Available online at www.sciencedirect.com
ScienceDirect
Journal of Environmental Sciences 20(2008) 1403–1408
JOURNAL OF ENVIRONMENTAL SCIENCES
ISSN 1001-0742
CN 11-2629/X
www.jesc.ac.cn

Assessment of toxicity potential of metallic elements in discarded electronics: A case study of mobile phones in China

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Received 12 November 2007; revised 27 December 2007; accepted 16 January 2008

Abstract

The electronic waste (e-waste) is increasingly flooding Asia, especially China. E-waste could precipitate a growing volume of toxic input to the local environment if it was not handed properly. This makes the evaluation of environmental impact from electronics an essentially important task for the life cycle assessment (LCA) and the end-of-life management of electronic products. This study presented a quantitative investigation on the environmental performance of typical electronics. Two types of disposed mobile phones (MPs), as a representative of consumer electronics, were evaluated in terms of toxicity potential indicator (TPI) with an assumption of worst-case scenario. It is found that the composition and the percentages of constituents in MPs are similar. More than 20 metallic elements make up 35 wt.%–40 wt.% of the total weight, of which 12 elements are identified to be highly hazardous and 12 are less harmful. With the TPI technique, the environmental performance of Pb is attributed to be 20.8 mg^{-1}. The total TPIs of metallic elements in the old and new type MP is 255,403 and 127,639 units, respectively, which is equivalent to the effect of releasing 6.14 and 12.28 g Pb into the environment. The average TPI of the old and new type MP is 4.1 and 4.5 mg^{-1}, respectively, which suggests a similar eco-efficiency per unit mass. The new model of MP is more eco-effective than the old one, which is not due to a reduction in the type of hazardous elements, but rather due to a significant miniaturization of the package with less weight. A single MP can have a considerable toxicity to the environment as referred to Pb, which suggests a major concern for the environmental impact of the total e-waste with a huge quantity and a heavy mass in China.

Key words: e-waste; enviromental impact; toxicity potential indicator (TPI); mobile phones (MPs)

Introduction

Each year hundreds of million tons of used electronic products are being thrown away to form electronic waste (e-waste) worldwidely, due to the blooming of electronic manufacturing and short cycle of product innovation. This situation is very serious in developing countries, especially for China which has been producing a large amount of e-waste since the 1990's. Moreover, China is recognized as a dumping ground for discarded electronics from other countries such as Japan, the US, and Europe. It is known that the discarded electronics will soon end up in landfill sites or incinerators where they will release toxic materials such as mercury, cadmium, lead, arsenic, dioxines and other hazardous materials into the air, soil or water. Many of these harmful substances can persist in the environment, bioaccumulate through the food chain, and pose a risk of causing adverse effects to human health and the environment.

To reduce the hazardous emissions and control the evironmental pollution, electroincs are turning towards green and their environmental performances are being considered, during which eco-design and the life cycle assessment (LCA) are important techniques. Eco-indicator methodologies (European Committee, 1998) are used often for the assessment of enviornmental impact of products, where emissions to human beings and ecosystems are evaluated. Prek (2004) has compared the enviromental aspects of three heating and air conditioning systems using the Eco-indicator 95 method. The results has shown that the indicator varied significantly with designs. Hur *et al*. (2004) has developed a green productivity index, which is defined as the ratio of productivity of a system to its environmental impacts, to evaluate the environmental performance. Soares *et al*. (2006) has proposed a new method for the identification of environmental impact category weights based on seven environmental criteria for the LCA. For electronics, Bhuie *et al*. (2004) have carried out a case study of computers and mobile phones (MPs) with environmental and economic trade-offs. The results over-emphasized the valuable metals than the environmental impacts. Yamaguchi *et al*. (2003) have introduced a life cycle inventory analysis of MPs with a focus on the energy consumption. The research group of environmental technology in the Fraunhofer Institute

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for Reliability and Microintegration (Fraunhofer IZM), Germany, has developed a modular assessment system named EE-Toolbox for the environmental optimization of electronics, which is a powerful tool for the LCA of electronic products (Meddendorf *et al*., 2000). It already has demonstrated some successful applications (Muller *et al*. 2001, Chung *et al*. 2003; Chen *et al*. 2005; Fujino *et al*. 2005), whereas further applications related to MPs are still needed. Material analysis and environmental assessment of electronics could help us on identifying improvements achievable through the use of intelligent and environmentally-responsible substances in the design. It could also provide reference data for the whole life cycle from the beginning of eco-design to the end-of-life (EOL) treatment.

