

Atmospheric deposition of polybrominated dibenzo-*p*-dioxins and dibenzofurans in Guangzhou, China: seasonal variations and sources†

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The atmospheric deposition of polybrominated dibenzo-*p*-dioxins and dibenzofurans (PBDD/Fs) was investigated at four locations in different suburban and urban functional districts of Guangzhou City. The annual deposition fluxes of total PBDD/Fs (eight 2,3,7,8-substituted tetra- to hexa-BDD/Fs) were in the range of 36–51 (mean 46) $\text{pg m}^{-2} \text{day}^{-1}$, and the corresponding TEQ fluxes were estimated to range between 7.9 and 11.3 (mean 10.3) $\text{pg I-TEQ m}^{-2} \text{day}^{-1}$, indicating a noticeable pollution level. The deposition fluxes of PBDD/Fs during the wet season were 2–4 times as high as those during the dry season. Both rainfall and temperature positively correlated with PBDD/F deposition fluxes. Ambient gas/particle partition coefficients (K_p) were predicted with SPARC. It appears seasonal variations of PBDD/F deposition fluxes were influenced by meteorological parameters and the local usage of brominated flame retardants (BFRs). The congener profiles of PBDD/Fs at four locations were similar either spatially or temporally, indicating that the main PBDD/F emission sources were similar to one another. Seasonal variations and congener patterns of PBDD/Fs indicated the possible sources included electronic waste recycling, industrial waste incinerators and products containing BFRs.

Introduction

Polybrominated dibenzo-*p*-dioxins and dibenzofurans (PBDD/Fs) are brominated analogues of the highly regulated polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) with all the chlorine atoms substituted by bromine atoms. Therefore, they have similar physicochemical properties, toxicity and geochemical behavior in the environment.¹ Due to their persistence and semivolatility, they can be transported over long

distances. Atmospheric deposition is an important pathway of transporting them from sources to environmental receptors.²

Generally, PBDD/Fs are not known to occur naturally. They are not intentionally produced (except for scientific purposes) but are generated as undesired by-products in various processes.³ They can be found as contaminants in brominated organic chemicals, particularly in brominated flame retardants (BFRs) (especially polybrominated diphenyl ethers (PBDEs)),^{4,5} and in final consumer products when using a secondary raw material containing BFRs, such as printed circuit boards and TV casing materials.⁶ They can be formed by chemical such as photochemical reactions from precursors, *e.g.* decabromodiphenyl ether (DeBDE) under UV;⁷ and can be formed during production and recycling processes of flame-retardant-containing plastic materials, *e.g.* shredders in recycling processes, extruders.⁸ Primarily, they are formed during combustion of flame-retardant-containing plastic materials, especially electronic waste (e-waste) burning of waste plastics containing BFRs.^{9,10}

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Environmental impact

Human and environmental exposures to polybrominated dibenzo-*p*-dioxins and dibenzofurans (PBDD/Fs) are likely to increase because brominated flame retardants (BFRs) are extensively used. Atmospheric deposition is the main pathway of transporting these micropollutants from sources to environmental receptors. However, there are few reports of PBDD/F atmospheric deposition. Guangzhou is a main manufacturing base of electronic products and automobiles and the largest market of electronic products, for which BFRs are commonly used. So Guangzhou is a suitable site to study PBDD/Fs. PBDD/F deposition fluxes, congener pattern distributions, the influences of meteorological factors on the seasonal variations and sources were investigated.

Furthermore, municipal solid waste incinerators (MSWIs), industrial waste incinerators (IWs), electric arc furnaces (EAFs) and open combustion of domestic waste also emit PBDD/Fs.^{11–13} Concerns about PBDD/Fs have increased because BFRs are extensively added in polymers, paints, textiles and other materials in electrical equipments, furnishings and vehicles.

