Published in final edited form as:

Waste Dispos Sustain Energy. 2019 ; 1(1): 79–89. doi:10.1007/s42768-019-00002-2.

Polybrominated Diphenylethers (PBDEs) in ambient air samples at the electronic waste (e-waste) reclamation site

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Abstract

Polybrominated Diphenylethers (PBDEs) were used as flame-retardants in various building materials, plastic and other polymers, airplanes, electronics etc. All or some of their congeners have been already banned in many countries, due to their persistency and adverse health effects. In this study, we are focusing on the e-wastes as a source of emission of PBDEs in ambient air during reclamation processes.

The ambient air particulate matter (PM) samples were collected at and near e-waste reclamation site in Bangkok, Thailand. Results showed the presence of various homologues viz: tri, tetra, penta, hexa, and hepta-PBDEs on both PM_{2.5} and Total Suspended Particle (TSP) samples. The comparison of samples as a function of distance from reclamation site indicated elevated levels of PBDEs in the close proximity to e-waste site. Interestingly, a shift in the congener pattern was observed with lower brominated PBDEs being more prevalent on nearby off-site samples as compared to the PM collected at the e-waste site. The total penta-PBDEs concentration is about double on e-waste site PM_{2.5} compared to control site samples. For TSP, tetra, penta, and hepta-PBDEs congeners are at higher concentrations at e-waste sites and its vicinity compared to reference sites. Overall, a clear trend can be observed indicating a debromination of PBDEs to more toxic tri and tetra congeners during reclamation process and PBDEs are being translocated from treated materials to ambient air PM. BDE 30 congener is identified as a specific marker of thermal reclamation processes of e-wastes as a most stable degradation product.

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This work indicates potential hazards related to the reclamation of e-wastes and remediation of sites containing PBDEs. In particular, thermal treatment methods can lead to congener transformation and increased emissions of more toxic lower-brominated congeners.

1. Introduction

Polybrominated Diphenylethers (PBDEs) are synthetic compounds having flame-retardant properties and applied in various products starting in ~early 1970^{1, 2} to meet fire resistance codes such as California Technical Bulletin 117.³ They can be found in many household materials like plastics and polymers (mainly polyurethane foam), electric and electronic devices (circuit boards, electrical insulation), rubber, textiles etc. and, in many other fields. Over time, it has been proven that PBDEs partition from the consumer products matrix to air and water. Due to their environmental persistency and toxicity, tetra to deca-PBDEs are listed on ANEX A of Stockholm convention.⁴

PBDEs' long lifetime in the environment results in ubiquitous presence in almost any environmental media such as sediment,⁵ water,⁶ in house dust and clothes dryer lint,⁷ and through bioaccumulation and biomagnification in various food products.⁸⁻¹² They have also been detected in the human specimens such as breast milk,¹²⁻¹⁵ and in human blood.^{15, 16}

As of 2001, PBDEs' global market was dominated by decabromo congener (83 %), with penta and octa brominated congeners occupying 11.1% and 5.6 % of the market, respectively.¹⁷ Since 2004, production of penta and octa PBDEs seized in the U.S. and was banned in Europe. Since 2006 many states have prohibited use of penta and octa PBDEs. According to 2012 EPA report, 5 sites were still manufacturing or importing decabromodiphenyl ether to the United States (over 18 million pounds in 2011).¹⁸ In 2013 manufacturers agreed to voluntarily seize the production of deca PBDE and 2015 production and import amount is estimated by EPA to be ~25000 lb.¹⁸

PBDEs are lipophilic compounds, that accumulate in fatty tissue, with lower brominated congeners being more bio accumulative and more soluble in water.^{19, 20} Toxicity of PBDEs is also highly dependent on the degree of bromination. Deca-PBDE is reported to be absorbed poorly during ingestion due to higher molecular weight.²¹ Furthermore, low brominated PBDEs (<5 Br) are metabolized slowly compared to high brominated counterparts resulting in their slow elimination and bioaccumulation leading to chronic interactions and are considered comparatively more toxic.^{21, 22} By comparison with polychlorinated biphenyls (structural and mode of action) it was suggested that only those PBDE congeners with no bromine in ortho position are considered toxic due to the co-planar orientation of the phenyl rings.²² PBDEs are known to affect the functions of estrogen and androgen,^{23, 24} metabolism, and adipogenesis processes.²⁵ PBDEs have been linked to obesity through a disruptive effect on endocrine system.²⁵⁻²⁷ Octa-PBDE is reported to be a teratogen,²⁸ and EPA has classified deca-PBDE congener as a possible carcinogen.²⁹ Children in particular are at high risk of PBDEs' exposure. PBDEs were found in notable concentration in infant blood due to prenatal exposure during pregnancy,³⁰ ingestion of house hold dust^{31, 32} or mouthing of toys.³³

