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Monitoring and Dispersion Modeling of Polybrominated Diphenyl Ethers (PBDEs) in the Ambient Air of Two Municipal Solid Waste Incinerators and a Coal-fired Power Plant

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ABSTRACT

The concentration of polybrominated diphenyl ethers (PBDEs) in the ambient air of two municipal solid waste incinerators (MSWIs) and one coal-fired power plant (TPP) were determined. Along with the sites mentioned above, eight ambient air samples were collected. Cluster analysis was carried out to determine the relationship of PBDE characteristics between each site. Finally, PBDE dispersion modeling in the atmosphere was applied by using ISCST3 (Industrial Source Complex Short Term 3) to assess the impact of the above two municipal solid waste incinerators and one coal-fired power plant on the ambient air. The total-PBDE concentrations in the ambient air were between 24.9 and 139 pg/Nm^3, averaging 59.8 pg/Nm^3 (n = 16). The BDE-209, BDE-47 and BDE-207 were the most predominant three among all 30 PBDE congeners, which contributed more than 58%, 9%, and 4% of total-PBDE mass to the ambient air, respectively. The results of cluster analysis indicated that no direct correlations existed among the emission sources (MSWI-A, MSWI-B, TPP) and the receptors (sampling sites). From the results of dispersion modeling, the annual total PBDE concentration in ambient air contributed by the MSWI-A, MSWI-B, TPP together were found to be 0.0259% ± 0.0208%. Hence, the results of both cluster analysis and dispersion modeling showed that MWSI-A, MSWI-B, and TPP were definitely not the major contributors of PBDEs to the ambient air environment. The ashes collected from the air pollution control devices of both the MSWIs and the TPP are probably a more important environmental issue and therefore should be paid more attention to.

Keywords: Polybrominated diphenyl ethers (PBDEs); Municipal solid waste incinerators; Coal-fired power plant; Stack flue gases; Dispersion.

INTRODUCTION

Polybrominated diphenyl ethers (PBDEs) are a group of persistent organic pollutants that have been extensively used as additives for flame retardation (FR) worldwide since the 1970's. This is due to the fact that they are the cheapest, yet most effective, fire retardants (FRs) (Rahman *et al.*, 2001). The most common PBDE products in the market are penta-, octa, and deca-BDE mixtures. Due to their high toxic effects on human beings and animals, the manufacturing and usage of these commercial penta- and octa-BDE mixtures were banned during August, 2004 in the European Union, with the exception of deca-BDE products. However, highly brominated BDEs can be debrominated into lesser brominated BDEs and still display adverse health effects (Soderstrom *et al.*, 2004); hence, the deca-BDE mixtures were banned as well on July 1st, 2008.

The United States also noticed the hazards of PBDE applications. All of the industries and companies in the U.S. have required a notification to the U.S. EPA 90 days prior to the manufacturing or importation, for any use, of commercial penta-BDE and octa-BDE products since January 1, 2005. Production in the United States of these two chemicals ceased at the end of 2004. Moreover, the U.S. EPA announced the phase out of deca-BDE in December of 2009, with production, importation, and sales of deca-BDE for most uses in the United States to end by December 31th, 2012, and all uses to end by December 31th, 2013 (EPA., 2010). Nevertheless, the use of PBDEs is still not restricted in

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The structure of PBDEs is similar to that of dibenzo-*p*-dioxins/furzns (PCDD/Fs) and polychlorinated biphenyls (PCBs) (Talsness, 2008). Deca-BDE (BDE-209) has been found to be photolytically debrominated and to form from nona- to tetra-BDEs as well as other PBDF homologues (Soderstrom, *et al.*, 2004). In a previous study, polybrominated dibenzo-*p*-dioxins, and dibenzofurzns (PBDD/Fs) were observed to be released from products containing BFRs during the incineration of the wastes of products or the processing of PBDE-containing plastics (Sakai *et al.*, 2001; Watanabe and Sakai, 2003; Weber and Kuch, 2003; Lai *et al.*, 2007). Once released during production, recycling, or usage, these PBDEs tend to persist in both terrestrial and aquatic environments (Soderstrom, *et al.*, 2004; Hites; Mandalakis *et al.*, 2009). For example, PBDEs have been observed at levels of the sum of PBDE-47, -99 and -100 and were found to be n.d.–4000 pg/L in the raw leachate of landfills (Osako *et al.*, 2004). Therefore, the use of unregulated deca-BDE products has caused less-brominated congeners, which are the highly toxic substances that are bio-accumulated in animals (Hale *et al.*, 2001; Darnerud, 2003; La Guardia *et al.*, 2006; Meng *et al.*, 2007; Kuiper *et al.*, 2008; Chen *et al.*, 2010). According to previous research on this topic, PBDEs have been detected in wild animal predators, such as peregrine falcon and blue fishes, which have a higher PBDE burden than other species (Bocio *et al.*, 2003; Chen *et al.*, 2008). Borghesi has confirmed that PBDE contamination of marine environments currently occurs on a global scale (Borghesi *et al.*, 2009).

