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Atmospheric bulk deposition of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) in the vicinity of MSWI in Shanghai, China

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ABSTRACT

Atmospheric bulk deposition samples were gathered month by month throughout a year at two sites in vicinity of a MSWI in Shanghai, to carry out an investigation on the atmospheric bulk deposition fluxes and seasonal variations of polychlorinated dibenzo-p-dioxinsand dibenzofurans (PCDD/Fs). The atmospheric bulk deposition fluxes of PCDD/Fs ranged from 23.5 to 560 pg $m^{-2}{\cdot}d^{-1}$ (1.01–23.9 pg WHO-TEQ$\cdot m^{-2}{\cdot}d^{-1}$), with an average value of 136 pg $m^{-2}{\cdot}d^{-1}$ (5.08 pg WHO-TEQ$\cdot m^{-2}{\cdot}d^{-1}$) in the Vicinity of the MSWI in Shanghai. The measured concentrations were well compared with those from urban or industrial sites in other regions in China and abroad. The seasonal trend of atmospheric bulk deposition fluxes of PCDD/Fs throughout a year exhibited as high levels in summer, moderate levels in winter, and low levels in spring and autumn. The principal component analysis (PCA) indicated not only the MSWI, but also vehicle emission was the indispensable source of PCDD/Fs in the vicinity of the MSWI, especially for the urban areas. The positive matrix factorization (PMF) apportioned 5 source categories: MSWI, diesel vehicles, atmosphere background, industrial combustion and un-leaded gas vehicles, accounting for 43.3%, 38.1%, 6.89%, 6.19% and 5.50% in average, respectively of PCDD/Fs in atmospheric bulk deposition in the vicinity of the MSWI in Shanghai, China.

1. Introduction

As is known, polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) were semi-volatile persistent organic pollutants (POPs), which could keep the nondegradable status in the nature for a long time. It was proved that the deposition of the semi-volatile compounds contributed to the primary pathway for the semi-volatile POPs to transfer from atmosphere to soil (Su et al., 2007; Lohmann and Jones, 1998) and plants. These long distance dispersed semi-volatile POPs can eventually bioaccumulate in the food chain (Tang et al., 2018). The deposition of PCDD/Fs in the worldwide and the emission each year showed the same order of magnitude based on the study of the mass balance (Brzuzy and Hites, 1996). The researches of the deposition specimens could figure out the extent of the environmental pollution of PCDD/Fs. PCDD/Fs were produced as the harmful side products by people's activities, such as the burning of the biomass and fossil fuels, the processes in the industry (paper mills, steel sintering, metal smelting and chemical manufacturing, etc.), medical waste incineration (MWI) and municipal solid waste incineration (MSWI) (Kulkarni et al., 2008). The PCDD/Fs emission from stack gas from MSWI is decreased significantly after Chinese ministry of environmental protection reduced the emission limit of a national standard in China to 0.1 ng I-TEQ$\cdot m^{-3}$(China MEP, 2014). Zhu et al. (2018) revealed that the concentrations of PCDD/Fs emissions in stack gas from 6 MSWIs in northern China were in the range of 0.007–0.059 ng I-TEQ$\cdot m^{-3}$, Which were generally decreased relative to those reported in stack gas emissions from Chinese MSWIs in 2009 (mean 0.423 ng I-TEQ$\cdot m^{-3}$) (Ni et al., 2009).

Apart from MSWI, metal production activities have been the predominant industrial sources of airborne PCDD/Fs. The secondary metallurgy manufacture has extremely high emissions of PCDD/Fs (Ba et al., 2009), especially secondary copper smelters can have extremely high emissions of PCDD/Fs at 2.7 ng TEQ$\cdot m^{-3}$ (Yang et al., 2020). Bibliometric analysis showed that the concentration of PCDD/Fs in the flue gas generated by sintering process is 2–5 ng TEQ$\cdot m^{-3}$, which is 4–10 times higher than that of the current standard (Xing et al., 2019).

The significance of unregulated atmospheric PCDD/Fs sources, such as vehicle emission, domestic combustion of coal and wood, and

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Table 1
Meteorological parameters , deposition fluxes and TEQ fluxes of PCDD/Fs near the MSWI in Shanghai.