Though the composition of commercially used mixtures of PBDEs are well known and the presence of PBDEs in the environment has been consistently observed, there is a large discrepancy between the congener pattern in the consumer products and those observed in environmental samples. In spite of fact that the BDE 209 accounts for the 75-80% of the world's production of PBDEs, environmental samples are dominated by lower PBDEs (< 6 Br) mainly BDE 47 and 99.³⁴⁻³⁶ It is suggested that due to the relatively low stability, deca-PBDE, both in the abiotic environment and in biota undergoes debromination resulting in mainly hepta to nona PBDEs.³⁷

Among the commercial mixture based on the penta-PBDEs (such as for example DE-71), BDE 99 (2,2',4,4',5 pentabromo diphenyl ether) is the dominant congener (~44-58%) with the BDE 47 (2,2',4,4' tetrabromo diphenyl ether) being major secondary component (~24-42%). Though BDE 47 and BDE 99 are indeed observed in environmental sample, their ratio is reversed (BDE 47 : BDE 99 ~2:1) compared to original mixtures.³⁸ There are a lot of speculations on the reasons for that reversal including varying chemical stabilities and differences in vapor pressure. In particular difference in vapor pressure of these two congeners is cited as the main cause of the relative concentration reversal in the environmental samples – BDE 47 has ~10 times higher solid air partitioning factor.³⁹⁻⁴¹ Models of the emission of PBDEs from the consumer products and other potential sources that include photolytic degradation of PBDEs in air, predict the reversal of the relative concentration of BDE 47 and BDE 99, however underestimates the overall concentration of each congener by the factor of 10.⁴¹

One of the major sources of PBDEs is electronic waste (e-waste). The global report had predicted a 33 % increase of amount of electronic waste worldwide by 2017.⁴² In 2012, European Union and the USA were the two larger e-waste generators (Figure 1). The same report highlights the substantial gap between the production and collection trends of electronics in the USA.

For many years export of electronic wastes to developing countries has been practiced and created entire e-waste recycling industry and potential environmental “ticking bomb”. Even now, despite a prohibitive regulation, electronic wastes still find the way to both official and illegal e-waste recycling sites in South East Asia and Africa.⁴³ Primitive and makeshift processes applied during the reclamation of precious and valuable materials from e-wastes result in significant emissions of particulates, metals, dioxins, PBDEs, and many other hazardous agents.

E-waste reclamation can be a significant source of PBDEs. Location of such facilities within the heavy populated areas creates a potential exposure risk not only for the on-site workers but also for local residents.^{44, 45} This manuscript presents the results of studies performed in Bangkok, Thailand, where informal e-waste reclamation site is located within the heavily populated residential area, with nearby schools, kindergartens and hospitals, raising a significant concern regarding potential exposure of PBDEs. This site typically utilizes a crude thermal/combustion method to recover metals, and thus related air and particulate emissions would be associated with thermal transformations of PBDEs and their transport on PM.

2. Experimental Section

2.1 Materials

Standards: Isotopically labeled internal standard solution ($^{13}\text{C}_{12}$, 99%) (IS Tetra PCB 52 and IS Hexa PCB 138 catalogue no: EO-5275) was purchased from Cambridge Isotope Laboratories, Inc. Method 1614 calibration solution ($^{13}\text{C}_{12}$, 99%/unlabeled, catalogue no: EO-5279-CS3) which is a mixture of PBDEs (tri-BDE 28, tetra-BDE 47, penta-BDE 99, penta-BDE 100, hexa-BDE 153, hexa-BDE 154, hepta-BDE 183, and deca-BDE 208) was also purchased from Cambridge Isotope Laboratories, Inc. Elution of standards and internal standards used during PBDEs analysis is depicted in Figure 2.

Solvents: Dichloromethane (DCM) (catalogue no: DX0838-1, EMD Millipore corporation) and n-hexane (catalogue no: BDH24575.400, VWR) solvents were of HPLC grade. Sand and washing soda used in the speed extractor system were pre-washed with DCM and dried in an oven at 105 °C for 48 hours.

2.2 Methodology

Sample Collection: Ambient air samples viz: Total Suspended Particle (TSP) and PM_{2.5} were collected on filters using the portable air samplers with an average sampling volume of 0.75 m³ from Bangkok, Thailand. The average sampling rate and time were 2000 ml/min and 6 hours respectively. Filters were loaded to the samplers on site. Field blanks were composed of the same filters, however placed flat on sampling sites at 1 m elevation, without mounting into sampler (passive sampling). Filter blanks were not taken to the site at all, and analyzed for PBDEs directly from the box. The study site was an informal e-waste recycling site located in the border of Chatuchak and Lat Phrao districts, Bangkok. Samples were collected directly at an informal e-waste site and off site at the approximate distance of 60 meters towards south east, 100 m towards west, 200 m towards north west and 200 m south west (Figure 3).

