



“Gheorghe Asachi” Technical University of Iasi, Romania



---

## REMOVAL OF FLAME RETARDANTS FROM THE NON-METAL FRACTION OF THE PROCESSED WASTE PRINTED CIRCUIT BOARDS USING ORGANIC SOLVENTS AND PYROLYSIS

Amit Kumar<sup>1\*</sup>, Maria E. Holuszko<sup>1</sup>, Travis Janke<sup>2</sup>

<sup>1</sup>NBK Institute of Mining Engineering, University of British Columbia, 517-6350 Stores Road, Vancouver, BC, V6T 1Z4, Canada

<sup>2</sup>Ronin8 Technologies Limited, 6-11411 Blacksmith Place, Richmond, BC, V7A 4T7, Canada

---

### Abstract

Printed circuit boards are the most important component of any electrical and electronic device. The average metal content in waste printed circuit boards is ~30-35% whereas the rest of the material is a non-metal fraction (NMF). Metals in the waste printed circuit boards are recycled for their value whereas the NMF is mostly sent to landfills or incinerators for disposal. The circuit board laminates contain flame retardant chemicals that pose potential hazards to the environment and to public health and safety. The concentration of polybrominated diphenyl ether (PBDEs) and polychlorinated biphenyls (PCBs) reported in literature is limited to circuit boards prior to any processing, or to dust and soil near recycling centers. This paper studied the concentration of these flame retardants in the NMF and showed a concentration of 294 mg/kg for PBDEs and 3200 µg/kg for PCBs. It also showed that 90-95% of these chemicals could be extracted using organic liquids such as toluene and n-hexane: acetone (1:1 v/v) even at a larger scale. The paper also analyzed the concentration of harmful dioxins and furans, which get released during the incineration process.

**Keywords:** flame retardants, non-metal fraction, PBDEs, PCBs, printed circuit boards

*Received: May, 2019; Revised final: November, 2019; Accepted: December, 2019; Published in final edited form: June, 2020*

---

### 1. Introduction

Printed circuit boards are the most important component of any electrical and electronic device. With the growing issue of electronic waste in the world, the end-of-life management of printed circuit boards has also become a challenging issue. The printed circuit boards are the most valuable parts of electronic waste, representing approximately 40% of the total value, while comprising only 6% of the total weight (Evangelopoulos et al., 2015; Golev et al., 2016; Kumar et al., 2018). The average metal content in waste printed circuit boards is ~30-35% whereas the rest of the material is referred to as non-metal, NMF (Bizzo et al., 2014; Luda, 2011; Szałatkiewicz, 2014). Waste printed circuit boards present an economic

incentive for the recycling of valuable metals such as copper, silver, gold, and palladium.

The circuit board contains multiple layers of reinforced laminate sheets where epoxy, phenolic, and polyester are major resins and cellulose and fiberglass are major reinforcement materials. Two of the most common types of boards are FR-2 and FR-4, which use cellulose reinforcement with phenolic resins, and fiberglass reinforced with epoxy resin, respectively (Guo et al., 2009; Weil and Levchik, 2004). The FR symbolizes the flame retardant (FR) boards where various chemicals are added to the resin manufacturing process to provide flame retardancy and thermal stability, but their presence also poses a potential hazard to the environment and to public health and safety (Brigden et al., 2005).

---

\* Author to whom all correspondence should be addressed: e-mail: amit.kumar.ism@gmail.com; Phone: +1 6043799093; Fax: +1 6048225599

Organo-halogen compounds such as polychlorinated biphenyls (PCBs) and polybrominated diphenyls (PBDEs) have been widely used as flame retardant chemicals in circuit boards and other electrical components. The production of PCBs has been banned in the USA since 1977 because of their harmful health effects (ATSDR, 2014). The Environmental Protection Agency (EPA) has set a limit of 0.0005 mg of PCBs per liter of drinking water as the safe limit. Europe also banned the use of penta- and octa-BDE in 2004 and deca-BDE in 2008 (Betts, 2008). The Environmental Protection Agency (2014b) reported a maximum reference dosage (RfD) of 0.0001 mg/kg/day for BDE-47 and BDE-99, 0.0002 mg/kg/day for BDE-153, and 0.007 mg/kg/day for BDE-209.

The concentration of PBDEs in waste circuit boards has been reported in various literature sources. Guo et al. (2015) reported 15.6-317.0 mg/kg in different parts of the waste printed circuit board workshops. 14567 mg/kg for penta-BDE and 2718 mg/kg for hexa-BDE in printed circuit boards themselves have been reported by Chen et al. (2012). Yu et al. (2017) reported 1.33-16.18 mg/kg of PBDEs in circuit boards of CRT TVs and printer/copiers whereas high values in the range of 2679-3045 mg/kg are reported in different waste printed circuit boards by Zhou et al. (2013). An average of 120 mg/kg of PBDEs is reported in all wiring boards from different electronic waste (Cai et al., 2018). The total PBDEs concentration was reported to be 0.67–9.2 mg/kg-dry in surface soils and 0.1–0.35 mg/kg-dry in river sediments around an e-waste recycling site in Vietnam (Matsukami et al., 2015). The concentration of the polybrominated biphenyls (PCBs) in printed circuit boards is not reported in any literature. The PCBs concentration in the 22 tree bark samples from an e-waste recycling area in China showed a concentration of 0.112 mg/kg of dry sample (Wen et al., 2009). The

PCBs concentration in the soil near different e-waste recycling sites showed a concentration of 0.08-21.06 ng/g and 3.27 -11.66 ng/g in snails found in the nearby area (Liu et al., 2008).

Similarly, the concentration of polychlorinated dibenzo-p-dioxin and dibenzofurans (PCDD/F) and polybrominated dibenzo-p-dioxin and dibenzofurans (PBDD/F) in unheated printed circuit boards was 4.7 ng Toxic Equivalent Quotient (TEQ)/kg and 16000 ng TEQ/kg (Duan et al., 2011). The PCDD/F concentration reported by Wen et al. (2009) in the 22 tree bark samples was 1800 pg/g (19.2 pg WHO-TEQ/g). The PCDD/F concentration in the soil and snails near various e-waste recycling sites in China was 53.39 pg WHO-TEQ/g, and 75.47 pg WHO-TEQ/g, respectively (Liu et al., 2008). The PCDD/F concentration from the soil and combusted residue from the e-waste recycling site in Guiyu, China was 0.8-506 pg WHO TEQ/g in various sample sources (Leung et al., 2007).