Month	Avg. Tem (°C)	Precipitation (mm)	Annual rainy days	Site A		Site B	
				Deposition fluxes ($pg{\cdot}m^{-2}{\cdot}d^{-1}$)	Deposition fluxes (pg WHO-TEQ $m^{-2}{\cdot}d^{-1}$)	Deposition fluxes ($pg{\cdot}m^{-2}{\cdot}d^{-1}$)	Deposition fluxes (pg WHO-TEQ$\cdot m^{-2}{\cdot}d^{-1}$)
Jan	7.0	72.6	9	79.51	3.03	163.35	6.10
Feb	6.9	20.8	6	69.41	4.42	125.89	7.03
Mar	10.4	93.7	13	138.78	5.28	171.61	6.64
Apr	17.1	103.4	11	77.29	2.14	96.63	3.18
May	21.6	51.5	7	75.24	2.94	71.93	2.19
Jun	23.7	208.3	17	212.14	8.28	195.38	7.61
Jul	31.3	72.2	14	560.26	27.45	439.54	20.67
Aug	29.5	155.6	15	101.01	3.43	88.37	2.61
Sep	24.6	278	17	109.05	3.40	41.96	1.17
Oct	19.4	88.3	11	51.90	2.39	23.47	1.53
Nov	13.8	84.6	12	96.93	4.15	86.83	2.83
Dec	7.2	20.4	6	78.65	3.27	113.76	5.15

chemical plant were also drew attention recently (Li et al., 2014; Laroo et al., 2012; Deng et al., 2011b; Hubner et al., 2005; Ma et al., 2019). A tailpipe emission research showed that PCDD/F emissions are 13.1, 7.1, and 13.6 pg I-TEQ· L^{-1} for three engines tested (Laroo et al., 2012). A tunnel study in Guangzhou, China, showed that the emission factors calculated based on the tunnel data were 230 pg I-TEQ $\cdot km^{-1}\cdot vehicle^{-1}$and 27.8 pg I-TEQ $\cdot km^{-1}\cdot vehicle^{-1}$ in winter and spring/summer season, respectively (Deng et al., 2011b). In Austria, most of the domestic heating appliances have shown PCDD/F emissions within a concentration range of 0.01–0.3 ng TEQ·MJ^{-1} (Hubner et al., 2005). And the emission factors of PCDD/Fs from coal and hardwood were 230 ng kg^{-1} and 50 ng kg^{-1} (Lee et al., 2005). Ma et al. (2019) investigated that the concentrations of PCDD/Fs emission of flu gas from a typical pesticide plant in eastern China were ranged from 0.056 to 1.412 ng TEQ·m^{-3} (Ma et al., 2019).

Although the absolute emission value of PCDD/Fs to air is not very high from MSWI, it is of the greatest significance, since these emissions may be dispersed through long distances, enter the food chains, and cause much public concern owing to their high toxicity and potential carcinogenic and mutagenic effects. And as continuous public criticisms and even recurrent anti-incineration protests are caused by the concern on the PCDD/Fs emissions in recent years, how to control dioxins emission is now a challenging task for China, who has large amounts of dioxin releases. MSWI was assumed as an important source of dioxin emissions in China also because it was acting an increasingly more significant role in waste management. In order to deal with the massive solid municipal waste, MSWIs were built in many urban areas in China, which made the MSWIs as very significant sources of PCDD/Fs in urban areas.

In the research area, the MSWI is located in the center of Pudong district, which is in the southeast of Shanghai. Because this plant is neighboring to the living communities, harmful pollutants emitted from MSWI, which could possibly impair people's health, results in serious worries in this area. A few researches focused on the short-term concentrations of flue gas from the source or the atmospheric samples from the surroundings. However, it is known that limited data on the atmospheric bulk deposition fluxes and seasonal variations of PCDD/Fs in the vicinity of MSWI in Shanghai for a long-term investigation until now was reported.

In this study, the Bergerhoff method was deployed, by setting up stainless steel pots to monitor PCDD/Fs at two sites in vicinity of the MSWI month by month for twelve consecutive sampling periods in 2017. This paper was aimed to investigate the atmospheric bulk deposition flux and seasonal variation of PCDD/Fs, and to analyze the possible sources of PCDD/Fs in this area.

2. Methods and materials

2.1. Sampling locations and sample collection

Shanghai, the most important region in east China, is the center of politics, economics and technology in China. The population of Shanghai is above 20 million. In the regions studied in this paper, the MSWI sits in the center of Pudong district, which is in the southeast of Shanghai. Southeasterly or northwesterly wind blows all the year in the research region, and varies in different seasons. Two sampling sites were established in the vicinity of this MSWI. According to the environmental impact assessment report of the MSWI, the predicted maximum ground-level concentration of PCDD/Fs was 714 m for typical days, and 1000 m for an annual average. And in our previous study (Deng et al., 2011a), maximum PCDD/Fs levels in soil samples were observed approximately at 1000 m from the MSWIs in Shanghai. And also considering the stability of the sampling site, as the sampling period was consecutive a year, Site A was established at the northwest (downwind direction of the prevailing wind direction in summer) of the MSWI, with the distance of 900 m in a garden. Site B was established at the southeast (downwind direction of the prevailing wind direction in winter) of the MSWI, with the distance of 750 m in a garden.