Since the 1970's, PBDE concentrations in the breast milk of Swedish mothers have increased almost 100-fold, doubling about every five years from 1972 to 1997 (Noren and Meironyte, 2000). However, a research survey from 1973 to 2000 in Japan indicated the PBDEs in Japanese mothers' breast milk are relatively low (Akutsu *et al.*, 2003). In Taiwan, the conducted research on breast milk in Taiwanese mothers found PBDE concentrations to be 1.6–2.3 times higher than those of Japanese mothers (Chao *et al.*, 2007; Horng *et al.*, 2010). The bio-accumulating effect in human bodies is of concern due to the fact that several toxicological effects of PBDE congeners have been detected in experimental animals, such as neurotoxicity, behavioral changes, and endocrine disruption (McDonald, 2002; Darnerud, 2003; Kuiper *et al.*, 2008; van der Ven *et al.*, 2009). The major sources of human PBDE exposure are through diet, accounting for 73% of daily intake (Bocio, *et al.*, 2003). Moreover, the major human dietary exposures are through meat products (Bocio, *et al.*, 2003; Harrad *et al.*, 2004). However, in a United States study, the major exposure routes were found to be both ingestion and dermal absorption (Johnson-Restrepo and Kannan, 2009). The different results in the U.S. could be caused by the massive usage of PBDEs.

In Taiwan, the fates and distribution of PCDD/Fs have been investigated thoroughly in many different areas (Chuang *et al.*, 2010; Lin *et al.*, 2010; Chen *et al.*, 2011; Chiu *et al.*, 2011; Lin *et al.*, 2011a; Lin *et al.*, 2011b; Lo *et al.*, 2011). Also, long term atmospheric PCDD/F monitoring has been done (Wu *et al.*, 2010). The main PCDD/F sources in MSWIs have been found to be from fly ashes (Chen *et al.*, 2008; Wang *et al.*, 2009). Moreover, not only PCDD/Fs emitted from joss papers burned in Taiwanese temples are noticed for their peak emissions during the festival period (Hu *et al.*, 2009), but also PCDD/Fs entering tap water via dry and wet deposition have drawn attention of people (Lin *et al.*, 2010). Wang (Wang *et al.*, 2010c) point out that the seasonal change of PCDD/Fs in air could be affected by heating and temperature inversion in winter or photodegradation and OH radical reaction in summer. In Taiwan, 72.2% of the electricity comes from thermal power plants, and 67% of those use coal as fuel. Not only have heavily oil-fueled power plants been found to contribute heavy metals in northern Taiwan (Wang *et al.*, 2010d), but also coal-fired power plants are now known to be very significant sources of PCDD/Fs, accounting for 56% of total PCDD/F emissions in southern Taiwan (Lin *et al.*, 2007). Lin (2007) indicated the dominant sources of PCDD/Fs in Kaohsiung area are coal-fired power plants, secondary aluminum smelting, electric arc furnaces, and open burning of rice straw, which were found to contribute 56%, 17%, 13%, and 3.3% to the total, respectively. However, in Taiwan, the dominant sources of PCDD/Fs are iron ore sintering, coal-fired power plants, electric arc furnaces, and open burning of rice straw, which have been found to contribute 32%, 28%, 23%, and 8.1% to the total, respectively. However, the emission inventories of PBDEs need to be investigated in more detail.

Schenker *et al.* (2008) calculated global PBDE discharges from production, use and waste-management, and found global PBDE emissions to be underestimated. PBDE emission estimation from the vapor pressures of PBDE congeners could be two orders higher than evaluated from their K_{OA} (Prevedouros *et al.*, 2004). The occurrence of PBDEs in the flue gases of power plants and vehicles, as well as their PBDE concentrations have been highly correlated with those of combustion-originated PCDD/Fs, revealing that PBDEs are likely to be the products of combustion (Wang *et al.*, 2010b). Artha (2011) also confirmed this finding. Wang *et al.* (2010b) also determined that in the U.S., combustion sources are larger PBDE emitters to the atmosphere (1260 kg/year) than are houses and garages (722 kg/year) (Batterman *et al.*, 2009). Furthermore, PBDEs have also been suspected to have similar formation conditions to those of PCDD/Fs during the combustion process (Wang *et al.*, 2010e). Tu (2011) and Wang (2010a, 2010f) all reported that the major PBDE emitting sources of MWSIs are bottom residues, but Wang (2010b) indicated that the amount of PBDEs emitted from stack flue gases annually are significant. Therefore, PBDEs contributed to the atmosphere via stack flue gases need to be further investigated. The primary objectives of this study were not only an attempt to measure the PBDE concentration in the ambient air and to create a PBDE dispersion model for two municipal solid waste incinerators (MSWIs) and a coal-fired power plant (TPP), but also to work on predicting the annual PBDE contribution to the vicinity under investigation.

MATERIALS AND METHODS

Basic Information for the Two MSWIs, One Coal-fired Power Plant and the Ambient Air Sampling Sites

Two continuously operating MSWIs (MSWI-A and MSWI-B) and a coal-fired power plant (TPP) located in southern Taiwan were investigated. The feeding wastes in both MSWIs were of municipal and industrial origins. The municipal vs. industrial wastes handled were 40% vs. 60% for MSWI-A, and 80% vs. 20% for MSWI-B. The capacity of each furnace in MSWI-A and MSWI-B was 450 and 300 metric tons per day, respectively. The operating installment of each furnace was a two-stage, starved-air modular type that included its own heat recovery system (a superheater and an economizer), semi-dry absorbers, activated carbon injection systems, fabric filters and stacks. The combination of the above air pollution control devices, known as ''the most effective technology for PCDD/F emission control'' (Buekens and Huang, 1998), is the most common system among MSWIs in Taiwan. For MSWI-A and MSWI-B, four ambient air sampling sites were selected, respectively. The combination of air pollution control devices (APCDs) in the TPP was focused on removing the particulate matters from the stack flue gases. The air pollution control devices for the TPP were a wet scrubber and a static precipitator, and the averaged amount of coal consumption was 16,442 tons/day (Tu *et al.*, 2011).