Various researchers have used different techniques with different solvent, temperature, masses, and volumes to estimate the concentration of flame retardants, especially PBDEs (Table 1). Wang et al. (2004) showed that extraction of flame retardants is possible using supercritical carbon dioxide at 313-353 K temperature and 10-25 MPa pressure. Xiu et al. (2014) used subcritical water oxidation at temperatures of 250-300°C for the removal of HBr from the brominated flame retardants, whereas Xing and Zhang (2012) used subcritical water at 400°C for the debromination purpose.

The literature study showed that the concentration of PBDEs, PCBs and PCDD/F in the area of electronic waste and circuit boards recycling are limited to the circuit boards themselves prior to any processing. Some researchers have also reported the PBDEs concentration in dust and in the soil near the e-waste recycling center.

**Table 1.** Procedure for estimating the concentration of flame retardants

| <i>Authors</i>               | <i>Sample wt.</i>                         | <i>Reagent</i>                         | <i>Reagent volume</i> | <i>Temp.</i>    | <i>Time</i> | <i>Apparatus</i>              |
|------------------------------|---|--|-----------------------|-----------------|-------------|-------------------------------|
| Kemmlein et al. (2002)       | Air                                       | Toluene                                | -                     | -               | 4 h         | Soxhlet                       |
| Leung et al. (2008)          | 3 g                                       | Acetone:DCM                            | -                     | 65°C            | 18 h        | Soxhlet                       |
| Kolic et al. (2009)          | 5-10 g                                    | Toluene                                | -                     | -               | 12-16 h     | Soxhlet                       |
| Ilyas et al. (2011)          | 5-7 g                                     | n-Hexane:Acetone                       | -                     | -               | 60 min      | Electric shaker               |
| Wang et al. (2011)           | 1 g                                       | n-Hexane:Acetone                       | 20 mL                 | 110°C           | 20 h        | Microwave                     |
| Sun et al. (2012)            | 1 g                                       | n-Hexane:MTBE                          | 5 mL                  | -               | 20 h        | Ultrasonic bath               |
| Xing and Zhang (2012)        | Oxygen combustion bomb-ion chromatography |  |                       |                 |             |                               |
| Huang et al. (2014)          | 10 g                                      | Ethyl acetate                          | 150 mL                | -               | 48 h        | Soxhlet                       |
| Abbasi et al. (2015)         | 0.1 g                                     | Hexane:DCM                             | -                     | -               | -           | Accelerated solvent extractor |
| EPA (2015)                   | -   | Methylene chloride followed by toluene | -                     | -               | 16 h each   | Soxhlet                       |
| Matsukami et al. (2015)      | 15 g                                      | n-Hexane:Acetone followed by Toluene   | 2 mL/min              | 35°C            | 40 min      | Soxhlet                       |
| Wu et al. (2016)             | 0.3 g                                     | n-Hexane:Acetone                       | 20 mL                 | -               | -           | Microwave                     |
| Evangelopoulos et al. (2017) | 1 g                                       | Isopropanol followed by toluene        | 100 mL                | -153°C & -132°C | 6 h         | Soxhlet                       |

However, concentrations of these harmful chemicals in the NMF of the processed waste circuit boards are not reported in any literature. Kumar et al. (2018) reported a PBDEs concentration of 194 mg/kg in the NMF of processed circuit boards obtained from a local e-waste recycling facility.

The present research analyzed the concentration of PBDEs, PCBs and PCDD/F in the NMF obtained from a local recycling facility. Since most waste circuit boards are processed in some fashion to recycle metals prior to disposal, consequently, the study was carried out on the separated NMF that will most likely be used as an alternative fuel or a secondary raw material for manufacturing.

It also analyzed the extraction of brominated and chlorinated flame-retardants from the NMF using organic solvents, n-hexane: acetone (HA) mixture (1:1 by vol.) and toluene. These reagents are most widely studied chemicals for the extraction of PBDEs and PCBs and also are relatively cheaper compared to other reagents. The residue left after extraction was analyzed for the residual PBDEs, PCBs and PCDD/F content, bromine and chlorine content, loss on ignition and calorific value. The results were also compared to the residue left after a pilot-scale pyrolysis process.

## **2. Material and methods**

### *2.1. Material*

A representative sample of NMF was received from the Ronin8 Technologies Limited pilot plant located in Richmond, British Columbia, representing an actual NMF generated at an industrial scale. The plant processed a mixture of FR-2 and FR-4 circuit boards obtained from computers, printers, televisions, servers, cell phones, and other household electronics using gravity separation (wet concentration table) to separate metals from non-metals. A representative sample of 25 kg NMF was sampled using the cone and quarter method from a 750-kg bulk bag and was oven dried at 60°C for 96 hours to remove any residual moisture.

Approximately 250 kg of NMF sample from the Ronin8 plant operation was sent to a third-party for the pyrolysis process. The reactor temperature was maintained at 600°C to 800°C during the process with a feed rate of ~43 kg/h. Approximately 120 kg (~48% of initial mass) of char residue was obtained after the process that was sent back to the Ronin8 facility. A subsample of ~25 kg was obtained from the char residue by the cone and quarter method for subsequent analysis.

### *2.2. Particle size analysis*

A 300 g subsample was obtained from the dry NMF from the 25 kg batch and collected for the particle size distribution analysis using screening for 20 minutes. A Ro-Tap machine manufactured by W.S.

Tyler, model RX-29, and was used for this analysis. The size distribution was plotted, and 80% and 50% cumulative passing size were determined.

### *2.3. Soxhlet extraction*

Approximately 100 grams of subsample was obtained from the dried NMF for each Soxhlet extraction test. The extraction was performed in 30 to 35-gram batches due to the volume limitation of the extraction unit. The sample was weighed and placed in a cellulose thimble. The thimble was placed in the extraction unit. Approximately 200 ml of the desired organic solvent was placed in the distillation/boiling flask. The set up was heated to the boiling point of the solvent with a condenser attached to the extraction unit. The extraction was carried out for 24 hours. After 24 hours, the fresh solvent was added to the flask to make up for the solvent loss and the extraction was continued with the next 30 to 35-gram batch. A total of 100 grams of samples were processed in three separate batches. After extraction, the solvent in the flask was transferred to a beaker and left in the fume hood for the solvent to evaporate, and the effluent left in the beaker was weighed. The process was repeated on the solid residue for another 24 hours to extract any residual chemical. The final residue was homogenized and was used for subsequent analysis.