This article aimed at assessing the worst-case toxicity of metallic elements in discarded electronics using the toxicity potential indicator (TPI) module in the EE-Toolbox. Two types of old MPs, as a representative of consumer electronics, were used for a case study, and their potential impacts on the environement were determined.

1 Materials and methods

Two types of discarded MPs, samples E and N, were collected from the recycler. Sample E was launched into the market in 1998, whereas sample N was a relatively new model that was first seen in 2003. First, they are dismantled into basic modules, including the case/housing, liquid-crystal-display (LCD) panel, keypad, printed circuit board (PCB), frame/plate, antenna, battery, speaker, and microphone (Fig.1).

Then, the weight of each module was measured using an analytical balance. Next, all parts were cut and ground into small pieces. Subsequently, the samples were digested in strong acids ($HCl:HNO_3$ = 1:5, *V/V*) following the procedures recommended in the IEC 62321 RoHS standard (IEC, 2005), the USEPA 3052 and 3056 Methods. The dissolution process was prolonged up to 144 h to extract as much metallic materials as possible. After filtration and diluting with de-ionized water, the concentration levels of the elements were determined using instrumental analysis techniques, including atomic absorption spectrometry (AAS, 3100, Perkin-Elmer, USA) and inductively coupled plasma-optical emission spectrometry (ICP-OES, Optima 5300^{TM} DV, Perkin-Elmer, USA). The filtration residues were also weighed and then studied using the energy dispersive X-ray (EDX) in the scanning electron microscope system (SEM, XL 40 FEG, Philips, The Netherlands). The compositional information from the EDX analysis were added into the extracted concentration to obtain the overall weight of substances in the whole MP.

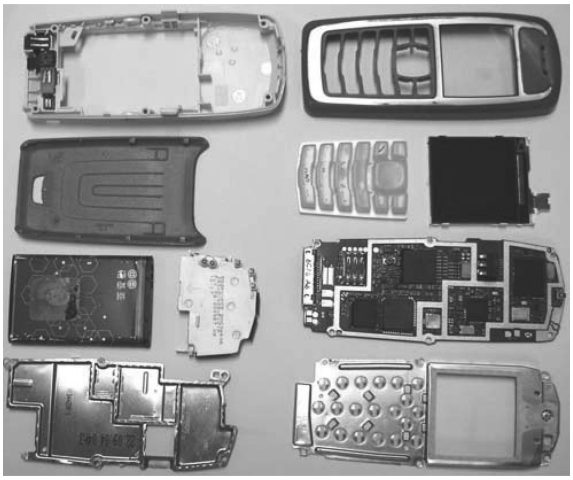

Fig. 1 Dismantled MPs with major modules.

2 Results and discussion

The main material groups in samples E and N are shown in Fig.2. The weight of sample E was about double of sample N. It is clear that although these sample MPs are quite different in specification (model, brand name, manufacturers, production year, location, weight, etc.), the overall composition and percentages of ingredients are more or less similar. This agrees well with the findings of other researchers (Lindholm, 2003; Huisman, 2003).

Plastics (not including epoxy based) give the highest contribution to the total weight, followed by metals, ceramics, and epoxies. The plastics are the main materials used for the housing, key pad, many components and connectors. A variety of metals are used in the PCB, components, frames, plates, screws, and other parts. The

