Annals of Tropical Research 33[2]:162-173(2011)

Heavy Metals Content of Two Red Soils in Samar, Philippines

Ian A. Navarrete[1, 2] and Victor B. Asio[2]

[1]Laboratory of Environmental Soil Science, Obihiro University of Agriculture and Veterinary Medicine, Inada-cho 080-8555, Japan; [2]Department of Agronomy and Soil Science, Visayas State University, Baybay City, Leyte 6521-A Philippines

ABSTRACT

The study evaluated the total and available heavy metal (Cd, Cu, Cr, Pb, Ni, and Zn) contents of two red soils in Samar, Philippines, one developed from slate near a mining site (Bagacay soil) and the other from serpentinite (Salcedo soil), a well-known source of heavy metals. Soil samples were collected from every horizon in each profile and samples were digested using *aqua regia* and NH_4NO_3 to determine total and available heavy metals content, respectively. Results revealed that Salcedo soil had high contents of total Cr (average: 1353 mg kg^{-1}), total Ni (average: 610 mg kg^{-1}), and available Cr (average: 0.19 mg kg^{-1}) that exceeded the maximum allowable contents in agricultural soils but it had low amounts of the available form of the heavy metals. Bagacay soil showed very low contents of both total and available heavy metals due to their low amounts in the parent rock. The red Bagacay soil showed no effect of the nearby mining activity.

Keywords: heavy metals, soil pollution, red soils, Samar island, mining, serpentinite

Correspondence: VBAsio *Address*: Department of Agronomy and Soil Science, Visayas State University, Baybay City, Leyte, 6521-A Philippines. *Tel*: 053-335-2627 *Email*: vbasio_ph@ yahoo.com
DOI: 10.32945/atr3329.2011

INTRODUCTION

Heavy metals generally occur in rocks in small amounts but concentrations in soils are frequently elevated as a result of human-caused contamination. The most important heavy metals with regard to potential hazards and occurrence in contaminated soils are: arsenic (As), cadmium (Cd), chromium (Cr), mercury (Hg), lead (Pb) and zinc (Zn). The sources of heavy metal pollutants are metal mining, metal smelting, metallurgical industries, and other metal-using industries, waste disposal, corrosions of metals in use, agriculture and forestry, fossil fuel combustion, and sports and leisure activities (Alloway, 1995 & 1997).

Heavy metal pollution of soils is a global environmental problem. The growing scientific and public awareness on this problem arises because heavy metal pollutants pose health risk for humans through food chain transfer from soils to crops (Alloway 1995; Oliver 1997; Chen and Lee, 1995; Chen *et al.,* 2000) especially in hot spots located close to industrial sites, around large cities, and in the vicinity of mining and smelting plants (Puschenreiter *et al.*, 2005).

Heavy metal pollution of soils can also be due to the high contents of heavy metals of the parent material particularly the ultramafic and serpentinite rocks (Huang, 1962; Reeves, 2003). The danger posed by such naturally polluted soils is that people living in the area may not be aware about the soil pollution. Thus, any soil studies and land evaluation activities in or close to ultramafic and serpentinite areas and mining sites should include an assessment of heavy metal contamination.

The present study evaluated the levels of total and available heavy metals of two major red soils in Samar island one of which developed from slate close to a mining site, and the other from serpentinite. We hypothesized that the two soils contain high levels of heavy metals coming from their parent material and possibly from the nearby mining activity.

MATERIALS AND METHODS

Study Site

The study was conducted in Samar, the 4th largest island member of the Philippine archipelago (Fig. 1). Two study sites were selected,

