

Full Length Research Paper

Characteristics of polybrominated diphenyl ethers in the indoor atmosphere of computer classrooms

C. C. Cheng¹, C. F. Chiu² and F. H. Chang^{2*}

¹Department of Materials Science and Engineering, Far East University, Tainan 744, Taiwan (R.O.C.).

²Department of Leisure, Recreation and Tourism Management, Tzu Hui Institute of Technology, Pingtung 926, Taiwan (R.O.C.).

Accepted 7 September, 2009

This study investigated the polybrominated diphenyl ether, PBDE, congeners present in the indoor atmosphere of computer classrooms with differing exposure sources. A total of six air samples were obtained from three classrooms. These samples were analyzed by high-resolution gas chromatography and high-resolution mass spectrometry, and the total PBDE concentration ranged from 34.4 - 488.7 $\mu\text{g}/\text{m}^3$. In one classroom without decoration, measurements were taken with the computers on in one day (one sample) and with the computers off in another day (one sample). When computers were switched on, the indoor total PBDE concentration was 10-fold that when they were switched off. When the computer power was on, the majority of the PBDE congeners found in two classrooms without decoration were of high molecular weight, i.e., on average, BDE209 (24.8%), BDE203 (12.8%), BDE183 (9.2%), BDE196 (7.4%) and BDE207 (6.3%); however, when the power was off in one classroom without decoration, the majority were of low molecular weight, i.e., BDE47 (18.2%), BDE17 (12.9%), BDE15 (11.3%), BDE28 (11.1%) and BDE99 (6.4%). The five most abundant PBDE congeners found in one decorated classroom where all computers were switched on (two samples) were BDE15 (30.7%), BDE7 (13.2%), BDE209 (10.1%), BDE28 (8.1%) and BDE17 (5.5%), indicating that materials used for decoration and PUF-containing chairs are a major source of di-BDE and tri-BDE. These two homologs constituted 57.4% of the total PBDE concentrations. This study confirmed that computer equipment, interior decoration and PUF-containing chairs, and whether the power is switched on or off, significantly affects the PBDE concentration.

Key words: Polybrominated diphenyl ethers, indoor, PBDE congeners.

INTRODUCTION

Polybrominated diphenyl ethers, PBDEs, are a class of additive flame retardants widely used in polyurethane foam (PUF), plastics, textiles and electronics. Research indicates that PBDEs may have a harmful effect on the thyroid gland, as well as on the endocrine, reproductive, liver and nervous systems (Birnbaum and Staskal, 2004; Darnerud et al., 2001). PBDE exposure may also impair infant brain development (Gruenewald et al., 2003). Recently, the indoor environment was recognized as being potentially the dominant exposure route of PBDEs (Harrad et al., 2004; Jones-Otazo et al., 2005; Lorber

2008). For example, exposure of vulnerable groups such as toddlers to PBDEs via inhalation and/or ingestion of contaminated indoor air/dust may constitute the principal exposure pathway (Jones-Otazo et al., 2005). However, Harrad and Diamond (2006) studied PBDEs as well as polychlorinated biphenyls (PCBs) and concluded that a simple ban on the manufacture and "new" use of PBDEs would be insufficient to reduce exposure, owing to the continued release from treated products already in use. In a study by Harrad et al. (2004) it was reported that the use of indoor electronic equipment and PUF chairs can significantly increase the indoor PBDE concentration. More recently, Chen et al. (2008) indicated that the primary indoor emission source of PBDEs in Guangzhou, China, is relatively old electronic/electrical appliances, especially computers, but not PUF-containing furniture.

*Corresponding author. E-mail: fhchang@ms18.hinet.net.

Table 1. Classroom information including number of computers (no.), number of PUF-containing chairs (no.), computer power status (on/off), decoration (with/without) and concentration of total PBDE (pg/m^3).

