Introduction

Polybrominated diphenyl ethers (PBDEs) are the most widely used flame retardants in various electrical and electronic products, including TV and computers, plastics, fibers and furniture [1-3]. PBDEs can induce toxicity in the endocrine, nervous, and reproductive systems by accumulating in the fat of humans, animals, fish, and shellfish due to their lipophilic characteristics. The manufacture and use of PBDEs are thus subject to prohibition or management in developed countries such as South Korea, the EU, the US and Japan; PBDEs have been added to the list of persistent organic pollutants (POPs) according to the Stockholm Convention in 2009 [3-6].

PBDEs do not decompose well in environmental media due to their nature as POPs. Furthermore, PBDEs are semi-volatile organic compounds (SOCs), present both in the gas and particle phases of the atmosphere. Accordingly, the gas fraction of PBDEs increases as its molecular weight decreases; on the other hand, the particle fraction of PBDEs decreases as its molecular weight decreases. In terms of POPs present in the atmosphere, dry and wet deposition occurs on environmental media such as plants, soil, and water bodies when the temperatures decrease or
during the rainy and winter seasons. On the contrary, when the temperatures increase, POPs are volatilized into the atmosphere from environmental media and transported across distances through the atmosphere. Hence, it is crucial to identify the concentration of POPs in the atmosphere to understand the circulation of POPs in the atmosphere, as well as in plant, soil, and water bodies [5-12].

To precisely measure and analyze POPs in the atmosphere, a polyurethane foam (PUF) high volume air sampler, which can collect samples by separating the particulate matter and gaseous matter at the same time, is used. However, since the PUF high volume air sampler is costly and requires power for its operation, it cannot be efficiently used when several air samples need to be collected from various places at the same time or in areas where power supply is not available [13,14]. In these cases, the passive air sampler (PAS) is often used. Although the PAS cannot perform measurements by separating the particulate matter and gaseous matter and shows lower accuracy than the PUF high volume air sampler, it is convenient and economical; thus, it could be effectively used in measuring the concentration of POPs at various places [11-15].

Several researchers have developed artificial PAS by using XAD-2 resin, PUF and semipermeable membrane devices. However, the artificial PAS has many disadvantages in that it is necessary to wash and clean the adsorbent before sampling and it requires installation and disassembly before and after each collection [15]. However, because leaves and tree barks can be directly used during each collection, They are more convenient and economical than their artificial counterparts. Despite the advantages of the PAS collected from the nature, the deposition mechanism of POPs present in the atmosphere varies with the type of PAS samples; if this factor is not carefully considered this can lead to erroneous results [16-18].

During the deposition of the atmospheric POPs such as polychlorinated biphenyls (PCBs) and polychlorinated dibenzo-p-dioxin/furans (PCDD/Fs), the deposition depends on the lipid contents and the morphological characteristics of tree barks such as its surface area and roughness of the surface. The deposition also depends significantly on the gas/particle fraction of POPs in the atmosphere [16-18]. POPs are present both in the gas phase and particulate phase since they are SOCs; because PBDEs have a greater molecular weight than PCBs and PCDD/ Fs, even lower brominated PBDEs have relatively greater particle fraction [16-21]. During the deposition of the atmospheric gaseous POPs on tree barks, several years are required to reach equilibrium between the atmospheric POPs concentration and the POPs concentration on the tree barks; thus, a cumulative deposition occurs. However, when more than a certain amount of particulate POPs is attached on tree barks, desorption of the particulate POPs can occur due to rainfall, snowfall and wind; therefore, cumulative deposition of more than a certain amount does not occur [16-18]. Chun [22] examined the depositional characteristics on tree barks for PCBs with a high gas fraction in the atmosphere. However, studies have not been conducted on the depositional characteristics on tree barks for PBDEs that have a high particle fraction in the atmosphere. Tree barks differ in terms of surface area, surface roughness and lipid content with species. Therefore, significant errors in the concentration of POPs are likely to occur when the characteristics of the species of the tree barks and its classification are not considered [22].