Reference sites were selected where no e-waste reclamation activity was performed in their vicinity. Reference sites were located in the Don Muang District, Bangkok (urban), and Pak Kret District (peri-urban) at the distance of 11072 meters north east and 17590 meters north west respectively. Sampling locations and sample details are presented in Figure 3.

Arc GIS software (version 10.5.1, ESRI (Environmental System Research Institute) was used to map the potential PBDEs exposure zone using a buffer tool. The GPS coordinates of e-waste and reference sampling sites were imported to Thailand base map of Administrative areas from DIVA-GIS program. Using shape file and focusing on e-waste site 225 m buffer was created, corresponding to the data obtained in these studies corresponding to observed PBDEs concentrations. The details of sampling collection sites are presented in Appendix 1.

Sample processing: Extraction of PBDEs from the filters was done using Buchi speed extractor (model E-916). Six extraction stainless steel vials were filled up to 90% volume with 1:1 layer of sand and Na₂SO₄. PM filters from the air sampler were placed on the sand bed (face down) and covered with additional sand/sodium sulfate layers to fill the vessels and spiked with 12.5 microliter of internal standards.

Before each extraction the Buchi extractor lines were flushed with a solvent for 10-15 minutes at extraction conditions. Extraction was performed at 150 bar and 80 °C using DCM as solvent for 40 minutes. Extracts were collected in collection glass tubes.

Speed evaporator was used to condense extracts (Buchi model with vacuum pump, V-700). Evaporation was performed at 513 mbar and temperature ramp from RT-60 °C for 30 minutes. Final volume of concentrated extract was around 0.5 ml. Remaining volume was transferred to 1ml vials, evaporated to dryness under nitrogen and reconstituted in 200 µl of nonane.

GC-MS and MS/MS Method: A specific method for analyzing PBDEs in ambient air samples was adopted from EPA Method 1614 (Brominated Diphenyl Ethers in Water, Soil, Sediment, and Tissue by HRGC/HRMS). The detection Limit for Gas chromatography-Mass Spectroscopy (GC-MS) analysis was established at 12 pg (which corresponds to 16 pg/m³ of ambient air samples) with sample recovery of ~90%. GC-MS analysis parameters are specified in Table 1.

Blank Filter paper were additionally analyzed on Agilent 7000 C Triple Quadrupole GC-MS/MS. A Multiple-Reaction-Monitoring (MRM) method was developed using a standard solution of the PBDEs. From the analysis, no prior contamination was detected. Detail analysis is shown in Appendix 3.

3. Results and Discussion

The list of detected PBDEs congeners on Total Suspended Particle (TSP) and Particulate Matter (PM_{2.5}) filter paper samples collected at the informal e-waste site, nearby e-waste site, and two reference sites is presented in Table 2. Though no PBDEs congeners were detected in the filter blanks, they were detected in the field blanks, particularly those placed at the e-waste site. We believe that this is a result of large quantities of dust particles present on the site, which settled on the sample's surface (passive PM collection). Details of the field blank data is presented in the supplement materials (see Appendix 2).

Ambient air samples collected at the e-waste site and nearby (within the buffer zone – see Figure 3), and two reference sites were all found to contain PBDEs with bromination level from tri to hepta. At e-waste site and within a buffer zone, 17 different PBDEs congeners were detected in TSP samples and 10 PBDEs congeners were detected in PM_{2.5} samples. Their concentrations within tri-hepta congener groups are presented in Figure 4. Both TSP and PM_{2.5} samples collected at the e-waste processing facility contained much higher concentration of penta-PBDEs than the reference sites 1 and 2. Commercial penta mixture (for example: DE-71) is one of the typical flame retarding additives in such products and one can anticipate that during reclamation PBDEs can be released into air and partition into PM. TSP samples contained more penta congeners compared to PM_{2.5}, which indicates that particles larger than 2.5 µm contained significant amounts of PBDEs.

The presence of tetra-PBDEs at the e-waste site was detected only for TSP samples, while PM_{2.5} samples did not show the presence of tetra congeners. The tetra PBDE decreased already within the buffer zone, with no detection (below threshold) of tetra congeners for

both TSP and PM_{2.5} samples for nearby sampling sites. Tetra-PBDEs congeners are the second largest component of commercial penta mixtures (>25 %) such as DE-71. We speculate that large fractions of penta and tetra PBDEs detected on larger particles (>2.5 µm) are a result of the direct entrainment of the e-waste material dust produced during the reclamation and represent the content of PBDEs in e-wastes. On the contrary, PM_{2.5} samples are typically associated with the thermal processes emission and PBDEs on PM_{2.5} deposit via desorption from e-waste and decomposition/transformation of PBDEs in thermal reclamation.