Sample Collection

In order to provide data on the levels of PBDEs in the surrounding area, samples of the stack flue gas and ambient air were collected during the same period of time for two seasons (Tu *et al.*, 2011). Five stack flue gas samples and eight ambient air samples were collected for each season. The sampling procedures for the stack flue gases and the ambient air complied with the requirements of NIEA A807.74C.

Sample Analysis

The ambient air PBDE samples were placed in a Soxhlet extractor spiked with 30 μL of an internal standard solution (23IS). The samples were extracted for 18 ± 2 hours, and the extract was then evaporated off to near dryness and was dissolved in dichloromethane three times before being transferred to a clean tube. Each extract was equally divided into two (A and B) flasks. Flask A was acid-washed, and flask B was stored.

The analyses of PBDEs were carried out by a high-resolution gas chromatographer/high-resolution mass spectrometer (HRGC/HRMS). Thirty PBDE congeners were analyzed. The column equipped by HRGC was heated up from 150°C to 190°C with a raise of 20°C/min, and was then raised up to 220°Cat 1.5°C/min. The temperature of the column was then increased to 310°C at 3°C/min and was maintained for 2 minutes. The HRMS was equipped with an electron impact (EI+) source, and the analytical mode of the selected ion monitoring (SIM) had a resolving power of 10,000. The temperature of the ion source was 250°C. The analytical procedures for the PBDEs have been described in more detail in previous reports (Wang *et al.*, 2010a; Wang *et al.*, 2010b).

Dispersion Modeling

Dispersion modeling was done using the Industrial Source Complex Short Term (ISCST3), which is the simulation program approved by the EPA in Taiwan. The modeling area was located in the vicinity of two MSWIs (MSWI-A and MSWI-B) and a coal-fired power plant (TPP) located in southern Taiwan. Southwest coordinates of the modeling area are (X = 155,224, Y = 2,500,133) (TWD97 coordinate system). The axis of the MSWI-A, MSWI-B and TPP are listed in Table 4 and the grid type used is a uniform Cartesian grid. On the grid, the distance between each point was set to 400 meters. Therefore, there were 100 points on both the X and Y axis, and the dispersion scenarios were set to rural. In this study, the meteorological data used was obtained from the Kaohsiung Weather Service Office, and the modeling work was done on an annual basis.

RESULTS AND DISCUSSION

PBDE Concentrations in the Ambient Air Sampling Sites

PBDE concentrations in the ambient air sampling sites around MSWI-A and MSWI-B are listed in Tables 1 and 2, respectively. The congener profiles of each site are presented in Figs. 1 and 2, respectively. The ambient air PBDE average concentrations are shown to be 70.8 ± 19.4 pg/Nm^3 and 48.9 ± 4.94 pg/Nm^3 for MSWI-A and MSWI-B, respectively. The reason why the average concentrations in the vicinity of MSWI-A are higher than those of MSWI-B could be a result of proximity to the MWSI-A industrial park, the influence of TPP emissions, and the elevated terrain in the vicinity of MSWI-B. BDE-209, BDE-47 and BDE-207 were the most predominant three among all 30 PBDE congeners, which contributed more than 58%, 9%, and 4% of total-PBDE mass in the ambient air, respectively. The average $\Sigma_{2-8\ Br}$ BDEs/$\Sigma_{9-10\ Br}$ BDEs ratios were shown to be 0.392 ± 0.107 and 0.449 ± 0.0300 for ambient air sampling sites for MSWI-A and MSWI-B, respectively. However, once BDE-209 was excluded, the ratios became 2.65 ± 0.473 and 2.43 ± 0.0973 for MSWI-A and MSWI-B, respectively. These ratios indicate that the lower borminated congeners are the dominating groups after BDE-209 was rooted out. BDE-209 is no doubt the most predominating PBDE congener. It can be seen that the average $\Sigma_{2-8\ Br}$ BDEs/$\Sigma_{9-10\ Br}$ BDEs ratio are 0.141 ± 0.0809 for the MSWI-A, MSWI-B, and TPP stack flue gases. The ratio became 0.827 ± 0.359 after the removal of BDE-209 influence. A comparison of the ratios for the ambient air sampling sites (BDE-209 excluded) with those of the stack flue gases (BDE-209 excluded) indicated that the content of lower brominated PBDE congeners was found to be rising. The results show that the BDEs were going through a photolytic process during transport and were debrominated.

Cluster Analysis for PBDEs in Ambient Air

Cluster analysis is an exploratory data analysis tool that aims at sorting different objects into groups in a way that the degree of association between two or more objects is maximal

Table 1. Ambient air concentration of PBDES in each MSWI A surrounding sampling site.

