Tetrabromobisphenol A in Indoor Dust from Houses and Internet Cafes

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ABSTRACT

Tetrabromobisphenol A or TBBPA is a widely used brominated flame retardant in modern materials such as electronic products, plastics and building materials. TBBPA can leach out of flame retardant-treated products during production, use, reuse, and final disposal of these consumer products. It has thus become a contemporary environmental contaminant. This study reports the levels of TBBPA in indoor dust from houses (n=4) and internet cafes (n=5) in Angono and Quezon City, in the Philippines. TBBPA in indoor dust was analyzed by ultrasonication-assisted hexane extraction and HPLC-UV determination. The instrument and method detection limits were 0.004 ng uL⁻¹ and 1275 ng g⁻¹, respectively. The standard calibration solutions ranged from 0.03 to 0.30 ng uL⁻¹ (r²=0.9956). The extraction recovery was 78% (n=3). TBBPA was found in six of the nine indoor dust samples studied where the concentrations ranged from not detected to 4916 ng g⁻¹. The occurrence and levels of TBBPA in indoor dusts are significant and suggest the need for further investigations especially in other microenvironments where people may be exposed to this contaminant.

Key words: tetrabromobisphenol A, indoor dust, ultrasonication, HPLC-UV

INTRODUCTION

Tetrabromobisphenol A (TBBPA) belongs to a group of chemicals known as brominated flame retardants. The structure of TBBPA (4,4'-isopropylidenebis(2,6dibromophenol); CAS no. 79-94-7) is shown in Figure 1. Brominated flame retardants are commonly found in modern-day materials such as electronic and electrical equipment, plastic products, upholstery and construction materials. These brominated flame retardant chemicals, including TBBPA as well as polybrominated biphenyls (PBBs), polybrominated diphenyl ethers (PBDEs) and hexabromocyclodecanes (HBCDs), are regarded as very efficient in reducing the flammability of modern consumer products. The world market for all types of flame retardants was reportedly over 2 billion US dollars in 2000 and was



Figure 1. Chemical structure of TBBPA

expected to increase each year (Tullo, 2000; Morf et al., 2005; Shaw et al., 2010). The commercial production of PBBs has ceased in the United States in the 1970s, while the higher molecular weight congeners were still in use until 1985 in Germany and

until 2000 in France (Alaee et al., 2003). The formulations of PBDEs particularly for penta- and octabromodiphenyl ethers were used in the United States until 2004, while decabromodiphenyl ether is still available until the scheduled phase-out in 2013 (US EPA, 2011). The ban and restrictions imposed on PBDE formulations consequently increased the demand for TBBPA and HBCDs. For TBBPA, the estimates of use in 2001 were 89,400 tons y⁻¹ in Asia, 18,000 tons y⁻¹ in the Americas, and 11,600 tons y⁻¹ in Europe (Covaci et al., 2009). Currently, it is the widely used flame retardant in the market (BSEF Fact Sheet, 2010). TBBPA is a reactive flame retardant such that it is covalently bonded to the polymeric material; it is also an additive flame retardant similar to PBDEs and HBCDs that are dissolved in the polymer. TBBPA is extensively used in electronic and electrical equipment including computers, televisions, vacuum cleaners, washing machines, office equipment and other high technology equipment (BSEF Fact Sheet, 2010; Watanabe and Sakai, 2003). As a reactive flame retardant, it is commonly found in printed circuit boards. In small waste electronic and electrical equipment dismantled in Australian treatment plants, for example, the average amount of TBBPA in printed circuit boards approximates those of tetra-, penta- and decabromodiphenyl ethers (Salhofer & Tesar, 2011). As an additive flame retardant, it is found in acrylonitrile-butadiene-styrene plastics used in casings for televisions or electronic devices. TBBPA, for instance, was among the flame retardants detected in rear and front covers of LCD TVs as well as in chassis, panels, adaptors, cooling fans or speakers of laptop computers in the Japanese market in 2008 (Kajiwara et al., 2011).

