonate, reducible, and oxidizable fractions of Cd, Pb, and Zn in contaminated soils of Poland. Martin (1996) employed the mixture of HF-HClO<sub>4</sub>-HNO<sub>3</sub> for the total analysis of Cd, Co, Cr, Cu, Pb, and Zn in alluvial soils of Germany. Charlesworth and Lees (1999) found the mixture of HClO<sub>4</sub>-HNO<sub>3</sub>-H<sub>2</sub>SO<sub>4</sub> suitable to digest river sediments for the determination of total contents of Cd, Cu, Ni, Pb, and Zn in England. Manz *et al.* (1999) used *aqua regia* to determine the Cu, Pb, and Zn contents in arable soils of central Germany. They measured the concentrations of the heavy metals in the final solution by X-ray Fluorescence analysis.

The *aqua regia* digestion method (USEPA Method 3050) was developed for the determination of heavy metals in the soils of U.S.A. (USEPA, 1986). In Taiwan, the *aqua regia* method is also one of the digestion methods recommended by the Environmental Protection Administration (EPA) for the total analysis of Cd, Cr, Cu, Ni, Pb, and Zn in sediments and soils (EPA-ROC, 1994). Simplicity and adaptability as a routine procedure have led to the widespread use of the *aqua regia* method for the determination of total amounts of Cd, Cr, Cu, Ni, Pb, and Zn in contaminated soils and sediments. The mixture of HF-HNO<sub>3</sub>-HClO<sub>4</sub>-H<sub>2</sub>SO<sub>4</sub> was recommended by Baker and Amacher (1982) for the total analysis of Cd, Cu, Ni, and Zn in soils. A similar digestion method using the reagents of HF-HNO<sub>3</sub>-HClO<sub>4</sub>-H<sub>2</sub>SO<sub>4</sub>, but modified in certain heating processes, was recommended for the total analysis of Cr in soils by Reisenauer (1982). Burau (1982) used HCl to replace H<sub>2</sub>SO<sub>4</sub> in the digestion mixture of HF-HNO<sub>3</sub>-HClO<sub>4</sub>-H<sub>2</sub>SO<sub>4</sub> for the total analysis of Pb in soil samples. Therefore, it is interesting and necessary to compare the different digestion methods for the total analysis of heavy metals in sediments and soils. The objectives of this study were to: (i) evaluate the total contents of Cd, Cr, Cu, Ni, Pb, and Zn in sediments and soils using different digestion methods, (ii) explain the dissolution effects of the digestion methods for sediments and soils using inorganic acid mixtures, and (iii) recommend the most appropriate digestion methods for the determination of these six heavy metals.

## 2. Materials and Methods

### 2.1. SAMPLE COLLECTION

#### 2.1.1. *Freshwater Sediments*

Two hundred and thirty-nine (239) freshwater sediment samples were taken from the Fei-Tsui Reservoir Watershed (FTRW), Taipei County, Taiwan (Figure 1). Sampling was done in 13 sampling stations along the Fei-Tsui Reservoir and its two main tributaries, the Nanse River and Beise River, with the use of a grab sampler. Sampling was performed every season from August 1996 to April 1998.

#### 2.1.2. *Soils*

Samples of forty-two arable soils were collected in 1994 from the surface (0–15 cm) and subsurface (15–30 cm) of 21 representative soil series distributed throughout Taiwan. The soils are derived from different parent materials including red earth, schist, argillite, sandstone and shale, and slate mixed with sandstone and shale. One hundred and ninety-four surface (0–15 cm) or subsurface (15–30 cm) layers of non-arable soils were also sampled from forest regions (hilly land forest, montane forest, and subalpine forests), industrial parks, residential and commercial areas in 1995.

### 2.2. DIGESTION METHODS

Air-dried samples of sediments and soils were ground and passed through a 2 mm sieve. The *aqua regia* method involving concentrated  $\text{HNO}_3$  and  $\text{HCl}$  (1:3 proportion) (EPA-ROC, 1994) and using a conical beaker heated on a hot plate was used as the standard method to digest the samples for the total analysis of Cd, Cr, Cu, Ni, Pb, and Zn. Prior to digestion by *aqua regia*, organic matter was destroyed by concentrated (35%)  $\text{H}_2\text{O}_2$ .

The method of Baker and Amacher (1982), which involved the digestion of samples in a mixture of  $\text{HF-HNO}_3\text{-HClO}_4\text{-H}_2\text{SO}_4$  in Teflon beakers placed on a hot plate, was also employed to analyze the total contents of Cd, Cr, Cu, Ni, Pb, and Zn. This method is described briefly as follows: A 2 g sample is transferred to a Teflon beaker and 25 mL of distilled water and 2 mL of concentrated  $\text{HNO}_3$  are added and allowed to dryness. This is followed by the addition of three drops of concentrated  $\text{H}_2\text{SO}_4$  and 10 mL of HF. The sample is then placed on a sand bath while the temperature slowly raised to 200 °C and is allowed to evaporate to dryness. This is followed by the addition of 15 mL of concentrated  $\text{HNO}_3$ , 2 mL of  $\text{H}_2\text{SO}_4$ , and 5 mL of  $\text{HClO}_4$ . Heating is continued until strong fumes of  $\text{SO}_3$  are produced. The Teflon container is cooled and the solution is transferred quantitatively to a 50 mL volumetric flask by adding distilled water.