The purpose of this study was to reduce the errors caused by incorrect sampling when using the tree barks as PAS; with this objective, four kinds of tree barks were collected from the same place and the depositional characteristics of atmospheric PBDEs on these tree barks were identified.

Materials and Methods

Reagents

For an analytical calibration curve, products of Wellington Laboratories (Guelph, ON, Canada) i.e., mixed standard solutions (calibration standards) (BDE-CVS-G: PBDE mixtures of 24 congeners), internal surrogate standards (MBDE-MXG: 13C12 PBDEs mixtures, 9 congeners) and recovery surrogate standard (BDE138L: International Union of Pure and Applied Chemistry [IUPAC] No. 13C13 BDE 138) were used. Pesticide residue analysis grade (J.T. Baker Inc., Phillipsburg, NJ, USA) solvents such as dichloromethane, n-hexane, and acetone and gas chromatography analysis grade solvents such as nonane (Sigma-Aldrich, St. Louis, MO, USA) were used in the present study.

Anhydrous granular solidium sulfate, potassium hydroxide, silver nitrate and sulfuric acid were obtained from GL Sciences (Tokyo, Japan). Silica gel (neutral, 70-230 mesh ASTM) was purchased from Merck (Darmstadt, Germany), bio-bead used in the gel permeation chromatography (GPC) column was purchased from Bio-Rad (S-X3, 40-80 µm, Hercules, CA, USA). All reagents were analytical grade. The physiochemical characteristics of the 24 congeners of target PBDEs analyzed are summarized in Table 1.

Sample Collection

Four kinds of tree barks were collected from Ginkgo, Pine, Platanus and Metasequoia; the trees showed relatively clear differences in external bark appearance and grew at the same place
within a 50 m radius in Hankyung National University located in Anseong, Gyeonggi-do Province, and received good ventilation. The outer skin of the tree barks was chiseled off by approximately 5 mm, and to exclude the influence of soil splashing during rainfall, samples were collected evenly from all directions within the height of 1-1.5 m from the ground by the end of October when the amount of rainfall was comparatively lower.

After collection, the samples were placed in a glass bottle and covered with an aluminum foil. The bottle was sealed with a lid, placed in an icebox, and transported to the laboratory. The samples was stored in a freezer at -20°C until analysis. The glass bottle and the aluminum foil were cleaned three times using n-hexane and dichloromethane, respectively. Figure 1 shows the tree barks used as samples.

Sample Extraction and Drying

The wet weight of tree bark samples was approximately 7-29 g; although the weight differences among samples were significant due to differences in gravity, the volume of the samples was similar. The samples were placed in a cellulose thimble (Sigma-Aldrich, size: φ43 mm × L123 mm) and spiked with internal surrogate standards. Extraction was then performed for 20-24 hours using an n-hexane:acetone (4:1) mixture solution in a Soxlet extraction apparatus. The wet/dry weight ratio of the samples was calculated by using the difference in the weight before and after drying of approximately 3-12 g of the wet samples at 95°C for approximately 24 hours. The lipid content of the samples was determined by the weight that was extracted from the dried samples used in the wet/dry sample weight ratio by placing the dried samples in a cellulose thimble and performing extraction for approximately 24 hours by using n-hexane in a Soxlet extraction apparatus. All samples were analyzed by preparing two subsamples (duplicate).

Pretreatment

The analysis and pretreatment of PBDEs were performed according to the POPs process test standards (Korean Official Test of POPs) [13] of the Ministry of Environment and the US Environmental Protection Agency (EPA) Method 1614 [14], which are described in the previous paper and summarized as follows [23]:

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**Table 1.** Selected physicochemical properties of polybrominated diphenyl ethers (PBDEs)

| Classification       | IUPAC No. | Molecular weight (g/mol) | LogKoa | No.   |
|----------------------|-----------|--------------------------|--------|-------|
| 2,2',4-T-BDE         | 17        | 406.9                    | 9.31   |       |
| 2,4',4'-T-BDE        | 28        | 94.0                     |        |       |
| 2,2',4,4'-T-BDE      | 47        | 485.8                    | 10.10  |       |
| 2,2',4,5'-T-BDE      | 49        | 9.89                     |        |       |
| 2,3',4,4'-T-BDE      | 66        | 10.25                    |        |       |
| 2,3',4,6'-T-BDE      | 71        | 10.20                    |        |       |
| 3,3',4,4'-T-BDE      | 77        | 10.46                    |        |       |
| 2,2',3,4,4'-P-BDE    | 85        | 564.7                    | 11.03  |       |
| 2,2',4,4',5'-P-BDE   | 99        | 10.96                    |        |       |
| 2,2',4,4',6'-P-BDE   | 100       | 10.82                    |        |       |
| 2,3',4,4',6'-P-BDE   | 119       | 11.17                    |        |       |
| 3,3',4,4',5'-P-BDE   | 126       | 11.39                    |        |       |
| 2,2',3,4,4',5',6-H-BDE | 138    | 643.6                    | 11.81  |       |
| 2,2',4,4',5',9'-H-BDE | 153    | 11.77                    |        |       |
| 2,2',4,4',5',6',9'-H-BDE | 154    | 11.66                    |        |       |
| 2,3',3,4,4',5',6',9'-H-BDE | 156    | 12.04                    |        |       |
| 2,2',3,4,4',5',6-H-BDE | 183    | 722.5                    | 12.56  |       |
| 2,2',3,4,4',6,6'-H-BDE | 184    | 12.50                    |        |       |
| 2,3',3,4,4',5',6-H-BDE | 191    | 12.85                    |        |       |
| 2,2',3,3',4,4',5',6'-O-BDE | 196   | 801.4                    | 13.72  |       |
| 2,2',3,3',4,4',6,6'-O-BDE | 197   | 13.47                    |        |       |
| 2,2',3,3',4,4',5',6'-N-BDE | 206  | 880.3                    | 14.36  |       |
| 2,2',3,3',4,4',5',6',6'-N-BDE | 207  | 14.39                    |        |       |
| 2,2',3,3',4,4',5',6',6'-O,9'-BDE | 209 | 959.2                    | 15.26  |       |

Koa, coefficient of octanol-air partitioning; IUPAC, International Union of Pure and Applied Chemistry.

*From Wang ZY, et al. Sci Total Environ 2008;389(2-3):296-305 [20].

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**Figure 1.** The four kinds of tree barks used in the present study. (A) Ginkgo (Ginkgo biloba), (B) Pine (Pinus densiflora), (C) Platanus (Platanus), (D) Metasequoia (Metasequoia glyptostroboide).
Gel Permeation Chromatography Column

Interfering substances were removed by using a GPC column (70 g of Bio Beads packed into a glass column of φ35 mm × L550 mm) and a silicagel cartridge of 0.5 g. The sample, which was extracted in a Soxlet, was concentrated to approximately 1-2 mL and then injected into the GPC column-silica gel cartridge. After injection, elution was performed using 200 mL of n-hexane:dichloromethane (1:1) mixture solution. The first 100 mL of eluate was discarded, and the remaining 100 mL of effluent was used in the analysis.

Multilayer Silicagel Column

The impurities present in the sample were not sufficiently removed by the GPC column-silicagel cartridge; for this reason, after the effluent was concentrated to 1-2 mL in a rotary evaporator, it was subsequently purified by using a multilayer silicagel column (φ15 mm × L300 mm), as shown in Figure 2. Once the sample was injected into the multilayer silicagel column, it was eluted with 150 mL of an n-hexane:dichloromethane (85:15) mixture solution. After concentrating the eluate to approximately 1 mL and spike recovery surrogate standard (BDE138L), a final solution was obtained by replacing the solvent with nonane; approximately 100 µL of the final volume was analyzed using a high-resolution gas chromatography/high-resolution mass spectrometer (HRGC/HRMS, JMS-800D; Jeol, Tokyo, Japan).

Analysis

The PBDE analysis conditions using HRGC/HRMS are summarized in Table 2.