In its foremost application as a reactive flame retardant, TBBPA is perceived to be stable and not easily released from the final product. Despite having no known natural source, however, it has been detected in the different environmental compartments. TBBPA may leak into the environment throughout the lifecycles of flame retardant-protected consumer products. TBBPA may enter the environment during its production, during use and reuse of TBBPA-treated products, and when these products reach their endof-life and final disposal. It is not surprising that TBBPA and the other brominated flame retardants are now among the emerging global contaminants. These environmental contaminants are receiving similar attention, particularly in reviews and assessments, as the classic twelve persistent organic pollutants or POPs (Alaee et al., 2003; Kemmlein et al., 2003; Covaci et al., 2007; De Wit et al., 2010). TBBPA has a melting point of 181°C, log K_{ow} of 5.903, reported water solubilities of <0.5 ug/L, 0.001 mg/L and <0.08 mg/L, and vapor pressure of $<1.19 \times 10^{-5}$ Pa at 20°C (US EPA, 2001). Shaw et al. (2010) summarized studies describing the effects and properties of TBBPA as a cytotoxicant, immunotoxicant, thyroid hormone agonist, or endocrine disruptor, among other effects. The occurrence and persistence of TBBPA in the environment have been documented. TBBPA has been detected in air, dust, soils, water, sediments, biota, mammalian tissues, and human serum and milk (Covaci et al., 2009; Jakobsson et al., 2002; Johnson-Restrepo et al., 2008; Watanabe and Sakai, 2003). Like the POPs compounds, TBBPA is now found in the Arctic region (De Wit et al., 2006; De Wit et al., 2010), revealing its capability to undergo long-range transport. And analogous to the traditional POPs, TBBPA is analyzed by standard chromatographic techniques such as high pressure liquid chromatography (HPLC) with ultraviolet (UV) or mass spectrometric detection and gas chromatography with diazomethane, N-methyltrimethylsilyltrifluoroacetamide or methyl chloroformate derivatization followed by mass spectrometry. The extraction of TBBPA from the different environmental matrices may involve methods such as Soxhlet extraction, sonication, microwaveasssisted extraction, accelerated solvent extraction, supercritical fluid extraction, pressurized liquid extraction, liquid-liquid extraction, or solid-phase extraction. The choice of extraction method depends on the sample matrix. Clean-up of the extracts may involve acid treatment, the use of alumina, silica or florisil columns, or in some instances, a solid-phase extraction step to remove extraneous interferents before instrumental analysis (Covaci et al., 2003; Covaci et al., 2009). The various techniques in the analysis of TBBPA and related compounds are described in review papers of Van Leeuven and De Boer (2008) and Covaci et al. (2003; 2007; 2009).

One of the causes of TBBPA contamination in the environment is the improper disposal of waste electronic and electrical equipment or electronic waste. In the Philippines, there is limited information available on the disposal of these wastes (Cardenas et al., 2006). Filipinos tend to store their electronic wastes for a long period of time before eventually giving them away or disposing of them, in many cases, into the ordinary garbage bin (Espino, 2008). This practice is common, perhaps due to the lack of guidelines on proper disposal or the expectation that a portion of the equipment's cost is recovered when a buyer is found. If left unchecked, this practice may pose threat to human and ecological health. There is potential for exposure to TBBPA in indoor environments where TBBPAtreated consumer products abound; there is also possible exposure to TBBPA in these places where Filipinos keep their outdated or broken electronic products for extended periods of time. Although TBBPA has been reported to be present in indoor air and dust elsewhere, mostly in developed countries, studies on TBBPA contamination in indoor environments in Asia are still scarce. In this paper, we present the first account on the occurrence of TBBPA in indoor places in the Philippines, specifically inside houses and internet cafes, and the latent exposure of Filipinos to this emerging environmental contaminant.

