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# Toxicity characterization of metals from various waste printed circuit boards

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ABSTRACT

Toxicity characterization (TC) of printed circuit board (PCB) of various obsolete electrical and electronic equipment (EEE) was performed. The end-of-life EEE considered in the study include personal computer (PC), laptop, washing machine (WM), television (TV) and air conditioner (AC). The standardized procedures i.e. EP, TCLP, ASTM Method D-3987 and SPLP were employed for toxicity characterization of PCBs in terms of metal leachability against their total metallic contents. Further, the standard SPLP was modified (MSPLP) to imitate Indian acid rain conditions to comparatively assess metal leachability. Except Se, there was statistically significant ($P < 0.05$) difference in metal contents of PCBs from different sources with Cu (maximum: $231133 \pm 3889$ mg/kg in laptop) and Pb (maximum: $73900 \pm 22100$ mg/kg in laptop) being the predominant metallic species. The TC test conditions showed statistically significant ($P < 0.05$) difference in metal leachability from respective EEE. Results indicated that Pb (maximum: $226.74 \pm 3.11$ mg/l in TCLP for laptop) and Ni (maximum: $0.942 \pm 0.053$ mg/l in SPLP for AC) in leachates exceeded the threshold toxicity limit. The general sequence of metal leachability, from most labile to least labile, from waste PCBs was: Pb > Cu > Zn > Al > Ni > Cd > Se > As > Ba. Except Pb, Cu and Zn, the ASTM procedure at neutral pH showed insignificant metal leachability. Standard SPLP and the MSPLP showed similar effect of Indian and western acid rain conditions on metal leachability. Greater leachability of Pb and Ni simultaneously indicated possible risk to the environment upon e-waste disposal.



## 1. Introduction

The rapid growth of electrical and electronic equipment (EEE) coupled with accelerated product obsolescence has led to build up of electronic waste (e-waste). The quantity of e-waste generated constitutes about 8% of municipal solid waste (MSW) and is the fastest growing waste stream in the world (Widmer et al., 2005). The United Nations University (UNU) reported that around 41.8 Mt of e-waste was generated worldwide in the year 2014. India ranks third in the list of Asian countries contributing to 1.7 Mt e-waste generations. Out of 41.8 Mt of e-waste generated worldwide in year 2014, only around 6.5 Mt of e-waste was collected formally by the take-back system while the rest of the e-waste was disposed of by landfilling, incineration or uncontrolled dumping (UNU, 2015). The global e-waste generation is predicted to increase at a growth rate of 4-5% per annum reaching to 49.8 Mt by 2018 (Baldé et al., 2015). Country-wise e-waste generation linking to their per capita purchasing power has been reviewed in detail elsewhere (Priya and Hait, 2017a). Depending on the adequacy of infrastructure for e-waste collection in a particular country, the end-of-life EEE collected through the take back system are usually subjected to recycling owing to their rich metal resource. E-waste that escapes from take back schemes is disposed of by incineration, landfilling or uncontrolled dumping in open drumpyards along with MSW stream. E-waste in incinerators leads to emission of harmful compounds causing air pollution whereas e-waste in landfills and open dumpyards lead to generation of toxic leachate which enters the environment and become available to biota.

Printed circuit boards (PCBs) are core components of e-waste and constitute 3–6% of the total weight of e-waste (Das et al., 2009; Li et al., 2004). The dramatic increase in the amount of waste PCBs with the increase in e-waste generation is indisputable (Widmer et al., 2005). A variety of inorganic and organic components including metals such as base metals, precious metals and toxic metals present in PCBs turn e-waste hazardous and also make it a potential reservoir of recyclable metals. Among the heavy and toxic metals, PCBs contain Cu, Zn, Al and Pb in abundance. Other toxic metals present in PCBs include Ni, Cd, Se, As, Ba, Cr, Ag and Hg. The assessment of toxicological properties of metals is well documented in literature (Demim et al., 2013a; DTSC, 2004; US Federal Register, 1980). Cu, Zn and Al being present in abundance in PCBs, their leaching in excess may pose serious threat to the biota. Their intake in