This hypothesis is supported by the detection of high content of tri-PBDEs in samples surrounding e-waste site (Figure 4). In fact, PM_{2.5} samples surrounding the e-waste site were dominated by tribrominated congeners, and their concentration increased with distance from the e-waste site, at close proximity. Such spatial profile indicates ongoing transformation (and specifically debromination) of PBDEs during reclamation, entrainment, and transport on PM_{2.5}. Tri-PBDEs are not a major component of commercial mixtures.

The concentration of hepta-PBDEs congeners was also directly proportional to the increasing distance from the e-waste site however only for TSP samples thus cannot be attributed to the similar mechanism as tri-PBDEs. Surprisingly, hexa-PBDEs congeners were only detected in the significant amount in the peri-urban sites of Pak Kret district. Furthermore, hepta-PBDEs were also detected in reference urban sites, Don Muang District at the levels comparable with nearby e-waste site (around border between Chatuchak and Lat Phrao districts).

Analysis of detected congeners provides additional insight into the transformation of PBDEs during and after reclamation of e-wastes. Surprisingly, PBDEs congeners commonly present in the commercial PBDEs mixture were not detected or not major contributors. For example, BDE 28 (tri-PBDE), BDE 47 (tetra-PBDE), BDE 99 (penta-PBDE), and BDE 153 (hexa-PBDE) are abundant in the US penta product (DE-71)^{17, 46} as well as in the European penta formulation (Bromokal 70-5DE).^{17, 46} However, we did not detect BDE 28 in any of the samples (except in the field blank). We found higher content of BDE 66, BDE 71, and BDE 79 compared to BDE 47. Likewise, for penta-PBDEs, we found BDE 85, BDE 105, and BDE 119/120 content surpassing that of BDE 99. Furthermore, in US octa product (DE-79)^{17, 46} and European octa formulation (Bromokal 79-8DE),^{17, 46} the most dominant congeners are BDE 175/183 (hepta-PBDEs) and BDE 209 (deca-PBDE) respectively. However, we found BDE 190 higher in our analysis.

Some of the congeners (such as for example BDE 30 and BDE 119) detected in our analysis were specifically reported as not present in air samples contaminated by evaporation of PBDEs from electronics⁴⁷ or generally not detected in common media type samples^{5, 6}. These observation lead to a conclusion that, particularly for PM_{2.5}, observed congeners are a product of decomposition of original Brominated Flame Retardants (BFRs), with the dominance of the congeners that are more thermodynamically stable. For example, tribromo congeners contribute the least in percentage in most common commercial mixture such as DE-71, Bromokal 70-5DE, DE-79, Bromokal 79-8DE, Saytex 102E, and Bromokal 82-0DE.⁴⁶ In spite of that, we observed the highest content of tri-PBDE and, more interestingly,

BDE 30 was only tribromo congener present in PM_{2.5} sample (0.47 ng/m³ of air) at e-waste site and surrounding areas (Figure 5). Among penta congeners, BDE 119 was the most dominant on TSP samples at the e-waste site.

Debromination pattern:

The detection of uncommon PBDE congeners typically not reported for different media sampling indicate a debromination pattern during reclamation. We assume that not all of the debromination products are detected, as they are subject to consequential reactions, and only those more stable can be observed. The proposed debromination scheme is presented in Figure 6. BDE 30 seems to be a final or stable debromination product of one of the debromination chains. For tetra PBDEs, BDE 75 and 71 were detected only at the e-waste site or close vicinity similarly as penta congener BDE 119. We believe, that these congeners are associated with a common pathway and can trace back to the BDE 190 (Figure 6). Other pathways presented in the scheme are also likely occurring, however due to lower stability of the products are subject to more complete debromination. However, it is BDE 30 uniquely detected in our studies as a dominant final debromination product that can be used as a marker of thermal e-waste activity, if detected on ambient air PM samples.

Comparison with other study:

In many developing countries open burning of e-waste, acid bath treatment of e-waste, and exposing electronic materials to open flame to remove attached worthwhile components are quite common.⁵¹ Typically PBDE studies in ambient air,⁴⁸⁻⁵⁰ concentrate on congeners present in the commercial mixtures namely BDE 28, BDE 47, BDE 49, BDE 75, BDE 99, BDE 100, BDE 153, and BDE154. Some of that results from the instrumentation limitation or difficulty in accurate quantification of PBDEs congeners. For example, PBDEs analyzed in e-waste site of Guiyu, China, Tsuen Wan site of Hong Kong and two sampling sites in Guangzhou, South China only measured mono-hepta PBDEs congeners due to the instrumentation limitation for higher PBDE congeners.⁴⁸ Similarly, the PBDEs analysis via passive sampling method across European countries analyzed PBDEs homologue from trihexa only.⁴⁹ Following the trend, only specific PBDEs congeners namely BDE 47, 99, 100, 153, 154 and 209 were looked via passive air sampling study conducted in the 139 households from California. Moreover, in this study BDE 209 was analyzed only in the dust samples and surface wiped samples but not in air particles.⁵⁰ Our studies indicate that a specific attention should be focused on the shift in congener pattern when analyzing ambient air concentration and the exposure of nearby populations. Incidentally, such lower brominated congeners are more toxicologically potent compared to their parent compounds before transformation. In here we report the emission of much larger group of congeners resulting from thermal recycling of e-waste including congeners usually not reported elsewhere: BDE 25, BDE 30, BDE 32, BDE 35, BDE 37, BDE 79, BDE 105, BDE 116, and BDE 128 (see Table 3).

4. Environmental Impact

Thermal reclamation of e-waste produces a unique pattern of PBDEs congeners, with the prevalence of the most stable, debrominated congeners. Pattern of the release of the PBDEs

was identified with the BDE 30 appearing as a clear marker of emissions from such activities. In fact, the ubiquitous presence of this congener in PM_{2.5} samples up to 250m from the e-waste site is an indication of exposure hazard to nearby population. Besides, debromination pattern leads to emission of lower brominated congeners which pose a much higher health risk compared to higher brominated ones. Identification of BDE 30 as a specific marker for e-waste thermal reclamation can improve the tracing of pollution sources and evaluate epidemiological studies of either workers at such sites or their household members (blood screening for specific metabolites). Additionally, PBDEs emitted during the e-reclamation process may act as a precursor for the formation of PBDD/Fs on PM surface.⁵² Thus, it is very likely that the presence of PBDE, on ambient air PM sample will be accompanied by the PBDD/Fs.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

ACKNOWLEDGEMENT:

This study was supported by National Institute of Environmental Health Sciences Superfund Research Program, Grant number P42ES013648.

5. References

1. Darnerud PO; Eriksen GS; Jóhannesson T; Larsen PB; Viluksela M, Polybrominated diphenyl ethers: occurrence, dietary exposure, and toxicology. *Environmental health perspectives* 2001, 109, (Suppl 1), 49. [PubMed: 11250805]
2. Keller JM; Alava JJ; Aleksa K; Young B; Kucklick JR, Spatial trends of polybrominated diphenyl ethers (PBDEs) in loggerhead sea turtle eggs and plasma. *Organohalogen Compounds* 2005, 67, 610–611.
3. Babrauskas V; Blum A; Daley R; Birnbaum L, Flame retardants in furniture foam: benefits and risks. *Fire Safety Science* 2011, 10, 265–278.
4. UNEP, S. C., Chemicals listed in Annex A. 2008.
5. Olutona GO; Oyekunle JA; Ogunfowokan AO; Fatoki OS, Assessment of polybrominated diphenyl ethers in sediment of Asunle stream of the Obafemi Awolowo University, Ile-Ife, Nigeria. *Environmental Science and Pollution Research* 2016, 23, (21), 21195–21205. [PubMed: 27491420]
6. Daso AP; Fatoki OS; Odendaal JP, Occurrence of polybrominated diphenyl ethers (PBDEs) and 2, 2', 4, 4', 5, 5'-hexabromobiphenyl (BB-153) in water samples from the Diep River, Cape Town, South Africa. *Environmental Science and Pollution Research* 2013, 20, (8), 5168–5176. [PubMed: 23361180]
7. Stapleton HM; Dodder NG; Offenberg JH; Schantz MM; Wise SA, Polybrominated diphenyl ethers in house dust and clothes dryer lint. *Environmental science & technology* 2005, 39, (4), 925–931. [PubMed: 15773463]
8. Hale RC; La Guardia MJ; Harvey EP; Mainor TM; Duff WH; Gaylor MO, Polybrominated diphenyl ether flame retardants in Virginia freshwater fishes (USA). *Environmental Science & Technology* 2001, 35, (23), 4585–4591. [PubMed: 11770759]
9. Sellström U; Kierkegaard A; de Wit C; Jansson B, Polybrominated diphenyl ethers and hexabromocyclododecane in sediment and fish from a Swedish river. *Environmental Toxicology and Chemistry* 1998, 17, (6), 1065–1072.
10. Domingo JL; Bocio A; Falcó G; Llobet JM, Exposure to PBDEs and PCDEs associated with the consumption of edible marine species. *Environmental science & technology* 2006, 40, (14), 4394–4399. [PubMed: 16903276]