In addition to the above digestion methods, the following two methods were also used for the determination of the total contents of Cr and Pb. The Reisenauer method, modified in certain heating procedures and which involves digestion in

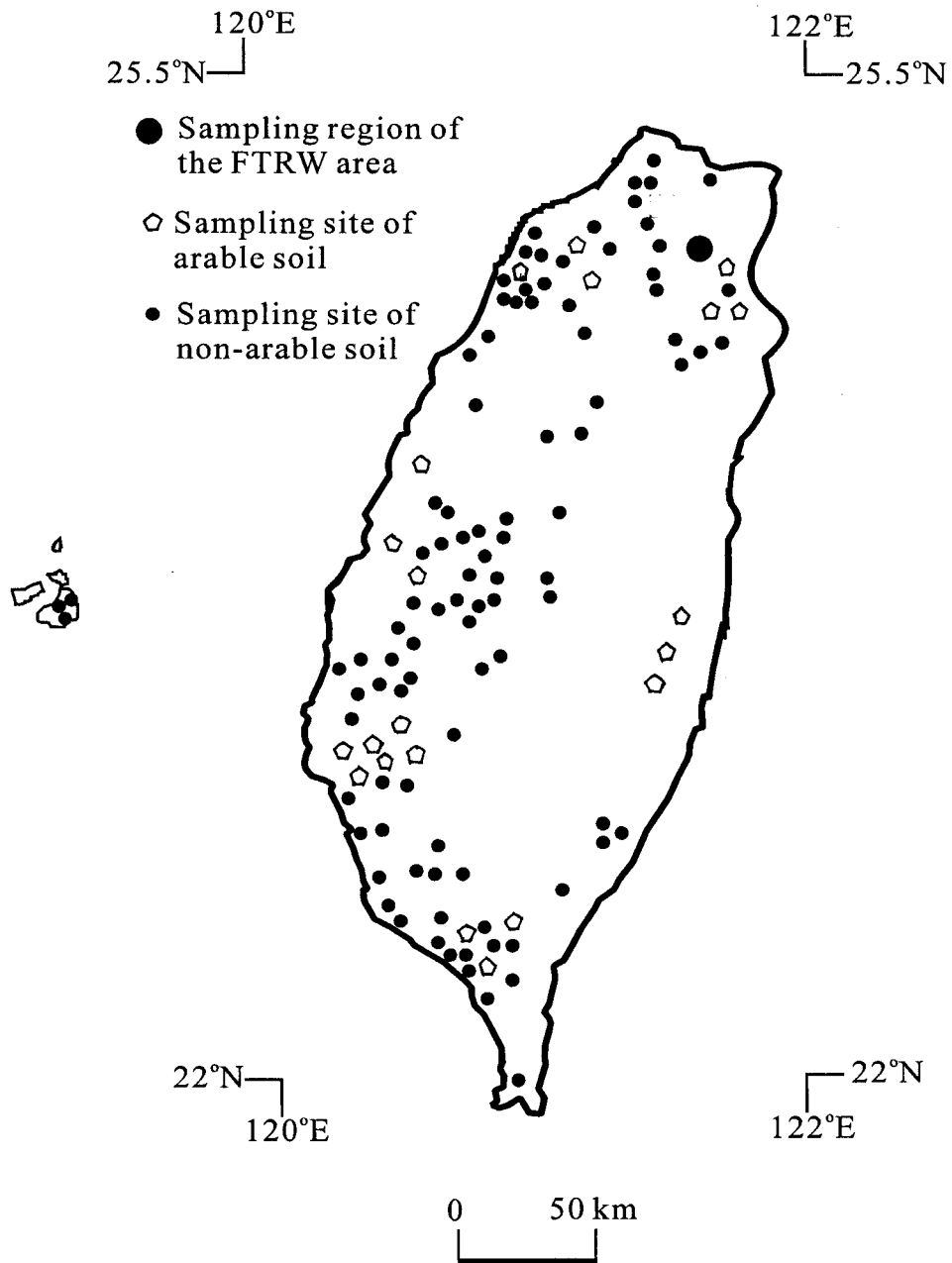


Figure 1. The sampling sites of the sediments at the FTRW area and soils through Taiwan.

a HF-HNO<sub>3</sub>-HClO<sub>4</sub>-H<sub>2</sub>SO<sub>4</sub> mixture, was also used for the total analysis of Cr (Reisenauer, 1982). This method is described briefly as follows: A 1 g sample is placed in a Teflon beaker, moistened with a few drops of distilled water and 0.2 mL of concentrated HNO<sub>3</sub>. Added the solution is then heated to dryness on a hot plate. This is followed by the addition of 2 mL of HClO<sub>4</sub>, 5 mL of HF, and 1 mL of H<sub>2</sub>SO<sub>4</sub>. The acid mixture is then heated on a hot plate at 80–90 °C inside a fume hood until the dark color disappears. The Teflon beaker, with about 90% of its top covered with a Pt lid, is transferred to a sand bath and evaporated to fumes of SO<sub>3</sub>. Since hydrated HF boils at 120 °C, it is heated cautiously at first and the temperature is not allowed to exceed 120 °C until the final traces of HF and HClO<sub>4</sub> are expelled. When the residue is completely dissolved, the container is cooled, and the solution is transferred quantitatively to a 50 mL volumetric flask by adding distilled water.

The second method is the Bureau method which involved the digestion of samples in HNO<sub>3</sub>-HClO<sub>4</sub> mixture using a block digester for the total analysis of Pb (Bureau, 1982). This method is described briefly as follows: A 2 g sample is placed in a tube and 10 mL of concentrated HNO<sub>3</sub>. The tube is connected to a funnel condenser overnight at a temperature from 80 to 90 °C. The apparatus is removed on the furnace support after heating to dryness at 125–130 °C. Then 1 mL of concentrated HNO<sub>3</sub> and 4 mL of concentrated HClO<sub>4</sub> are added and the mixture is heated to dryness at 200–210 °C. The tube container is then cooled and 4 mL of HCl and 50 mL of distilled water are added. The solution is passed through an acid-washed filter membrane and is then transferred quantitatively to a 100 mL volumetric flask by adding enough volume of 1% HNO<sub>3</sub>. Fifty mL of the solution is used for liquid-liquid separation by adding 1% ammonium pyrrolidine dithiocarbamate (APDC), 1% diethylammonium diethyldithiocarbamate (DDDC), and 5 mL of saturated methylisobutylketone (MIBK) to form Pb chelates soluble in CHCl<sub>3</sub> layer.