PBDEs	A		B		C		D	
	S1	S2	S1	S2	S1	S2	S1	S2
BDE-7	0.0219	0.55	0.0563	0.0011	0.0133	0.0011	0.0178	0.274
BDE-15	0.17	0.569	0.298	0.477	0.116	0.0017	0.116	0.331
BDE-17	0.228	0.538	0.531	0.439	0.203	0.414	0.171	0.286
BDE-28	0.846	0.88	1.27	0.726	0.653	0.621	0.598	0.458
BDE-49	0.758	1.03	1.03	0.86	0.506	0.918	0.686	0.573
BDE-71	0.083	0.101	0.127	0.152	0.0626	0.148	0.0667	0.0714
BDE-47	9.18	5.44	10.3	3.92	6.02	4.33	6.89	1.94
BDE-66	0.63	0.574	0.486	0.435	0.392	0.535	0.378	0.343
BDE-77	0.0445	0.115	0.033	0.0936	0.0261	0.102	0.0247	0.0751
BDE-100	0.849	0.672	1.02	0.44	0.501	0.541	0.651	0.25
BDE-119	0.0678	0.137	0.0732	0.0851	0.0133	0.113	0.0418	0.0759
BDE-99	3.15	3.2	3.29	2.15	1.84	2.5	2.99	1.26
BDE-85	0.0852	0.0829	0.113	0.0495	0.0359	0.0681	0.049	0.0363
BDE-126	0.0004	0.0433	0.0003	0.0403	0.0003	0.0369	0.0003	0.0263
BDE-154	0.324	1.18	0.399	0.879	0.187	0.988	0.245	0.659
BDE-153	0.446	2.56	0.484	2.05	0.24	1.75	0.281	1.32
BDE-139	0.0516	0.184	0.0529	0.166	0.0253	0.195	0.0341	0.132
BDE-140	0.0357	0.188	0.0277	0.158	0.0178	0.185	0.0193	0.122
BDE-138	0.0427	0.298	0.058	0.239	0.0267	0.29	0.0026	0.198
BDE-156	0.0012	0.0301	0.0008	0.0242	0.0008	0.0008	0.0008	0.0162
BDE-184	0.0401	0.149	0.0307	0.132	0.0189	0.164	0.0365	0.116
BDE-183	0.602	4.02	0.531	2.77	0.361	3.12	0.559	2.65
BDE-191	0.0562	0.32	0.0475	0.246	0.0247	0.338	0.117	0.186
BDE-197	0.348	1.53	0.252	1.22	0.159	1.49	0.535	1.19
BDE-203	0.715	1.66	0.282	1.46	0.184	1.93	1.35	0.974
BDE-196	0.612	0.928	0.28	0.832	0.184	0.992	1.34	0.595
BDE-208	1.77	2.18	0.793	1.78	0.645	2.44	1.6	1.23
BDE-207	2.93	3.93	1.42	3.08	1.1	4.12	2.77	2.16
BDE-206	2.88	5.35	1.13	4.16	0.951	5.75	1.87	2.69
BDE-209	18.9	101	8.93	69.7	10.4	97.4	11.7	37.8
$\Sigma_{2-8\ Br}$ BDEs	19.4	27	21	20	11.8	21.8	17.2	14.2
$\Sigma_{9-10\ Br}$ BDEs	26.4	112	12.3	78.7	13.1	110	17.9	43.9
Total BDE (pg/Nm^3)	45.8	139	33.3	98.7	24.9	131	35.1	58.1

if they belong to the same group and minimal if they are not part of the same group. It also provides the fingerprint characteristics of PBDEs in the ambient air and serves as a useful index for different emission sources. This work applied cluster analysis of 30 individual congeners, PBDE concentrations, $\Sigma_{2-8\ Br}$ BDE and $\Sigma_{9-10\ Br}$ BDE concentrations, $\Sigma_{2-8\ Br}$ BDEs/$\Sigma_{9-10\ Br}$ BDEs ratios, total PBDE concentrations among the MSWI-A, MSWI-B, TPP, and sites A, B, C, D, E, F, and G. The results of cluster analysis are shown in Fig. 3. The current investigation classified these sampling sites into three clusters according to k-means cluster analysis. Cluster 1 included sites A and C; Cluster 2 included sites B, D, E, F, G, and H; Cluster 3 included MSWI A, MSWI B, and TPP. The statistically significant differences on $\Sigma_{9-10\ Br}$ BDEs concentrations, $\Sigma_{2-8\ Br}$ BDEs/$\Sigma_{9-10\ Br}$ BDEs ratios, and total PBDE concentrations formed the basis of the classification. The results showed a probable direct correlation between site A and site C. However, no obvious direct correlations existed among the MSWI-A, MSWI-B, TPP and sampling sites. The TPP and the MSWI-A, and MSWI-B are probably not the main contributors of PBDE emissions in the surrounding ambient air. Both MSWI-B, and TPP to ambient air in the modeling area were all less than 0.1%, according to the ISCST3 modeling results. Accordingly, the off-shore contribution of PBDE concentrations on the ambient atmosphere along the coast probably had a deeper impact on sites A and D than did the other contributors. The results of cluster analysis in this study can provide useful information for the local city government regarding the formation of air pollution control strategies.