11. Christensen JH; Glasius M; Pécseli M; Platz J; Pritzl G, Polybrominated diphenyl ethers (PBDEs) in marine fish and blue mussels from southern Greenland. *Chemosphere* 2002, 47, (6), 631–638. [PubMed: 12047074]
12. Ohta S; Ishizuka D; Nishimura H; Nakao T; Aozasa O; Shimidzu Y; Ochiai F; Kida T; Nishi M; Miyata H, Comparison of polybrominated diphenyl ethers in fish, vegetables, and meats and levels in human milk of nursing women in Japan. *Chemosphere* 2002, 46, (5), 689–696. [PubMed: 11999792]
13. Norén K; Meirionyté D, Certain organochlorine and organobromine contaminants in Swedish human milk in perspective of past 20–30 years. *Chemosphere* 2000, 40, (9–11), 1111–1123. [PubMed: 10739053]
14. Meirionyté D; Norén K; Bergman A, Analysis of polybrominated diphenyl ethers in Swedish human milk. A time-related trend study, 1972–1997. *Journal of Toxicology and Environmental Health Part A* 1999, 58, (6), 329–341. [PubMed: 10580757]
15. Bi X; Qu W; Sheng G; Zhang W; Mai B; Chen D; Yu L; Fu J, Polybrominated diphenyl ethers in South China maternal and fetal blood and breast milk. *Environmental pollution* 2006, 144, (3), 1024–1030. [PubMed: 16564120]
16. Fängström B; Hovander L; Bignert A; Athanassiadis I; Linderholm L; Grandjean P; Weihe P; Bergman Å, Concentrations of polybrominated diphenyl ethers, polychlorinated biphenyls, and polychlorobiphenyls in serum from pregnant Faroese women and their children 7 years later. *Environmental science & technology* 2005, 39, (24), 9457–9463. [PubMed: 16475322]
17. La Guardia MJ; Hale RC; Harvey E, Detailed polybrominated diphenyl ether (PBDE) congener composition of the widely used penta-, octa-, and deca-PBDE technical flame-retardant mixtures. *Environmental science & technology* 2006, 40, (20), 6247–6254. [PubMed: 17120549]
18. EPA, Preliminary Information on Manufacturing, Processing, Distribution, Use, and Disposal: Decabromodiphenyl Ether. 2017.
19. Watanabe I; Sakai S.-i., Environmental release and behavior of brominated flame retardants. *Environment international* 2003, 29, (6), 665–682. [PubMed: 12850086]
20. Act, C. E. P., Environmental Screening Assessment Report on Polybrominated Diphenyl Ethers (PBDEs). 1999.
21. Hooper K; McDonald TA, The PBDEs: an emerging environmental challenge and another reason for breast-milk monitoring programs. *Environmental health perspectives* 2000, 108, (5), 387. [PubMed: 10811563]
22. Rahman F; Langford KH; Scrimshaw MD; Lester JN, Polybrominated diphenyl ether (PBDE) flame retardants. *Science of the Total Environment* 2001, 275, (1–3), 1–17.
23. Legler J; Hamers T; van Eck van der Sluijs-van de Bor M; Schoeters G; van der Ven L; Eggesbo M; Koppe J; Feinberg M; Trnovec T, The OBELIX project: early life exposure to endocrine disruptors and obesity–. *The American journal of clinical nutrition* 2011, 94, (suppl_6), 1933S–1938S. [PubMed: 21543539]
24. Ceccatelli R; Faass O; Schlumpf M; Lichtensteiger W, Gene expression and estrogen sensitivity in rat uterus after developmental exposure to the polybrominated diphenylether PBDE 99 and PCB. *Toxicology* 2006, 220, (2–3), 104–116. [PubMed: 16414171]
25. Hoppe AA; Carey GB, Polybrominated diphenyl ethers as endocrine disruptors of adipocyte metabolism. *Obesity* 2007, 15, (12), 2942–2950. [PubMed: 18198302]
26. Janesick A; Blumberg B, Endocrine disrupting chemicals and the developmental programming of adipogenesis and obesity. *Birth Defects Research Part C: Embryo Today: Reviews* 2011, 93, (1), 34–50.
27. Legler J; Brouwer A, Are brominated flame retardants endocrine disruptors? *Environment international* 2003, 29, (6), 879–885. [PubMed: 12850103]
28. Karlsson M; Ericson I; van Bavel B; Jensen J-K; Dam M, Levels of brominated flame retardants in Northern Fulmar (*Fulmarus glacialis*) eggs from the Faroe Islands. *Science of the Total Environment* 2006, 367, (2–3), 840–846.
29. EPA, Technical Fact Sheet – Polybrominated Diphenyl Ethers (PBDEs). 2017.