The concentrations of Cd, Cr, Cu, Ni, Pb, and Zn in the final solutions were determined with an atomic absorption spectrometer (Hitachi 180–30, Japan). The method detection limits (MDL) in sediments and soils were as follows: Cd 0.02, Cr 0.1, Cu 0.04, Ni 0.03, Pb 0.1, and Zn 0.02 (all in mg kg<sup>-1</sup> samples).

### 2.3. QUALITY ASSURANCE AND QUALITY CONTROL

For quality assurance and control (QA/QC), standard reference materials, such as No. 1646 (estuarine sediment) and 2704 (Buffalo river sediment) selected from the National Institute of Standards and Technology (NIST), U.S.A., and BCR 141 (calcareous loam soil) and 142R (light sandy soil) selected from the Commission of the European Communities, Belgium, were digested in triplicate and analyzed using the above mentioned procedures. Satisfactory recoveries of heavy metals in the standard reference materials were found for most metals excluding Cd, Pb and Zn (Table I). In each batch of sediment and soil samples, several (10% of the total

number of samples) duplicate samples were used to check precision by analytical splits.

### 3. Results and Discussion

#### 3.1. HEAVY METALS IN SEDIMENTS

The mean values of the total contents of heavy metals in the sediment determined by the different digestion methods are shown in Table II. These data showed the background levels of heavy metals in the freshwater sediments of northern Taiwan with no or slight contamination. The preliminary data in this study indicated that the clay content of the sediments ranged from 30 to 60%, organic carbon was less than 1.5%, and the pH values ranged from 6.2 to 7.0 (Chen *et al.*, 1998).

Results also revealed that the mean total Cd content ( $0.61 \text{ mg kg}^{-1}$ ) of sediments digested by the *aqua regia* method was lower than by the Baker and Amacher method ( $0.91 \text{ mg kg}^{-1}$ ). The total Cd content of sediments digested by the *aqua regia* method ranged from  $<0.02$  to  $3.43 \text{ mg kg}^{-1}$  as compared to  $<0.02$  to  $4.01 \text{ mg kg}^{-1}$  by the Baker and Amacher method (Figure 2a). For the non-contaminated sediments, the measured values of Cd ( $<4 \text{ mg kg}^{-1}$ ), were probably due to Cd existing in the structures of minerals (Chen, 1998). A higher digesting effectiveness was shown by the Baker and Amacher method (Figure 2a) as reflected by the greater range of values of total Cd in the sediments.

For the most sediment samples, the total Cr content measured in samples digested by the Baker and Amacher method or the Reisenauer method was higher than that by the *aqua regia* method (Figures 2b and 3a). The mean total Cr content determined by the *aqua regia* method was  $20.9 \text{ mg kg}^{-1}$  as compared to  $44.3$  and  $52.0 \text{ mg kg}^{-1}$  by the Baker and Amacher method and the Reisenauer method (Table II).

The mean total contents of Cu, Ni, and Zn in the sediments ( $n = 239$ ) digested by the *aqua regia* method were slightly higher than those by the Baker and Amacher method (Table II). All values of Cu, Ni, and Zn total contents in the sediments clustered around the 1:1 ratio lines between the Baker and Amacher method and the *aqua regia* method, except for 3 samples for Cu, 1 sample for Ni, and a few samples for Zn (Figures 2c, d, and f). Using the *aqua regia* method, the mean total contents of Cu, Ni, and Zn in the sediments were  $18.2$ ,  $30.2$ , and  $56.2 \text{ mg kg}^{-1}$ , respectively.

The mean total content of Pb in the sediments digested by the *aqua regia* method was  $28.3 \text{ mg kg}^{-1}$  which was much higher than that by the Baker and Amacher method ( $11.6 \text{ mg kg}^{-1}$ ) (Table II). We randomly selected 119 from 239 sediment samples and digested them using the Bureau method for total Pb analysis in order to compare the results with the other digestion methods. The mean total Pb content ( $28.8 \text{ mg kg}^{-1}$ ) in the sediments ( $n = 119$ ) digested by the Bureau method was slightly higher than that ( $24.7 \text{ mg kg}^{-1}$ ) by the *aqua regia* method (Table II).

TABLE I  
The recovery analysis of total metal content in two certified reference materials