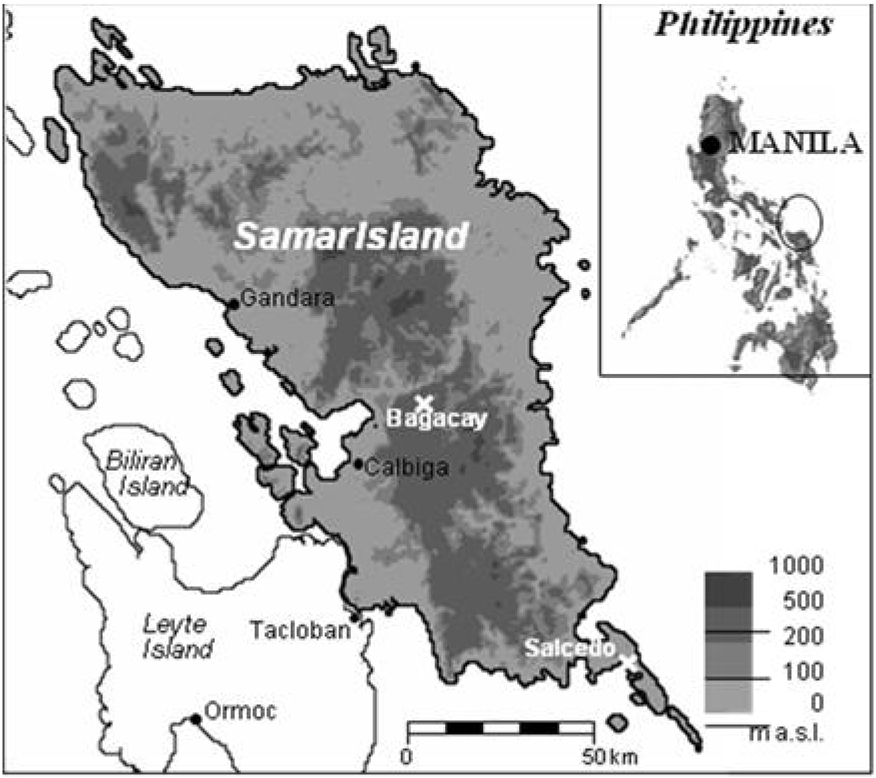

Figure 1. Map of Samar, Philippines and the location of the research sites marked X.

the first located at an altitude of 600-650 m ASL on a dissected plateau in the central portion of the island in a place called Bagacay, which is widely known for its copper and pyrite mines (stopped some years ago). The site is underlain by slate of Lower Miocene age, which developed into the red soil classified as Haplic Acrisol (World Reference Base), or Typic Paleudult (Soil Taxonomy) (Navarrete *et al.,* 2007). The area is a residual forest dominated by dipterocarp tree species. The second site is located in the southeastern portion of the island in the coastal town of Salcedo. The area is hilly with an altitude of 50 m ASL and is covered with patches of dipterocarp trees and grasses. A major plant common to both sites is the fern *Pteridium aquilinum*. The red soil in the area which is classified as Haplic Ferralsol (World Reference Base) or Rhodic Hapludox (Soil Taxonomy) developed from serpentinite of Upper Cretaceous origin. Both red soils are highly weathered and contain considerable amounts of hematite, which explains their deep red color (Navarrete *et al.*, 2007; Asio and Jahn, 2007). The climate of the two sites falls within the Köppen's Am type (tropical rain forest climate, monsoon type) having an annual rainfall of 2700 mm and average temperature of 28°C. Selected physicochemical properties and clay mineralogy of the two soils are presented in Table 1 and Figure 2, respectively.

Table 1. Selected characteristics of the two red soils in Samar, Philippines

	Depth	pH	Clay	OM	$CECpH_7$	Fed	Ald	Feo	Alo
Horizon	cm	H_2O	%		cmol kg^{-1}	g kg^{-1}			
Bagacay soil									
Ah	0-5	5.8	27.1	4.42	29	64	8.3	5.2	2
BA	5-20	5.8	32.7	5.07	30.1	62	8.0	5.4	2
Bt1	20-60	5.3	33.3	1.70	21.8	73	9.8	5.4	2.3
Bt2	60-100	5.2	36.9	0.97	16.1	79	10.6	1.6	2.5
Bt3	100-165	5.1	36.4	0.52	18	84	10.0	1.4	2.6
Bt4	165-225	5.1	47.6	0.22	16.1	83	8.7	1.3	2.7
Bt5	225-275	5.2	59.1	0.13	14.6	71	7.3	1.2	2.3
Bt6	275-350	5.1	55.0	0.08	25.8	80	8.4	1.6	3.7
Bt7	350-500	5.1	60.2	0.10	22.8	84	8.5	1.7	3.5
Bt8	500-550	5.3	n.d.	0.07	19.8	71	7.1	2	2.2
Salcedo soil									
Ah	0-21	5.8	59.8	1.38	9.7	164	21.6	1.4	1.4
Bo1	21-54	5.7	63.6	0.43	9.7	191	24.0	1.4	1.7
Bo2	54-92	5.5	69.0	0.33	10.9	194	23.2	1.4	1.8
Bo3	92-130	5.6	75.8	0.28	11.1	180	20.0	1.3	1.7
Bo4	130-191	5.6	83.8	0.23	10.9	170	16.4	1.4	1.8
Bo5	191-291	5.5	85.3	0.16	20.7	154	13.6	1.1	2
Bo6	291-391	5.3	86.6	0.11	16.4	151	13.3	1.3	2.1
Bo7	391-500	5.3	88.2	0.10	22.3	144	12.3	1.3	2.1

*Selected data from Navarrete et al. (2007).