Guangzhou is the largest industrial city in southern China with a dense population and heavy traffic. About 40% of the annual gross industrial output in 2004 was attributed to the manufacture of electronics, automobiles, and petrochemicals. Tremendous increases in the economy, industrial productivity, and the utilization of natural resources have resulted in serious environmental pollution. Some studies have shown that the contamination levels of PCDD/Fs and DeBDE are high in the ambient air in Guangzhou compared to those in other countries.^{14,15}

However, few data are available for the atmospheric deposition of PBDD/Fs. In this study, we present novel data on the monthly atmospheric deposition of PBDD/Fs collected in Guangzhou City from April 2005 to March 2006. PBDD/F deposition fluxes, congener pattern distributions and sources were investigated. In addition, the influences of meteorological factors on the seasonal variations of PBDD/F deposition fluxes are also discussed.

Experimental section

Sample collection and extraction

Locations for sampling of atmospheric deposition are shown in Fig. 1. Bulk atmospheric deposition samples were collected at four points in Guangzhou, including Wushan (Ws for short, urban), Yuancun (Yc for short, urban), Haizhu (Hz for short, urban), and Changban (Cb for short, suburban). Here Wushan, Yuancun and Haizhu were commercial, industrial and residential districts, respectively; Changban was near a farming district in the outskirts of the city.

Each sample was collected monthly (28 ± 3 days) over a one-year period (April 2005–March 2006) using two glass pots (50 cm long, 50 cm wide, and 40 cm high) 50 cm above the ground supported by a stainless steel bracket. Prior to sampling, 20 L pure water was added to the pots to prevent the re-suspension of particles, and 20 mL of 1 mol L⁻¹ copper sulfate was used as a kind of algicide.



Fig. 1 Sampling locations in Guangzhou, China.

Methods for the detailed analysis were reported elsewhere.¹⁶ Samples were filtered through glass fiber filters (GFFs, 1.0 μ m, Whatman, England) to separate liquid and particle phases. The water fraction was then extracted with solid phase extraction disks (ENVI-18 DISK 47 mm, Supelco, USA). Subsequently, the filters and disks were dried in a desiccator, and then Soxhlet extracted with toluene (Merck, Germany, pesticide quality grade) for 24 h after being spiked with a mixture of ¹³C₁₂-labeled internal standards (EDF-5071, CIL; EDF-8999, CIL). The extracts were concentrated to 1 mL with a rotary evaporator. Sample cleanup was accomplished successively according to the following steps: slurry of 20 g of 40% H₂SO₄/silica gel, a multi-layer silica gel column, and a 5 g florisil column. Finally, injection standards (EDF-5073, CIL; EDF-5999, CIL) were added to the corresponding extracts, and the final volume was adjusted to 20 μ L. A detailed method of extract cleanup for the co-analysis of PBDD/Fs and PCDD/Fs is presented in the ESI†.

Instrumental analysis

Identification and quantification were performed with HRGC/HRMS (Trace GC 2000 and Finnigan MAT 95 XP). A DB-5ms column (30 m, 0.25 mm ID, 0.1 mm film, J&W Scientific, USA) was used for PBDD/Fs. The oven temperature program was as follows: 150 °C (held for 2 min) increased to 220 °C at a rate of 40 °C min⁻¹, then to 300 °C (held for 5 min) at a rate of 7.4 °C min⁻¹. For PCDD/F analysis, a DB-5ms column (60 m, 0.25 mm ID, 0.25 mm film, J&W Scientific, USA) was used, and the oven temperature program was: 120 °C increased to 160 °C at 20 °C min⁻¹, 220 °C (held for 16 min) at 7.5 °C min⁻¹, 235 °C (held for 7 min) at 5 °C min⁻¹, and 320 °C (held for 6 min) at 5 °C min⁻¹.