EXPERIMENTAL

Standards and solvents. The standards 3,5,3',5'-tetrabromobisphenol A (TBBPA, 98.8%) and pentachloronitrobenzene (PCNB, 96.4%, 5 mg mL⁻¹ in methanol) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Stock solutions of TBBPA and PCNB were prepared in methanol at 10 ng uL⁻¹ each. These were diluted to appropriate concentrations in the same solvent using volumetric equipment to make the calibration and spiking solutions. The HPLC-grade methanol (100.0%), acetonitrile (99.9%), water (2 ppm maximum residues), and *n*-hexane (99.8% as C6-isomers) were purchased from JT Baker (Philipsburg, NJ, USA). The solvents used for



Figure 2. Sampling sites in Quezon City and in Angono, Rizal [Maps adapted and modified from http://mapsof.net/ uploads/static-maps/metro_manila_politicalmap.png and http://www.mapcentral.ph/]

preparing the mobile phase were passed through 0.45 um x 47 mm nylon membrane filters (Whatman International Ltd., Maidstone, England) and degassed under vacuum in a Buchner flask set-up.

Sampling, sample preparation and extraction of TBBPA in indoor dust. Indoor dust samples were collected from filters of air conditioning units in five internet cafes near the University of the Philippines Diliman campus in Quezon City and in four houses in Angono, Rizal during the period of February to September 2010. The choice of sampling sites was mainly based on easy access and permission granted by owners to enter their houses and internet cafes. Figure 2 shows the locations of the sampling sites. The dust samples were carefully loosened and scraped from the filters using a 3.5 cm x 1 cm wire brush with a 13 cm length handle (Home Solutions, Philippines). A new brush was used for each sample. The dust samples were placed in 20-mL vials (RPI Corporation, Mt. Prospect, IL, USA), covered with aluminum foil, and stored in the freezer at 0 to 4°C until analysis.

The dust samples were homogenized by passing through a 500 um mesh sieve (W.S. Tyler, Mentor, OH, USA). Triplicates of 0.1 g dust samples (duplicates for limited sample masses collected) were weighed accurately in 4-mL vials and extracted with 2 mL hexane using a Power Sonic 410 ultrasonicator (Hwashin Technology, Gyeonggi-do, Korea). The ultrasonicator has a 10-L bath capacity, 40 kHz ultrasonic frequency and power consumption of 600 W. The ultrasonication-assisted hexane extraction was carried out for 15 min at room temperature. The hexane extract was filtered through a 0.2 um x 13 mm nylon membrane filter (Whatman International Ltd., Maidstone, England). A 500 uL of the hexane extract was placed in a microvial, evaporated to almost dryness using a water bath at temperature below 80°C, and reconstituted in 500 uL methanol. Added to this final extract was a 50 ng PCNB internal standard. PCNB was chosen as internal standard because it gave a high UV activity at the optimum wavelength of TBBPA and its use resulted in an acceptable analysis time with TBBPA.

The dust samples used for recovery experiments were prepared by exhaustive extraction using 100% hexane followed by 100% methanol. These were air dried at room temperature, fortified with TBBPA, equilibrated and air dried overnight, and taken through the entire ultrasonication-assisted hexane extraction procedure.

HPLC-UV analysis. A Shimadzu UV1700 spectrophotometer (Kyoto, Japan) was used to measure the wavelengths at which the TBBPA and PCNB registered maximum absorbances. The optimum wavelength suitable for the simultaneous determination of these compounds was 207 nm which was then used in the HPLC-UV analysis of TBBPA in the indoor dust extracts.

The system used for the analysis of TBBPA was a LC-10AS/SPD-10AV chromatograph equipped with a UV detector (Shimadzu, Kyoto, Japan). The analytical column was a ThermoHypersil C18 column 250 mm x 5 um x 4.6 mm i.d. (Thermo Fisher Scientific, MA, USA). Attached to this column was a Phenomenex C18 guard column 4 mm x 3.0 mm i.d. (Torrance, CA, USA). The following are the optimum HPLC-UV conditions used in the analysis: the mobile phase was 70:30 acetonitrile:water; the flow rate was 1 mL min⁻¹ which resulted in a total pressure of 77 kgf-cm²; the oven temperature was maintained at 30°C; and the UV detector was set at 207 nm. A 25 uL of the standard solution or sample extract was manually injected into the 20-uL sample loop. Data acquisition and processing were done using a Class LC-10 Shimadzu Analysis System and Software version 1.64. Figure 3 shows a HPLC-UV chromatogram of TBBPA and the internal standard.