Classroom	Number of computers	Number of PUF-containing chairs	Computer power	Decoration	Concentration of total PBDE	
					Mean	Range
A	61	61	on	with	94.5 (n = 2)	89.8 - 99.2
B	51	0	on	without	155.5 (n = 2)	107.0 - 204.0
C	59	0	off	without	34.4 (n = 1)	34.4
C	59	0	on	without	488.7 (n = 1)	488.7

Therefore, the issue of PBDE exposure in computer classrooms is worthy of investigation. The air PBDE concentrations inside three computer classrooms in a southern Taiwan college were measured in this study, and the PBDEs present were analyzed. The results of this analysis may help us to evaluate the effect of computer usage and decoration on indoor PBDE emission and understand the characteristics of the PBDEs present in the atmosphere of computer class-rooms.

MATERIALS AND METHODS

The sample areas were three computer classrooms in a southern Taiwan college campus, one with interior decoration (with fiber glass wall paper and plastic laminate wood flooring) and 61 PUF-containing chairs (classroom A), the others without decoration and without any PUF-containing chairs (classrooms B and C). The detailed classroom characteristics including the number of computers, number of PUF-containing chairs, computer power status (on/off), and decoration are shown in Table 1. A total of six indoor air samples were collected between September 7 and September 9, 2007, and between November 22 and November 24, 2007.

Air samples were collected using a PS-1 high-volume air sampler (General Metal Works, U.S.A.) fitted with a total suspended particulate inlet modified to hold a glass fiber filter and a pre-cleaned PUF, as described previously (Harrad et al., 2004). The typical sampling flow rate was $0.25 \text{ m}^3/\text{min}$. To minimize underestimation of the concentration, the total volume of air drawn from the computer classroom did not exceed its indoor volume and was allowed to re-equilibrate for an identical period of time (Harrad et al., 2004). Indoor air sampling was conducted over a period of approximately 24 h for each sample and in the absence of the classroom occupants. Depending on the research requirements, electrical appliances including computers, monitors, lights, and air conditioners were either switched on or off during sampling.

Chemical analyses

In this study, filter and PUF plugs were analyzed as units to avoid the confounding effects of low analyte quantities in the samples. The method of PBDE analysis has been described in detail elsewhere (Chang et al., 2009). Briefly, the filters and PUF plugs were spiked with isotope-labeled PBDE standard solutions including ^{13}C -BDE15, ^{13}C -BDE28, ^{13}C -BDE47, ^{13}C -BDE99, ^{13}C -BDE153, ^{13}C -BDE154, ^{13}C -BDE183, ^{13}C -BDE197, ^{13}C -BDE207 and ^{13}C -BDE209 (Wellington Laboratories, Canada and AccuStandard, U.S.A.), and Soxhlet extraction with toluene was then performed for 22 ± 2 h. The concentrated extracts were cleaned and fractionated on acid/basic multi-layer silica gel columns and then alumina columns. The final extracts containing PBDEs were then

concentrated to near dryness and added to $10 \mu\text{l}$ of internal standard ^{13}C -BDE138 for instrumental analyses.

Instrumental determination was performed using an HP6890 high-resolution gas chromatographer (HRGC) (Agilent, U.S.A.) and a high-resolution mass spectrometer (HRMS) (Micromass Autospec Ultima, U.K.). Qualitative and quantitative analyses of pretreated samples of thirty PBDE congeners including BDE7, BDE15, BDE17, BDE28, BDE47, BDE49, BDE66, BDE71, BDE77, BDE85, BDE99, BDE100, BDE119, BDE126, BDE138, BDE139, BDE140, BDE153, BDE154, BDE156, BDE183, BDE184, BDE191, BDE196, BDE197, BDE203, BDE206, BDE207, BDE208 and BDE209 were performed using the ^{13}C isotope dilution method and HRGC/HRMS. The instrumental analysis conditions have been reported previously (Chang et al., 2009). The method detection limits (MDL) were calculated as three times the signal to noise ratio in the sample for all congeners, and was found to range from 0.29 - 11.35 pg (except for BDE209); the MDL for BDE209 was 105.37 pg.