The atmospheric bulk deposition samples were gathered month by month for twelve consecutive sampling periods in 2017, by the stainless steel pots with the height of 50 cm and the inner diameter of 50 cm, from two sites (Site A and Site B) in vicinity of the MSWI, Pudong, Shanghai, China.

Before collecting the samples, in order to avoid the re-suspension of the dry deposition, 5 L purified water was filled into the sampler. Simultaneously 1.5 L isopropanol was used as algaecide. Atmospheric bulk deposition samples suspended in the water were then moved into the glass bottles and the inside of those samples was cleaned up with the glass wool pre-cleaned using the toluene. Table 1 shows the sampling periods and meteorological parameters (Shanghai Pudong new district bureau of statistics, 2018).

2.2. Pre-treatment and chemical analysis

The particle phases were obtained by filtering the collected water-deposition mixtures using glass fiber filters (GFFs, 0.45 μm, millipore, USA). The water phase was then liquid-liquid extracted by 500 mL dichloromethane for three times. Finally the filtered fiber filters were dried by lyophilizer (ALPHR 1-2LD; Christ, Germany).

The samples were analyzed for 17 PCDD/Fs based on the US environmental protection agency Method 1613 b. The dried filtered glass fiber filters were spiked with $^{13}C_{12}$-labelled compound stock solution (Wellington Laboratories, Canada) before extraction to promise the

efficiency of extraction and measure the amount of the losses at the stages of the extraction and the purification processes. Then by applying the accelerated solvent extraction system (ASE 200; Thermo, USA), each portion of the dried filtered fibers was extracted by the mixture of hexane and dichloromethane (volume ratio of 1:1). Following that, the extracts were concentrated by multi-samples quantitative concentrator (Syncore Analyst; Büchi Switzerland), and then purified by passing through an acid silica (44 wt % sulfuric) bed and a multi-layer silica column. The PCDD/Fs were separated via an activated florisil column with 40 mL mixture of hexane and dichloromethane (volume ratio of 1:1) as the eluent. The eluent was then concentrated to about 10 μL using a gas blowing concentrator (Multivap TM 118; Organomation Associates, USA)with gentle flow of nitrogen. The concentrated eluent was finally blended with 10 μL $^{13}C_{12}$-internal standard spiking solution to quantify the recovery of the labelled compound stock solution standards. The instrument analysis was then performed by a 6890 high resolution gas chromatograph (HRGC; Agilent Technologies, USA) linked to an Autospec Premier high resolution mass spectrometer (HRMS; Waters, USA) equipped with a DB-5MS column (60 m × 0.25 mm × 0.25 μm). The ion-monitoring mode was chosen in the experiment on the HRMS with a resolution of at least 10 000.

2.3. Quality control and quality assurance

Dioxins in the reference samples could be ignored because of a low level. The toxic equivalent quantity (TEQ) was achieved based on the toxicity equivalency factor (TEF), which was constructed by the World Health Organization (WHO) in 2005 (Berg et al., 2006). The concentrations less than the detection limits were defined as 1/2 of the detection limits. The limit of detection was obtained as three times the standard deviation of the smallest calibration point, which exhibited values of 0.02, 0.05–0.1 and 0.3 pg/sample for 4 chlorinated PCDD/Fs, 5–7 chlorinated PCDD/Fs and 8 chlorinated PCDD/Fs, respectively. The recovery ranges of the labelled compound stock solution standards for PCDD/Fs were 34.3–98.1% (average ± SD), which satisfied the requirements of the standards.

2.4. Data analysis

The XLSTAT version 2018 was used to perform the principal component analysis (PCA). The normalization of the PCDD/Fs homologue data set was run before the PCA. Positive matrix factorization (PMF) was performed using the PMF model (V5.0). For the PMF method, a 17 × 24 dataset (17 PCDD/F congeners and 24 atmospheric deposition samples were used to distinguish possible sources of PCDD/Fs in atmospheric deposition based on the composition or fingerprints of the sources. Detailed data processing was according to the user guide of the PMF model (V5.0) (US-EPA, 2014).