30. Herbstman JB; Sjödin A; Kurzon M; Lederman SA; Jones RS; Rauh V; Needham LL; Tang D; Niedzwiecki M; Wang RY, Prenatal exposure to PBDEs and neurodevelopment. *Environmental health perspectives* 2010, 118, (5), 712. [PubMed: 20056561]
31. Bradman A; Castorina R; Sjödin A; Fenster L; Jones RS; Harley KG; Chevrier J; Holland NT; Eskenazi B, Factors associated with serum polybrominated diphenyl ether (PBDE) levels among school-age children in the CHAMACOS cohort. *Environmental science & technology* 2012, 46, (13), 7373–7381. [PubMed: 22668079]
32. Chao H-R; Shy C-G; Huang H-L; Koh T-W; Tok T-S; Chen SC-C; Chiang B-A; Kuo Y-M; Chen K-C; Chang-Chien G-P, Particle-size dust concentrations of polybrominated diphenyl ethers (PBDEs) in southern Taiwanese houses and assessment of the PBDE daily intakes in toddlers and adults. *Aerosol Air Qual. Res* 2014, 14, 1299–1309.
33. Chen S-J; Ma Y-J; Wang J; Chen D; Luo X-J; Mai B-X, Brominated flame retardants in children's toys: concentration, composition, and children's exposure and risk assessment. *Environmental science & technology* 2009, 43, (11), 4200–4206. [PubMed: 19569352]
34. Strandberg B; Dodder NG; Basu I; Hites RA, Concentrations and spatial variations of polybrominated diphenyl ethers and other organohalogen compounds in Great Lakes air. *Environmental Science & Technology* 2001, 35, (6), 1078–1083. [PubMed: 11347917]
35. Keum Y-S; Li QX, Reductive debromination of polybrominated diphenyl ethers by zerovalent iron. *Environmental science & technology* 2005, 39, (7), 2280–2286. [PubMed: 15871265]
36. Alaei M; Arias P; Sjödin A; Bergman Å, An overview of commercially used brominated flame retardants, their applications, their use patterns in different countries/regions and possible modes of release. *Environment international* 2003, 29, (6), 683–689. [PubMed: 12850087]
37. Chain E. P. o. C. i. t. F., Scientific opinion on polybrominated diphenyl ethers (PBDEs) in food. *Efsa Journal* 2011, 9, (5), 2156.
38. Birnbaum LS; Staskal DF, Brominated flame retardants: cause for concern? *Environ Health Perspect* 2004, 112, (1), 9–17. [PubMed: 14698924]
39. Wei WJ; Mandin C; Blanchard O; Mercier F; Pelletier M; Le Bot B; Gloennec P; Ramalho O, Distributions of the particle/gas and dust/gas partition coefficients for seventy-two semi-volatile organic compounds in indoor environment. *Chemosphere* 2016, 153, 212–219. [PubMed: 27016817]
40. Prevedouros K; Jones KC; Sweetman AJ, Estimation of the Production, Consumption, and Atmospheric Emissions of Pentabrominated Diphenyl Ether in Europe between 1970 and 2000. *Environ Sci Technol* 2004, 38, (12), 3224–3231. [PubMed: 15260317]
41. Rauert C; Harrad S, Mass transfer of PBDEs from plastic TV casing to indoor dust via three migration pathways - A test chamber investigation. *Sci Total Environ* 2015, 536, 568–574. [PubMed: 26247685]
42. Lewis T, World's E-waste to grow 33 % by 2017, says global report. 2013.
43. Li J; Liu L; Zhao N; Yu K; Zheng L, Regional or global WEEE recycling. Where to go? *Waste management* 2013, 33, (4), 923–934. [PubMed: 23337392]
44. Muenhor D; Moon HB; Lee S; Goosey E, Polybrominated diphenyl ethers (PBDEs) in floor and road dust from a manual e-waste dismantling facility and adjacent communities in Thailand. *J Environ Sci Heal A* 2017, 52, (14), 1284–1294.
45. Qu WY; Bi XH; Sheng GY; Lu SY; Fu H; Yuan J; Li LP, Exposure to polybrominated diphenyl ethers among workers at an electronic waste dismantling region in Guangdong, China. *Environ Int* 2007, 33, (8), 1029–1034. [PubMed: 17618686]
46. Redfern FM; Lee W-J; Yan P; Mwangi JK; Wang L-C; Shih C-H, Overview and perspectives on emissions of polybrominated diphenyl ethers on a global basis: Evaporative and fugitive releases from commercial PBDE mixtures and emissions from combustion sources. *Aerosol Air Qual. Res* 2017, 17, (5), 1117–1131.
47. Cahill TM; Groskova D; Charles MJ; Sanborn JR; Denison MS; Baker L, Atmospheric concentrations of polybrominated diphenyl ethers at near-source sites. *Environ Sci Technol* 2007, 41, (18), 6370–6377. [PubMed: 17948781]