Quality assurance and quality control

At the beginning of the development of the PBDE analytical method, the initial precision and recovery (IPR) was evaluated. When analyzing the practical samples, recoveries of the isotope-labeled standards of tri-BDE, tetra-BDE, penta-BDE, hexa-BDE, hepta-BDE and deca-BDE were evaluated. After each batch analysis, or after every ten practical samples, blank matrix analyses were performed using the same procedures as those for the practical sample analyses. All evaluation results met the criteria for the PBDE analytical method used in this study (data not shown).

Data treatment and analysis

Data were recorded and analyzed in EXCEL 2003 (Microsoft, U.S.A.). Sample values lower than the MDL were set to MDL/2 in order to construct the concentration distribution profiles of the PBDE congeners and for further data analysis.

RESULTS AND DISCUSSION

Comments on the indoor total PBDE concentrations

The indoor total PBDE concentrations in the computer classrooms were 89.9, 99.2 (classroom A, power on, decorated, 2 samples), 107.0, 204.0 (classroom B, power on, undecorated, 2 samples), 34.4 (classroom C, power off, undecorated) and $488.7 \text{ pg}/\text{m}^3$ (classroom C, power on, undecorated). These results and other information on the classroom settings are provided in Table 1. It is noted that in classroom C, the indoor PBDE concentration when

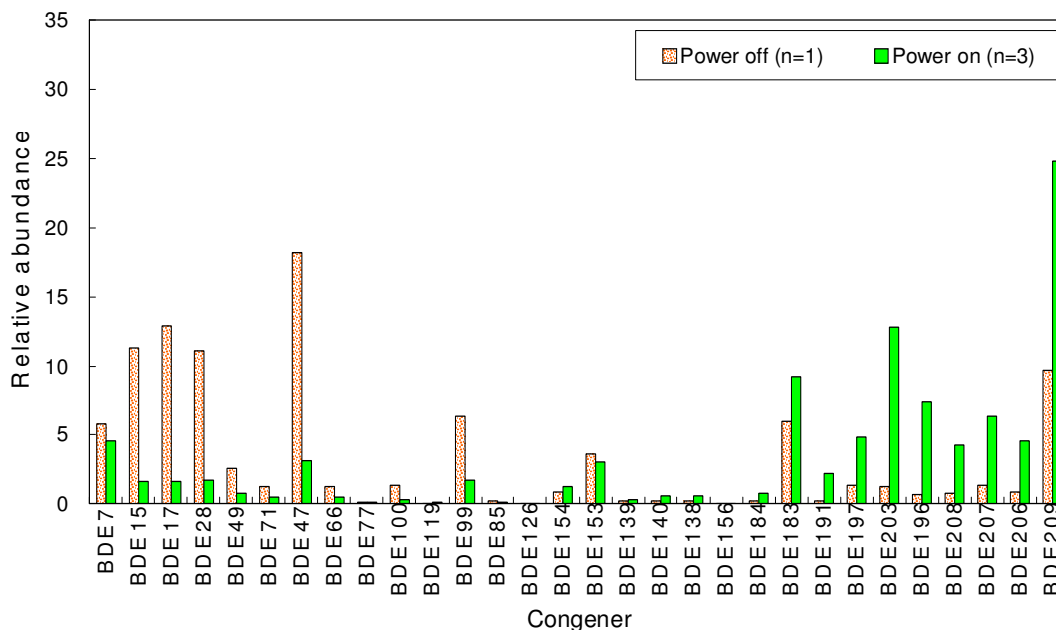


Figure 1. The relative abundances of PBDE congeners in the air of indoor computer classrooms without decoration.

the power was switched on was 10-fold that measured when the power was off.