3. Results and discussion

3.1. Atmospheric bulk deposition fluxes of PCDD/Fs

Table 1 shows the atmospheric bulk deposition fluxes of PCDD/Fs and the corresponding TEQ fluxes. Fig. 1 depicts the atmospheric bulk deposition fluxes of PCDD/Fs and meteorological parameters. The atmospheric bulk deposition fluxes PCDD/Fs changed from 51.9 to 560 pg $m^{-2}{\cdot}d^{-1}$ for the Site A, with an average value of 138 pg $m^{-2}{\cdot}d^{-1}$; while 23.5–440 pg $m^{-2}{\cdot}d^{-1}$ for the Site B, with an average value of 135 pg $m^{-2}{\cdot}d^{-1}$. In this study, the atmospheric bulk deposition fluxes of PCDD/Fs were comparable with that near an iron and steel making plant in Korea (204–608 pg $m^{-2}{\cdot}d^{-1}$) (Fang et al., 2011), the MSWIs in Taiwan (518–595 pg $m^{-2}{\cdot}d^{-1}$) (Wu et al., 2009), and other areas in China, such as Guangzhou (58–900 pg $m^{-2}{\cdot}d^{-1}$) (Ren et al., 2007). Global average deposition fluxes for the temperate zone was 767 pg $m^{-2}{\cdot}d^{-1}$ (Brzuzy and Hites, 1996). Therefore, the atmospheric bulk deposition fluxes PCDD/Fs in vicinity of the MSWI in Shanghai was comparable with other places in the temperate zone.

The TEQ bulk deposition fluxes of PCDD/Fs were 2.14–23.9 pg WHO-TEQ$\cdot m^{-2}{\cdot}d^{-1}$ and 1.01–17.6 pg WHO-TEQ$\cdot m^{-2}{\cdot}d^{-1}$ at the Site A and Site B, with the average values of 5.26 and 4.84 pg WHO-TEQ$\cdot m^{-2}{\cdot}d^{-1}$, respectively. And annual TEQ bulk deposition flux of PCDD/Fs was 0.37–8.73 ngWHO-TEQ$\cdot m^{-2}{\cdot}year^{-1}$, with an average value of 1.85 ng WHO-TEQ$\cdot m^{-2}{\cdot}year^{-1}$. In Table 2, the comparison of annual TEQ bulk deposition flux of PCDD/Fs in this study and the literature data of other regions showed that the annual TEQ bulk deposition flux of PCDD/Fs of this research was higher than that in urban areas from Lagoon of Venice, Italy (Guerzoni et al., 2004), lower than those in Yokohama, Japan (Ogura et al., 2001) and Taiwan (Wu et al., 2009), comparable to those in Guangzhou (Ren et al., 2007) and Harbin (Zhu et al., 2017), China, in Busan, Korea (Moon et al., 2005), in Porto Marghera, Italy (Rossini et al., 2005), in Pohang, Korea (Fang et al., 2011), in industrial area of Taiwan (Ngo et al., 2018) and Saitama, Japan (Minomo et al., 2018).

3.2. Seasonal variations for the deposition flux of PCDD/Fs

The total TEQ and 2378-substituted PCDD/Fs were strongly correlated with each other with the R2 of 0.9781. The atmospheric bulk deposition fluxes of PCDD/Fs behaved obviously higher in June and July than other months. Seasonal variation for the atmospheric bulk deposition fluxes of PCDD/Fs in vicinity of the MSWI in Shanghai is shown in Fig. 2. The atmospheric bulk deposition fluxes of PCDD/Fs throughout the year was higher in summer (Jun to Aug) than in winter (Dec to Feb), spring (Mar to May) and autumn (Sep to Nov). This trend was different from most of other dioxin deposition researches (Moon et al., 2005; Venier et al., 2009; Fang et al., 2011). In these research areas, the higher atmospheric deposition fluxes of PCDD/Fs in winter were observed because of the house warming by biofuel (Venier et al., 2009) or colder temperatures leading to the transportation onto surfaces followed with clearance by snow (Lei and Wania, 2004; Lohmann and Jones, 1998). The results of the correlation analysis showed that the ambient temperature, precipitation or the rainy days were not much related with the atmospheric bulk deposition fluxes of PCDD/Fs. Atmospheric deposition is a very complex process. Generally, ultraviolet light, solar radiation and precipitation have been found to be the most important meteorological parameters and may have an effect on the concentration of PCDD/Fs in the atmosphere (Zhang et al., 2019).