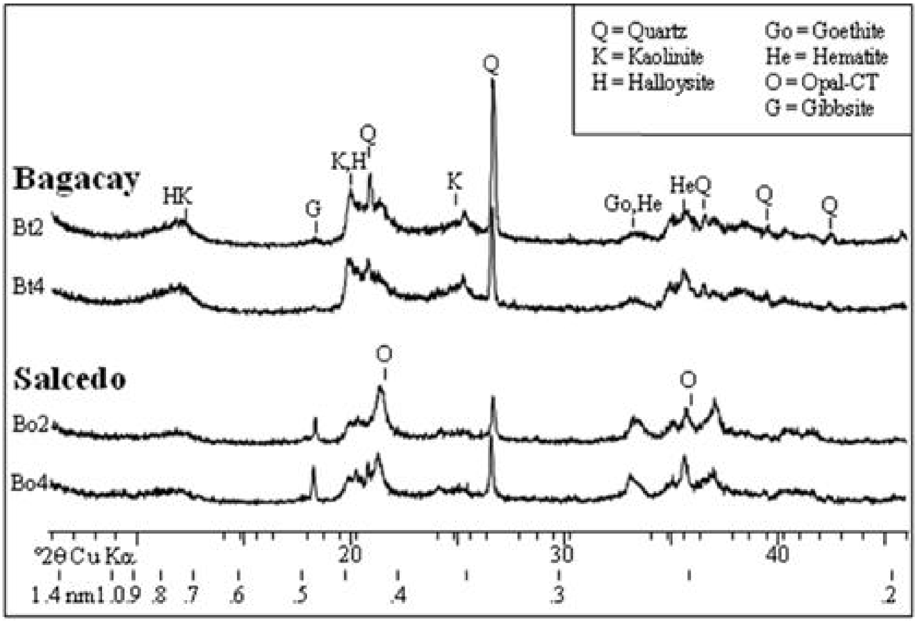

Figure 2. X-ray patterns of selected powdered soil samples.

Soil Sampling and Analysis

The two red soils were examined and sampled from recent road cuts after removing at least 30 cm thickness of surface to expose the fresh soil (Fig 3). Samples were collected from every horizon in each profile, freed of large plant residue, air-dried, and passed through a 2 mm sieve.

The total Cd, Cu, Cr, Pb, Ni, and Zn were determined by *aqua regia* digestion method (USEPA 1986), which uses a mixture of concentrated HNO_3 and HCl (1:3 proportion). This method is briefly described as follows: A 3 g soil is transferred into a digestion tube and 7 mL of concentrated HNO_3 and 20 mL of concentrated HCl were added and allowed to stand overnight. Samples were digested with intermittent heat treatments at 50°C (5 min), 100°C (30 min), and 120°C (1.5 h). After digestion, the solution was cooled and 50 mL of doubled distilled water was added. The solution was filtered and the contents of total Cd, Cu, Cr, Pb, Ni, and Zn were quantified using ICP-AES (Yves Yobin JY

Bagacay soil Salcedo soil

Figure 3. Soil profile of the two red soils evaluated in Samar, Philippines

70 plus). The available Cd, Cu, Cr, Ni, Pb, and Zn were determined by NH_4NO_3 method (Schlichting et al. 1995) and the contents were quantified using ICP-AES. All analyses were done in duplicate samples and values are reported as mean.

Statistical Analysis

Pearson correlation analysis was done on selected measurable soil properties (clay, pH, OM, CEC, Fe_d, Al_d, Fe_o, and Al_o) and total heavy metals (Table 2: Cd, Cu, Cr, Ni, Pb, and Zn) to assess the soil properties that control the behavior of heavy metals in the soils. The Pearson correlation analysis was done using the JMP software package (Version 8, SAS Institute, USA).