The average PBDE concentration found in our study, 170.5 pg/m^3 , was much lower than those reported for the work places tested by Harrad et al. (2004) (2788 pg/m^3) and Chen et al. (2008) (4700 pg/m^3). However, our result was the same order of magnitude of the findings of Harrad et al. (2004) (525 pg/m^3) and Wilford et al. (2004) (260 pg/m^3) for homes, but was an order of magnitude less than that observed by Chen et al. (2008) in homes (3016 pg/m^3).

PBDE concentration measurements in indoor environments may be affected by many sources, such as electrical appliances and PUF-containing chairs (Chen et al., 2008; Harrad et al., 2004), and are complicated by additional factors such as ventilation rate, temperature, proximity of the sampler to potential sources, age of those sources, and so on (Chen et al., 2008; Wilford et al., 2004). Therefore, without a specific and detailed experimental design, the total PBDE concentration measured in different indoor spaces can only be used as a reference of personal exposure level, and cannot be used to identify the characteristics and contributions of PBDEs resulting from a particular pollution source.

Comments on the congener composition

Figure 1 illustrates the relative abundances of PBDE congeners in the air of the computer classrooms without decoration. Classroom A, which had decoration, was not included in this analysis because we just sought to

identify whether the computer power was switched on or off affecting the PBDE concentration. The data displayed in Figure 1 includes, therefore, 2 samples from classroom B which had the power on, and 2 samples from classroom C, one with power off and one with power on. When all computers were in the power-off mode, the single sample from Classroom C, the five most abundant PBDE congeners were BDE47 (18.2%), BDE17 (12.9%), BDE15 (11.3%), BDE28 (11.1%) and BDE99 (6.4%), comprising 59.9% of the total PBDE concentration. By comparison, in the power-on mode, the five most abundant PBDE congeners, which comprised 60.5% of the total PBDE concentration, were BDE209 (24.8%), BDE203 (12.8%), BDE183 (9.2%), BDE196 (7.4%) and BDE207 (6.3%). Figure 2 demonstrates the contribution of various PBDE homologs to the total PBDE concentrations measured in the air of the computer classrooms without decoration. This figure was developed using the same data and clustering of data points as Figure 1 (described above). The predominant PBDE homologs found in the indoor air of the classrooms in terms of relative abundance when the power was switched off were di-BDE (17.1%), tri-BDE (24.0%) and tetra-BDE (23.4%), which comprised 64.5% of the total PBDE concentration. In contrast, when all computers were switched on, the predominant PBDE homologs, which comprised 77.1% of the total PBDE concentration, were hepta-BDE (12.2%), octa-BDE (25.0%), nona-BDE (15.1%) and deca-BDE (24.8%). When the computers were off, our findings showed that air might be expected to be relatively enriched with lower brominated PBDEs, that is, di-BDE, tri-BDE and tetra-BDE (Figures 1 and 2), and were in