### *2.4. Polybrominated diphenyl ether (PBDEs) analysis*

Approximately 20 g samples were obtained from the as-received NMF, pyrolysis and extraction residue and sent to an external laboratory for PBDEs analysis. The laboratory only reported the concentration of 17 congeners of PBDEs. The PBDEs extraction was performed using standard EPA 3541 procedure (EPA, 1994a) followed by EPA 8270D (EPA, 2014a) for analysis.

### *2.5. Polychlorinated biphenyls (PCBs) analysis*

Approximately 20 grams of representative samples from the as-received NMF, pyrolysis and extraction residue were prepared and sent to an external laboratory for PCBs analysis. The laboratory reported the concentration of all 209 congeners of PCBs. The analysis was performed using the standard EPA 1668C method (EPA, 2010).

### *2.6. Polychlorinated dibenzodioxin and dibenzofurans (PCDD/F) analysis*

Approximately 30 grams of representative samples from the as-received NMF, pyrolysis and extraction residue were prepared and sent to an external laboratory for PCDD/F analysis. The test was performed using the standard EPA 1613B method (EPA, 1994c). It provided the concentration of all homologs of PCDD from tetra- to octa-chlorinated dioxins and furans.

### 2.7. Chlorine and bromine content analysis

The chlorine and bromine concentration were determined using standard EPA 5050 (EPA, 1994b) procedure followed by EPA 9056 to determine inorganic halogen anions using ion chromatography (EPA, 2007) by an external laboratory.

### 2.8. Loss on ignition (LOI) analysis

Approximately 1g sample was heated in the presence of air from room temperature to 500°C in 30 mins (150°C/min) and then to 750°C in the next 30 mins (8°C/min). The sample was left at 750°C for another 3 hours for complete combustion. The residual mass was used to estimate the loss on ignition. This test was performed in triplicates and the average value was reported. To ensure the complete removal of the organic materials, the procedure for the coal ash content analysis, as defined by American Society for Testing and Materials (ASTM) D3174 – 12, was used (ASTM International, 2012).

### 2.9. Calorific value determination

The calorific value testing was performed using a Parr 6100 Calorimeter and a Parr 4510 nickel alloy wire following ASTM D5865 guidelines (ASTM International, 2013). Approximately 5 grams of subsamples were obtained for testing and was sent to an external laboratory.

## 3. Results and discussion

The NMF used for this research represented an actual NMF generated at an industrial scale and was obtained from a 750 kg bulk bag. It showed that most of the particle ranged from 300-600 µm size whereas only 0.5% of the particles were coarser than 1180 µm

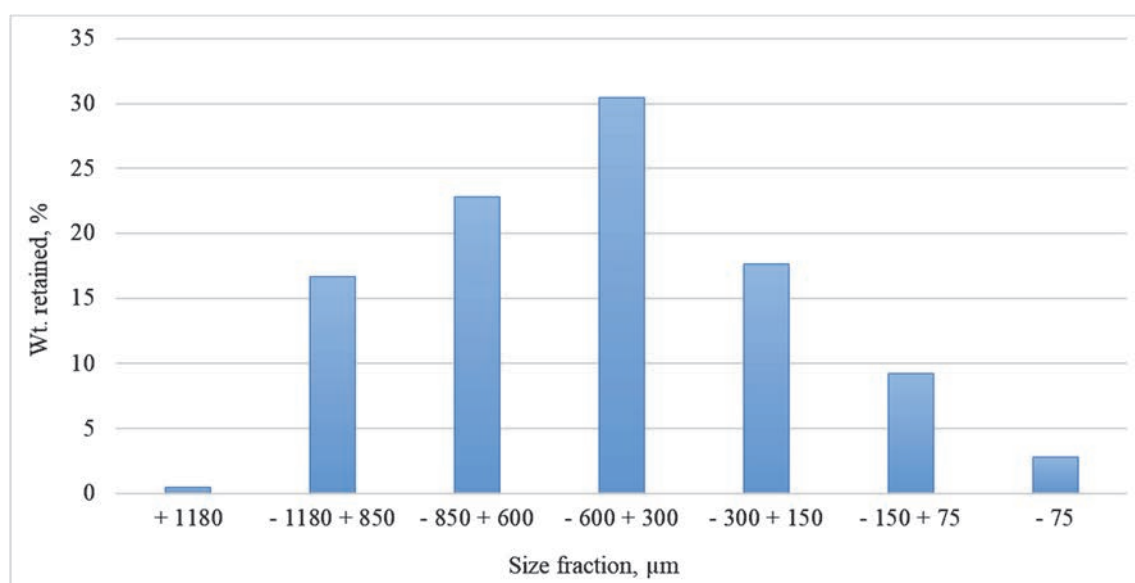
(Fig. 1). The 80% passing and 50% passing sizes were approximately 820 µm and 500 µm, respectively.

The as-received dry NMF was processed in a Soxhlet extraction unit (SX) to remove flame retardants in two 24-hour stages. The mass/yield of effluent extracted is shown in Table 2. The result showed that most of the extraction was completed within 24 hours and both reagents showed similar recovery. Kiguchi et al. (2006) also showed that PCBs have similar solubility and extraction for both solvents for soil and sediment samples, however, a time-based extraction test would be required to establish the optimum time and the rate of extraction. Some of the research listed in Table 1 also used these solvents with small samples for the characterization of flame retardants. The test showed that the process can be scaled up with larger sample masses.

**Table 2.** Percentage of extracted effluent from NMF using different solvents

| Reagents              | Extracted effluent, % |         |       |
|-----------------------|-----------------------|---------|-------|
|                       | Stage 1               | Stage 2 | Total |
| n-hexane:acetone (HA) | 2.67                  | 0.34    | 3.01  |
| Toluene               | 2.72                  | 0.34    | 3.06  |

To evaluate the degree of extraction of flame retardants, all residue samples were analysed for PBDEs, PCBs, and PCDD/F content. The results of the PBDEs content analysis is shown in Table 3 and an overall reduction in the PBDEs concentration is shown in Fig. 2. The EPA method 3541 uses n-hexane:acetone (1:1 v/v) for the extraction of PBDEs in a Soxhlet extractor using 10 g samples (EPA, 1994a). Since the HA residue was obtained in a similar manner, it is expected to have low PBDEs concentration, as evident in Table 3. The results also showed that toluene is capable of extracting PBDEs from the sample at a higher extent.