Element	Certified (mg kg <sup>-1</sup> )	Measured (mg kg <sup>-1</sup> )	Recovery (%)
SRM 1646 estuarine sediment			
Baker and Amacher method			
Cd	0.36	0.39 (±0.04) <sup>a</sup>	96 (±16)
Cr	76	62.7 (±2.16)	83 (±3.0)
Cu	18	17.3 (±2.57)	96 (±14)
Ni	32	31.5 (±2.26)	97 (±7.2)
Pb	28.2	26.3 (±4.04)	93 (±14)
Zn	138	74.5 (±2.69)	54 (±2.0)
SRM 2704 Buffalo river sediment			
Baker and Amacher method			
Cd	3.45	2.97 (±0.22)	86 (±6.4)
Cr	135	106 (±3.10)	79 (±2.3)
Cu	98.6	76.1 (±4.47)	77 (±4.5)
Ni	44.1	35.2 (±2.75)	80 (±6.2)
Pb	161	122 (±28.8)	76 (±18)
Zn	438	166 (±30.7)	38 (±7.0)
BCR 142R light sandy soil			
<i>Aqua regia</i> method			
Cd	0.25	0.14 (±0.08)	57 (±33)
Ni	61.1	62.1 (±2.55)	102 (±4.4)
Pb	25.7	29.9 (±4.27)	116 (±17)
Zn	93.3	58.5 (±2.90)	63 (±3.2)
Baker and Amacher method			
Cd	0.34	0.35 (±0.05)	103 (±15)
Cu	69.7	56.1 (±1.01)	81 (±1.2)
Ni	64.5	56.6 (±2.73)	88 (±4.6)
Pb	40.2	13.0 (±4.22)	32 (±10)
BCR 141 calcareous loam soil			
<i>Aqua regia</i> method			
Cd	0.30	0.28 (±0.03)	94 (±3.8)
Cr	53.0	37.5 (±1.28)	71 (±2.7)
Cu	31.2	27.4 (±1.37)	88 (±4.9)
Ni	28.0	29.0 (±0.45)	104 (±1.5)
Pb	26.3	37.6 (±3.73)	143 (±14)
Zn	70.0	58.9 (±11.5)	84 (±16)

<sup>a</sup> The values in the parentheses are standard deviations.

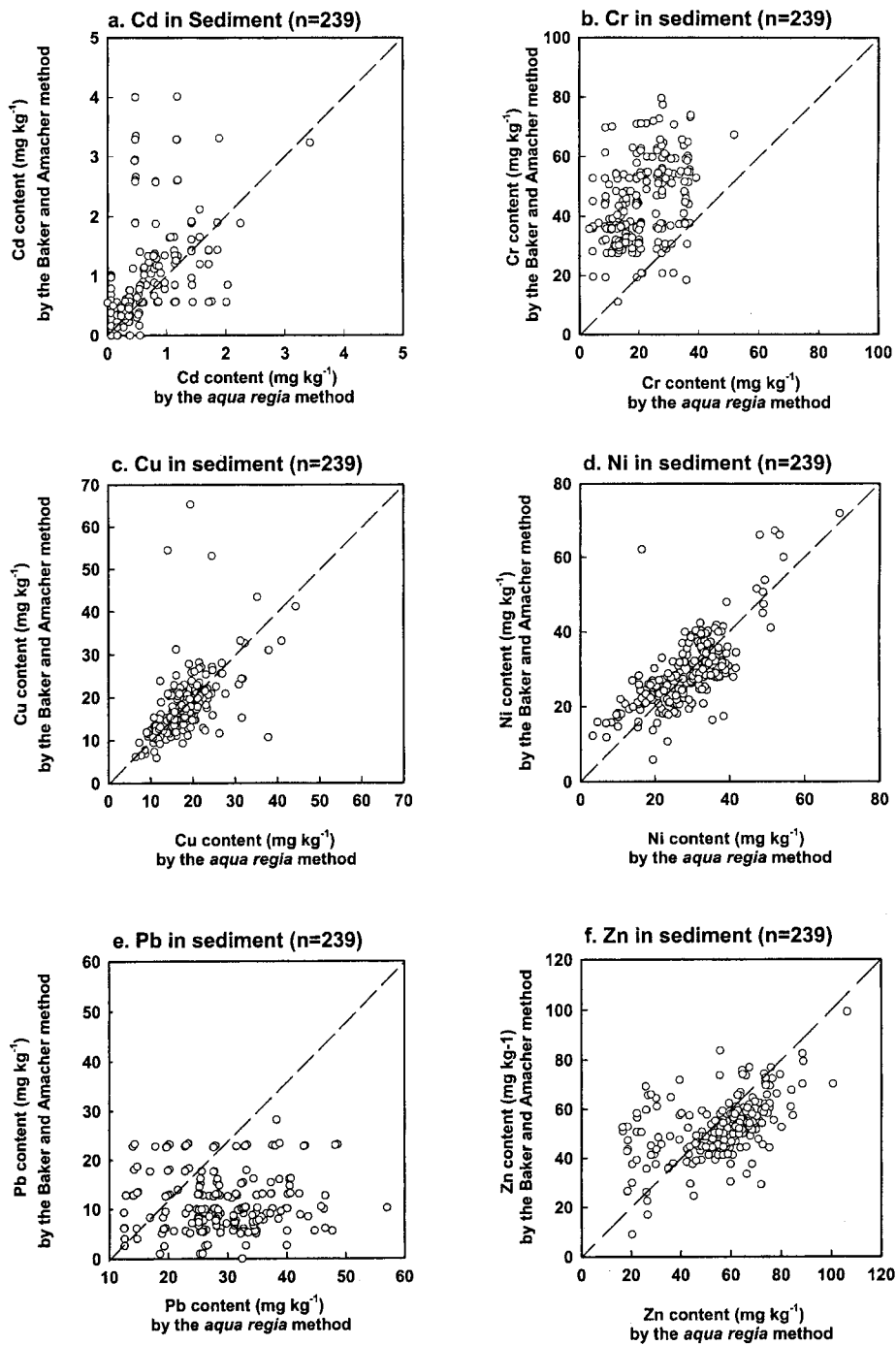


Figure 2. The total contents of Cd, Cr, Cu, Ni, Pb, and Zn digested by the *aqua regia* method and the Baker and Amacher method by a mixture of inorganic acids for the freshwater sediments (n = 239) of the FTRW area.