Method performance and validation. A solution of 0.03 ng uL⁻¹ TBBPA in methanol was used to evaluate the reproducibility of the optimized HPLC-UV detection method. The calibration range for the analysis was established using standard solutions in linear response intervals of the optimized detection method. The statistical detection limit of the instrument was obtained using the equation

 $DL = student's t \times SD$



Figure 3. HPLC-UV chromatogram of TBBPA and PCNB measured at 207 nm. The mobile phase was 70:30 acetonitrile:water.

where the student's t value is 3.1438 with n-1 degrees of freedom at 99% confidence, and SD is the standard deviation of the measured TBBPA concentrations (n=7) in the spike level of 0.03 ng uL⁻¹ in methanol. The statistical method detection limit (MDL) was similarly obtained using Equation 1 but based on the standard deviation of seven replicate measurements of 2000 ng g-1 TBBPA spiked in indoor dust. The extraction recovery of TBBPA in indoor dust was evaluated from measurements of spiked TBBPA in previously cleaned indoor dust. The indoor dust was spiked with 2000 ng g-1 TBBPA and allowed to stand overnight. Three replicates of 0.1 g of this spiked dust were extracted with hexane by ultrasonication and the TBBPA was measured by HPLC-UV determination. The recovery was calculated using the equation

% Recovery = $[(TBBPA_{extract}/PCNB_{extract}) / (TBBPA_{standard}/PCNB_{standard})] \times 100$ (Equation 2)

where TBBPA_{extract} is the area of TBBPA in the extract of indoor dust at 2000 ng g⁻¹ spike concentration; PCNB_{extract} is the area of the internal standard in the extract at 0.1 ng uL⁻¹; TBBPA_{standard} is tha area of TBBPA in the standard solution at 0.1 ng uL⁻¹ concentration corresponding to the spiked TBBPA concentration in the indoor dust; and PCNB_{standard} is the area of the internal standard in the standard solution at 0.1 ng uL⁻¹ concentration at 0.1 ng uL⁻¹ concentration. Data analyses as well as calculations of concentrations, standard deviations and recovery were performed using Excel Microsoft Office 2003.

Determination of TBBPA in indoor dust. The indoor dust samples were analyzed using the optimized ultrasonication-assisted hexane extraction and HPLC-UV determination. The TBBPA in the extracts was determined and quantified using calibration solutions of 0, 0.03, 0.05, 0.08, 0.1, 0.2 and 0.3 ng uL⁻¹TBBPA in methanol; the extracts and calibration solutions also contained 0.1 ng uL⁻¹ PCNB. The TBBPA con-

| Replicates (spike level =0.03 ng | TBBPA Retention time, min | PCNB Reten- tion time, | Retention time ratio, TBBPA/ | Area of TBBPA | Area of PCNB | Area ratio, TBBPA/ PCNB |
|-------------------------------------------|---------------------------------|---------------------------------|---------------------------------------|---------------------|--------------------|----------------------------------|
| <u>uL</u>) | | min | PUNB | 2524 | 107(0 | 0.1702 |
| 1 | 5.95 | 9.83 | 0.605 | 3524 | 19/69 | 0.1/83 |
| 2 | 5.90 | 9.81 | 0.601 | 3816 | 22251 | 0.1715 |
| 3 | 5.93 | 9.86 | 0.601 | 3565 | 20047 | 0.1778 |
| 4 | 6.18 | 10.27 | 0.602 | 3712 | 19516 | 0.1902 |
| 5 | 6.09 | 10.12 | 0.602 | 3414 | 20197 | 0.1690 |
| 6 | 6.07 | 10.08 | 0.602 | 3515 | 20460 | 0.1718 |
| 7 | 6.06 | 10.06 | 0.602 | 3383 | 20090 | 0.1684 |
| Mean | 6.03 | 10.00 | 0.602 | 3561 | 20332 | 0.1752 |
| SD | 0.10 | 0.18 | 0.002 | 155 | 898 | 0.0076 |
| % RSD | 1.68 | 1.76 | 0.283 | 4.36 | 4.42 | 4.36 |

Table 1. Repeatability of TBBPA determination by HPLC-UV detection

centrations in the extracts were measured by linear regression analysis and the corresponding concentrations in the 0.1 g indoor dust samples were then calculated from these measurements. Solvent and procedural blanks (pooled indoor dust cleaned by extraction using 100% hexane followed by 100% methanol) were likewise analyzed together with the indoor dust samples to check for interferences or background peaks from laboratory conditions and equipment. In these blanks, no peaks were detected at the retention times of the target analytes.