Dispersion Modeling for PBDEs

PBDE emission data from two municipal solid waste incinerators (MSWIs) and one coal fired power plant (TPP) have been published on Tu *et al.* (2011) and were cited in this study. The results of ISCST3 dispersion modeling is illustrated in Fig. 4. The prevailing wind direction seriously affects the transport of stack flue gases. As shown in Fig. 4, the annual prevailing wind direction is northwest. The ambient air sampling site A is located in where there is the highest concentration of stack flue gas emission from the TPP. The stack height of the TPP is higher than that of the

Table 2. Ambient air concentration of PBDES in each MSWI B surrounding sampling site.

PBDEs	E		F		G		H	
	S1	S2	S1	S2	S1	S2	S1	S2
BDE-7	0.0206	0.0011	0.0264	0.0011	0.0302	0.147	0.0011	0.17
BDE-15	0.181	0.0017	0.139	0.0017	0.162	0.368	0.219	0.364
BDE-17	0.189	0.326	0.209	0.321	0.308	0.323	0.242	0.302
BDE-28	0.656	0.673	0.67	0.606	0.813	0.587	0.673	0.574
BDE-49	0.387	0.781	0.487	0.643	0.657	0.649	0.463	0.664
BDE-71	0.0598	0.0473	0.0506	0.117	0.0905	0.0934	0.0591	0.0663
BDE-47	4.19	5.18	4.81	3.62	6.35	4.07	4.67	3.9
BDE-66	0.255	0.425	0.365	0.327	0.367	0.376	0.32	0.356
BDE-77	0.0182	0.0397	0.0249	0.0659	0.0387	0.0497	0.0293	0.0529
BDE-100	0.336	0.571	0.484	0.51	0.607	0.433	0.497	0.481
BDE-119	0.0319	0.0469	0.0336	0.0642	0.0135	0.0728	0.0321	0.0469
BDE-99	1.56	2.13	1.83	2.13	3.33	1.77	1.94	2.04
BDE-85	0.0466	0.0508	0.0607	0.065	0.0549	0.0472	0.0651	0.052
BDE-126	0.0003	0.0114	0.0003	0.0201	0.0003	0.017	0.0003	0.0156
BDE-154	0.15	0.493	0.239	0.75	0.281	0.557	0.192	0.636
BDE-153	0.264	0.726	0.388	1.71	0.48	0.681	0.281	1.1
BDE-139	0.0202	0.109	0.038	0.207	0.0455	0.12	0.033	0.123
BDE-140	0.0161	0.0946	0.0376	0.151	0.0357	0.108	0.0254	0.117
BDE-138	0.0257	0.16	0.051	0.341	0.0552	0.145	0.0356	0.145
BDE-156	0.0008	0.0107	0.0008	0.0008	0.0008	0.0169	0.0008	0.0102
BDE-184	0.0233	0.0626	0.0352	0.182	0.0579	0.0925	0.0227	0.0863
BDE-183	0.559	1.72	0.707	2.61	1.16	1.59	0.43	1.87
BDE-191	0.035	0.16	0.0557	0.399	0.11	0.181	0.0233	0.178
BDE-197	0.26	1.04	0.293	1.97	0.691	0.862	0.188	1.02
BDE-203	0.35	1.06	0.41	3.01	1.26	1.17	0.257	1.16
BDE-196	0.336	0.683	0.362	2.51	1.12	0.77	0.237	0.582
BDE-208	1.15	1.24	1.33	1.99	1.86	1.44	0.902	1.37
BDE-207	2.03	2.11	2.26	3.22	3.05	2.31	1.61	2.28
BDE-206	1.85	2.47	2.15	3.66	2.64	2.9	1.52	2.89
BDE-209	17.1	32.2	20.6	40.4	17.4	36	17.1	38.7
$\Sigma_{2-8\ Br}$ BDEs	9.97	16.6	11.8	22.3	18.1	15.3	10.9	16.1
$\Sigma_{9-10\ Br}$ BDEs	22.1	38.1	26.3	49.3	24.9	42.7	21.1	45.3
Total BDE (pg/Nm^3)	32.1	54.7	38.1	71.6	43	58	32.1	61.4

MSWIs, which can be seen in Table 3, and the TPP is located near the coastline. Therefore, under the influence of strong wind from the sea and the stack height, the stack flue gas emissions from the TPP will have a longer transportation range in the air than will be the case for the MSWIs .The maximum 10 1-hour average concentrations, which are listed in Table 4, were also obtained by the dispersion modeling. The average of these 10 maximum 1-hour average concentrations was found to be 1550 ± 74 fg/Nm^3. Most of these scenarios occurred in the morning during the month of February, which means the meteorological conditions at that time were especially tending toward a high PBDE concentration.

The annual PBDE concentrations in the ambient air contributed by MSWI-A, MSWI-B, and TPP are shown in Table 5. The highest concentration and the second highest concentration are 60.9 fg/Nm^3 and 54.7 fg/Nm^3, respectively. From the results of dispersion modeling, the annual total PBDE concentration in ambient air contributed by the MSWI-A, MSWI-B, TPP together were found to be 0.0259% ± 0.0208% (Table 5). It was very clear that MWSI-A, MSWI-B, and TPP were definitely not the major contributors of PBDEs to the ambient air environment. However, the source of major pollution from PBDEs in the ambient air of receptors needs to be investigated in more detail. In addition, PBDEs have a low vapor pressure and a high boiling point. The ashes collected from the air pollution control devices of both the MSWIs and the TPP are probably a more important environmental issue and therefore should be investigated more thoroughly (Li *et al.*, 2003; Lai *et al.*, 2007; Tu *et al.*, 2011).

