

Trace Element Contamination around the E-waste Recycling Site at Agboghloshie, Accra City, Ghana

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Abstract—E-waste has become a subject of growing environmental concern in developing countries due to legal/illegal import from developed nations. In this study, we investigated the levels and speciation of trace metals in and around the largest e-waste recycling site, Agboghloshie market in Accra city, Ghana. Concentrations of 15 elements in soil/ash mixtures collected around Agboghloshie markets were measured by handheld X-ray fluorescence (XRF) analyzer. Concentrations of Cu (50 to 22000 mg/kg), Zn (200 to 160000 mg/kg), Pb (100 to 14000 mg/kg) and Sn (<50 to 1000 mg/kg) were extremely high in residual ash derived from the combustion of coatings on metal wires. Bromine (Br) (20 to 1500 mg/kg), As (<50 to 1100 mg/kg) and Hg (<20 to 150 mg/kg) were also at moderately high levels. X-ray absorption fine structure measurements revealed that majority of Br was possibly in the inorganic form rather than organic contaminants. Predominance of inorganic Br in soil/ash mixtures might be attributed to the conversion of organic Br by thermal decomposition. Formation of dioxin like compounds is probably high in this area and hence further comprehensive monitoring is needed to assess the health risk for the e-waste recycling workers.

Keywords: Ghana, e-waste, trace element, XANES, dioxin

INTRODUCTION

E-waste encompasses a broad and growing range of electronic devices ranging from large household appliances such as refrigerators, air conditioners, stereos and consumer electronics to computers and hand-held cellular phones (Puckett *et al.*, 2002). E-waste produces higher volumes of waste in comparison to other consumer goods. For example, consumers buy a stereo console or television set with the expectation that it would last for a decade or more, but the increasingly rapid evolution of technology combined with rapid product obsolescence make everything disposable. The growing quantity of e-waste is beginning to reach disastrous proportions and industrialized countries all over the world are just now beginning to grapple with the problem (Schmidt, 2006). Recently, e-waste has become a subject of growing environmental concern in developing countries due

to the large volume of legal and illegal import from developed nations. The nations which are claiming to send recyclable materials are actually sending the pollution to developing countries. Many toxic substances including BFRs, PCBs and heavy metals contained in e-waste are released into the environment during disposal and recycling. Furthermore, inappropriate thermal treatment and combustion processes widely employed by recyclers in developing countries to retrieve valuable metals are known to generate unintentional highly toxic chemicals such as PCDD/Fs, PBDD/Fs and mixed halogenated homologues (Robinson, 2009). Lack of data is most concerning on the e-waste recycling sites in Asian and African developing countries, where the pollution has often been overlooked. In this study, we investigated the levels and speciation of trace metals around the largest e-waste recycling site, Agbogbloshie market in Accra city, the capital of Ghana. At the Agbogbloshie market, the main electronic wastes being processed are obsolete computers, monitors and televisions. These are manually dismantled at numerous small workshops within the market. Certain materials, mainly plastic coated wires and cables, are subsequently taken to sites on the edge of the market where they are burnt to separate metals from plastic coatings. These wires are commonly attached to other types of materials, including pieces of printed circuit boards, which consequently are also burnt. Materials of no value are disposed of in a large area on the edge of the market that is also used for the disposal of a wide range of other types of wastes (Brigden *et al.*, 2008). Korle Lagoon in the nearby estuary has become one of the most polluted water bodies on earth (Nixon *et al.*, 2007). It is the principal outlet through which all major drainage channels in the city empty their wastes into the sea. Large amounts of untreated industrial waste emptied into surface drains has led to severe pollution in the lagoon and disrupted its natural ecology. The increased levels of industrial activity and consumption of various materials by the urban population is leading to the generation of copious quantities of waste. Managing the volume of wastes poses a major challenge for the city authorities, particularly, ensuring all the waste generated is collected for disposal is a major problem (Boadi and Kuitunen, 2002).

MATERIALS AND METHODS

A total of 10 soil/ash mixtures were collected from Agbogbloshie market, Accra, Ghana, in August 2010 (Table 1). Accra is the largest city in Ghana in terms of industrial establishment and infrastructural development. It is a coastal city and one of the major e-wastes dumping sites in West Africa. All soil/ash mixture samples were stored at -25°C in the Environmental Specimen Bank (*es-BANK*) of Ehime University until chemical analysis. Concentrations of 15 elements in soil/ash mixture collected around Agbogbloshie market were measured by a Field Portable X-ray fluorescence (FP-XRF) spectrometer (Innov-X systems). Accuracy of XRF measurement was preliminarily evaluated by measuring 18 certified geological materials distributed by Geological Society of Japan. Certified geological materials are Igneous rock (JA-3, JB-1b, JB-3, JG-3, JGb-2, JR-1, JR-3, JP-2), Sedimentary rock/Sediments (JLs-1, JSI-1, JSI-2, JLk-1, JSd-1, JSd-2, JMS-1, JMS-2), Coal fly ash (JCFA-1) and Ore sample (JMn-1). Chemical

Table 1. Sampling locations of soil/ash mixture samples.