TABLE II

Means of heavy metal contents in the freshwater sediments by different digestion methods (mg kg<sup>-1</sup>)

Element	<i>Aqua regia</i>	Baker and Amacher (1982)	Reisenauer (1982)	Bureau (1982)
Cd (n = 239)	0.61 (±0.52) <sup>a</sup>	0.91 (±0.80)		
Cr (n = 239)	20.9 (±9.31)	44.3 (±19.5)	52.0 (±19.4)	
Cu (n = 239)	18.2 (±5.44)	17.9 (±7.17)		
Ni (n = 239)	30.2 (±21.7)	29.4 (±9.99)		
Pb (n = 239)	28.3 (±8.37)	11.6 (±6.14)		
Pb (n = 119) <sup>b</sup>	24.7 (±8.89)			28.8 (±15.4)
Zn (n = 239)	56.2 (±16.8)	52.0 (±13.2)		

<sup>a</sup> Numbers in parentheses are standard deviations.

<sup>b</sup> The data were produced by 119 subsamples of 239 samples by the Bureau method for correlating with the corresponding data by the *aqua regia* method.

The results of this study indicate that the sediments taken from the FTRW area in northern Taiwan were not contaminated by Cd, Cr, Cu, Ni, Pb, and Zn when the samples were taken from 1996 to 1998.

### 3.2. HEAVY METALS IN SOILS

Samples of natural and non-contaminated arable soils with various soil textures, ranging from clayey Oxisols (clay >40%) to sandy Entisols (sand >70%), were evaluated for their total contents of heavy metals using different methods. Results revealed that some non-arable soils were more contaminated than the arable ones, especially for the urban soils such as those in industrial parks, residential and commercial areas. Therefore, the wide range of values of the heavy metals in the non-arable soils indicated the influence of human activities (Figure 4). Mean values for the total contents of Cd, Cr, Cu, Ni, Pb, and Zn in the arable and non-arable soils digested by the *aqua regia* were lower than those by the other digestion methods, except for Cu in the non-arable soils (Tables III and IV). Using the Baker and Amacher method, the mean total Cu contents in the arable and non-arable soils were 21.5 and 21.6 mg kg<sup>-1</sup>, respectively. In comparison, the mean Cu contents in the arable and non-arable soils digested by the *aqua regia* method were 19.4 and 25.1 mg kg<sup>-1</sup>, respectively.

The mean total Cd content in the arable soils digested by the Baker and Amacher method was 1.84 mg kg<sup>-1</sup> which was much higher than that by the *aqua regia* method (0.74 mg kg<sup>-1</sup>). The difference in the average content of Cd between the two digestion methods was larger for the non-arable soils than for the arable. The Baker and Amacher method was not used for analysis of the total Cr and Pb contents of the soil samples, but instead, the Reisenauer and the Bureau methods

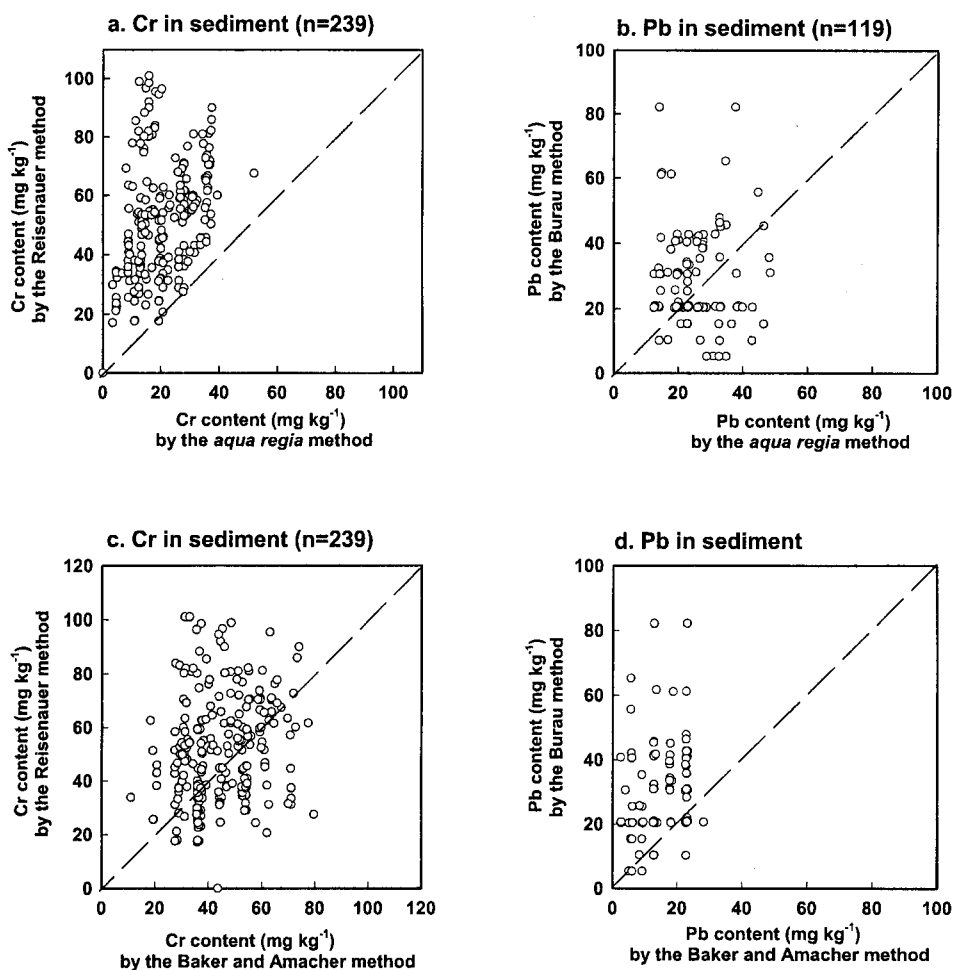


Figure 3. (a) The total Cr contents digested both by the *aqua regia* method and the Reisenauer method for all the 239 sediment samples, (b) The total Pb contents digested both by the *aqua regia* method and the Burau method for the 119 of 239 sediment samples, (c) The total Cr contents digested both by the Baker and Amacher method and the Reisenauer method for all the 239 sediment samples, and (d) The total Pb contents digested both by the Baker and Amacher method and the Burau method for the 119 of 239 sediment samples at the FTRW area.