CONCLUSIONS

The total-PBDE concentrations in the ambient air were between 24.9 and 139 pg/Nm^3, averaging 59.8 pg/Nm^3 (n = 16). Among all 30 detected PBDE congeners, the BDE-209, BDE-47 and BDE-207 were the most predominant three and contributed more than 58%, 9%, and 4% of the total-PBDE mass in the ambient air, respectively. The average $\Sigma_{2-8\ Br}$ BDEs/$\Sigma_{9-10\ Br}$ BDEs ratios indicated that the lower borminated congeners are the dominating groups

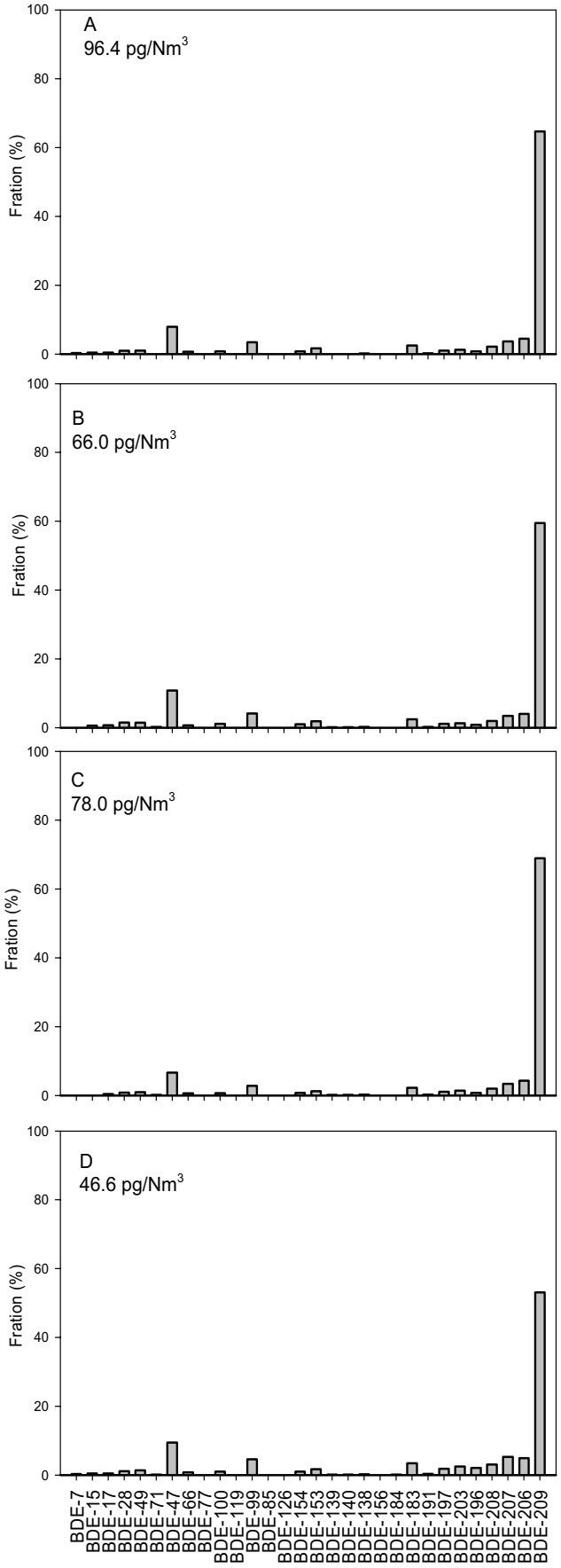

Fig. 1. PBDE congener profiles in the vicinity of MSWI A.