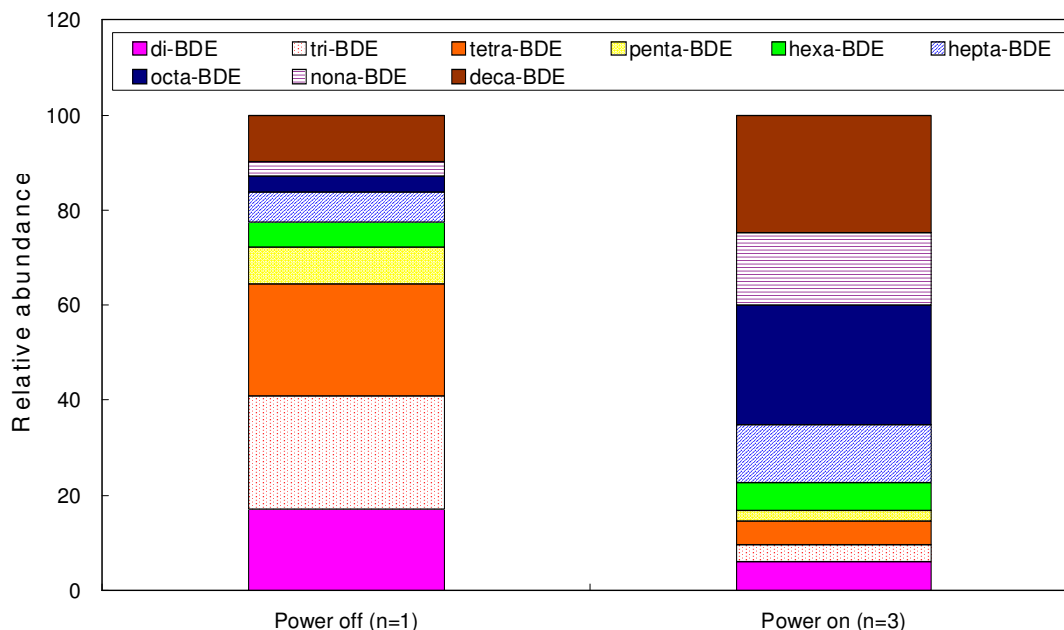


Figure 2. Contributions of various PBDE homologs to the total PBDE concentration measured in the air of indoor computer classrooms without decoration.

good agreement with those reported in the study by Wilford et al. (2004). In addition, Bergman et al. (1999) reported that BDE47 and BDE99 were found in the air of computer and electronic product assembly plants, and Julander et al. (2005) stated that workers in electronic dismantling factories had elevated plasma BDE28 concentrations, which increased with increased working hours. These results were similar to those obtained in our study in the computer classrooms when the power was switched off, which showed higher proportions of BDE28, BDE47 and BDE99. Furthermore, Jakobsson et al. (2002) reported that technicians involved in intensive computer work had serum concentrations of BDE-153, BDE-183 and BDE-209 that were significantly higher than those of staff with less computer usage. Moreover, elevated BDE209 serum levels were observed among the electronic waste dismantling workers in Guangdong and Guiyu, China (Bi et al., 2007; Qu et al., 2007). Our PBDE measurement when the power was on was similar to this result; however, our study demonstrated that BDE15, BDE17, BDE28, BDE47, BDE99, BDE153, BDE183, BDE203, BDE196, BDE207 and BDE209 were the PBDE congeners related to and derived from the computer equipment present, and only with differing indoor environments did the relative abundance of the congeners vary. Figure 3 shows the relative abundances of PBDE congeners in the air of the computer classrooms where all computers were being switched on. The data includes not have decoration. The five most abundant PBDE congeners found in the air of the decorated classroom, 2 samples in classroom A which had decoration, a sample in each of classrooms B and C, both of which did

classroom A, were BDE15 (30.7%), BDE7 (13.2%), BDE209 (10.1%), BDE28 (8.1%) and BDE17 (5.5%); these five congeners comprised 67.6% of the total PBDE concentration. Figure 4 shows the contribution of various PBDE homologs to the total PBDE concentration measured in the air of computer classrooms with all computers in power-on mode. The predominant PBDE homologs found in the air of decorated classrooms in terms of relative abundance were di-BDE (43.8%), tri-BDE (13.6%) and deca-BDE (10.1%), which comprised 67.5% of the total PBDE concentration. We found that, in the computer classrooms with or without decoration, BDE183, BDE203 and BDE209 congeners were the most abundant when the power was on; in the computer classrooms with decoration, the concentrations of low molecular weight BDE7, BDE15 and BDE28 were significantly higher than in the computer classrooms without decoration (Figure 3). Our results indicated that interior decorating and PUF-containing chairs may be important sources of di-BDE and tri-BDE, and these two homologs constituted 57.4% of the total PBDE concentration (Figure 4).