As for the ambient temperature, on the one hand, the photolysis process interferes with PCDD/Fs in the environment, and the sunlight is strong in summer, so the concentration of OH groups is high, which causes the dioxin in the air to react with these groups, reducing the concentration of PCDD/Fs in the atmosphere, especially in gaseous phase (Chen et al., 2011). On the other hand, Shanghai is a subtropical monsoon climate. During the sampling period (2017), the average temperature for Pudong District (sampling sites) in Shanghai, in winter, was 7.03 °C. No domestic heating and rarely snowing in winter made Shanghai experience limited PCDD/Fs emission and snow scavenging, compared to other research regions.

As for precipitation or the rainy days, there is more rainfall in summer, which may defuse the PCDD/Fs in atmosphere. But also relatively higher precipitation and more rainy days could make the PCDD/Fs emitted from the MSWI quickly be captured by atmospheric deposition sampler.

All the reason above may lead the largest amounts of precipitation and the highest temperature exhibiting the highest PCDD/Fs deposition flux, and no obvious variations for other seasons. This trend was consistent with some dioxin deposition researches (Ren et al., 2007; Kaupp and Mclachlan, 1998), in which the PCDD/Fs deposition fluxes within the rainy seasons with tremendously larger values than those within the dry seasons was demonstrated.

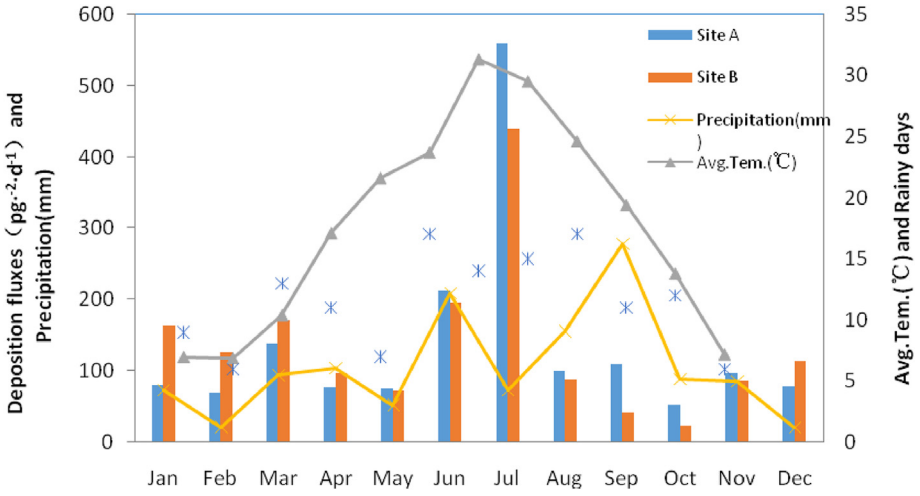


Fig. 1. Deposition fluxes, as well as meteorological parameters in the vicinity of MSWI in Shanghai.

Table 2
The comparison of the atmospheric deposition fluxes of PCDD/Fs (ng TEQ·m^{-2}·year^{-1}) in other regions.

Type of flux	Type of data	Reported flux ng TEQ·m^{-2}·year^{-1}	Location	Site description	Study date	Reference
Bulk deposition	Measured	5.7–17 (I-TEQ)	Yokohama, Japan	urban area	1996–1998	Ogura et al. (2001)
Bulk deposition	Measured	0.77–15.0 (WHO-TEQ)	Guangzhou, China	urban area	2004–2005	Ren et al. (2007)
Bulk deposition	Measured	0–3.36 (WHO-TEQ)	Venice, Italy	urban area	1998–1999	Guerzoni et al. (2004)
Bulk deposition	Measured	1.0–3.7 (2.1)	Busan, Korea	urban area	2002	Moon et al. (2005)
Bulk deposition	Measured	0.73–4.4 (WHO-TEQ)	Porto Marghera, Italy	industrial area	2003–2004	Rossini et al. (2005)
Dry deposition	Estimated	1.36–20.7 (I-TEQ)	Taiwan	MSWI	2005	Wu et al. (2009)
Bulk deposition	Measured	1.31–4.829 (I-TEQ)	Pohang, Korea	Steel complex	2008–2009	Fang et al. (2011)
Bulk deposition	Measured	2.04–8.87 (WHO-TEQ)	Taiwan	industrial area	2011–2012	Ngo et al. (2018)
Bulk deposition	Measured	0.657–12.8 (3.3) (WHO-TEQ)	Saitama, Japan	urban area	2012–2013	Minomo et al. (2018)
Bulk deposition	Estimated	4.12–15.5 (8.62) (WHO-TEQ)	Harbin, China	urban area	2014	Zhu et al. (2017)
Bulk deposition	Measured	0.37–8.73 (1.85) (WHO-TEQ)	Shanghai, China	MSWI	2017	This study