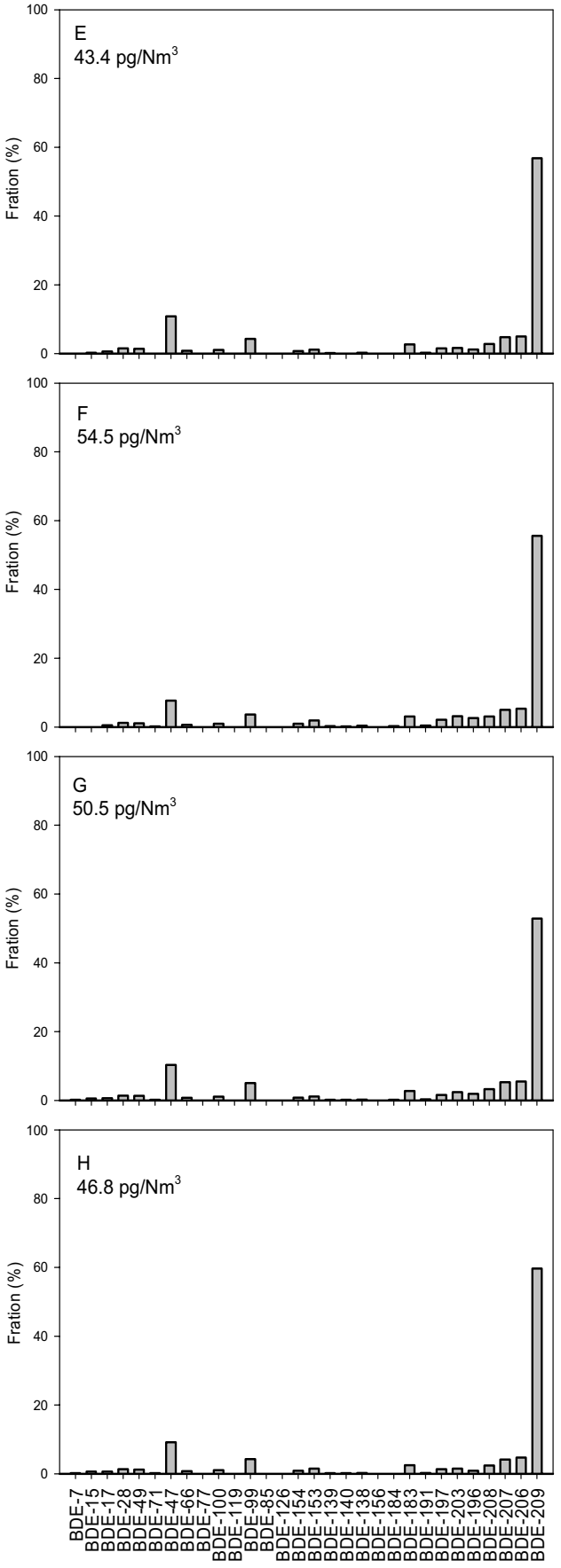

Fig. 2. PBDE congener profiles in the vicinity of MSWI B.

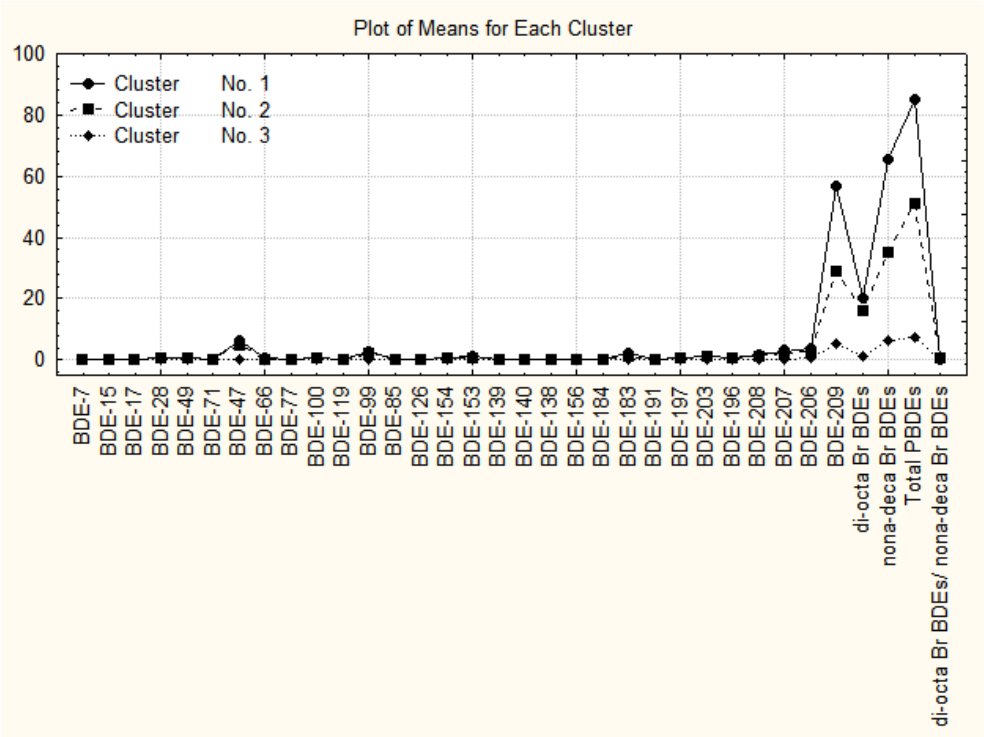

Fig. 3. K-mean cluster analysis for MSWIs, TPP and each ambient air sampling sites. Cluster No.1: A, C; Cluster No.2: B, D, E,F, G, H; Cluster No.3: MSWI A, MSWI B, TPP.