RESULTS AND DISCUSSION

Analytical determination of TBBPA in indoor dust

The analysis of TBBPA by high pressure liquid chromatography and UV detection at 207 nm wavelength was optimized with 70:30 acetonitrilewater as mobile phase. After testing various twosolvent combinations of acetonitrile, methanol and water, the 70:30 acetonitrile-water eluent resulted in the best chromatographic conditions, i.e., having the optimal area response and shortest analysis time. This HPLC-UV determination is very reproducible with less than 5% and 2% relative standard deviations for peak areas and retention times, respectively (Table 1). The analytical parameters are summarized in Table 2. The six-level calibration curves in the linear response range of 0.03 to 0.3 ng uL⁻¹ have regression r² greater than 0.99 for both area of TBBPA and area response of TBBPA against PCNB. The determination can thus be carried out with or without PCNB, i.e., by internal standard calibration or by external calibration, respectively. However, it should be noted that in the analysis of real samples and especially with manual injection, internal standard addition is preferred. The instrument detection limit is 0.004 ng uL⁻¹ which can allow for trace analysis of TBBPA in an extract dissolved in methanol. This instrument detection limit is lower than the 1.1 ng uL⁻¹ reported by Pöhlein et al. (2005) in a similar HPLC-UV determination of TBBPA but using aqueous buffered methanol as chromatographic eluent and 205 nm wavelength for detection.

For limited amounts of samples such as indoor dust, an ultrasonication extraction procedure was deemed ideal because it can support small-volume glassware to contain small-size samples. In addition, ultrasonication extraction is less solvent-requiring, less time-consuming, and less costly. Different solvents were tested and hexane was found to be the suitable extraction solvent for TBBPA in indoor dust. Methanol and ethyl acetate were observed to extract extraneous compounds along with TBBPA from the indoor dust

| Parameters | Method performance |
|------------------------------------------|----------------------------------|
| TBBPA calibration range | $0.03 - 0.30 \text{ ng uL}^{-1}$ |
| PCNB internal standard spike level | 0.10 ng uL^{-1} |
| Calibration equation using area ratio of | y = 6.0714x - 0.0185 |
| TBBPA/PCNB | $(\mathbf{R}^2 = 0.9956)$ |
| Calibration equation using TBBPA | y = 12.495x - 0.086 |
| area only | $(\mathbf{R}^2 = 0.9980)$ |
| RSD of measured TBBPA concentration at | 3.96% |
| spike level of 2000 ng g ⁻¹ | (n=7) |
| Extraction recovery | 78% |
| | (n=3; SD=24) |
| Instrument detection limit | 0.004 ng uL^{-1} |
| Method detection limit | 1275 ng g ⁻¹ |

 Table 2. Analytical parameters for TBBPA determination and quantitation in indoor dust

samples. The coextractives imparted color in the extract thus requiring further clean-up. This was not the case with hexane where the extract was colorless. Also, hexane evaporates easily when reconstituting the extract in methanol prior to instrumental analysis.