Conclusion

This study confirmed that the presence of computer equipment, interior decoration and PUF-containing chairs significantly increases the indoor PBDE concentration. However, different PBDE sources give rise to different PBDE congeners. When computers are in power-on or power-off mode, different PBDE congeners are generated, including BDE15, BDE17, BDE28, BDE47,

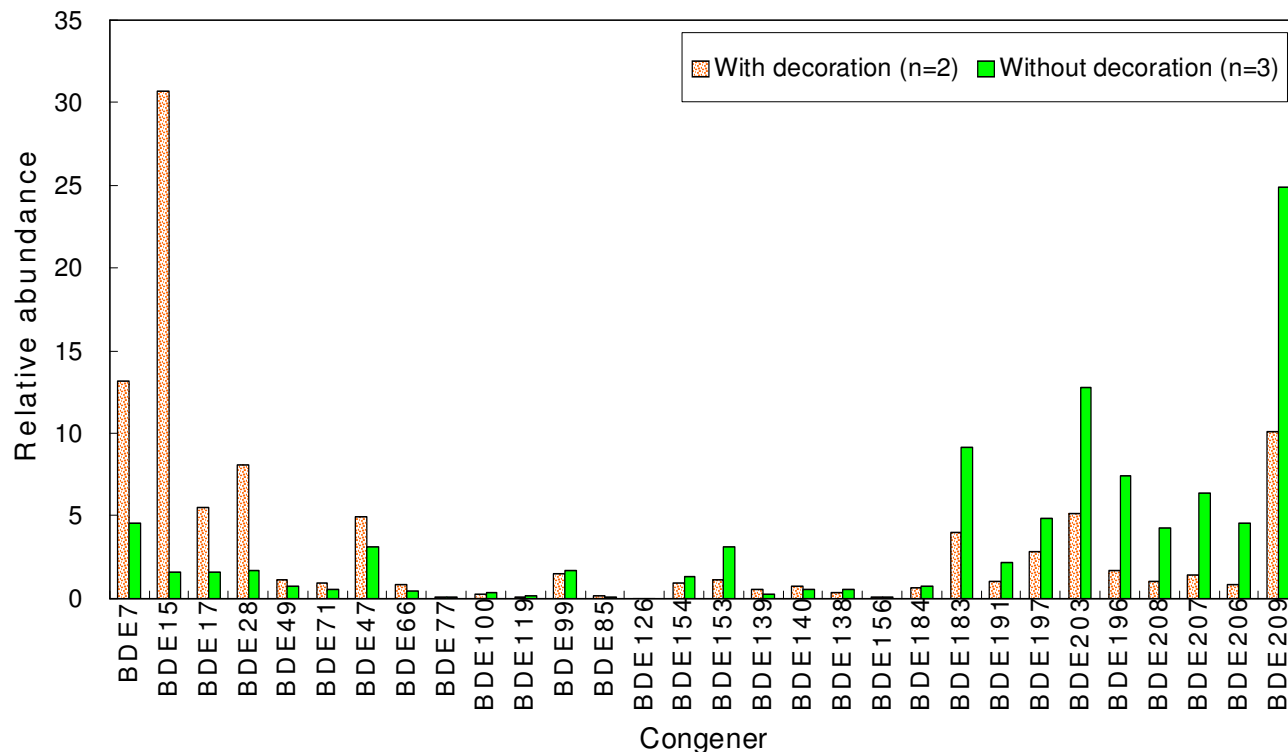


Figure 3. The relative abundances of PBDE congeners in the air of indoor computer classrooms when all computers were being switched on.