RESULTS AND DISCUSSION

Total and Available Heavy Metals Content

Table 2 shows the contents of total Cd, Cu, Cr, Ni, Pb, and Zn of Bagacay and Salcedo soils. As can be seen, total Cd contents were below 0.09 mg kg^{-1} in both soils. The total Cu contents ranged from 56 to 96 mg kg^{-1} and 32 to 44 mg kg^{-1} in Bagacay and Salcedo soils, respectively. The total Pb contents ranged from 3 to 12 mg kg^{-1} with slightly higher values in Salcedo soil than in Bagacay soil, while the total Zn contents ranged from 58 to 69 mg kg^{-1} and the values did not vary considerably between the two soils. In Salcedo, the prolonged weathering of the serpentinite, which is known to contain high amounts of Cr and Ni (Huang, 1962; McGrath, 1995; Ellis *et al.*, 2002), has

Table 2. Total heavy metal contents of the two red soils in Samar, Philippines

Horizon	Depth cm	Cd mg kg^{-1}	Cu	Cr	Ni	Pb	Zn
Bagacay soil							
Ah	0-5	0.08	56	30	12	6.7	63
BA	5-20	0.08	57	29	12	6.4	65
Bt1	20-60	0.03	61	33	14	6.3	64
Bt2	60-100	0.03	66	34	15	7.5	72
Bt3	100-165	0.09	60	10	12	6.8	68
Bt4	165-225	0.06	63	11	10	5.3	69
Bt5	225-275	0.06	69	8	7	4.9	69
Bt6	275-350	0.07	84	7	13	3.9	58
Bt7	350-500	0.06	96	8	11	3.2	58
Salcedo soil							
Ah	0-21	0.00	32	1635	428	12	60
Bo1	21-54	0.04	40	1592	473	12	65
Bo2	54-92	0.05	44	1450	521	12	69
Bo3	92-130	0.01	41	1381	526	12	65
Bo4	130-191	0.03	39	1383	534	11	62
Bo5	191-291	0.00	37	1293	707	10	63
Bo6	291-391	0.00	40	1044	957	9	68
Bo7	391-500	0.00	37	1045	738	8	67
Critical value*		3-8	60-125	75-100	100	100-400	70-400

*According to Kabata-Pendias and Pendias (2001).

resulted in elevated soil contents of total Cr (average:1340 mg kg^{-1}) and total Ni (average: 693 mg kg^{-1}). The contents of total Cr and total Ni were 18 and 7 times larger than the critical soil total concentration of 75-100 and 100 mg kg^{-1} for Cr and Ni, respectively (Kabata-Pendias and Pendias, 2001). Although a small fraction of the total Cr and total Ni in the soil are labile, mobile or biologically available (Kabata-Pendias and Pendias, 2001; McGrath, 1995), this fraction can enter the food chain through plant uptake and has the potential to pollute ground waters. Susaya *et al.* (2009) found that most farmers in the Salcedo site are growing food crops many of which contain elevated levels of Cr and Ni due to the high soil contents of these metals. These results suggest that the soil could pose health hazard to the farmers through dust inhalation or soil ingestion (Oliver, 1997) and consumption of food crops such a vegetables and root crops that are commonly grown in the area. Although no detailed health studies have yet been done in the area, many farmers reported unexplained health problems, which may be related to heavy metal toxicity. Another problem is that crops grown in soils high in Ni are more susceptible to mosaic virus infection than those in low Ni soils (Davis *et al.*, 2001), suggesting that Salcedo soil is probably problematic when used for crop production. Under oxidizing condition, Cr is highly soluble and mobile in the soil as the Cr (VI) anion chromate (CrO_4^{2-}) and bichromate ($HCrO_4^-$) that are suspected to be carcinogenic (Ellis *et al.*, 2002). On the other hand, the total Cr and total Ni contents were generally low in Bagacay soil since the slate parent material contained low amounts of these heavy metals. It likewise indicates that the half century of copper and pyrite mining activity a few kilometers away has not affected the soil studied probably because of the distance and it is not within the path of the dust coming from the mining site. However, it would be interesting to evaluate the level of contamination in the red soil very close or around the now abandoned mining site.