were used for Cr and Pb, respectively, for comparison with the *aqua regia* method. The mean total content of Cr ( $43.3 \text{ mg kg}^{-1}$ ) in samples of arable soils digested by the Reisenauer method was more than twice greater than that ( $21.4 \text{ mg kg}^{-1}$ ) digested by the *aqua regia* method. The mean total content of Cr ( $48.7 \text{ mg kg}^{-1}$ ) in non-arable soils digested by the Reisenauer method was also more than twice greater than that ( $18.2 \text{ mg kg}^{-1}$ ) by the *aqua regia* method. The mean total content of Pb in all the soils evaluated using the Burau method was higher than that by the *aqua regia* method (Tables III and IV).

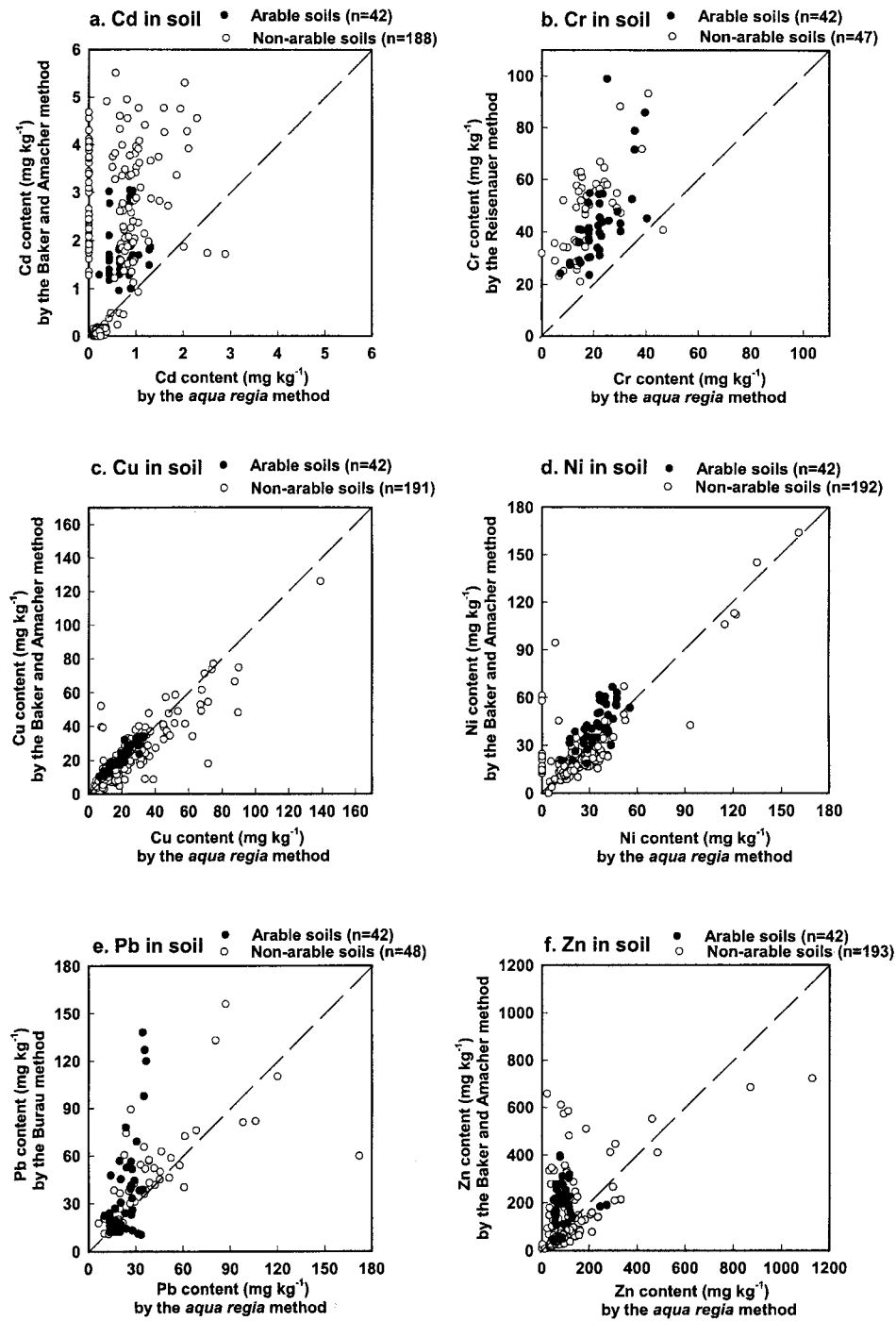


Figure 4. The total contents of Cd, Cr, Cu, Ni, Pb, and Zn digested by the *aqua regia* method and the other methods by a mixture of inorganic acids for the arable (n = 42) and non-arable (n = 47 to 193) soils through Taiwan.

TABLE III

Means values of heavy metal contents in the arable soils by different digestion methods (mg kg<sup>-1</sup>)

Element	<i>Aqua regia</i>	Baker and Amacher (1982)	Reisenauer (1982)	Bureau (1982)
Cd (n = 42)	0.74 (±0.27) <sup>a</sup>	1.84 (±0.62)		
Cr (n = 42)	21.4 (±7.82)		43.3 (±16.0)	
Cu (n = 42)	19.4 (±7.86)	21.5 (±7.50)		
Ni (n = 42)	34.6 (±9.56)	43.3 (±12.9)		
Pb (n = 42)	23.9 (±7.54)			39.5 (±31.7)
Zn (n = 42)	93.7 (±16.8)	197 (±82.8)		

<sup>a</sup> Numbers in parentheses are standard deviations.