**Fig. 1.** Particle size distribution of the as-received dry NMF

The test results showed that deca-BDE is the major contributor to the total PBDEs content in the NMF, followed by tetra-, penta- and hexa- BDE. Results showed that the concentration of the total PBDEs in NMF was 294 mg/kg, compared to 1.33 – 14567 mg/kg reported for different circuit boards in various literature (Cai et al., 2018; Chen et al., 2012; Jie Guo et al., 2015; Yu et al., 2017; Zhou et al., 2013). Since circuit boards are most likely to be processed in some manner before any disposal, it is important to establish the concentration in a representative NMF.

The pyrolysis process was most effective for the removal of PBDEs from the sample due to the high-temperature effect, whereas the Soxhlet extraction removed 92-98% of the total PBDEs (Fig. 2). It suggests that a batch or continuous extraction

process can be used for the removal of harmful PBDEs from the NMF prior to disposal without going through high temperature and energy-intensive pyrolysis process.

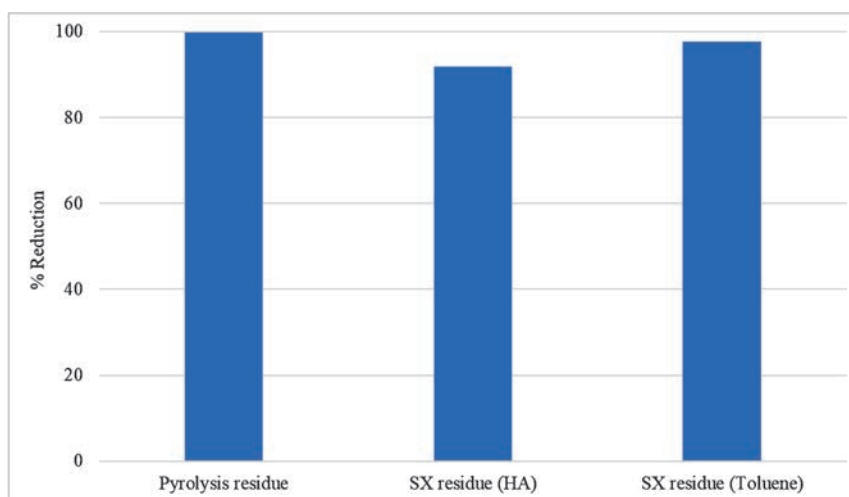
However, a cost study would be required to make an economic decision and a study is needed to test the process at a pilot scale. The other harmful flame-retardants added to circuit boards are PCBs. The PCBs content of the as-received NMF and all residues were also analyzed, and the results are shown in Table 4 and Fig. 3. The EPA method 1668C was adopted to analyze the PCBs concentration which uses toluene as the solvent (EPA, 2010), suggesting that the toluene residue in this test should have negligible PCBs concentration compared to NMF, as evident in Table 4.

**Table 3.** PBDEs content (mg/kg) of as-received NMF and different residues

| Type         | NMF, as received | Pyrolysis residue | HA residue   | Toluene residue |
|--------------|------------------|-------------------|--------------|-----------------|
| Tri-BDE      | 15.60            | 0.02              | 0.01         | 0.03            |
| Tetra-BDE    | 71.70            | 0.01              | 0.02         | 0.10            |
| Penta-BDE    | 54.80            | 0.00              | 0.02         | 0.06            |
| Hexa-BDE     | 16.35            | 0.00              | 0.01         | 0.02            |
| Hepta-BDE    | 5.69             | 0.00              | 0.02         | 0.00            |
| Octa-BDE     | 0.73             | 0.00              | 0.02         | 0.00            |
| Nona-BDE     | 9.00             | 0.00              | 0.95         | 0.10            |
| Deca-BDE     | 120.00           | 0.36              | 23.00        | 6.50            |
| <b>Total</b> | <b>293.87</b>    | <b>0.39</b>       | <b>24.04</b> | <b>6.81</b>     |

**Table 4.** PCBs content ( $\mu\text{g}/\text{kg}$ ) of as-received NMF and different residues

| Type         | NMF, as-received | Pyrolysis residue | HA residue  | Toluene residue |
|--------------|------------------|-------------------|-------------|-----------------|
| Mono-CB      | 16.0             | 10.4              | 0.2         | 0.5             |
| Di-CB        | 284.0            | 15.7              | 3.0         | 8.1             |
| Tri-CB       | 1200.0           | 38.7              | 10.4        | 25.3            |
| Tetra-CB     | 988.0            | 21.6              | 5.1         | 11.5            |
| Penta-CB     | 342.0            | 6.8               | 2.1         | 6.0             |
| Hexa-CB      | 287.0            | 2.5               | 1.5         | 2.8             |
| Hepta-CB     | 59.5             | 0.2               | 0.2         | 0.6             |
| Octa-CB      | 15.4             | 0.0               | 0.0         | 0.1             |
| Nona-CB      | 1.4              | 0.0               | 0.0         | 0.0             |
| Deca-CB      | 0.2              | 0.0               | 0.0         | 0.0             |
| <b>Total</b> | <b>3193.6</b>    | <b>96.0</b>       | <b>22.7</b> | <b>55.0</b>     |



**Fig. 2.** Percent reduction in the PBDEs concentration after pyrolysis and Soxhlet extraction

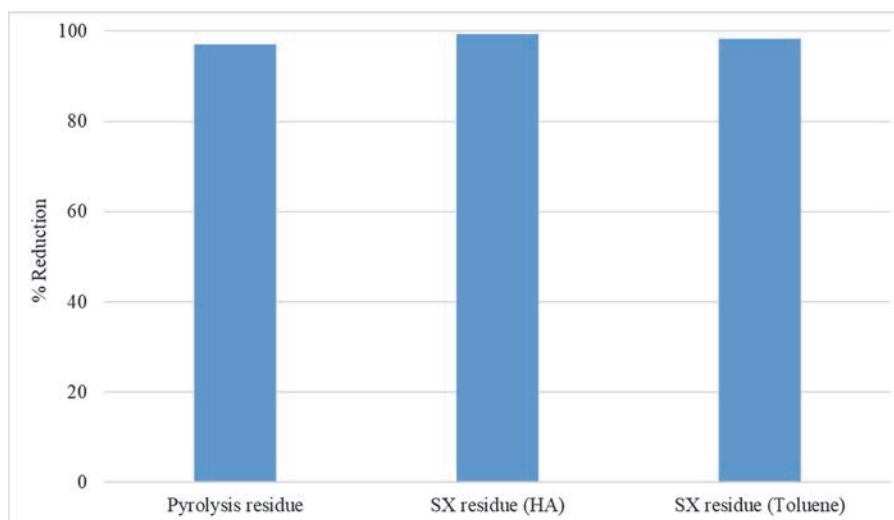


Fig. 3. Percent reduction in the PCBs concentration after pyrolysis and Soxhlet extraction