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excess is likely to cause human health effects like gastrointestinal distress, anaemia, digestive disturbances and kidney dysfunction (Raikwar et al., 2008). Pb is the most common toxic constituent of PCBs which is present as Pb-Sn solders with 60:40 ratio of Sn to Pb which have been found to leach at higher concentrations in landfills and dumpyards (Jang and Townsend, 2003). Metals such as Pb, Ni, Cd, Se, As, Ba, Cr and Hg are known to be more widespread contaminants of the environment causing severe effects to the biota including those related to survival, growth, reproduction, development, behavior and metabolism (Demim et al., 2013b; DTSC, 2004; Florea and Busselberg, 2006). They are lethal to animals, humans and plants beyond the maximum concentration for characteristic toxicity (DTSC, 2004; US Federal Register, 1980). In humans and animals, excess concentrations of these metals are reported to cause renal toxicity, hepatotoxicity, carcinogenicity, kidney dysfunction, respiratory disorders, skin allergy, selenosis and chronic pulmonary toxicity while in plants they affect the photosynthetic apparatus inhibiting growth and reproduction (Demim et al., 2013b; DTSC, 2004; US Federal Register, 1980; Florea and Busselberg, 2006). Ag and Hg are extremely toxic metals which cause human ailments such as allergic dermatitis, narcosis, gastrointestinal, respiratory, cardiovascular, endocrinological and renal disorders (Florea and Busselberg, 2006; Raikwar et al., 2008). Metals such as Ba cause abdominal cramps, diarrhoea, respiratory problems and impairment of cardiovascular systems in humans (Florea and Busselberg, 2006; Raikwar et al., 2008). Se in excess leads to selenosis, bronchial spasms and also respiratory disorders in humans (DTSC, 2004; Florea and Busselberg, 2006; US Federal Register, 1980).

The Resource Conservation and Recovery Act (RCRA) of 1976 promulgated criteria to differentiate hazardous and non-hazardous wastes and administer management of solid and hazardous waste (RCRA, 1976). One of the most significant dangers posed by hazardous wastes streams is leaching of toxic metals into soil and groundwater (Chang et al., 2001; Dubey and Townsend, 2004; Kendall, 2003; Sorini and Jackson, 1988; Wadanambi et al., 2008). Based on this concern, several toxicity characteristic (TC) tests have been prescribed by international organisations for the determination of toxicity of solid waste to be classified as hazardous waste and restrict their improper disposal. The United States Environmental Protection Agency (USEPA) Extraction Procedure (EP) test was the earliest to be designed to simulate leaching of a solid hazardous waste co-disposed with municipal waste in a sanitary landfill (USEPA, 1980). Followed by EP, the USEPA developed the Toxicity Characteristic Leaching Procedure (TCLP), the EPA Method 1311, the second generation extraction procedure to address the shortcomings of EP (USEPA, 1986). TCLP promulgated for use in determination of mobility of primarily organic and inorganic constituents present in waste that may pose a threat to the environment. Both the tests, EP and TCLP simulate solid waste leaching in landfill conditions. The pH values as prescribed to conduct EP and TCLP tests are $5.00 \pm 0.20$ and $4.93 \pm 0.05$, respectively. However, EP addressed only a few toxic semi-volatiles and metal leachates while TCLP waste characterization is based on the leaching of extensive list of volatile, semi-volatile organics as well as inorganic pollutants. Another TC test proposed by the American Society for Testing and Materials (ASTM), Method D-3987 (ASTM, 1995), outlined a procedure for determining the toxicity of solid waste so as to categorize it as hazardous waste. This method uses distilled water as the leaching medium to estimate the mobility of inorganic constituents from the waste under the specified test conditions. The distilled water extraction in the ASTM method simulates conditions where the dominant factor determining the pH of the extract is the solid waste itself. Later, the USEPA proposed the Synthetic Precipitation Leaching Procedure (SPLP), the EPA Method 1312 (USEPA, 1996) for assessment of mobility of both organic and inorganic analytes of waste dumped in-situ, in or on the ground surface exposed to rainfall. SPLP was based on assumption that rainfall causing waste leaching is acidic in nature. Standard SPLP test was designed by the USEPA with pH of $4.20 \pm 0.05$ simulating the pH of acid rain in the western countries.