Table 3 reveals that the available Cr in Salcedo soil was higher (0.14-0.33 mg kg^{-1}; except Bo1 horizon) than the critical risk value of 0.05 mg kg^{-1}, above which toxicity is considered to be possible. The acidic condition of Salcedo soil, which enhances Cr solubility, explains the elevated contents of available Cr in the soil (McGrath, 1995). The available Cd, Cu, Pb, and Zn were low in the two soils, which is consistent

Table 3. Available heavy metal contents of the two red soils in Samar, Philippines

Horizon	Depth cm	Cd	Cu	Cr	Ni	Pb	Zn
		mg kg^{-1}					
Bagacay soil							
Ah	0-5	0.01	0.03	bdl	0.02	0.01	0.25
Bt1	20-60	0.01	0.04	bdl	0.02	0.01	0.26
Bt2	60-100	0.01	0.12	bdl	0.05	0.06	0.28
Bt3	100-165	0.01	0.13	bdl	0.04	0.22	0.20
Salcedo soil							
Bo1	21-54	bdl	0.01	0.01	0.10	bdl	0.02
Bo2	54-92	bdl	0.02	0.14	0.46	0.02	0.04
Bo3	92-130	bdl	0.03	0.33	0.57	bdl	0.09
Bo4	130-191	bdl	0.03	0.26	0.71	bdl	0.09
Threshold value		0.02	1.00	0.05	1.50	0.30	2.00

bdl: below detectable limit (0.01 mg kg^{-1}).

with the low total contents of these heavy metals in the soils (Table 2). Despite the remarkably high total Ni contents, the available Ni was low and is likely due to the strong binding between Ni and soil clay minerals and Fe and Al oxides (Navarrete *et al.*, 2007). This probably explains why no plants investigated in the Salcedo site met the criterion for a Ni hyperaccumulator plant (Susaya *et al.*, 2009). However, prolonged consumption of different food crops with high Ni levels can induce accumulation of Ni above the recommended daily intake that could cause health problems (Susaya *et al.*, 2009).

The total Cr and total Ni were positively correlated with clay (p<0.001), dithionite extractable Fe (Fe_d: p<0.001) and Al oxides (Al_d: p<0.001), but were negatively correlated with OM (p<0.05), CEC (p<0.001), and oxalate extractable Fe (Fe_o: p<0.001) and Al (Al_o: p<0.001) (Table 4). This result implies strong affinity of clay, Fe and Al oxides to bind with Cr and Ni in the soils studied. This results conforms to the findings of Navarrete *et al.* (2007) who reported that 82-97% of Cr and 38-67% of Ni in Salcedo soil are strongly bounded to Fe oxides and other clay minerals (for example see Fig. 2). Similarly, Susaya et al. (2009) reported a strong correlation between total Ni and clay in the Salcedo soil. In the present study, the negative correlation between Ni and OM (p<0.05) conforms to the findings of Kabata-Pendias and Sadurki

(2004) who showed that the association of metals to OM was generally insignificant for Ni. The total Cu ($p<0.05$) and total Cd ($p<0.05$) were positively correlated with CEC.

Table 4. Pearson correlation analysis between total heavy metals and selected soil properties of the two red soils in Samar, Philippines

	pH	Clay	OM	CEC_7	Fe_d	Al_d	Fe_o	Al_o
Total Cd	-0.13	-0.53[c]	0.47	0.55[b]	-0.46	-0.42	0.23	0.41
Total Cu	-0.66[b]	-0.93[a]	0.43	0.69[b]	-0.93[a]	0.85[a]	0.47	0.92[a]
Total Cr	0.55[b]	0.94[a]	-0.56[c]	-0.82[a]	0.99[a]	0.95[a]	-0.59[c]	-0.88[a]
Total Ni	0.52[b]	0.97[a]	-0.57[c]	-0.81[a]	0.98[a]	0.91[a]	-0.60[c]	-0.87[a]
Total Pb	0.47	0.93[a]	-0.61[b]	-0.86[a]	0.99[a]	0.96[a]	-0.68[b]	-0.83[a]
Total Zn	-0.56[c]	-0.38	-0.13	-0.03	-0.22	-0.10	-0.31	0.52[c]

[a]Correlation is significant at the 0.001 level.

[b]Correlation is significant at the 0.01 level.

[c]Correlation is significant at the 0.05 level.