The results also showed that tri- and tetra-CBs are the major contributors to the total PCBs concentration, followed by penta-, hexa-, and di-CBs. The nona- and deca-CBs have a very low concentration in the sample. It also showed that even after the production ban in 1977, circuit boards derived from electronic waste streams still have a significant amount of PCBs associated with them, mostly due to old electronic and electrical appliances that are still found in the waste stream. This also establishes the total concentration of PCBs in NMF to be  $\sim 3200$   $\mu\text{g}/\text{kg}$ , which is not reported in any other literature. In the case of pyrolysis, some of the PCBs might have melted and coated the char residue, thus increasing their final concentration.

The results showed that the n-hexane:acetone mixture is the most effective solvent for the extraction of PCBs from samples and had almost similar results to toluene. The overall extraction for all the residue samples was over 95% suggesting that all the studied processes also remove most of the harmful PCBs. Kiguchi et al. (2006) also showed an almost 100% extraction of PCBs from soil and sediment samples using these solvents.

The production and use of PBDEs and PCBs have been banned in the USA and Europe but results in Tables 3 and 4 showed that the analyzed NMF contains a significant amount of PBDEs and PCBs. The NMF sample used in this study was produced from waste printed circuit boards processed by the recycling company Ronin8 Technologies Limited which was collected by the provincial programs such as Electronic product recycling association, Encorp pacific, Return-it and some other local dismantling facilities. However, these programs don't record the type, model and year of the collected e-waste which makes it impossible to track the source and production year of the processed printed circuit boards.

Most of the e-waste processed in Canada is collected from Canadian households but the e-waste could have been manufactured in countries like China

or India where the PBDEs and PCBs might still be in use. Many of the Canadians are immigrants that suggested that some of the e-waste processed might have been manufactured outside Canada and arrived in Canada with these immigrants. The high levels of these chemicals in the NMF suggests that the processed waste printed might have been originated/manufactured in countries where PBDEs and PCBs are still used.

The presence of the PBDEs and PCBs in the NMF posed the risk of release of toxic PCDD/F with incineration, hence it is necessary to establish the concentration of these substances in the NMF. The as-received NMF and all residues were analyzed for the PCDD/F content to study the possible emission of harmful substances during incineration. The results from the PCDD/F analysis is shown in Table 5 and Fig. 4. The value for the tetra-CDF for pyrolysis residue was significantly higher (311  $\text{pg}/\text{g}$ ) than expected which may have been due to an analysis error. A duplicate study will be required to confirm this behavior. The tetra-CDF concentration in the pyrolysis residue was not considered while estimating the total reduction in PCDD/F after pyrolysis.

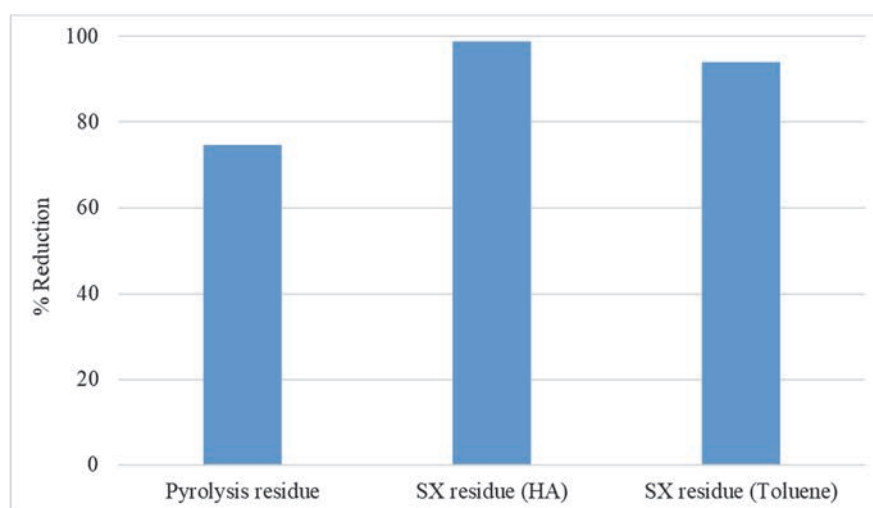
Since the EPA method 1613 used for the analysis of PCDD/F uses toluene as the extraction solvent (EPA, 1994c), it is expected to see a similar trend as to the PCBs concentrations, as can be seen in Table 5. The Soxhlet extraction process residue had a very low concentration of PCDD/F, suggesting that the extraction residue can be used for incineration. However, the analysis of the fly ash (incineration residue) is needed to estimate the residual heavy metal concentrations. The toxicity equivalency (TEQ) is a tool to assess cumulative toxicity of a mixture of PCDD/F and PCBs. Toxicity levels (TEFs) for all compounds are assessed relative to the toxicity of 2,3,7,8-tetrachlorodibenzo-p-dioxin (tetra-CDD), which is the most toxic dioxin. TEQ represents the product of the concentrations of individual congeners and their respective TEFs.