TABLE IV

Mean values of heavy metal contents in the non-arable soils by different digestion methods (mg kg<sup>-1</sup>)

Element	<i>Aqua regia</i>	Baker and Amacher (1982)	Reisenauer (1982)	Bureau (1982)
Cd (n = 188)	0.49 (±0.58) <sup>a</sup>	2.14 (±1.47)		
Cr (n = 47)	18.2 (±9.31)		48.7 (±15.9)	
Cu (n = 191)	25.1 (±23.2)	21.6 (±16.9)		
Ni (n = 192)	23.7 (±17.1)	24.2 (±20.6)		
Pb (n = 48)	41.2 (±32.1)			48.6 (±30.4)
Zn (n = 193)	102 (±101)	121 (±119)		

<sup>a</sup> Numbers in parentheses are standard deviations.

### 3.3. COMPARISONS OF DIFFERENT DIGESTION METHODS

For the determination of total Cd in sediments and soils, the Baker and Amacher method gave higher values than the *aqua regia* method for most samples, the latter method actually showing non-detectable values of total Cd in the samples analyzed (Figures 2a and 4a). Likewise, for most samples of sediments and soils, the Baker and Amacher method and the Reisenauer method produced higher values of total Cr compared to the *aqua regia* method (Figures 2b and 3a). Thus, the Reisenauer method is recommended for the total analysis of Cr in sediment samples because this digestion method appears to be slightly better than the Baker and Amacher method (Figure 3c).

In terms of total Cu, Ni, and Zn determination, no significant differences were observed between the *aqua regia* method and the Baker and Amacher method for all the sediment and soil samples (Figures 2c, 2d, 2f, 4c, 4d, and 4f). In Figure 2c,

the most biased sediment sample was found to have a total Cu content of only 19.5 mg kg<sup>-1</sup> using the *aqua regia* method, but showed a total Cu of 65.3 mg kg<sup>-1</sup> when digested by the Baker and Amacher method. Likewise, in Figure 2d, the most clearly biased sediment sample had a total Ni content of 16.5 mg kg<sup>-1</sup> when digested by the *aqua regia* method, but showed a value of 62.1 mg kg<sup>-1</sup> by the Baker and Amacher method. Both cases indicate that the freshwater sediments in the upstream region of the FTRW area might be slightly contaminated when compared with the data from other countries such as the United States of America (Horowitz *et al.*, 1991). Few biased soil samples were found for the non-arable soils. These results indicate that some soil samples with higher potential for anthropogenic contamination tended to be more biased between the *aqua regia* method and the Baker and Amacher method based on the soil quality proposed by several workers (Alloway, 1991; Chen, 1991, 1998; Kabata-Pendias *et al.*, 1992; Chen *et al.*, 1996). In Figure 4c, an extremely high Cu content in the samples of non-arable soil taken from the industrial park was found when digested by the Baker and Amacher method (126 mg kg<sup>-1</sup>) and by the *aqua regia* method (140 mg kg<sup>-1</sup>). A similar trend of extremely high Ni and Zn contents were also found in some samples from some non-arable soils in the highly industrialized areas in west parts of Taiwan (Figures 4d and f). These results indicate that the *aqua regia* method does not completely dissolve the residual heavy metal in the silicate minerals of highly weathered soils or highly contaminated soils. In addition, it can destroy the organic matter through the addition of H<sub>2</sub>O<sub>2</sub> and probably dissolves most metal oxides and other most parts of mineral phases like silicate minerals. Thus, near complete extraction can be achieved in many cases (Hossner, 1996). In this study, we also found that the total content of Cu, Ni, and Zn in samples of sediments and soils digested by the *aqua regia* method can still reflect the potential contaminated situations of the study area.

For the determination of total Pb, the *aqua regia* method showed much better heavy metal dissolution compared to the Baker and Amacher method (Figure 2e). The concentrated H<sub>2</sub>SO<sub>4</sub> in the HF-HNO<sub>3</sub>-HClO<sub>4</sub>-H<sub>2</sub>SO<sub>4</sub> digestion mixture of the Baker and Amacher method seemed to have caused the poorer digestion. The low Pb recovery was probably caused by the precipitation of Pb and the potential interference of PbSO<sub>4</sub> during the subsequent analysis. However, the better dissolution effect by the Bureau method in 119 of 239 sediment samples was due to the fact that the concentrated H<sub>2</sub>SO<sub>4</sub> was replaced by concentrated HCl in the acid mixture (Figure 3b). The Bureau method for total content of Pb in soil samples also indicated better dissolution effect than the *aqua regia* method (Figure 4e).

#### 3.4. RECOMMENDATION OF DIGESTION METHOD

The results in the present study show a significant correlation between the Baker and Amacher method and the *aqua regia* method for the total Cd content of sediments ( $p < 0.01$ ), but not of soils (Tables V and VI). The digestion of silicate

TABLE V

Correlation of linear regression ( $Y = X_0 + aX$ ) of heavy metal content by different digestion methods in the freshwater sediments

Y	Element (Sample no.)	a (coefficient of X)	$X_0$	$R^2$
The Baker and Amacher method	Cd (n = 239)	0.77 <sup>a</sup>	0.44	0.25**
	Cr (n = 239)	0.59 <sup>a</sup>	32.1	0.16*
	Cu (n = 239)	0.72 <sup>a</sup>	4.94	0.31**
	Ni (n = 239)	0.74 <sup>a</sup>	8.20	0.55**
	Pb (n = 239)	0.03 <sup>a</sup>	12.6	<0.01
	Zn (n = 239)	0.37 <sup>a</sup>	31.9	0.28**
The Reisenauer method	Cr (n = 239)	0.73 <sup>a</sup>	37.0	0.12
The Bureau method	Pb (n = 119)	0.49 <sup>a</sup>	21.7	0.05
The Reisenauer method	Cr (n = 239)	0.26 <sup>b</sup>	40.6	0.03
The Bureau method	Pb (n = 119)	0.49 <sup>b</sup>	21.7	0.05

\* Significantly at  $P < 0.05$ , and \*\* significantly at  $P < 0.01$ .