Quality Assurance/Quality Control

Procedural blank was performed on each sample group as shown in the pretreatment process of the actual solution; a signal to noise ratio (signal/noise) value < 3 was considered as a non-detection. The average recovery by the congeners of internal surrogate standards that was spiked into the sample prior to extraction was 63.4% (39.4-113.9%), thus satisfying both the process test standards of POPs [13] and the 25-150% standard range (deca-BDE was 20-200%) as specified by the US EPA Method 1614 [14]. The limit of detection was 0.5 (BDE 17)-5.0 (BDE 209) pg/g. SRM 2585 (National Institute of Standards and Technology), which was the reference material, was analyzed to evaluate the whole analysis processes, and the concentration value as specified by the manufacturer was satisfied.

Recovery of internal surrogate standard was examined by analyzing the standard solution of the intermediate stage of a calibration curve standard solution when analyzing each of the 10 samples to check the stability of the equipment during the target material analysis. All the samples were analyzed by preparing two subsamples; the average coefficient of variance between two subsamples was 16.4% (0.0-37.4%).

Results

The lipid content and the total concentration of the 24 congeners of PBDEs deposited on each tree barks are shown in Figure 3. The total concentration of PBDEs was in the following order: Metasequoia (83,159.0 pg/g dry) > Ginkgo (53,538.4 pg/g dry) >...
dry) > Pine (20,266.4 pg/g dry) > Platanus (12,572.0 pg/g dry).
The lipid content was in the following order: Ginkgo (7.82 mg/g dry)
> Pine (4.85 mg/g dry) > Platanus (3.61 mg/g dry) > Metasequoia (0.97 mg/g dry). The lipid content of Metasequoia was the lowest, whereas the concentration of PBDEs deposited on Metasequoia was the highest.

Figure 4A and 4B show the concentration of the 24 congeners of analyzed target PBDE deposited on the tree barks, which were classified based on the lower brominated PBDEs (tri-penta BDE: BDE 17, 28, 47, 49, 66, 71, 77, 85, 99, 100, 119, 126: molecular weight [MW] = 406.9-564.79) and the higher brominated PBDEs (hexa-deca BDE: 138, 153, 154, 156, 183, 184, 191, 196, 197, 206, 207, 209: MW = 643.6-959.2). The sum of BDE 206, 207, and 209 concentrations accounted for 90.5% (84.3-95.6%) of the total concentration; in particular, the concentration of BDE 209 was the highest at 76.3% (71.0-80.7%) of the total concentration and the PBDEs deposited on the tree barks were mostly the higher brominated PBDEs.

Discussion

Although PBDEs are lipophilic chemicals, as shown in Figure 3, there was no correlation between the total concentration of PBDEs deposited on the tree barks and the lipid content of the tree barks ($R^2 = 0.1011, p = 0.6820$) [20].

Figure 4 shows the concentrations of the lower brominated PBDEs and higher brominated PBDEs deposited on the tree barks, according to tree species. The concentrations of the lower brominated PBDEs in Figure 4A did not show any regularity according to the tree species; however, the concentrations of the higher brominated PBDEs in Figure 4B showed regularity according to the tree species in the following order: Metasequoia > Ginkgo > Pine > Platanus.

Generally, the gas fraction of POPs, including PBDEs in the atmosphere, increases as the molecular weight of POPs decreases; on the other hand, the particle fraction of POPs increases as the MW of POPs increases [10,16,21,23]. The principal depositional mechanism of the lipophilic atmospheric gaseous POPs on the tree barks includes dry deposition on the lipids of the tree barks, whereas the principal depositional mechanism of particulate POPs includes dry and wet deposition (adhesion) on the surfaces of tree barks [10,16,22,24,25]. Chun [22] stated in previous study that the concentration of PCBs that were mostly present in the gas phase of the atmosphere and were deposited on the tree barks showed a strong correlation with the lipid content of the tree barks. However, most of the atmospheric PBDEs that are deposited on tree barks are the highly brominated PBDEs with a high particle fraction and the low brominated PBDEs whose particle fraction in the atmosphere is also considerably high compared to those of the other POPs [11,12]. The adhesion of the particulate POPs on the tree barks largely depends on the morphological characteristics of tree barks such as its surface area and roughness. Moreover, the adhesion shows a low correlation with lipid content [22,24,25]. Therefore, it was shown that there was a low correlation between the total concentration of PBDEs deposited on the tree barks and the lipid content of the tree barks. No correlations between the lipid content of the tree barks and the concentration of the lower brominated PBDE homologue with relatively high gas fraction in the atmosphere were also observed. Because the lower brominated PBDEs co-exist both in the gas phase and particle phase of the atmosphere, the lower brominated PBDEs showed concurrent characteristics of the two deposition mechanisms: the first is the dry gaseous deposition on the lipids of the tree barks and the second is a simple dry and wet deposition (adhesion) on the tree barks. The correlation between the concentration of the lower
brominated PBDEs homologue and the lipid content of the tree barks was thus low and regularity according to tree species was not observed [22,25].