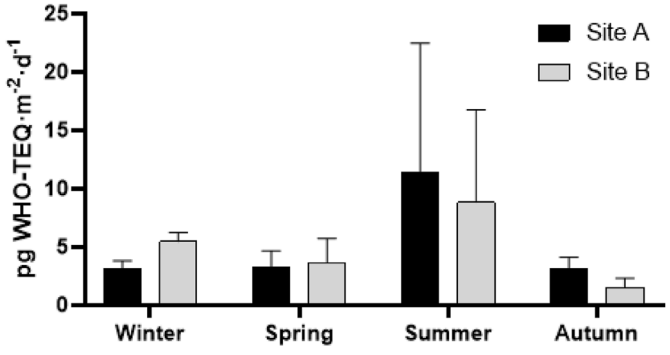


Fig. 2. Seasonal variation of PCDD/Fs in the atmospheric bulk samples in the vicinity of a MSWI in Shanghai, China.

Statistical analysis proved that the atmospheric bulk deposition fluxes of PCDD/Fs from Site B were higher than that of Site A in the winter season (Dec, Jan and Feb) with the P-value of 0.018. Although the atmospheric bulk deposition fluxes of PCDD/Fs showed no significant differences between the two sampling sites in summer, but the atmospheric bulk deposition fluxes of PCDD/Fs from Site A were a little higher than that of Site B in summer season (Jun, Jul and Aug). In winter, northwesterly wind prevailed in the specific research area. And Site B was established at the southeast direction of the MSWI, which is the downwind directionof the MSWI in winter. The PCDD/Fs concentrations of atmospheric deposition may be elevated at the downwind direction of the MSWI in winter, compared to the upper wind direction in winter; on the contrast, in summer, southeasterly wind prevailed in the specific research area. And Site A was established at the northwest of the MSWI, which is the downwind directionof the MSWI in summer. The PCDD/Fs concentrations of atmospheric deposition may also be elevated at the downwind direction of the MSWI in summer, compared to the upper wind direction in summer. The spatial variations of the deposition concentrations at the downwind direction in different seasons may indicate that MSWI could be an important PCDD/Fs source for its vicinity areas.

3.3. Average congener and homologue profiles of PCDD/Fs

Fig. 3 shows the average profiles of 17 2378-substituted congeners of PCDD/Fs in atmospheric bulk deposition specimens. Generally, no

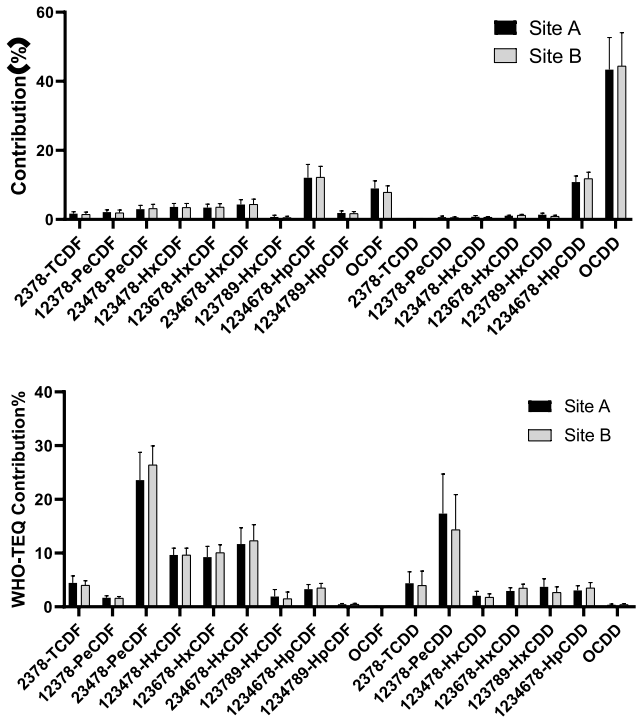


Fig. 3. The normalization profiles of 17 2378-substituted congeners of PCDD/Fs in the atmospheric bulk deposition specimens in the vicinity of a MSWI in Shanghai, China.