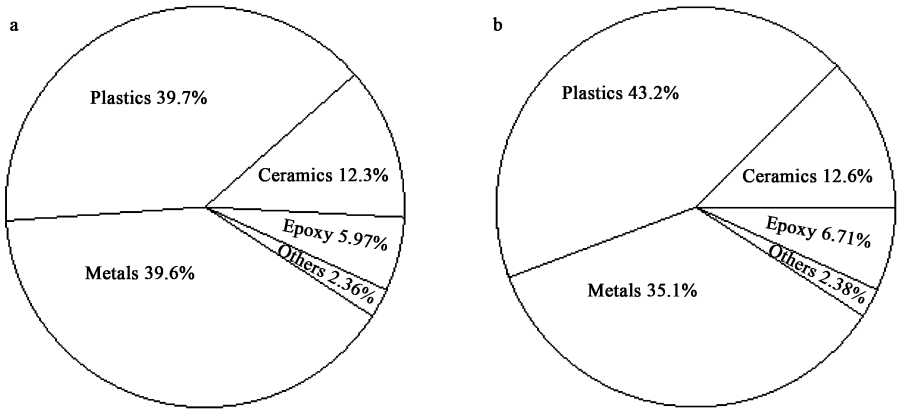

Fig. 2 Main material constitutes in the MP sample E (a) (total weight 153.38 g) and sample N (b) (total weight 80.25 g).

ceramics includes the glasses in the LCD and PCB as well as the ceramics in the components. Epoxy resin is a dominant substance for the PCB. Other constitutes like organic solutions in the battery and the polycyclic aromatic hydrocarbon of the LCD, are estimated to be 2%–3%. Both the plastics and PCB are likely to contain bromine in organic compounds which was used as a flame retardants, which may pose the threat of forming dioxins and furans in poorly combusted and controlled exhaust gas streams. Importantly, the metallic constituents, with more than 20 elements, make up 35%–40% of the total mass. The detailed metallic contents (24 elements) are presented in Table 1 according to the analyses. Some trace elements are not included due to their appearance at the less than mg/L level.

The total weight of metallic constituents in sample E is more than double of that in sample N. However, the percentages of each element in the total weight for two MPs are similar. The primary metallic constitutes are Al, Fe, Cu, Co, Zn, Ni, Sn, Cr, and Pb. It should be pointed out that Pb is a rather problematic substance, which is known to be very hazardous, and is strongly restricted or banned in electronics by the European Union (EU) legislation, "Restriction of Hazardous Substances (RoHS) Directive". Another 15 elements are also confirmed to be in very small quantities, some of which, such as Be, Cd, As and Sb, may be highly toxic to the environment and human beings. According to the comparative analysis of materials in MPs, it is found that although the products are quite different in model and production year, the type of elements and their relative ratio do not change. Moreover, the overall usage of toxic substances in electronics is expected to increase substantially since the growth speed of product quantity is generally much higher than the reduction speed of product weight.

Table 1 Metallic content in MPs

Element	Metallic content (g)	
	Sample E	Sample N
Al	17.1636	9.6814
Fe	16.3912	5.1121
Cu	13.1702	7.0213
Co	9.6921	4.1331
Zn	1.4492	0.0770
Ni	1.3070	0.6652
Sn	0.7665	0.4778
Cr	0.5714	0.5432
Pb	0.4328	0.1250
Mg	0.1919	0.0013
Ag	0.1052	0.0712
Mn	0.0855	0.0478
Ba	0.0658	0.0826
Nd	0.0628	0.1167
Sb	0.0478	0.0070
Au	0.0265	0.0133
Pd	0.0099	0.0039
Ti	0.0089	0.0283
Be	0.0070	0.0020
W	0.0056	0.0006
Bi	0.0032	0.0008
As	0.0026	0.0031
Cd	0.0004	0.0002
Hg	0.00008	0.00001
Total	61.5672	28.2149

Only with a quantitative technique, can the negative impact of metals in MPs be assessed. Here, the TPI module in the EE-Toolbox (Meddendorf *et al*., 2000) is used to calculate the potential impacts of these 24 elements in a worst-case scenario. The TPI (mg^{-1}) for the evaluation of a product is based on the environmental properties of the materials contained in the product. Different ecological impacts are integrated into one number, so the numerical result can express the possibility of harm to both humans and the environment when the substances are released in an uncontrolled manner. An uncontrolled, fine spread release, e.g., as dust or through groundwater is assumed to be the worst impact case, even though it might not occur in the real life cycle of the product under investigation. According to the name of the chemical substance and its material safety data sheet, the model considers the potential impact by mathematical aggregation with equal weights for legally-defined items, including human toxicity (like allowable workplace concentration (MAK)), damage to aquatic systems (water pollution classification (WGK)) and declared hazardous properties (hazardous substances declarations of risk phrase (*R* value)). After projection onto a numerical scale and logarithmic aggregation, each material is attributed one number which describes the relative worst-case ecological impact of the material on a scale of 0 to 100. Since Pb is a rather problematic element in electronics, here it was used as an example to calculate the TPI according to the following process:

Step 1: input value confirmation

MAK = 0.1 mg/m^3; WGK = 0; *R*20 (harmful by inhalation); *R*22 (harmful if swallowed); *R*33 (danger of cumulative effects); *R*61 (may cause harm to the unborn child); and *R*62 (risk of impaired fertility)

Step 2: evaluation on standard scale from 0 (harmless) to 7 (extremely hazardous)

$$N_{\mathrm{MAK}} = \log(\frac{10^4}{\mathrm{MAK}}) = 5$$

$$\mathrm{WGK} = 0 \rightarrow N_{\mathrm{WGK}} = 3 \text{ (low hazard to water)}$$

Two *R* items related to the inhalation:

$R20 \longrightarrow N_1 = 3$; $R22 \longrightarrow N_2 = 3$;

$$N_{\text{R-MAK}} = \ln \sum_i^n e^{N_i} = \ln(e^3 + e^3 + e^4) = 3.69$$

Three items related to cumulative effects:

$R33 \longrightarrow N_3 = 4$; $R61 \longrightarrow N_5 = 6$; $R62 \longrightarrow N_6 = 4$;

$$N_{\mathrm{R}} = \ln \sum_i^n e^{N_i} = \ln(e^4 + e^6 + e^4) = 6.24 \quad (1)$$

Step 3: aggregation with elimination of overlaps

$$N_{\mathrm{stoff}} = \mathrm{Aggr}\,(N_{\mathrm{R}}, \max(N_{\mathrm{MAK}}, N_{\text{R-MAK}}), \max(N_{\mathrm{WGK}}, N_{\text{R-WGK}}))$$

Elimination of $N_{\text{R-MAK}}$ (3.69), adoption of higher MAK–evaluation with $N_{\mathrm{MAK}} = 5$

$$N_{\mathrm{Pb}} = \ln(e^{6.24} + e^5 + e^3 - 3 + 1) = 6.52$$

Step 4: projection on exponential scale of 0 to 100

A scaling factor is obtained by assuming that the impacts concerning MAK, WGK, and *R* phrase are extremely toxic ($N_{MAK} = N_{WGK} = N_R = 7$).

$$\text{Scaling factor} = \frac{3 \times e^7 - 3}{100} = 32.9 \quad (2)$$

then, the unit TPI (mg^{-1}) of Pb is:

$$TPI_{Pb} = (e^{N_{Pb}} - 1)/\text{scaling factor} = (e^{6.52} - 1)/32.9 = 20.8$$

Then, the potential environmental impact of Hg is represented by a quantiative value of TPI, 39.9 mg^{-1}. Likewise, the TPIs of other elements are determined and shown in Fig.3. Obvious differences in the environment impact of individual elements are found, according to which highly hazardous elements are summarized in Fig.3a and less harmful ones are collected in Fig.3b. Generally, Cd, Hg, As, and Sb are regarded as dangerous metals that have significant health hazards. It is interesting to identify that Be, Ni, Ag, and Cr are also potentially dangerous, rather than the restriction to Pb with a TPI of 20.8 mg^{-1}. Be is often used as a Be-Cu alloy in MPs for the sake of helping expand and contract the springs and contacts. Over exposure to this material can give irreversible and sometimes fatal scaring of the lungs. Ni is classified by the EPA as a Group B2, probable human carcinogen. It also has long-term respiratory effects and can cause lung and nasal cancers. Ag is given a high TPI ranking of 37.8 mg^{-1} due to its toxicity to water organisms and its maximum workplace concentration. Unfortunately, there is a less chance for manufacturers to eliminate Ag since SnAgCu alloy has become a dominant Pb-free solder in electronics (Mulugeta, 2000), and some components and keypad contacts also contain Ag. Cr is also classified as a toxin because all forms of Cr can be dangerous at high concentration levels; and in particular, the RoHS Directive has already banned Cr^{6+} in electronics.