CONCLUSION

Based on the results of the study, it maybe concluded that: a) the contents of total Cr and total Ni in the red Salcedo soil derived from sepentinite were high and exceeded the maximum allowable concentrations in agricultural soils; b) the total heavy metal contents of the red Bagacay soil from slate were low due to their low concentrations in the parent material; c) the contents of available form of the heavy metals studied were low in both red soils (except for available Cr in Salcedo soil); and d) there was no noticeable effect of the nearby mining site on the heavy contents of the slate-derived red Salcedo soil.

REFERENCES

ALLOWAY, B. J. 1995. Soil processes and the behaviour of metals. In: *Heavy Metals in Soils (2nd ed.)* (B. J. Alloway, ed). Blackie Academic and Professional, London, pp. 11-37.

ALLOWAY, B. J. 1997. Soil pollution and land contamination. In:

Pollution: Causes, Effects and Control (3rd ed.) (R. M. Harrison, ed). Spriner, Berlin, pp: 318-338.

ASIO, V. B. and R. JAHN. 2007. Weathering of basalt and clay mineral formation in Leyte, Philippines. *Philippine Agricultural Scientist* **90**:204-212.

CHEN, Z. S. and D. R. LEE. 1995. Heavy metals contents of representative agricultural soils in Taiwan. *Journal of the Chinese Institute of Environmental Engineering* **5**:205-211.

CHEN, Z. S., G. J. LEE, and J. C. LIU. 2000. The effects of chemical remediation treatments on the extractability and speciation of cadmium and lead in contaminated soils. *Chemosphere* **41**:235-342

DAVIS, M. A., J. F. MURPHY, R. S. BOYD. 2001. Nickel increases susceptibility of a nickel hyperaccumulator to *Turnip mosaic* virus. *J Environ Qual* **30**:85-90.

ELLIS, A. S., T. M. JOHNSON, and T. D. BULLEN. 2002. Chromium isotope and the fate of hexavalent chromium in the environment. *Science* **295**:2060-2062.

HUANG, W. T. 1962. *Petrology*. McGraw-Hill Book Co., New York.

KABATA-PENDIAS, A., and H. PENDIAS. 2001. *Trace Elements in Soils and Plants (3rd ed)*. CRC Press, Boca Raton.

KABATA-PENDIAS, A., and W. SADURSKI. 2004. Trace elements and compounds in soil. In: *Elements and Their Compounds in the Environment* (E. Merian, M. Anke, M. Ihnat, and M. Stoeppler, eds). Occurrence, Analysis and Biological Relevance (2nd ed). New York: Wiley-VCH.

McGRATH, S. P. 1995. Chromium and nickel. In: *Heavy Metals in*

Soils (2nd ed.) (B. J. Alloway, ed). Blackie Academic and Professional, London, p. 152-178.

NAVARRETE, I. A., V. B. ASIO, R. JAHN, and K. TSUTSUKI. 2007. Characteristics and genesis of two strongly weathered soils in Samar, Philippines. *Aust J Soil Res* **45**:153-163.

OLIVER, M. A. 1997. Soil and human health: a review. *Eur J Soil Sci* **48**:573-592.

PUSCHENREITER, M., O. HORAK, W. FRIESEL, and W. HARTL. 2005. Low-cost agricultural measures to reduce heavy metal transfer into the food chain- a review. *Plant Soil Environ* **51**: 1-11.

PEREZ-SIRVENT, C., M. J. MARTINEZ-SANCHEZ, M. L. GARCIA-LORENZO, J. MOLINA, and M. L. TUDELA. 2009. Geochemical background levels of zinc, cadmium and mercury in anthropically influenced soils located in a semi-arid zone (SE, Spain). *Geoderma* **148**: 307-317.

SCHLICHTING, E., H. P. BLUME, and K. STAHR. 1995. *Bodenkundliches Practicum (2nd ed).* Blackwell, Berlin.

REEVES, R. D. 2003. Tropical hyperaccumulators of metals and their potential for Phytoextraction. *Plant and Soil* **249**:57-65.

SUSAYA, J. P., K. H. KIM, V. B. ASIO, Z. S. CHEN, I. A. NAVARRETE. 2009. Quantifying nickel in soils and plants in the ultramafic area in Philippines. *Environmental Monitoring and Assessment* **167**:504-514.

U.S. ENVIRONMENTAL PROTECTION AGENCY. 1986. Acid digestion of sediments, sludge, and soils. In: *Test Methods for Evaluating Soil Waste* (USEPA, ed). SW-846, USEPA, Cincinnati, OH, U.S.A.