great variations during the twelve sampling periods were observed for 17 2378-substituted congener profiles at two sampling sites. Among all deposition specimens, OCDD was the dominated congeners, occupying around 40.8% of the overall concentration of 17 congeners, followed by the high-chlorinated congeners including 1234678-HpCDF, 1234678-HpCDD and OCDF, which accounted for 13.9%, 10.8% and 9.13%, respectively. The distribution property was alike with those findings of the deposition samples from the industrial and urban areas (Fang et al., 2011; Moon et al., 2005; Ren et al., 2007). With respect to the TEQ concentrations, 23478-PeCDF made the most important contribution and accounted for 38.9% of the total TEQ on average, followed by 234678-HxCDF and 123678-HxCDF. This result also agreed with those of the former deposition researches (Fang et al., 2011; Moon et al., 2005; Ren et al., 2007).

For the ten homologue characters, OCDD, followed by HpCDF and HxCDF, exhibited the largest abundance in all the specimens, which were accounted for 40.8%, 15.7% and 13.4%, respectively. The homologue profiles of PCDD/Fs displayed in this study was described as increased the concentrations with the increased level of chlorination, except for OCDF. In general, there were no obvious differences in homologues profiles of spatial and seasonal distribution of PCDD/Fs in this study. But when we compared the homologue profiles of 6 winter specimens with that of 6 summer specimens, 4–6 chlorinated homologues of PCDD/Fs were a little higher in winter than in summer by 0.05–1.5%; and the 7–8 chlorinated homologues of PCDDs were a little lower in winter than in summer by 0.59–5.25%. The profiles of the homologues of PCDD/Fs are affected by many factors, including meteorological conditions, pollution sources, air trajectories, and atmospheric deposition (Lohmann and Jones, 1998). And wet deposition dominates, accounting for 85% of the total deposition flux of the higher chlorinated homologues (Schröder et al., 1997). On one hand, the low chlorinated PCDD/Fs trend to bound in gaseous phase in summer due to higher temperature, which makes relatively higher abundance of high chlorinated homologues in the particle phase in summer. On the other hand, there are more rainfall in summer than in winter, so that the homologues of PCDD/Fs in summer were influenced more by wet deposition, which is more related to high chlorinated PCDD/Fs (Zhang et al., 2019). Above all may explain that low chlorinated homologues of PCDD/Fs were a little lower and the high chlorinated homologues of PCDDs were a little higher in summer in this study. For the specimens of February and July, as the homologue profiles represented as obviously higher HpCDF (21.4%) and HxCDF (17.7%), but lower OCDD (28.5%). The PCDF to PCDD ratios were ranged from 1.24 to 1.94, which were obviously higher than the average level (0.80). High abundances of PCDFs are linked to thermal processes, e.g., air emissions from MSWI (Sundqvist et al., 2010), which is indicated that there may be distinct pollution sources influenced the homologue profiles of PCDD/Fs in the atmospheric bulk deposition samples in February and July in study area.

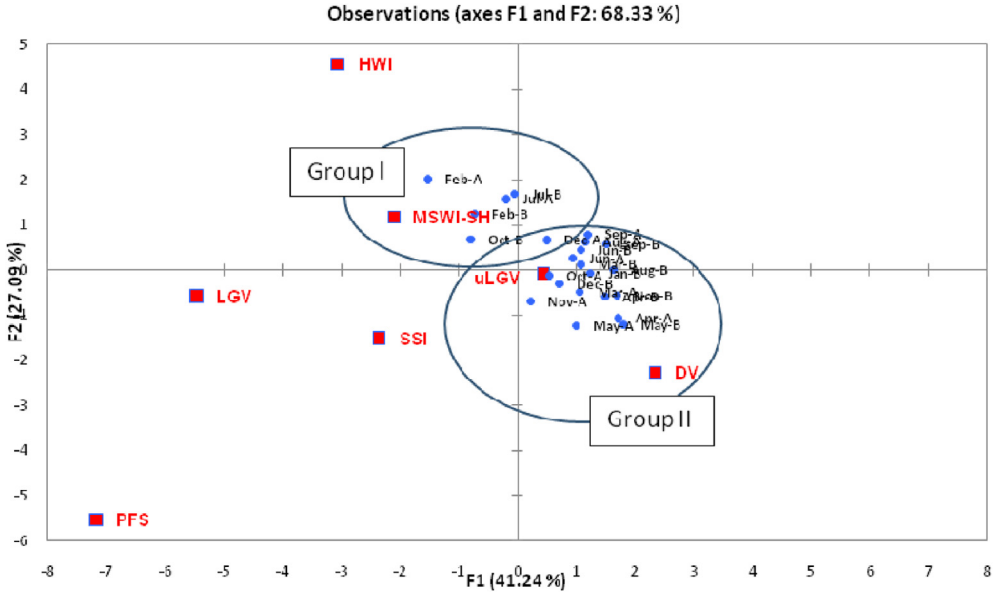


Fig. 4. The principal component plot of the 24 atmospheric deposition specimens and several emission sources.