<sup>a</sup> (X = the *aqua regia* method).

<sup>b</sup> (X = the Baker and Amacher method).

minerals is affected by the reaction of HF with Si to form the gaseous SiF<sub>4</sub>. Both HClO<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub> are powerful oxidizers and dehydrating agents. The HNO<sub>3</sub> is used to prevent the explosive reactions of the organic matter with HClO<sub>4</sub> prior to the sample's digestion in the Baker and Amacher method. The recoveries (%) of Cd in the standard samples of SRM 1646 and BCR 142R by the Baker and Amacher method were close to 100%, but the poorer recoveries of BCR 142R and BCR 141 was found by the *aqua regia* method (Table I). Therefore, the Baker and Amacher method is more effective than the *aqua regia* method for Cd.

It is valuable to note that the dissolution effects of both the Baker and Amacher method and the Reisenauer method were better than the *aqua regia* method for the total analysis of Cr in the sediment samples associated with identification of recovery of standard reference materials. However, the observed Cr total content in sediment and soil samples determined by these two methods varied greatly, indicating the metal's wide distribution and its large standard deviations in the sediment and soil samples collected. For simplicity, the Baker and Amacher method is also recommended as the most appropriate method for the total analysis of Cr in sediments and soils.

For the sediment and soil samples, the mean values of total contents of Cu, Ni, and Zn were not different between the *aqua regia* method and the Baker and Amacher method (Tables II, III, and IV). Unfortunately, poorer recoveries for Zn

TABLE VI  
Correlation of linear regression ( $Y = X_0 + aX$ ) of heavy metal content by different digestion methods in the soils (including arable and non-arable soils)

Y	Element (Sample no.)	a (coefficient of X) <sup>a</sup>	X <sub>0</sub>	R <sup>2</sup>
The Baker and Amacher method	Cd (n = 230)	0.73	1.69	0.09
	Cu (n = 233)	0.76	3.78	0.76**
	Ni (n = 234)	0.85	4.70	0.67**
	Zn (n = 235)	0.68	64.5	0.31**
The Reisenauer method	Cr (n = 89)	1.04	25.7	0.32**
The Burau method	Pb (n = 90)	0.69	21.6	0.31**

\*\* Significantly at  $P < 0.01$ .

<sup>a</sup> (X = the *aqua regia* method).

in SRM 1646, SRM 2704 and BCR 142R by the Baker and Amacher method were found. A significant correlation ( $p < 0.01$ ) was observed in the values of total contents of Cu, Ni, and Zn determined by the Baker and Amacher method and the *aqua regia* method in the sediment and soil samples (Tables V and VI). The *aqua regia* method may be applicable for the determination of Cu, Ni, and Zn in soils affected by anthropogenic practices, and thus may be suitable for the routine assessment of metal contamination in soils (Hossner, 1996). Therefore, the *aqua regia* method is recommended for the total analysis of Cu, Ni, and Zn attributed to QA/QC processes. However, the Baker and Amacher method is also a good method for the baseline study of Cu, Ni, and Zn in sediments and soils but with higher cost in consuming inorganic acids.

The Baker and Amacher method is not recommended for the total analysis of Pb, because of the precipitation of Pb with  $H_2SO_4$  and greater variability of recovery in standard reference material. On the other hand, the Burau method showed better dissolution effect for Pb in both sediment and soil samples especially when the Pb content was more than  $60 \text{ mg kg}^{-1}$  (Figures 3b and 4e). Therefore, the Burau method is the most appropriate digestion method for the total analysis of Pb, because the chelating agents are applied to concentrate Pb during the digestion.

#### 4. Conclusions

The best digestion methods for the total analysis of Cd, Cr, Cu, Ni, Pb, and Zn in the freshwater sediment and soil samples are as follows: the Baker and Amacher method for Cd, Cr, Cu, Ni, Pb, and Zn; the Reisenauer method for Cr, but for simplicity, the Baker and Amacher method is also the flexible method for the total

analysis of Cr in sediments and soils; the *aqua regia* method for Cu, Ni and Zn; and the Burau method for Pb. The Baker and Amacher method is also an alternative to evaluate the background levels of total Cu, Ni and Zn in sediments and soils, but with poorer recovery from standard samples. The Baker and Amacher method is not appropriate for the total analysis of Pb because of its precipitation with H<sub>2</sub>SO<sub>4</sub>. The *aqua regia* reagent can destroy the organic matter, metal oxides and other most parts of mineral phases like silicate minerals, but recommended for Cu, Ni and Zn in the present study with higher recovery from standard samples.

### Acknowledgements

The authors thank the Environmental Protection Administration of Republic of China (Grant No. EPA-82-E3H1-09-01 and EPA-83-E3H1-09-01) and Taipei Water Resource Management Committee for providing the financial support in this study. We gratefully thank Mr. T. M. Lee, Y. I. Leu, G. J. Lee and M. Y. Wu, and Miss M. Y. Cheng, for their help in field sampling and laboratory analysis. The authors also thank Dr. Victor B. Asio of the Institute of Tropical Ecology, Visayas State College of Agriculture, Baybay, Leyte, Phillipines for giving valuable comments on the manuscript.

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