Quality control

Quality assurance and quality control were conducted including method blanks, ongoing precision and recovery (OPR), initial precision and recovery (IPR), and duplicate samples. The recoveries of all the labeled compounds were 50–110%. The detection limits were quantified as three times the standard deviations of the mean concentrations in the blanks, which were 0.05–0.3 pg g⁻¹ for PBDD/Fs and 0.1–0.8 pg g⁻¹ for PCDD/Fs.

Results and discussion

Deposition fluxes

Eight 2,3,7,8-substituted tetra- to hexa-BDD/F congeners were quantified. The deposition flux for each month was calculated with the amount (pg) of the analytes of interest divided by the sampling area (0.5 square metres) and sampling time (28 ± 3 days). Detailed results are shown in Table S1†. As shown in Table 1 the mean deposition fluxes of PBDD/Fs for a year (sum of the eight congeners, \sum 8PBDD/Fs) at Yuancun, Wushan, Haizhu, and Changban were 51 (range: 14.9–101), 50 (range: 12.6–115), 48 (range: 12.9–143), and 36 (range: 10.5–71) pg m⁻² day⁻¹, respectively. Because the toxic equivalency factors (TEFs) had not been determined for PBDD/Fs, the I-TEFs of PCDD/Fs were used for the corresponding congeners of PBDD/Fs to calculate their toxicity, which was suggested by the WHO.¹ It should be noted that this conversion of exposure values for

Table 1 Deposition fluxes ($\text{pg d}^{-1} \text{m}^{-2}$) of total PBDD/Fs ($\sum 2,3,7,8\text{-PBDD/Fs}$)

Location	Mean	Median	Min	Max
Yuancun	50.9	38.9	14.9	100.9
Wushan	49.8	37.6	12.6	115.2
Haizhu	48.3	32.2	12.9	142.7
Changban	35.8	31.8	10.5	71.4

PBDD/F to TCDD toxicity equivalents was only an estimate and is by no means accepted. The mean TEQ deposition fluxes at Yuanchan, Wushan, Haizhu, and Changban were 11.3 (range: 3.5–23), 11.3 (range: 3.0–26), 10.6 (range: 3.0–28), and 7.9 (range: 2.4–16.3) $\text{pg TEQ m}^{-2} \text{day}^{-1}$, respectively. It was found that the deposition fluxes of PBDD/Fs varied largely with the sampling time. For example, at Haizhu, the highest flux of deposition is $28.2 \text{ TEQ m}^{-2} \text{day}^{-1}$ in May and the lowest one is $3.0 \text{ TEQ m}^{-2} \text{day}^{-1}$ in December, the former was about 9 times the latter one. However, the fluxes did not vary significantly with the sampling location, especially in urban areas. Slightly higher levels of PBDD/Fs were found in samples from urban than those from suburban sites. The mean value for the four locations was $10.3 \text{ pg TEQ m}^{-2} \text{day}^{-1}$. Without consideration of the limited number of sampling locations, the annual loading of PBDD/Fs to land through atmospheric deposition in Guangzhou was roughly estimated to be 28 g TEQ in Guangzhou City (the surface area was 7434.4 km^2).

There were only limited data on PBDD/F bulk deposition elsewhere. The bulk deposition fluxes of $\sum 8\text{PBDD/Fs}$ were reported to vary largely in the range of $13\text{--}969 \text{ pg m}^{-2} \text{day}^{-1}$ in three samples from Kyoto.¹⁷ Li *et al.*¹⁰ reported that the PBDD/F concentrations in air at Wushan in Guangzhou were, respectively, 0.20 and $0.27 \text{ pg I-TEQ m}^{-3}$ in the winter and summer, accounting for 32% and 48% of the total TEQ of PCDD/Fs and PBDD/Fs, indicating that the pollution was noticeable.