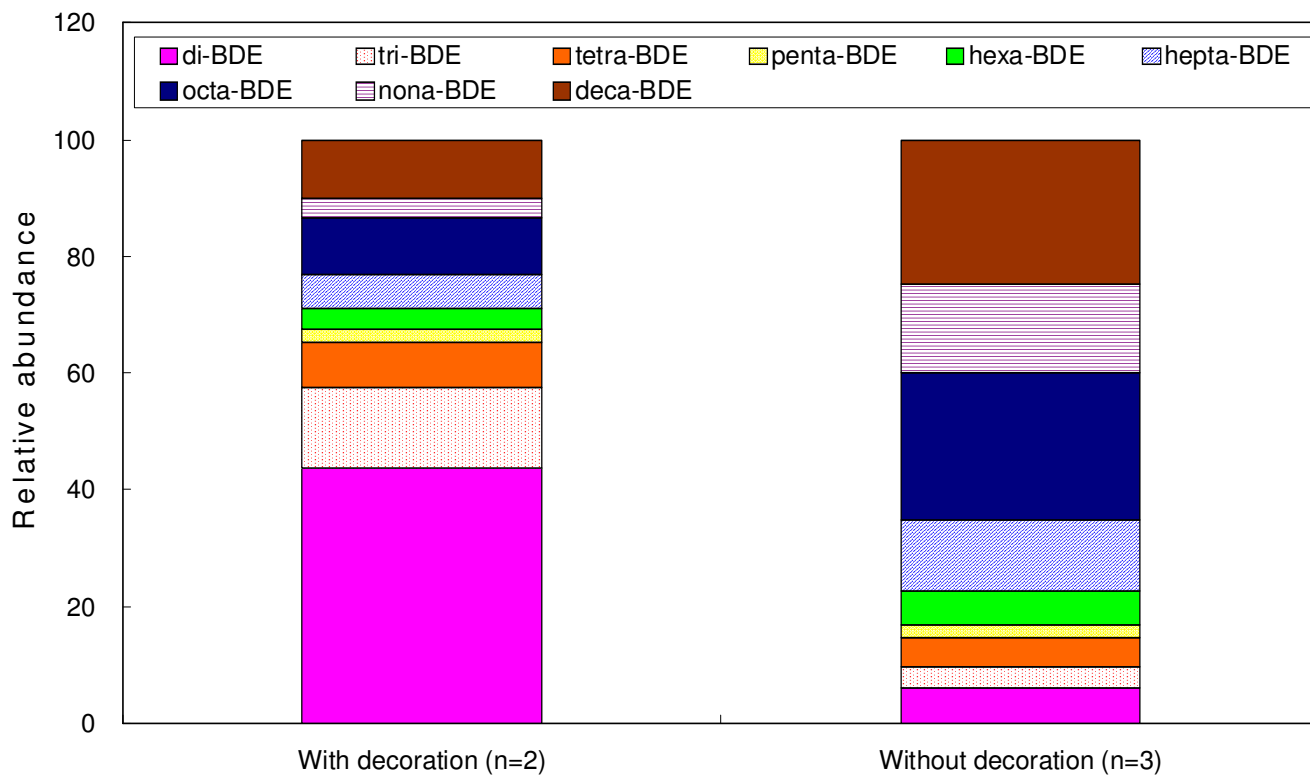


Figure 4. Contributions of various PBDE homologs to the total PBDE concentration measured in the air of indoor computer classrooms when all computers were being switched on.

BDE99 and BDE153 (dominant when power off), and BDE183, BDE203, BDE196, BDE207 and BDE209 (when power on). Lower brominated PBDE congeners (e.g. di-BDE, tri-BDE and tetra-BDE) are predominant in the air of computer classrooms with interior decorating and PUF containing chairs when the power is switched off. In contrast, higher brominated PBDE congeners (e.g. hepta-BDE, octa-BDE, nona-BDE and deca-BDE) are predominant in the air of computer classrooms without interior decorating or PUF-containing chairs when the power is switched on.

ACKNOWLEDGEMENTS

We gratefully acknowledge the financial support (Grant NSC95-2314-B-470-001) of the National Science Council (NSC) of the Republic of China (R.O.C.), and the Super Micro Mass Research and Technology Center, Cheng-Shiu University, Taiwan (R.O.C.) for assistance during sampling and sample analyses.