The TPI value of these elements based on a unit can provide useful information for screening toxic substances and for the examination of environmental performance during the LCA of electronic products. The total potential toxicity of metals, considering the weight and evaluation factor, can be calculated by summing up the TPI value of an individual material and the mass of that material. In this way, the contribution of each metal is also known.

Figure 4 shows the total TPI values and main contributions of metallic elements in sample E and sample N, respectively. It appears that the distribution of element type and portion in the pie for both samples is comparable. Co makes the largest contribution because of its high environmental weight factor and the large amount of presence. Ni is the second dominant contribution, which is ascribed to its high TPI per unit, rather than the weight present. Cu has a relatively high contribution because of high content, meanwhile Cr also makes a relatively large contribution due to high risk of toxicity. Some other

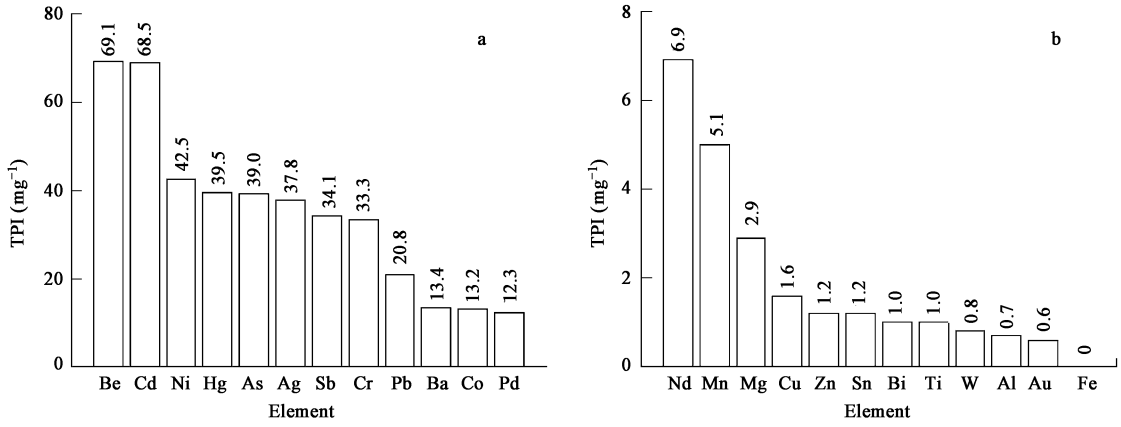

Fig. 3 Toxicity potential indicator of metallic element. (a) high hazard; (b) low hazard.

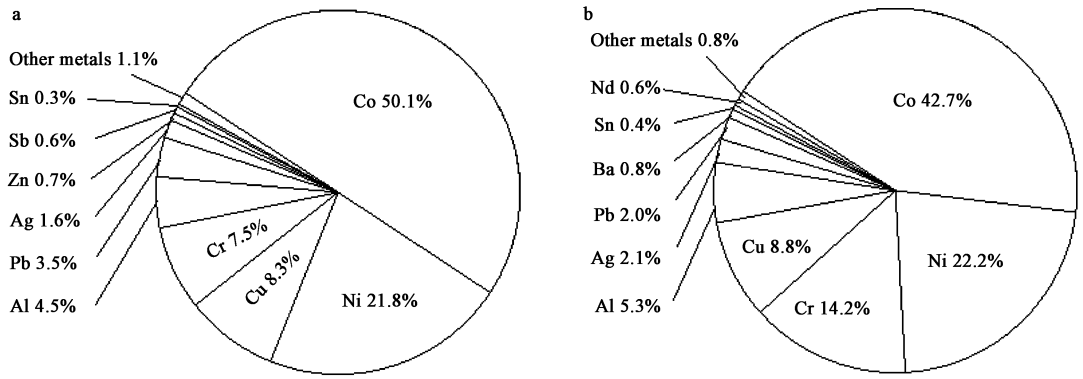

Fig. 4 TPI evaluation of old type MP sample E (a) and sample N (b). Total TPI of metals in sample E was 255,403.4 mg^{-1} and in sample N was 127,639.2 mg^{-1}.

metals make a total contribution of about 1%, which is mainly due to their minor content. However, they should not be underestimated because some are quite harmful, as indicated in Fig.3a, and the cumulative total toxicity from hundreds of millions of MPs could be dreadful.