Sample	Latitude	Longitude
GH10-E1	05.33'06.93" N	00.13'33.63" W
GH10-E2	05.33'06.34" N	00.13'34.87" W
GH10-E3	05.33'05.27" N	00.13'36.02" W
GH10-E4	05.33'03.28" N	00.13'35.43" W
GH10-E5	05.33'03.16" N	00.13'33.15" W
GH10-E6	05.33'01.22" N	00.13'37.39" W
GH10-E7	05.33'02.40" N	00.13'36.70" W
GH10-E8	05.33'03.80" N	00.13'37.02" W
GH10-E9	05.33'03.76" N	00.13'36.10" W
GH10-E10	05.33'01.13" N	00.13'32.09" W

extraction by 1N HCl was also made to assess bioavailable fraction. Three-hundred milligram of freeze-dried soil/ash mixtures were put into Teflon vessel and shaken under darkness at 185 rpm by reciprocating shaker for 2 hours. After filtration of extractant through 0.45 μm membrane filters, concentrations of trace elements were measured by Inductively Coupled Plasma Mass Spectrometer (ICP-MS, Agilent7500cx). Elemental speciation of soil/ash mixtures for Cu, Zn and Br was performed using X-ray absorption near edge structure (XANES) spectroscopy at a beamline (BL-9C) of the Photon Factory in the Institute of Material Structure Science, High Energy Accelerator Research Organization (KEK-PF). The KEK-PF storage ring was operated at 2.5 GeV with a 450 mA maximum current. A Si(111) double-crystal monochromator was used to produce a monochromatic X-ray beam. Color of soil/ash mixtures were measured by portable soil color meter (SPAD-503, Konica Minoruta, Japan). The color was expressed numerically using L*a*b* color space.

RESULTS AND DISCUSSION

Validation of XRF measurements

Accuracy of XRF measurement was preliminarily evaluated by measuring 18 certified geological materials distributed by Geological Society of Japan. In most cases, accuracy was within an order of magnitude. In this study, the elements evaluated the accuracy were placed in any one of the following three categories with respect to instrumental linear response (r^2) between replicate analyses for all standard reference materials (SRMs) measured (Fig. 1). Elements showing high correlation coefficient between SRMs measured by FP-XRF and SRMs certified concentration were classified into category 1. Copper, Zn, Sr and Pb were classified into this category. Iron and Ti showed good agreement with certified values at low concentration range and not good in high concentration. These elements were classified into category 2. Elements placed in category 3 (i.e., As

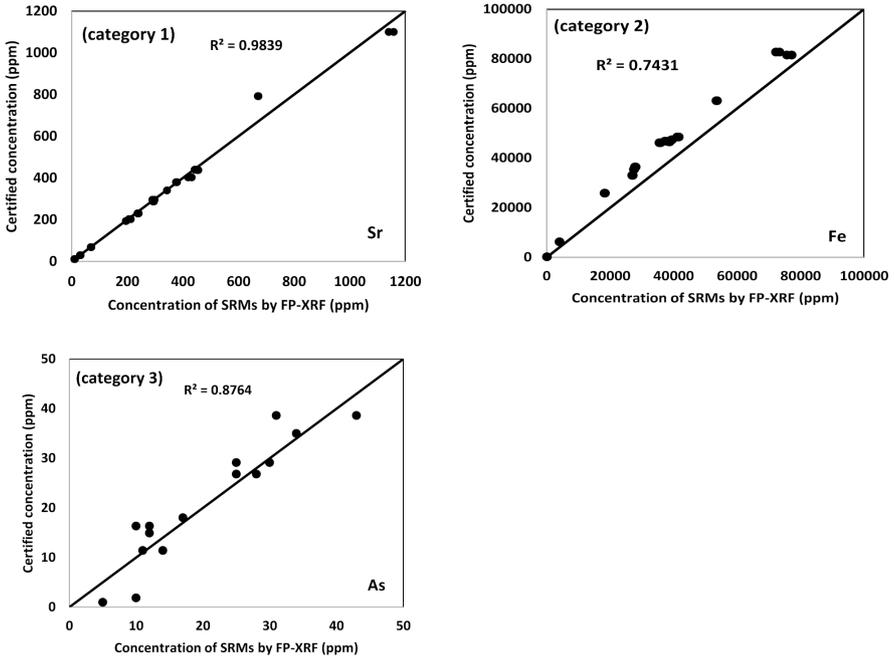


Fig. 1. Comparison of trace element concentrations in SRMs measured by FP-XRF and certified values. The line shows a 1:1 relationship.

and Co) showed low degree of correlation between SRMs measured by FP-XRF and SRMs certified concentration. In general, concentrations of many elements measured by the FP-XRF were in good agreement with certified values, although some elements placed under categories 2 and 3, showed poor accuracy possibly due to matrix effect, or wide range of concentrations and very low concentrations. Although we have to modify analytical condition in future, to improve these data, the accuracy for most of metals is within an acceptable range, at present.