The concentration of the atmospheric PBDEs deposited on the tree barks depended on characteristics such as the phase of PBDEs in the atmosphere and the morphological characteristics of the tree barks such as surface area and roughness. However, if these characteristics were not considered and the PBDE concentrations were compared by collecting barks of different tree species grown in different areas or the samples were used by mixing the tree barks of various species, the conclusions would likely vary from the practical results.

This study was conducted to find the depositional characteristics of 24 congeners of atmospheric PBDEs that were deposited on the tree barks of Ginkgo, Pine, Platanus, and Metasequoia that are often used as PAS of atmospheric POPs.

The total concentration of PBDEs deposited on the tree barks could be arranged in the following order: Metasequoia (83,159.0 pg/g dry) > Ginkgo (53,538.4 pg/g dry) > Pine (20,266.4 pg/g dry) > Platanus (12,572.0 pg/g dry). The lipid content could be arranged in the following order: Ginkgo (7.82 mg/g dry) > Pine (4.85 mg/g dry) > Platanus (3.61 mg/g dry) > Metasequoia (0.97 mg/g dry). The correlation between the total concentration of PBDEs deposited on the tree barks and the lipid content

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**Figure 4.** Polybrominated diphenyl ether (PBDE) congener concentrations (pg/g dry) in tree barks from four species for (A) lower brominated PBDEs and (B) higher brominated PBDEs.
was insignificant ($R^2 = 0.1011, p = 0.6820$). Among the PBDE congeners deposited on the tree barks, the sum of the BDE 206, 207 and 209 concentrations accounted for 90.5% (84.3-95.6%) of the total concentration, indicating that most PBDEs deposited on tree barks were highly brominated PBDEs via deposition of particulates. The deposition of the atmospheric particulate PBDEs on the tree barks largely depends on the morphological characteristics of the tree barks such as its surface area and surface roughness than on the lipid content of the tree barks. Therefore, when using the tree barks as the PAS of the atmospheric PBDEs, samples belonging to same tree species should be collected to reduce errors and to obtain reliable data.

**Conflict of Interest**

The author has no conflicts of interest with material presented in this paper.