**Table 5.** PCDD/F content (pg/g) of as-received NMF and different residues

| Type         | NMF, as-received | Pyrolysis residue | HA residue | Toluene residue |
|--------------|------------------|-------------------|------------|-----------------|
| Tetra-CDD    | 12.9             | 17.3              | <0.24      | <0.090          |
| Penta-CDD    | 11.7             | 7.2               | <0.083     | 0.9             |
| Hexa-CDD     | 6.4              | 4.8               | <0.14      | 0.3             |
| Hepta-CDD    | 7.1              | 1.6               | <0.20      | 0.8             |
| Octa-CDD     | 128.0            | 0.8               | 4.0        | 20.3            |
| Tetra-CDF    | 55.6             | -                 | <0.15      | 1.0             |
| Penta-CDF    | 82.3             | 63.5              | <0.077     | 0.2             |
| Hexa-CDF     | 79.4             | 12.4              | <0.11      | 0.7             |
| Hepta-CDF    | 21.6             | 1.8               | <0.12      | <0.22           |
| Octa-CDF     | 25.8             | 0.5               | 0.9        | 2.3             |
| <b>Total</b> | <b>430.8</b>     | <b>109.8</b>      | <b>4.9</b> | <b>26.3</b>     |

**Table 6.** WHO toxic equivalency (TEQ) for as-received NMF and all residues in pg/g

| Type   | Level | NMF, as-received | Pyrolysis residue | HA residue | Toluene residue |
|--------|-------|------------------|-------------------|------------|-----------------|
| PCBs   | Lower | 8.5              | 0.0               | 0.0        | 0.0             |
|        | Mid   | 11.2             | 2.6               | 2.4        | 2.2             |
|        | Upper | 13.9             | 5.3               | 4.8        | 4.5             |
| PCDD/F | Lower | 2.9              | 2.2               | 0.0        | 0.0             |
|        | Mid   | 3.1              | 2.2               | 0.2        | 0.2             |
|        | Upper | 3.2              | 2.2               | 0.5        | 0.2             |

**Fig. 4.** Percent reduction in the PCDD/F concentration after pyrolysis and Soxhlet extraction

Greene et al. (2003) have suggested that maintaining a lifetime average daily bodily dosage below 1-10 pg/kg/day (TCDD TEQ) is required to eliminate the risk of cancer. The lower limit is calculated by substituting zero (0) for any non-detectable compound whereas the upper bound represent the worst-case scenario where the detection limit is used for the non-detectable compounds (Johnston, 2016). The TEQ for PCBs and PCDD/F is shown in Table 6. Comparing the limits, the results showed that the Soxhlet extraction could achieve a reduction in the TEQ value for all the cases similar to the pyrolysis process.

The as-received NMF and all residues were also analysed for the total chlorine and bromine concentration to evaluate the effectiveness of the used process in the removal of total chlorine and bromine. Reduction of chlorine to below 0.15% is necessary if

the NMF fraction is to be used as an alternative fuel source. The results from the test are shown in Table 7. For comparison, Duan et al. (2011) reported a chlorine and bromine concentration of 0.02% and 5.99% in FR-4 NMF and 0.07% and 9.99% in NMF from the circuit boards in the printer using XRF. The sample used for this test was a more representative sample often found at any recycling facility and the test was performed using EPA standards, hence it represents a more realistic scenario.

EPA flame-retardants in the printed circuit board's handbook (2015) showed that standard epoxies used in the laminate production contain 0.1-0.25 % chlorine. This chlorine would not be completely removed during the pyrolysis process and would not be extracted during the Soxhlet extraction process either. Hence, the residues still have a significant amount of chlorine content left.



**Table 7.** Chlorine and bromine concentration in as-received NMF and different residues

| Sample id         | Chlorine, % | Bromine, % |
|-------------------|-------------|------------|
| NMF, as-received  | 0.33        | 2.69       |
| Pyrolysis residue | 0.13        | 1.72       |
| HA residue        | 0.22        | 2.68       |
| Toluene residue   | 0.23        | 2.71       |

**Table 8.** Loss on ignition and calorific value of as-received NMF and different residues

| Sample id         | LOI, % | Calorific value, GJ/t |
|-------------------|--------|-----------------------|
| NMF, as-received  | 63.5   | 16.3                  |
| Pyrolysis residue | 40.7   | 11.9                  |
| HA residue        | 57.6   | 15.4                  |
| Toluene residue   | 59.2   | 15.2                  |

In the case of bromine, the pyrolysis process caused the greatest decrease in the concentration whereas other extraction processes have not reduced the bromine concentration significantly. It suggests that the PBDEs is not the major bromine species in the sample. Other flame retardants such as Tetrabromobisphenol A (TBBPA), brominated cyclohydrocarbons and polybrominated biphenyls (PBB), might also be present in the sample which don't get released in the tested processes and would be responsible for the high bromine concentration. TBBPA is widely used in electronic equipment, added in reactive mode and thus is less likely to escape during the process used for testing in this study (Birnbaum and Bergman, 2010), which would justify the higher concentration of bromine in all samples. Once the TBBPA is chemically bound, the finished epoxy resin typically contains about 18 to 21 % bromine (Weil and Levchik, 2004). A test on the pyrolysis of TBBPA in the paper laminated printed circuit boards showed that most of the bromine is released in the form of hydrogen bromide (HBr) and approximately 1.8% was left in the residue (EPA, 2015). The TBBPA content analysis of all samples would be required for confirming this hypothesis.

Finally, the as-received NMF, Soxhlet extraction residues and pyrolysis residues were tested for the loss on ignition and the calorific value. The results in Table 8 showed that the LOI for the pyrolysis residue has dropped significantly due to the removal of ~52% of the organic materials (section 2.1.2) whereas the LOI for the SX residue remained unchanged compared to the received NMF due to a low mass removal (3-5%) during the extraction process. The calorific value of the sample had a similar trend to the LOI. This shows that the Soxhlet extraction can remove the flame-retardant materials without reducing the energy content of the NMF significantly, which is necessary if the NMF is to be used as an alternative source of fuel for energy recovery. However, a cost study would be required to make an economic decision and a study program is needed to test the process on a pilot scale.

#### 4. Conclusions

This paper addressed the evaluation of the concentration of harmful flame-retardants such as PBDEs and PCBs in the rejected NMF of processed printed circuit boards from a representative sample, which was obtained from an industrial e-waste recycling facility. These estimates are currently only available for unprocessed individual circuit boards. The test work showed a PBDEs concentration of 294 mg/kg and PCBs concentration of 3200 µg/g in NMF. It also showed that the concentration of harmful dioxins and furans that would be released during the incineration process is over 430 pg/g.

The results indicated that organic solvents such as toluene and n-hexane:acetone are able to extract these chemicals at a larger scale in an efficient manner and can be used as an alternative to a high-energy, intensive pyrolysis process. However, a cost study would be required to make an economic decision and a test program is needed to test the process on a pilot scale. The test work also showed that even pyrolysis is not an efficient method to remove all bromine and chlorine for the NMF of processed waste printed circuit boards.

#### Acknowledgements

The author acknowledges Ronin8 Technologies Limited (Richmond, British Columbia) for their financial support as well as for providing samples, expert advice, and other necessary technical details. The author also acknowledges the Canadian funding agency MITACS Inc. for their financial assistance and ALS Environmental (Burnaby, British Columbia) for performing the external laboratory analysis.