Contamination levels

Concentrations of Cu (50 to 22000 mg/kg), Zn (200 to 160000 mg/kg), Pb (100 to 14000 mg/kg) and Sn (<50 to 1000 mg/kg) were extremely high in residual ash derived from combustion of coatings of wire, and Br (20 to 1500 mg/kg), As (<50 to 1100 mg/kg) and Hg (<20 to 150 mg/kg) were also at moderately high levels (Fig. 2). Concentrations of these metals were found to increase with higher L* value (data not shown), which represents darkness of soil color suggesting that these levels can be simply controlled by dilution of residual ash with uncontaminated soil. As the black color of the soil is due to the burning of e-waste materials, it can be presumed that these metals were from e-waste products, and released into the surrounding environment through open burning. In Environment

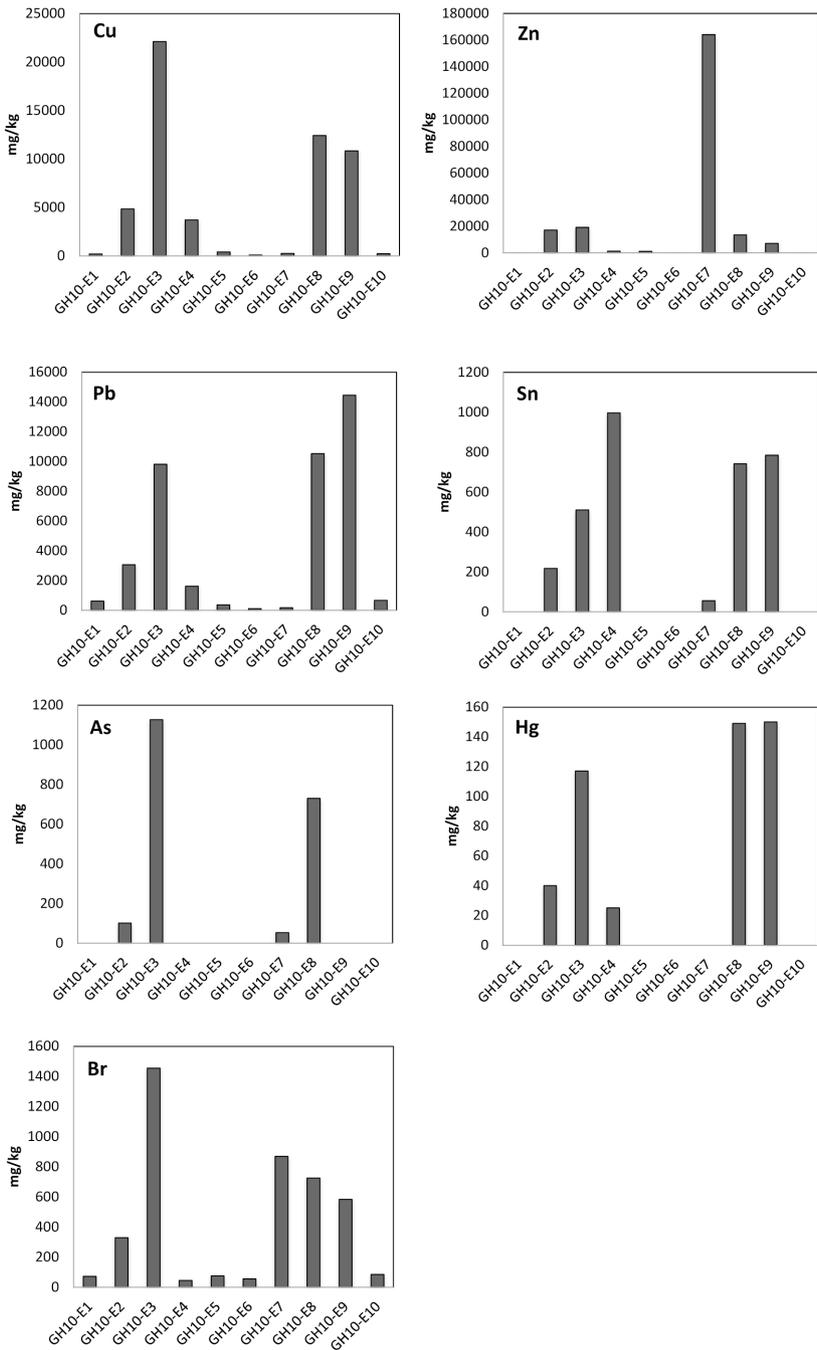


Fig. 2. Concentrations (XRF) of trace elements in bulk soil/ash mixtures collected from Agbogbloshie market.