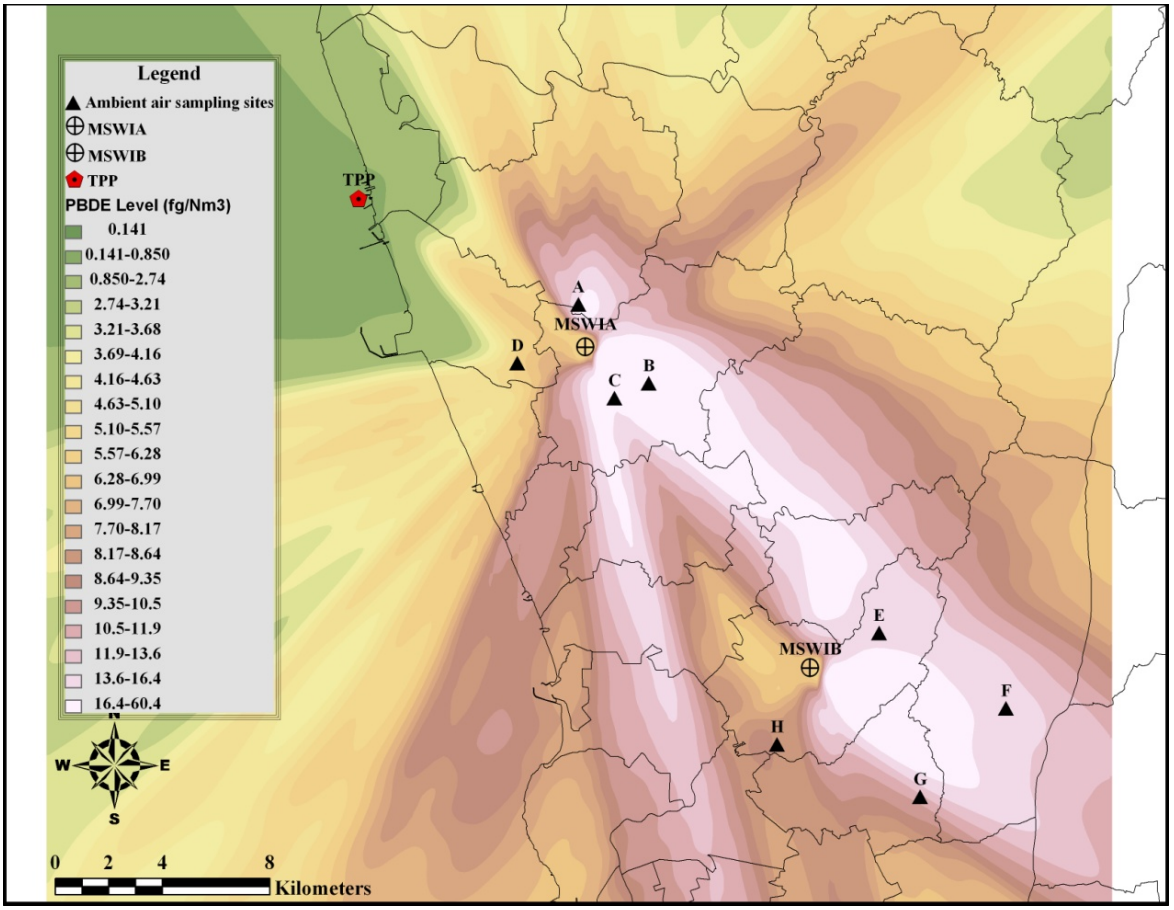

Fig. 4. ISCST3 Modeling Results.

Table 3. Basic information of the three PBDE emitting sites.

	MSWI-A	MSWI-B	TPP
x	175260	183647	166801
y	2523346	2511392	2528874
z	13	33	20
Mean PBDE concentrations in stack flue gases (ng /Nm^3)	9.32	7.62	5.43
stack flow rates (Nm^3/s)	20.1	30.4	609
Number of stacks	3	3	1
PBDE emission rates (g/s)	5.63E-07	6.96E-07	3.31E-06
stack heights (m)	60	120	250
Temperature of stack flue gases (K)	273	273	273
Speeds of stack flue gases (m/s)	13.0	17.3	27.2
Stack diameters (m)	2	1.8	6.7

Table 4. Maximum 10 1-hour average total PBDE concentration.

Ranking	TWD97 Coordinates		Concentration fg/m^3	Time & Date
	X	Y		
1	176024	2523333	1663	2009/9/3 0900 hours
2	174824	2522533	1631	2009/4/3 0900 hours
3	175224	2524133	1610	2009/8/30 0900 hours
4	184424	2510933	1592	2009/1/19 1200 hours
5	184424	2512133	1577	2009/2/19 1000 hours
6	184424	2511333	1515	2009/8/27 0900 hours
7	175224	2522533	1501	2009/3/25 0900 hours
8	176024	2523733	1490	2009/10/12 1000 hours
9	175224	2522533	1464	2009/2/1 1000 hours
10	184424	2511333	1454	2009/2/7 1000 hours

Table 5. Annual total PBDE concentrations contributed by MSWI-A, MSWI-B and TPP.

Ambient air sites	TWD97 Coordinates		Concentration fg/m^3
	X	Y	
A	175000	2524925	15.3
B	177619	2521988	38.5
C	176344	2521429	18.9
D	172716	2522743	5.89
E	186216	2512681	15.7
F	190939	2509878	14.6
G	187742	2506584	11.5
H	182406	2508533	8.52
The 1st highest annual average total PBDE concentration	176424	2522533	60.9
The 2nd highest annual average total PBDE concentration	176824	2522133	54.7

after BDE-209 was removed from consideration. Cluster analysis shows that no direct correlations existed between the emission sources (MSWI-A, MSWI-B, TPP) and the receptors (sampling sites). Furthermore, according to the results of ISCST3 dispersion modeling, the annual total PBDE concentration in ambient air contributed by the MSWI-A, MSWI-B, TPP together were found to be 0.0259% ± 0.0208%. This means that the PBDE contribution fraction from the above three emission sources to the ambient air were all far below 0.1%. Hence, from the results of both cluster analysis and dispersion modeling, it was shown that MWSI-A, MSWI-B, and TPP were definitely not the major contributors of PBDEs to the ambient air environment. The ashes collected from the air pollution control devices of both MSWIs and TPP are probably a more crucial environmental issue with regard to PBDEs, and more attention is necessary to eliminate this threat to both human health and to the environment.

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