#### References

- Abbasi G., Buser A.M., Soehl A., Murray M.W., Diamond M.L., (2015), Stocks and flows of PBDEs in products from use to waste in the U.S. and Canada from 1970 to 2020, *Environmental Science and Technology*, **49**, 1521-1528.
- ATSDR (2014), (2014), *Polychlorinated Biphenyls - ToxFAQsTM*, Agency for Toxic Substances and Disease Registry, Atlanta, Georgia, On line at: <https://www.atsdr.cdc.gov/toxfaqs/tfacts17.pdf>.
- ASTM International, (2012), D3174 - 12: Standard Test Method for Ash in the Analysis Sample of Coal and Coke from Coal, West Conshohocken, PA, On line at: <https://compass.astm.org/download/D3174.28556.pdf>
- ASTM International, (2013), D5865 - 13: Standard Test Method for Gross Calorific Value of Coal and Coke, West Conshohocken, PA, On line at: <https://compass.astm.org/download/D5865.3397.pdf>.
- Betts K.S., (2008), New thinking on flame retardants, *Environmental Health Perspectives*, **116**, A210-213.
- Birnbaum L.S., Bergman Å., (2010), Brominated and chlorinated flame retardants: The San Antonio Statement, *Environmental Health Perspectives*, **118**, 514-515.
- Bizzo W., Figueiredo R., de Andrade V., (2014), Characterization of printed circuit boards for metal and



- energy recovery after milling and mechanical separation, *Materials*, **7**, 4555-4566.
- Brigden K., Labunska I., Santillo D., Allsopp M., (2005), *Recycling of electronic wastes in China & India: Workplace & environmental contamination*, University of Exeter, Exeter, UK, On line at: <http://www.greenpeace.org/international/PageFiles/25134/recycling-of-electronic-waste.pdf>.
- Cai C., Yu S., Liu Y., Tao S., Liu W., (2018), PBDE emission from E-wastes during the pyrolytic process: Emission factor, compositional profile, size distribution, and gas-particle partitioning, *Environmental Pollution*, **235**, 419-428.
- Chen Y., Li J., Chen L., Chen S., Diao W., (2012), Brominated flame retardants (BFRs) in waste electrical and electronic equipment (WEEE) plastics and printed circuit boards (PCBs), *Procedia Environmental Sciences*, **16**, 552-559.
- Duan H., Li J., Liu Y., Yamazaki N., Jiang W., (2011), Characterization and inventory of PCDD/Fs and PBDD/Fs emissions from the incineration of waste printed circuit board, *Environmental Science and Technology*, **45**, 6322-6328.
- EPA, (1994a), Automated Soxhlet Extraction, Washington, D.C., On line at: <https://www.epa.gov/sites/production/files/2015-06/documents/epa-3541.pdf>.
- EPA, (1994b), Bomb preparation method for solid waste, Washington, D.C., On line at: <https://www.epa.gov/sites/production/files/2015-12/documents/5050.pdf>.
- EPA, (1994c), Tetra- through octa-chlorinated dioxins and furans by isotope dilution HRGC/HRMS, Washington, D.C., On line at: [http://www.well-labs.com/docs/epa\\_method\\_1613b\\_1994.pdf](http://www.well-labs.com/docs/epa_method_1613b_1994.pdf).
- EPA, (2007), Determination of inorganic anions by ion chromatography, Washington, D.C., On line at: <https://www.epa.gov/sites/production/files/2015-12/documents/9056a.pdf>.
- EPA, (2010), Chlorinated biphenyl congeners in water, soil, sediment, biosolids, and tissue by HRGC/HRMS, Washington, D.C., On line at: [https://well-labs.com/docs/epa\\_method\\_1668c\\_2010.pdf](https://well-labs.com/docs/epa_method_1668c_2010.pdf).
- EPA, (2014a), Semi-volatile organic compounds by gas chromatography/mass spectrometry, Washington, D.C., On line at: <https://www.epa.gov/sites/production/files/2015-12/documents/8270d.pdf>.
- EPA, (2014b), Technical fact sheet - polybrominated diphenyl ethers (PBDEs) and polybrominated biphenyls (PBBs), Washington, D.C., On line at: [https://www.epa.gov/sites/production/files/2014-03/documents/ffirofactsheet\\_contaminant\\_perchlorate\\_january2014\\_final\\_0.pdf](https://www.epa.gov/sites/production/files/2014-03/documents/ffirofactsheet_contaminant_perchlorate_january2014_final_0.pdf).
- EPA, (2015), Flame retardants in printed circuit boards, Washington, D.C., On line at: [https://www.epa.gov/sites/production/files/2015-08/documents/pcb\\_ch6.pdf](https://www.epa.gov/sites/production/files/2015-08/documents/pcb_ch6.pdf).
- Evangelopoulos P., Arato S., Persson H., Kantarelis E., Yang W., (2017), *Brominated Flame Retardants (BFRs) Reduction in Plastics from Electric and Electronic Equipment Waste (WEEE) Fraction as a Treatment Method Prior to Pyrolysis*, 16th Inter. Waste Management and Landfill Symp., Cagliari, Italy.
- Evangelopoulos P., Kantarelis E., Yang W., (2015), Investigation of the thermal decomposition of printed circuit boards (PCBs) via thermogravimetric analysis (TGA) and analytical pyrolysis (Py-GC/MS), *Journal of Analytical and Applied Pyrolysis*, **115**, 337-343.
- Golev A., Schmeda-Lopez D.R., Smart S.K., Corder G.D., McFarland E.W., (2016), Where next on e-waste in Australia?, *Waste Management*, **58**, 348-358.
- Greene J., Hays S., Paustenbach D., (2003), Basis for a proposed reference dose (RfD) for dioxin of 1-10 pg/kg-day: A weight of evidence evaluation of the human and animal studies, *Journal of Toxicology and Environmental Health, Part B*, **6**, 115-159.
- Guo J., Zhang R., Xu Z., (2015), PBDEs emission from waste printed wiring boards during thermal process, *Environmental Science and Technology*, **49**, 2716-2723.
- Guo J., Guo J., Xu Z., (2009), Recycling of non-metallic fractions from waste printed circuit boards: a review, *Journal of Hazardous Materials*, **168**, 567-590.
- Huang D.Y., Zhao H.Q., Liu C.P., Sun C.X., (2014), Characteristics, sources, and transport of tetrabromobisphenol A and bisphenol A in soils from a typical e-waste recycling area in South China, *Environmental Science and Pollution Research*, **21**, 5818-5826.
- Ilyas M., Sudaryanto A., Setiawan I.E., Riyadi A.S., Isobe T., Ogawa S., Takahashi S., Tanabe S., (2011), Characterization of polychlorinated biphenyls and brominated flame retardants in surface soils from Surabaya, Indonesia, *Chemosphere*, **83**, 783-791.
- Johnston J., (2016), *Dioxins, Furans, and Dioxin-Like PCB Congeners: Ecological Risk Calculation Methodology for Upland Soil*, Lacey, WA, On line at: <https://fortress.wa.gov/ecy/publications/documents/1609044.pdf>.
- Kemmlin S., Hahn O., Jann O., Kalus S., Stolle D., (2002), *Emission of Flame Retardants from Consumer Products and Building Materials*, Federal Institute for Materials Research and Testing (BAM), Berlin (Germany); Federal Environment Agency, Berlin (Germany), On line: <http://hdl.handle.net/10068/198540>
- Kiguchi O., Kobayashi T., Saitoh K., Ogawa N., (2006), Effects of extraction solvents on the extraction efficiencies of polychlorinated dibenzo-p-dioxins and dibenzofurans, and polychlorinated biphenyls in reference materials, *International Journal of the Society of Materials Engineering for Resources*, **13**, 81-85.
- Kolic T.M., Shen L., MacPherson K., Faye L., Gobran T., Helm P.A., Marvin C.H., Arsenault G., Reiner E.J., (2009), The analysis of halogenated flame retardants by GC-HRMS in environmental samples, *Journal of Chromatographic Science*, **47**, 83-91.
- Kumar A., Holuszko M.E., Janke T., (2018), Characterization of the non-metal fraction of the processed waste printed circuit boards, *Waste Management*, **75**, 94-102.
- Leung A.O.W., Zheng J.S., Wong M.H., (2008), PBDEs in dust from printed circuit board recycling at Ane-waste hotspot in Southeastern China, *Organohalogen Compounds*, **70**, 174-177.
- Leung A.O.W., Luksemburg W.J., Wong A.S., Wong M.H., (2007), Spatial distribution of polybrominated diphenyl ethers and polychlorinated dibenzo-p-dioxins and dibenzofurans in soil and combusted residue at Guiyu, an electronic waste recycling site in Southeast China, *Environmental Science and Technology*, **41**, 2730-2737.
- Liu H., Zhou Q., Wang Y., Zhang Q., Cai Z., Jiang G., (2008), E-waste recycling induced polybrominated diphenyl ethers, polychlorinated biphenyls, polychlorinated dibenzo-p-dioxins and dibenzo-furans