48. Deng W; Zheng J; Bi X; Fu J; Wong M, Distribution of PBDEs in air particles from an electronic waste recycling site compared with Guangzhou and Hong Kong, South China. *Environment International* 2007, 33, (8), 1063–1069. [PubMed: 17631964]
49. Jaward FM; Farrar NJ; Harner T; Sweetman AJ; Jones KC, Passive air sampling of PCBs, PBDEs, and organochlorine pesticides across Europe. *Environmental science & technology* 2004, 38, (1), 34–41. [PubMed: 14740714]
50. Bennett D; Moran R; Wu XM; Tulse N; Clifton M; Colón M; Weathers W; Sjödin A; Jones R; Hertz-Picciotto I, Polybrominated diphenyl ether (PBDE) concentrations and resulting exposure in homes in California: relationships among passive air, surface wipe and dust concentrations, and temporal variability. *Indoor Air* 2015, 25, (2), 220–229. [PubMed: 24832910]
51. Liebmann A, ICT Waste Handling: Regional and Global End-of-Life Treatment Scenarios for ICT Equipment. In 2015.
52. Zhang M; Buekens A; Li X, Brominated flame retardants and the formation of dioxins and furans in fires and combustion. *Journal of hazardous materials* 2016, 304, 26–39 [PubMed: 26546701]

Figure 1:
Electronic waste generation by major countries in 2012 (million in tons).⁴²

Figure 2:
Chromatograms of Standards and Internal Standards elution in the GC-MS analysis.

Figure 3: Sampling locations and location description. Buffer zone marked in polar diagram is made at 225 m from the e-waste site.

Figure 4:
Distribution of PBDEs congeners at the e-waste, nearby e-waste site, and reference sites.

Figure 5:
BDE 30 as a debrominated product and acting as a finger print in PM2.5 as a result of the thermal treatment done in the e-waste site.

Figure 6:

Proposed debromination pattern of PBDEs congeners detected in the current study. Marked in bold is a pathway to BDE 30 observed in this study.

Table 1:

GC-MS parameters for PBDEs analysis.

Model	Bruker Scion 456 TQ GC-MS/MS
Mode	Selective Ion Monitoring (SIM)
Ionization Method	Electron Ionization (EI)
Column Volatiles	Zebron ZB-Semi
Dimensions	20m × 0.18mm × 0.18µm
Injection	Splitless @ 300 °C, 1µl
Oven Program	100 °C for 3min to 320 °C @ 5 °C /min hold for 20 min

Table 2:

Detected PBDEs congeners on TSP and PM2.5 filter samples at the informal e-waste site, close proximity of e-waste site, and two references sites. Symbol 'x' represents presence and '–' represents absence of PBDE congener.

BDE congener	E-waste site and Vicinity		Reference Site 1		Reference Site 2	
	TSP	PM2.5	TSP	PM2.5	TSP	PM2.5
Tri-BDE						
BDE 17	-	-	-	x	-	-
BDE 25	x	-	-	-	-	x
BDE 28	-	-	-	-	-	-
BDE 30	x	x	-	-	-	-
BDE 32	-	-	-	x	-	-
BDE 35	x	-	-	-	-	-
BDE 37	x	-	-	-	x	x
Tetra-BDE						
BDE 47	x	x	-	-	-	-
BDE 49	-	-	-	x	x	-
BDE 51	-	-	-	x	x	-
BDE 66	-	-	-	x	x	x
BDE 71	x	-	-	x	x	x
BDE 75	-	x	-	-	-	-
BDE 79	x	-	-	-	x	x
Penta -BDE						

Table 3:

Difference in PBDEs congeners in various part of the world vs Bangkok, Thailand (our study). Yellow mark corresponds to the PBDE congener that we did not see in our analysis. Symbols 'x' and '–' indicate presence and absence of the particular PBDE congener.

BDE congeners	⁴⁸ ref	⁴⁸ ref	⁴⁸ ref	⁴⁹ ref	⁵⁰ ref	Our study
BDE 17	-	-	-	-	-	x
BDE 25	-	-	-	-	-	x
BDE 28	x	x	x	x	-	-
BDE 30	-	-	-	-	-	x
BDE 32	-	-	-	-	-	x
BDE 35	-	-	-	-	-	x
BDE 37	-	-	-	-	-	x
BDE 47	x	x	x	x	x	x
BDE 49	-	-	-	x	-	x
BDE 51	-	-	-	-	-	x
BDE 66	x	x	x	-	-	x
BDE 71	-	-	-	-	-	x
BDE 75	-	-	-	x	-	x
BDE 79	-	-	-	-	-	x
BDE 85	-	-	-	-	-	x
BDE 99	x	x	x	x	x	x