PCDD/Fs in these deposition samples were also analyzed (see Table S1†). The total deposition fluxes of the seventeen 2,3,7,8-substituted PCDD/F congeners were in the range of $161\text{--}874$ (mean 430) $\text{pg m}^{-2} \text{day}^{-1}$. The WHO₉₈-TEQ fluxes were in the range of $4.8\text{--}50 \text{ pg TEQ m}^{-2} \text{day}^{-1}$, with a mean value of $20 \text{ pg TEQ m}^{-2} \text{day}^{-1}$, which were in agreement with the levels previously reported (range: $2.1\text{--}41 \text{ pg TEQ m}^{-2} \text{day}^{-1}$, mean: $20 \text{ pg TEQ m}^{-2} \text{day}^{-1}$).¹⁴ PBDD/Fs accounted for 36% of the total TEQ of the deposited PCDD/Fs and PBDD/Fs, which also indicated that PBDD/F pollution was noticeable.

Congener profiles

The congener profiles of 2,3,7,8-substituted PBDD/Fs in atmospheric deposition are presented in Fig. 2. It is found that the congener profiles of PBDD/Fs are consistent both temporally and spatially. The sequence based on the relative contribution to the total deposition fluxes of PBDD/Fs was as follows: 2,3,7,8-TBDF (mean 45%) > 2,3,4,7,8-PeBDF (mean 28%) > 1,2,3,7,8-PeBDF (mean 20%) > others. PBDFs were dominant in all samples, and the average mass fractions of PBDFs at the four locations ranged between 92% and 94%, which were in accordance with the previously reported data regarding PBDD/Fs in

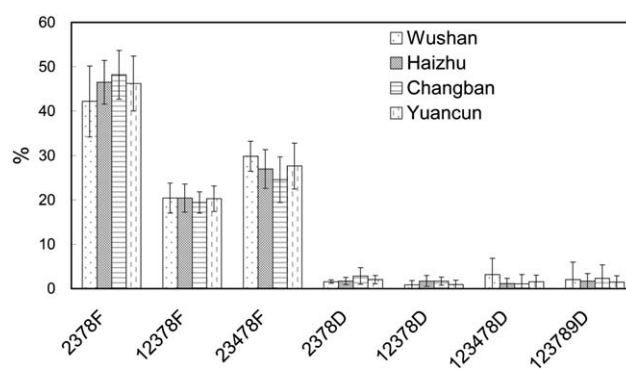


Fig. 2 Average congener profiles of PBDD/Fs in atmospheric deposition of Guangzhou (1,2,3,6,7,8-HxBDD: coeluted with 1,2,3,4,7,8-HxBDD).

the atmosphere of urban areas from Taiwan and in sediments from the East River in the Pearl River Delta (PRD).^{18,19} With regard to the relative contribution of individual PBDD/F congeners to the total TEQ fluxes, 2,3,4,7,8-PeBDF was the most important contributor, accounting for an average of 61% of the total TEQ, followed by 2,3,7,8-TBDF (20%), 2,3,7,8-TBDD (9%), and 1,2,3,7,8-PeBDF (5%).

Seasonal variation

Guangzhou is subject to a typical sub-tropical monsoon climate characterized by year-round warm to high temperatures and abundant rainfall. Meteorological data in Guangzhou, such as the monthly rainfall and the monthly average temperature, are obtained from the Chinese National Bureau of Statistics. The seasonal variation of PBDD/F deposition fluxes was investigated at all sampling sites for a year. The deposition fluxes of PBDD/Fs at all sampling locations varied monthly, and the average flux at each location during the wet season (from April to September) was about 2–4 times higher than that during the dry season (from October to March), which was similar to the case of PCDD/Fs. Sources including the metallurgical, electronics, and automobile manufacturing industries, IWIs, and MSWIs emit pollutants at a relatively constant flow and do not vary monthly. Biomass combustion sources, such as straw burning and fossil fuel heating, occur seasonally, yet they are not considered to be the important sources of such pollutants in Guangzhou, not only because they contain trace levels of brominated precursors, but also because they rarely occur. Thus, meteorological factors are considered to be important determinants of deposition flux.