**References**

1. Covaci A, Harrad S, Abdallah MA, Ali N, Law RJ, Herzke D, et al. Novel brominated flame retardants: a review of their analysis, environmental fate and behaviour. Environ Int 2011;37(2):532-556.
2. Wania F, Dugani CB. Assessing the long-range transport potential of polybrominated diphenyl ethers: a comparison of four multimedia models. Environ Toxicol Chem 2003;22(6):1252-1261.
3. Hites RA. Polybrominated diphenyl ethers in the environment and in people: a meta-analysis of concentrations. Environ Sci Technol 2004;38(4):945-956.
4. Yeo HG, Cho KC, Chun MY. Concentration and characteristic of PBDEs in pine needle and soil of Ansung-city. Korean J Environ Health 2006;32(2):111-117 (Korean).
5. Yeo HG, Cho KC, Chun MY. Composition, source, and regional concentration of PBDEs in pine needles. J Korean Soc Environ Eng 2006;28(8):829-835 (Korean).
6. Kim KK. Contents characteristics of polybrominated diphenyl ethers (PBDEs) in indoor household dust. Anal Sci Technol 2013;26(2):113-119 (Korean).
7. Eitzer BD, Hites RA. Atmospheric transport and deposition of polychlorinated dibenzo-p-dioxins and dibenzofurans. Environ Sci Technol 1989;23(11):1396-1401.
8. Thomas G, Sweetman AJ, Ockenden WA, Mackay D, Jones KC. Air–pasture transfer of PCBs. Environ Sci Technol 1998;32(7):936-942.
9. Bacci E, Cerejeira MJ, Gaggi C, Chemello G, Calamari D, Vighi M. Chlorinated dioxins: volatilization from soils and bioconcentration in plant leaves. Bull Environ Contam Toxicol 1992;48(3):401-408.
10. Yeo HG, Choi MK, Chun MY, Kim TW, Sunwoo Y. Temperature dependence of PCBs in urban area of Seoul City. J Korean Soc Atmos Environ 2002;18(3):193-204 (Korean).
11. Hayakawa K, Takatsuki H, Watanabe I, Sakai S. Polybrominated diphenyl ethers (PBDEs), polybrominated dibenzo-p-dioxins/dibenzofurans (PBDD/Fs) and monobromo-polychlorinated dibenzo-p-dioxins/dibenzofurans (MoBPXDD/Fs) in the atmospheric and bulk deposition in Kyoto, Japan. Chemosphere 2004;57(5):343-356.
12. Mandalakis M, Besis A, Stephanou EG. Particle-size distribution and gas/particle partitioning of atmospheric polybrominated diphenyl ethers in urban areas of Greece. Environ Pollut 2009;157(4):1227-1233.
13. Ministry of Environment. Korean Official Test of POPs. Notification No. 2011-125, Gwacheon: Ministry of Environment; 2011, p.1728-1789 (Korean).
14. US Environmental Protection Agency. Method 1614: brominated diphenyl ethers in water, soil, sediment, and tissue by HRGC/HRMS; 2007 [cited 2014 Apr 14]. Available from: http://water.epa.gov/scitech/methods/cwa/bioindicators/upload/2007_09_11_methods_method_1614.pdf.
15. Shoeb M, Harner T. Characterization and comparison of three passive air samplers for persistent organic pollutants. Environ Sci Technol 2002;36 (19):4142-4151.
16. Chun MY. A study on the deposition of PCBs in air on coniferous needles. J Korean Soc Environ Eng 1998;20(10):1377-1383 (Korean).
17. Chun MY. Sampling rate evaluation of atmospheric PAHs to pine needles for passive air sampler. J Korea Soc Environ Anal 2011;14(2):83-88 (Korean).
18. Chun MY. Estimation of PCBs concentrations in ambient air using pine needles as a passive air sampler (PAS). J Health Environ Sci Health Sci 2012;38(4):360-368 (Korean).
19. Cetin B, Odabasi M. Atmospheric concentrations and phase partitioning of polybrominated diphenyl ethers (PBDEs) in Izmir, Turkey. Chemosphere 2008;71(6):1067-1078.
20. Wang ZY, Zeng XL, Zhai ZC. Prediction of supercooled liquid vapor pressures and n-octanol/air partition coefficients for polybrominated diphenyl ethers by means of molecular descriptors from DFT method. Sci Total Environ 2008;389(2-3):295-305.
21. Heo JW, Kim DG, Song IS, Lee G. Concentration and gas-particle partitioning of PCDD/Fs and dipoxy groups in the ambient air of Ansan area. J Korean Soc Atmos Environ 2010;26(5):517-532 (Korean).
22. Chun MY. Depositional characteristics of atmospheric PBDEs on tree barks. J Korea Soc Environ Anal 2013;16(2):92-98 (Korean).
23. Chun MY. Characteristics of atmospheric polybrominated diphenyl ethers (PBDEs) deposited on tree leaves. J Korea Soc Environ Anal 2014;17(1):1-8 (Korean).
24. Welsch-Pausch K, McLachlan MS, Umlauf G. Determination of the Principal Pathways of Polychlorinated Dibenzo-p-dioxins and Dibenzo-p-dioxins to Lolium multiflorum (Welsh Ray Grass). Environ Sci Technol 1995;29(4):829-835 (Korean).