The average TPI value of samples E and N is 4.1 and 4.5 mg^{-1}, respectively. This suggests that an equal unit of metallic subtances from these two MP samples presents a similar level of threat to the environment. Neverthless, the total TPI value of metallic elements in sample E (255,403.4 mg^{-1}) is about double of that (127,639.2 mg^{-1}) in sample N. Thus, the overall environmental impact of sample E is about double of sample N, which is mainly due to the mass difference.

Since Pb is now a great concern for the electronic manufacturing and recycling industry, we set the TPI of Pb (20.8 mg^{-1}) to be as a control. Then, the total impact of metallic elements from sample E and sample N under a worst-case scenario is equal to the effect of releasing 6.14 and 12.28 g Pb, respectively, into the environment without a control. As compared to the old-type MP sample E, the relatively new-type sample N offers a great improvement in environmental performance, which is mainly due to a substantial miniaturization of the package. However, no major changes in the type of hazardous elements are found with product model and manufacturing time. This is mainly because more functionality per unit weight is emphasized over the eco-efficiency by the manufacturers.

Despite the small mass contained per unit, a single MP can have a considerable toxicity when referred to Pb. Thus, the potential polluting impact of MPs in China should not be underestimated since the number of them is significantly large. It is of great concern that other heavy electronic products, such as TVs and PCs, may have an even more serious polluting effect since most electronics are similar in composition, but these products are far heavier than the MPs. According to Li *et al*. (2006), a forecast of the amount of the EOL electronics in typical household appliances and PCs was made. In 2010, it is expected that the number of obsolete TVs, refrigerators, washing machines, air conditioners, and PCs will be about 58, 9, 11, 12, and 72 million units, respectively. It is also estimated that each year about 70 million MPs are discarded in China (CCTV News, 2005). Then, we can image that the e-waste in China would persist a great threat to the safety of the environment with tremendous toxicity potential units. To clean our environment and have a sustainable development, the electronics must really go green. Therefore, reduction of hazardous materials and absolute weight in the design phase of production is as important as careful EOL management of electronics. At the same time, the recycling ratio should be improved due to the ever-increasing growth of users and rapid replacement of old electronic products.

3 Conclusions

Irrespective of model and time of production, the general composition and the percentages of constituents in MPs are more or less similar, in which more than 20 metallic elements make up 35 wt.%–40 wt.% of the total mass. There were 12 highly hazardous elements and 12 less harmful elements being present in both MPs, which make these phones a considerable potential threat to the environment if substantial numbers of phones are improperly treated at the end of their lives. The total TPI of metallic elements in sample E (153.38 g) and N (8.25 g) is 255,403.4 and 127,639.2 mg^{-1}, respectively, which is equivalent to the effect of releasing 12.28 and 6.14 g Pb (TPI 20.8 mg^{-1}) into the environment. The average TPI of sample E and N is 4.1 and 4.5 mg^{-1}, respectively, which suggests a similar eco-efficiency per unit mass. Thus, the overall environmental impact of sample E is about double of sample N, which is mainly due to the mass difference. The relatively new model of MP is more eco-effective than the old one, which is not due to a reduction in the type of hazardous elements, but rather due to a significant miniaturization of the package with less weight. A single MP can have a considerable toxicity to the environment as referred to Pb. This suggests a major concern for the environmental impact of the total e-waste with such a large mass in China since most electronics are similar in composition, but the PCs and household appliances such as TVs, refrigerators, washing machines and conditioners are much far heavier than MPs.

Acknowledgments

This project has been supported by the CityU Strategic Research Grant (No. 7001976). The authors would like to thank Prof. B. Ralph in the Brunel University, UK, for the helpful discussion.

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