The relationship between the average monthly deposition fluxes of PBDD/Fs and the monthly rainfall is depicted in Fig. 3. As shown in this figure, the bulk deposition fluxes of PBDD/Fs significantly are correlated with the monthly rainfall with a correlation coefficient of 0.93 ($p < 0.002$). Most PBDD/Fs (70%) in the air were absorbed on particles during the summer, and almost all (90%) were found in the particulate phase during the winter in Guiyu Town, PRD.¹⁰ Thus, rainwater plays an important role in scavenging PBDD/Fs associated with impacting/diffusing particles and even partially gaseous PBDD/Fs, which results in the higher deposition level of PBDD/Fs during the wet season.

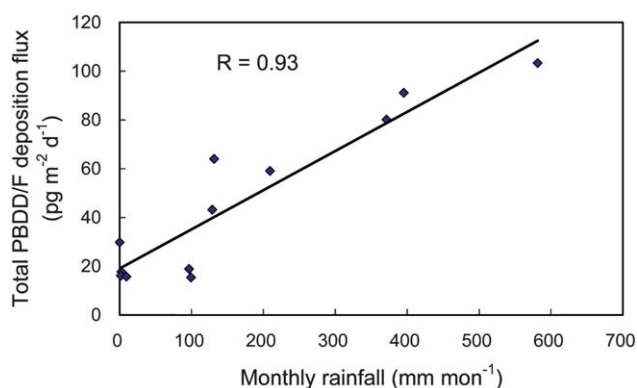


Fig. 3 Relationship between PBDD/F deposition fluxes and the monthly rainfall.

It is interesting that the correlation coefficient between the deposition fluxes of PBDD/Fs and the monthly rainfall is larger than that between the deposition fluxes of PCDD/Fs and the monthly rainfall ($R = 0.62$, $p < 0.01$). We think this is because the molecular weights of PBDD/F congeners are larger than their chlorinated counterparts, so their vapor pressures are smaller and gas/particle partitioning coefficients (K_p) are larger. Because few data of K_p of PBDD/Fs have been reported, we predict K_p with SPARC using the method presented by Arp and Goss.²⁰ SPARC is a free, online Web application (<http://archemcalc.com/sparc/>) that explicitly calculates sorbate-sorbent interactions by using various empirical molecular descriptors that are derived from a molecular structure. The results are shown in Table 2. As shown in Table 2, K_p values of tetra- to hexa-brominated DD/Fs are about 40–500 times higher than their chlorinated counterparts at common temperatures (15–25 °C). Therefore, relatively more PBDD/Fs are expected to absorb onto particles and be prone to particle-associated washout of PBDD/Fs than their chlorinated counterparts.

The relationships between the average monthly deposition fluxes of PBDD/Fs and the monthly average temperature are depicted in Fig. 4. The bulk deposition fluxes of PBDD/Fs positively correlate with the monthly average temperature, and the correlation coefficient was 0.77 ($p < 0.02$). We also analyzed the correlation between fluxes of PCDD/Fs and temperature. No obvious relationships are found ($R = 0.31$, $p < 0.01$), which is in agreement with the previous study.¹⁴

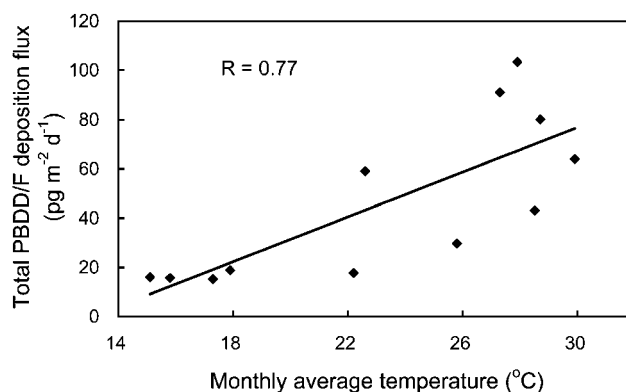


Fig. 4 Relationship between PBDD/F deposition fluxes and the monthly average temperature.