REFERENCES

- Bergman Á, Athanasiadou M, Klasson Wehler E, Sjödin A (1999). Polybrominated environmental pollutants: human and wildlife exposures. *Organohalogen Compd.* 43: 89-92.
- Bi XH, Thomas GO, Jones KC, Qu WY, Sheng GY, Martin FL, Fu JM (2007). Exposure of electronics dismantling workers to polybrominated diphenyl ethers, polychlorinated biphenyls, and organochlorine pesticides in South China. *Environ. Sci. Technol.* 41: 5647-5653.
- Birnbaum LS, Staskal DF (2004). Brominated flame retardants: Cause for concern? *Environ. Health Persp.* 112: 9-17.
- Chang FH, Yang CR, Tsai CY, Lin WC (2009). Airborne polybrominated diphenyl ethers in a computer classroom of college in Taiwan. *Iran. J. Environ. Health Sci. Eng.* 6: 121-130.
- Chen LG, Mai BX, Xu ZC, Peng XC, Han JL, Ran Y, Sheng GY, Fu JM (2008). In- and outdoor sources of polybrominated diphenyl ethers and their human inhalation exposure in Guangzhou, China. *Atmos. Environ.* 42: 78-86.
- Darnerud PO, Eriksen GS, Johannesson T, Larsen PB, Viluksela M (2001). Polybrominated diphenyl ethers: Occurrence, dietary exposure, and toxicology. *Environ. Health Persp.* 109: 49-68.
- Gruenewald DM, Aronsson A, Ekman-Ordeberg G, Bergman A, Noren K (2003). Human prenatal and postnatal exposure to polybrominated diphenyl ethers, polychlorinated biphenyls, polychlorobiphenyls, and pentachlorophenol. *Environ. Health Persp.* 111: 1235-1241.
- Harrad S, Diamond M (2006). New directions: Exposure to polybrominated diphenyl ethers (PBDEs) and polychlorinated biphenyls (PCBs): Current and future scenarios. *Atmos. Environ.* 40: 1187-1188.
- Harrad S, Wijesekera R, Hunter S, Halliwell C, Baker R (2004). Preliminary assessment of UK human dietary and inhalation exposure to polybrominated diphenyl ethers. *Environ. Sci. Technol.* 38: 2345-2350.
- Jakobsson K, Thuresson K, Rylander L, Sjödin A, Hagmar L, Bergman A (2002). Exposure to polybrominated diphenyl ethers and tetrabromobisphenol A among computer technicians. *Chemosphere* 46: 709-716.
- Jones-Otazo HA, Clarke JP, Diamond ML, Archbold JA, Ferguson G, Harner T, Richardson GM, Ryan JJ, Wilford B (2005). Is house dust the missing exposure pathway for PBDEs? An analysis of the urban fate and human exposure to PBDEs. *Environ. Sci. Technol.* 39: 5121-5130.
- Julander A, Karlsson M, Hagstrom K, Ohlson CG, Engwall M, Bryngelsson IL, Westberg H, van Bavel B (2005). Polybrominated diphenyl ethers - plasma levels and thyroid status of workers at an electronic recycling facility. *Int. Arch. Occ. Environ. Health* 78: 584-592.
- Lorber M (2008). Exposure of Americans to polybrominated diphenyl ethers. *J. Expo. Sci. Environ. Epidemiol.* 18: 2-19.
- Qu WY, Bi XH, Sheng GY, Lu SY, Fu H, Yuan J, Li LP (2007). Exposure to poly-brominated diphenyl ethers among workers at an electronic waste dismantling region in Guangdong, China. *Environ. Int.* 33: 1029-1034.
- Wilford BH, Harner T, Zhu JP, Shoeib M, Jones KC (2004). Passive sampling survey of polybrominated diphenyl ether flame retardants in indoor and outdoor air in Ottawa, Canada: Implications for sources and exposure. *Environ. Sci. Technol.* 38: 5312-5318.