Several flame retardants measurements in indoor dust reported in literature do not provide recoveries of the extraction, likely because of the lack of reference materials. Since a certified reference material for TBBPA in indoor dust was also not available in this study, the accuracy of the ultrasonication-assisted hexane extraction was assessed by replicate analyses of blank indoor dust spiked with 2000 ng g⁻¹ TBBPA. This provided an estimation of the extraction performance and recovery which was defined as the percent ratio of the measured amount divided by the spiked or expected amount. An acceptable recovery of 78% was obtained which demonstrates the efficiency of the ultrasonication-assisted hexane extraction in TBBPA removal from the sample matrix. The method detection limit is 1275 ng g⁻¹ which is relatively high for use in environmental monitoring of trace organic pollutants. This is expected because preconcentration was not done during the extract preparation and before instrumental analysis. Nonetheless, this method detection limit is acceptable for the present purpose wherein the method was used in indoor dust samples anticipated to be highly contaminated with TBBPA. The method can thus be useful in the analysis of indoor dust from enclosed environments where TBBPA-laden consumer products are present. For TBBPA determination in less contaminated samples, such as in outdoor dust where TBBPA is more dispersed, a sample size greater than 0.1 g may be used or a two- to four-fold preconcentration may be carried out to significantly lower the method detection limit.

Overall, the analysis of TBBPA in indoor dust is fast, requires minimal solvent or sample preparation, and does not need rigorous clean-up prior to HPLC-UV determination.

Concentrations and possible sources of TBBPA in the indoor dust samples

Dust and airborne particulates provide sinks for organic pollutants. TBBPA is also expected to adhere in this matrix. TBBPA contamination in dust collected in houses, pubs, offices, schools or cars has been reported (Abb et al., 2011; Abdallah, et al., 2008; D'Hollander et al., 2010; Geens et al., 2009; Harrad et al., 2010; Harrad et al., 2011; Takigami et al., 2009). Hence, these microenvironments are likely places for exposure to TBBPA. The TBBPA concentrations in

| Dust samples | Site Description | TBBPA concentration, ng g ⁻¹ (n=3) | Corrected ^c TBBPA concentration, ng g ⁻¹ | |
|-----------------|-----------------------------------------|-----------------------------------------------------|----------------------------------------------------------------------|--|
| House | | | | |
| HA | Bedroom: 1 TV, 1 PC | nd | nd | |
| HB | Bedroom: 1 PC, 1 laptop computer | < MDL ^a (388) | < MDL | |
| HD | Bedroom: 1 TV | 1348 | 1728 | |
| HE | Bedroom: 1 TV, 1 DVD player | nd | nd | |
| Internet Cafe | | | | |
| IA | Internet room: 9 PCs | 2220 ^b | 2846 | |
| IB | Internet room: 20 PCs | 2235 | 2865 | |
| IC | Internet room: 15 PCs, 1 photocopier | 2368 | 3036 | |
| IE | Internet room: 11 PCs | 4916 ^b | 6300 | |
| IF | Internet room: 8 PCs | nd | nd | |

| Table 3. TBBPA | concentrations | in the | indoor | dust | samples |
|----------------|----------------|--------|--------|------|---------|
| | | | | | |

nd = Not detected;

^a < MDL (TBBPA was detected; the calculated 388 ng g⁻¹ is below the statistical MDL);

^baverage of duplicate analyses; ^ccorrected for recovery.

indoor dust samples from houses and internet cafes in the present study are summarized in Table 3. TBBPA was detected in 67% of these samples. To our knowledge, this shows for the first time TBBPA contamination in indoor dust in the Philippines particularly in internet cafes where young people spend considerable time. Higher concentrations were found in internet cafe indoor dusts than in house indoor dusts. In the internet cafe dust samples where TBBPA was detected, the average concentration was 2934 ng g⁻¹. Of the dust samples taken from the houses, only one had TBBPA concentration above the method detection limit. Since TBBPA determination in internet cafe indoor dusts has never been done before, only the TBBPA concentrations in house dusts were compared to those reported in other countries (Table 4). The 1348 ng g⁻¹ concentration in one of the house dust samples in this study is notably higher than those reported elsewhere. This concentration may be comparable to some samples collected in Belgium (Geens et al., 2009). The comparability, however, may be limited since different sampling techniques and analytical methods were followed. In addition, there are studies that involve only a small sample size such that the measurements of TBBPA contamination may not provide a general assessment of human exposure to TBBPA in houses. Despite very few investigations on human exposure to brominated flame retardants, it has been proposed that this can be through food intake, dust ingestion and inhalation (Abdallah et al., 2008;