Temperature is generally thought to be an important factor to control the behaviors of organic pollutants, such as partition between gas and particle phase and photolysis. As temperature increases, PBDD/F is expected to migrate more from the particle to gas phase. As shown in Table 2, the change in gas/particle partitioning of PBDD/Fs will be an increase in sorption by an average factor 9 with a drop of 15 degrees (from 30 to 15 °C). Thus, gas/particle partitioning depending on temperature cannot explain the phenomena observed.

In addition, the increase in temperature might improve the degradation of relatively unstable higher brominated congeners, such as hepta- to octa-BDD/Fs, to relatively stable ones, such as tetra- to hexa-BDD/Fs, which will result in not only an increase of the deposition flux of tetra- to hexa-BDD/Fs but also a change of congener profiles. However, no obvious differences were found in the congener profiles of PBDD/Fs between samples collected in the summer (May–September, monthly average temperature: 27–30 °C) and in the winter (December–February, monthly average temperature: 15–17 °C). Thus, the variation of deposition fluxes is unlikely to be attributed to the degradation.

On the other hand, in Guangzhou, the climate is characterized by high rainfall and warm temperatures at almost the same time. Rainfall weakly correlated with the temperature ($R = 0.58$, $p = 0.05$) during the sampling period. October was an exception, when it was warm but dry, with the average temperature and the rainfall being 25.8 °C and 0 mm, respectively. PBDD/F deposition fluxes in October were 2–3 times as high as those in

Table 2 Ambient gas/particle partitioning coefficients (K_p) of PBDD/Fs and PCDD/Fs at different temperatures and the enthalpy of partitioning into the water insoluble organic matter (WIOM) phase (predictions were done using SPARC v4.5, accessed on July 11, 2001)

	$\log K_p^a/\text{m}^3 \text{g}^{-1}$			$K_p(15^\circ\text{C})/K_p(30^\circ\text{C})$	$\Delta H_{\text{WIOM}}/\text{kJ mol}^{-1}$	$\log K_p^b/\text{m}^3 \text{g}^{-1}$		$\frac{K_p(\text{PBDD/F})}{K_p(\text{PCDD/F})}$		
	15 °C	25 °C	30 °C			15 °C	25 °C	15 °C	25 °C	
2,3,7,8-TeBDD	5.65	4.88	4.68	9.3	110.8	2,3,7,8-TeCDD	3.76	3.19	78	49
1,2,3,7,8-PeBDD	6.90	6.07	5.89	10.2	116.1	1,2,3,7,8-PeCDD	4.57	3.93	215	139
1,2,3,7,8,9-HxBDD	8.20	7.29	7.18	10.5	119.1	1,2,3,7,8,9-HxCDD	5.52	4.78	482	326
2,3,7,8-TeBDF	4.86	4.30	4.04	6.6	91.3	2,3,7,8-TeCDF	3.19	2.74	47	37
1,2,3,7,8-PeBDF	6.25	5.54	5.30	8.9	107.4	1,2,3,7,8-PeCDF	4.11	3.57	139	94

^a $\log K_p$ of PBDD/F was calculated based on $f_{\text{WIOM}} = 0.1$ and WIOM B. ^b Data of $\log K_p$ of PCDD/F were predicted with SPARC by Arp and Goss.²⁰

December and January when it was cold (respectively 15 °C and 16 °C) and dry, with the exception of the Wushan location. Atmospheric concentrations of PBDD/Fs are likely built up in the atmosphere quicker when hot and with low wind, due to increased volatilization from surfaces and perhaps increased use of air conditioners, and they are readily washed out by rainfall. During long dry spells with little wind, particles rich in PBDD/Fs, and not just vapor phase PBDD/Fs, can increase in the atmosphere. Thus, the maximum PBDD/F deposition events should come after heavy rainfall events that occur after several dry days at elevated temperature, with little wind and with no precipitation. The climate characteristics can explain the positive correlation between both rainfall and temperature and deposition fluxes of PBDD/Fs, although they cannot explain the lack of correlation between the temperature and PCDD/F fluxes.