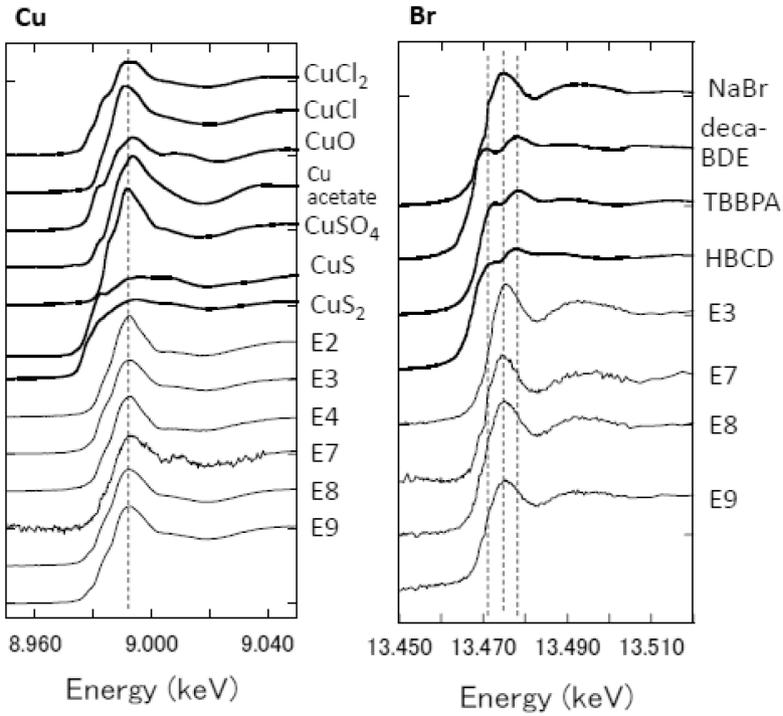


Fig. 3. Comparison of Cu and Br K-edge XANES spectra of soil/ash mixtures.

Agency Notification No. 19, Japanese environmental standards values for Pb, As, Se and Cd in the soil are 150 mg/kg, and for Cr is 250 mg/kg. Japanese environmental standards values (Environment Agency Notification No. 18) for concentration of HCl extractable Pb, As, Se and Cd are 0.01 mg/L and for Cr that is 0.05 mg/L. By comparison of these values to the present results, Pb and As in soil/ash mixtures were in serious toxic levels. Concentrations of HCl extractable Cu (1 to 200 mg/L), Zn (3 to 1100 mg/L) and Pb (1 to 360 mg/L) were considerably high. Arsenic (0.03 to 0.2 mg/L), Cr (0.05 to 0.4 mg/L), Se (0.1 to 0.3 mg/L) and Cd (0.03 to 0.9 mg/L) were also high. It is clear that soil/ash mixture has significant negative effects on human health. As a result, it is expected that recycler's health might be affected by accidental ingestion of toxic heavy metals through soil.

XANES

Copper and Br XANES spectra of soil/ash mixtures and reference materials are shown in Fig. 3. The XANES spectra were clearly different between organic Br (PBDE, HBCD, and TBBPA) and inorganic salt (NaBr). The peak observed around 13.471 keV is the typical feature of organic Br. However, that peak was

not observed from all spectra of soil/ash mixtures, and these XANES spectra were identical to NaBr. Hence, it seems that majority of Br was probably in the inorganic salt form rather than organic contaminants. Generally, Br in electronic products is mainly in organic form such as brominated flame retardants. Since soil/ash mixtures were collected from wire-burning site, dominant form of Br might be organic Br. Actually, highest Br concentration in black ash implied that original form of Br might be organic Br. Predominance of inorganic Br in soil/ash mixtures revealed by XANES might be attributed to the conversion of organic Br by thermal decomposition during burning activity. In such environment, possible formation of dioxins, toxic byproducts, is of high concern.

Various experimental studies have suggested that formation of dioxins by burning process of waste products could be catalyzed by trace metals (Stieglitz *et al.*, 1989). Fujimori and Takaoka (2009) suggested that presence of CuCl_2 during thermal combustion is important to chlorination of carbon. The XANES spectra for all soil/ash mixtures are similar to CuCl_2 suggesting that dominant Cu form in the soil/ash mixtures is CuCl_2 . As the Cu level in residual ash was high (Fig. 1), and CuCl_2 was likely the dominant form (Fig. 3), formation of dioxins seems quite plausible. Hence, further comprehensive monitoring is needed to assess the health risk for the e-waste recycling workers in Agbogbloshie market, Ghana.

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