Scientific studies have mainly focused on the leachability and toxicity assessment of metals from plastic housing and PCBs of waste mobile phones and PCs only using TCLP and SPLP (Chen et al., 2016; Jang and Townsend, 2003; Nnorom and Osibanjo, 2008; Townsend, 2004; Townsend et al., 2008). Owing to the complexity in manufacturing of EEE and heterogeneous metallic content, it is necessary to assess metal leachability and toxicity from PCBs from a wide range of discarded EEE using standardized TC test procedures. Further, the minimum value for the decadal mean pH of rainwater in India encompassing ten Global Atmospheric Watch (GAW) stations across the country during 2001–2012 is reported to be 4.77 (Bhaskar and Rao, 2017). Therefore, it is pertinent to investigate the metals leachability from a wide range of PCBs by modifying the SPLP to simulate Indian acid rain conditions. In these contexts, the objective of this research was to assess leachability and toxicity characteristics of a wide range of PCBs of obsolete EEE viz., personal computer (PC), laptop, washing machine (WM), television (TV), air conditioner (AC) in terms of twelve heavy and toxic metals namely, Cu, Zn, Al, Pb, Ni, Cd, Se, As, Ba, Cr, Ag and Hg against their total metallic contents employing standardized TC procedures i.e., EP, TCLP, ASTM D-3987 and SPLP to simulate various conditions of e-waste dumping. Moreover, the paper also aimed at assessing the metal leachability from the PCBs by the modified SPLP (MSPLP) to imitate pH of 4.8 under Indian acid rain condition in comparison to the SPLP.

## 2. Materials and methods

### 2.1. PCB collection and processing

Five end-of-life EEE viz., PC, laptop, WM, TV and AC were selected for the study. The make, model and year of manufacture (YoM) of the end-of-life EEE used for the study were: PC (Make: HP Compaq; Model: dx2068; YoM: 2009), laptop (Make: Lenovo; Model: G-570-59-068335; YoM: 2011), WM: (Make: LG; Model: WF – S7012DN; YoM: 2004), TV (Make: Sony; Model: Trinitron KV-27FV17; YoM: 2005), AC (Make: LG; Model:AS-H0764DM0; YoM: 2004). The end-of-life EEE were disassembled manually at the local repair shops and scrapyards in Patna, Bihar, India to separate the PCBs from other components. The PCBs of respective end-of-life EEE were collected in triplicate after disassembling. Representative photographs of the PCBs are shown in Fig. 1. Waste PCBs were then manually dismantled to remove mounted electronic components like capacitors, resistors, semiconductor chips before comminution. Further, PCBs were mechanically comminuted using cutting mill (SM200, Retsch GmbH, Germany) to particle size <9.5 mm. Three replicates of comminuted samples were taken from each of the PCBs of respective end-of-life EEE and were subjected to subsequent leaching.

### 2.2. Quantification of toxic metals content of waste PCBs

For quantification of selected heavy and toxic metal contents, the respective comminuted samples of waste PCBs were subjected to the USEPA 3052 acid digestion procedure (Priya and Hait, 2017b; USEPA, 1995). The digestate obtained after acid digestions were transferred to volumetric flasks to make up to 100 ml volume with distilled water. The resulting solutions were filtered through 0.22 μm Millipore filter paper under pressure using vacuum filtration unit. The corresponding filtrates were subjected to analysis by inductively coupled plasma-atomic emission spectrometry (ICP-