Another possible explanation is that the warm temperature improves the emission of PBDD/Fs from products containing BFRs, such as computers, furnishings, vehicles, *etc.* Therefore, we speculate the high deposition fluxes of PBDD/Fs, occurring during the hot and rainy season, are caused by the high rainfall and elevated emission from products with high temperature together. The seasonal variations of PBDD/F deposition fluxes are influenced by the meteorological parameters and the local usage of BFRs. Yet for PCDD/Fs, temperature does not play an important role in the deposition fluxes, which is in agreement with the likelihood that PCDD/Fs came mainly from combustion and not from the material surface *via* evaporation. From the above analysis, the difference of PCDD/Fs and PBDD/Fs in the correlation of the deposition fluxes with temperature also suggests a difference in their main sources.

Source analysis

The relative profiles of congeners are almost the same despite the difference amongst stations, which suggests that the main sources of PBDD/Fs were similar for the four locations. E-waste recycling emits a huge amount of PBDD/Fs, especially open combustion. For example, open combustion emits about 4 mg kg⁻¹ (printed circuit boards) of PBDD/F homologues, and atmosphere PBDD/F abundances were 1.6–2104 pg TEQ m⁻³ in an e-waste dismantling area.^{9,10} Although crude e-waste recycling is illegal, there are still several e-waste dismantling family workshops in outskirts of Guangzhou. A large scale of crude e-waste recycling occurred in Qinyuan City, a notorious e-waste recycling area about 60 km away from Guangzhou city center. During the sampling period, there were five MSWIs, one IWI and several EAFs located in the suburbs. Concentrations of PBDD/Fs in the stack flue gas of such incinerators and furnaces in Taiwan were reported to be 0.557, 4.17 and 1.88 pg TEQ N⁻¹ m⁻³, respectively.^{11,12} Several small factory-owned IWIs were present in Yuancun. In addition, products containing BFRs, such as computers, furnishings, vehicles, *etc.* might also emit PBDD/Fs. A large number of these products are being produced, sold and consumed, for Guangzhou is a main manufacturing base of electronic products and automobiles, the largest electronic products market and the largest city with 10 million people in southern China.

We compared the congener patterns in the deposition samples with those in possible sources, based on the extent of available data from the literature.^{10–12} As seen from Fig. 5, the bulk

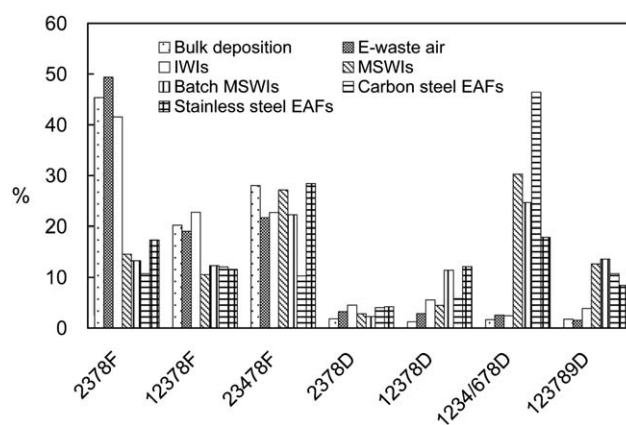


Fig. 5 PBDD/F congener patterns in bulk deposition and some sources (bulk deposition: in this study; e-waste air;¹⁰ flue gas of IWIs, MSWIs and batch MSWIs;¹¹ flue gas of carbon steel EAFs and stainless steel EAFs¹²).