| Country | Samples | Range (ng g ⁻¹) | Collection/ sampling year | Reference |
|-------------|---------------------------|--------------------------------|------------------------------|-----------------------------|
| Philippines | House dust $(n-4)$ | nd – 1348 | 2010 | This study |
| Japan | House dust $(n-2)$ | 490 - 520 | 2006 | Takigami, et al., |
| Belgium | (II-2) House dust | < 3 – 419 | 2008 | D'Hollander, et |
| Belgium | (n=45) Domestic | 0.85 - 1481 | 2008 | al., 2010 Geens, et.al., |
| UK | dust (n=18) House dust | < MQL - 382 | 2006-2007 | 2009 Abdallah, et al., |
| Germany/ | (n=45) House dust | nd 470 | not reported | 2008 Abb. et al |
| USA | (Germany, | $\operatorname{IId} = 470$ | not reported | 2011 |
| | n=24; USA, n=2) | | | |

Table 4. Comparison of TBBPA concentrations in house dust in different countries

nd = Not detected; < MQL = less than the reported method quantitation limit.

Geens et al., 2009; Harrad et al., 2010). Geens et al. (2009) illustrated that dietary intake is the major path of exposure to environmental contaminants including TBBPA, while contaminated dust is a minor contributor. Kose et al. (2008) and Jakobsson et al. (2002) demonstrated that electronic products are among the causes of brominated flame retardants contamination in indoor environments and contamination increases when these flame retardant-treated products are present.

In the houses and internet cafes where we collected the indoor dusts, we recorded information on the would-be sources of TBBPA. The house dust samples were taken from air-conditioned bedrooms which contained at least one television set or one computer. In the internet cafes, the number of computers ranged from 8 to 20. The higher concentrations of TBBPA and the frequency of TBBPA occurrence in indoor dust from the internet cafes may be associated with the more number of computers present in these places. It should be noted, however, that the collection of indoor dust was not controlled nor simultaneously timed so as to respect the private and business activities in these places. As such, caution should be made in interpreting the TBBPA concentrations as these relate to the number of computers inside the internet cafes. Nevertheless, the data obtained here provide insights on the occurrence of TBBPA in indoor environments and the potential exposure of Filipinos to TBBPA from electronic products which are commonplace in these modern times. The results of this study can also serve as basis or baseline for future studies.

While there is no other information yet on TBBPA contamination in indoor environments in the Philippines, the findings in this study prompt the need to look at TBBPA occurrence in other enclosed places (viz. offices, classrooms, libraries, malls and other public microenvironments) where Filipinos stay for many hours. And while there is no health-based guideline against this contaminant, the effects of storage and disposal of electronic products should also be studied. A report on organohalogens in breast milk from mothers living in Payatas dumpsite in the Philippines showed higher levels of the flame retardants PBDEs compared to those reported in other Asian countries (Malarvannan et al., 2009). TBBPA was not among the flame retardants they investigated. It would be an interesting further study to determine the occurrence and levels of TBBPA in breast milk and serum from this exposed group. In this country where there is still no clear guideline on electronic waste disposal, comprehensive studies on the levels of brominated flame retardants in the local environment is important. When brominated flame retardant-treated things end up in dumpsites, soil contamination may ensue. These wastes may emit brominated flame retardant chemicals including TBBPA which can contaminate not only the soil but also the air and water. Scientific data on the environmental levels of these contaminants are important to the relevant government authorities as they formulate guidelines on the reduction of indoor or outdoor contamination and as they implement policies on electronic waste storage, handling, treatment and disposal.

CONCLUSIONS

An ultrasonication-assisted hexane extraction and determination by HPLC-UV detection were optimized and applied in the analysis of TBBPA in indoor dust. In six of the nine indoor dust samples analyzed, TBBPA was detected in concentrations up to 4916 ng g⁻¹. This study presented primary measurements of TBBPA in indoor dust from houses and internet cafes in the Philippines. The relatively high levels of TBBPA in most of the samples are believed to be caused by leaching of TBBPA from flame retardant-treated electronic products present in the sampling sites. Furthermore, this study provided indication suggesting that indeed dust represents one of the potential sources of human exposure to TBBPA in these indoor environments.

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