- pollution in the ambient environment, *Environment International*, **34**, 67-72.
- Luda M.P., (2011), *Recycling of Printed Circuit Boards*, In: *Integrated Waste Management - Volume II*, Kumar S. (Ed.), Intech, London, UK, 285-298, On line at: [http://cdn.intechopen.com/pdfs/18491/InTech-Recycling\\_of\\_printed\\_circuit\\_boards.pdf](http://cdn.intechopen.com/pdfs/18491/InTech-Recycling_of_printed_circuit_boards.pdf).
- Matsukami H., Tue N.M., Suzuki G., Someya M., Tuyen L.H., Viet P.H., Takahashi S., Tanabe S., Takigami H., (2015), Flame retardant emission from e-waste recycling operation in northern Vietnam: Environmental occurrence of emerging organophosphorus esters used as alternatives for PBDEs, *Science of the Total Environment*, **514**, 492-499.
- Sun J., Liu J., Liu Q., Qu G., Ruan T., Jiang G., (2012), Sample preparation method for the speciation of polybrominated diphenyl ethers and their methoxylated and hydroxylated analogues in diverse environmental matrices, *Talanta*, **88**, 669-676.
- Szałatkiewicz J., (2014), Metals content in printed circuit board waste, *Polish Journal of Environmental Studies*, **23**, 2365-2369.
- Wang H., Hirahara M., Goto M., Hirose T., (2004), Extraction of flame retardants from electronic printed circuit board by supercritical carbon dioxide, *The Journal of Supercritical Fluids*, **29**, 251-256.
- Wang J., Lin Z., Lin K., Wang C., Zhang W., Cui C., Jin J., Dong Q., Huang C., (2011), Polybrominated diphenyl ethers in water, sediment, soil, and biological samples from different industrial areas in Zhejiang, China, *Journal of Hazardous Materials*, **197**, 211-219.
- Weil E.D., Levchik S., (2004), A review of current flame-retardant systems for epoxy resins, *Journal of Fire Sciences*, **22**, 25-40.
- Wen S., Yang F., Li J.G., Gong Y., Zhang X.L., Hui Y., Wu Y.N., Zhao Y.F., Xu Y., (2009), Polychlorinated dibenzo-p-dioxin and dibenzofurans (PCDD/Fs), polybrominated diphenyl ethers (PBDEs), and polychlorinated biphenyls (PCBs) monitored by tree bark in an e-waste recycling area, *Chemosphere*, **74**, 981-987.
- Wu Y., Li Y., Kang D., Wang J., Zhang Y., Du D., Pan B., Lin Z., Hunag C., Dong Q., (2016), Tetrabromobisphenol A and heavy metal exposure via dust ingestion in an e-waste recycling region in Southeast China, *Science of the Total Environment*, **541**, 356-364.
- Xing M., Zhang F., (2012), A novel process for detoxification of BERs in waste PCBs, *Procedia Environmental Sciences*, **16**, 491-494.
- Xiu F.R., Qi Y., Zhang F.S., (2014), Co-treatment of waste printed circuit boards and polyvinyl chloride by subcritical water oxidation: Removal of brominated flame retardants and recovery of Cu and Pb, *Chemical Engineering Journal*, **237**, 242-249.
- Yu D., Duan H., Song Q., Liu Y., Li Y., Li J., Shen W., Luo J., Wang J., (2017), Characterization of brominated flame retardants from e-waste components in China, *Waste Management*, **68**, 498-507.
- Zhou X., Guo J., Lin K., Huang K., Deng J., (2013), Leaching characteristics of heavy metals and brominated flame retardants from waste printed circuit boards, *Journal of Hazardous Materials*, **246-247**, 96-102.