deposition congener pattern is similar to that in the stack flue gas of IWIs and in the air from an e-waste recycling area. HxBDD is obviously higher in relative proportion to the stack flue gas of MSWIs and EAFs than that in bulk deposition. Regarding the concentrations of PBDD/Fs in the flue gas, the sequence is e-waste recycling > IWIs > EAFs > MSWIs, based on a review of the available literature.^{9,11,12} Consequently, MSWIs and EAFs are likely to be less significant PBDD/F emission sources compared to others. Because congener patterns of 2,3,7,8-substituted tetra- to hexa-BDD/Fs in many other sources had been rarely reported, including products containing BFRs, it is difficult to identify sources precisely. From the above analysis of a tendency to see an increase in deposition rates with temperature, PBDD/F evaporating from products such as electronics and automobiles which contain BFRs is also likely to be an important source. Therefore, we speculate that the possible important sources of PBDD/Fs in Guangzhou include e-waste recycling, IWIs and products containing BFRs.

Correlation between PBDD/Fs and PCDD/Fs

The deposition fluxes of PCDD/Fs and PBDD/Fs are plotted in Fig. 6. There are no obvious correlations between the deposition

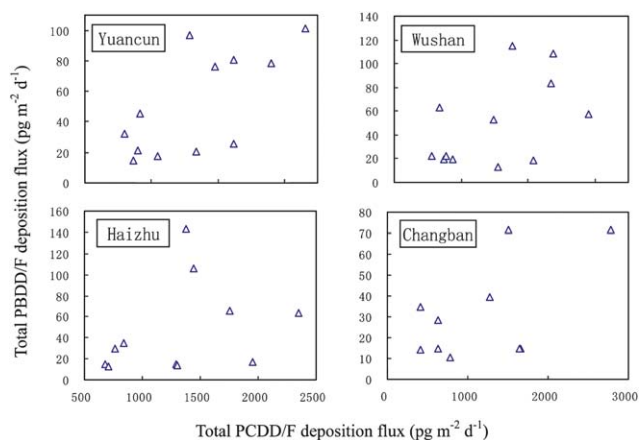


Fig. 6 Relationship between PBDD/F and PCDD/F deposition fluxes.

fluxes of PCDD/Fs and PBDD/Fs at Changban, Wushan, and Haizhu, further suggesting that the main source of PCDD/Fs was different from that of PBDD/Fs. We hypothesize that the metallurgical industry, including steel-making plants and secondary copper smelters, which were among the main sources of PCDD/Fs in Guangzhou, were unlikely to be the predominant sources of PBDD/Fs. In addition, MSWI is also the important source for PCDD/Fs in Guangzhou, but is considered a less important source of PBDD/Fs, not only because of the very small contribution ratio of PBDD/Fs compared to PCDD/Fs but also because of the differences in PBDD/F congener profiles between atmospheric deposition and MWI stack flue gas. In contrast, there is a positive correlation between the deposition fluxes of PCDD/Fs and PBDD/Fs in Yuancun ($R = 0.69$, $p = 0.01$), suggesting that deposition samples from Yuancun were likely to share a similarly important source of PCDD/Fs and PBDD/Fs. Some factory-owned IWIs were present in the industrial area near the sampling site of Yuancun, which emitted both PCDD/Fs and PBDD/Fs and might explain the relationship.

Conclusion

A remarkable deposition level of PBDD/Fs was observed based on a year-around sampling at monthly intervals in Guangzhou, China. Seasonal variations of PBDD/Fs deposition fluxes were influenced by meteorological parameters and the local usage of BFRs. The similar deposition fluxes and almost same congener profiles of PBDD/Fs amongst the four locations suggested they had similar sources, which were likely to be e-waste recycling, IWIs and products containing BFRs. The trend that PBDD/Fs deposition flux increases with temperature might provide evidence of the local extensive usage of BFRs.

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