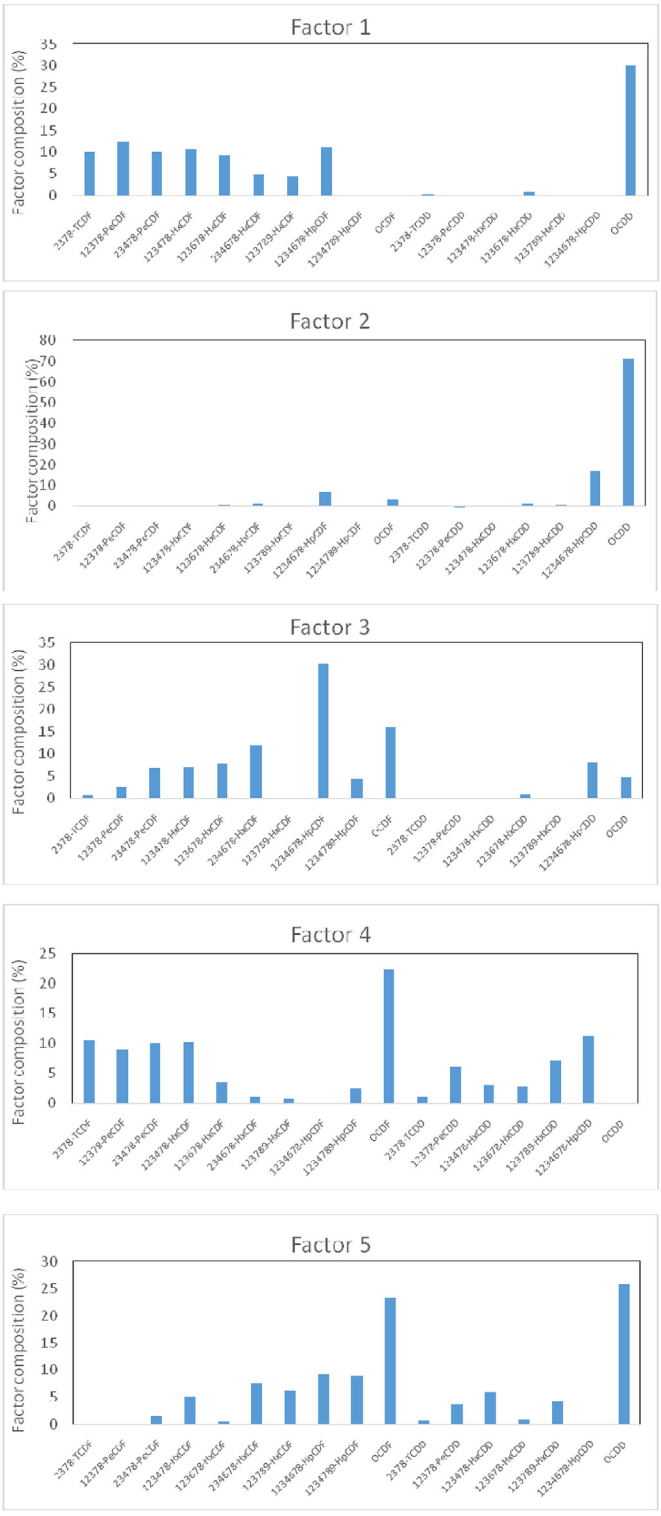


Fig. 5. Source profiles of PCDD/Fs as obtained from PMF method.

3.4. Source identification

3.4.1. Principal component analysis (PCA)

Based on the investigation of the possible emission sources and the preliminary PCA in the study area, MSWI, hazardous waste incineration source (HWI) (USEPA, 2001), vehicle emission source (unleaded gas vehicles (ULGV), leaded gas vehicles (LGV), diesel vehicles (DV), sludge incineration (SSI)and metal smelting (PFS) (USEPA, 2001) were considered as the possible emission sources in study area. The PCDD/F homologue profiles of the atmospheric bulk deposition specimens in the vicinity of the MSWI, together with above mentioned possible emission sources were analyzed by PCA.

Three main compositions, accounting for 88.3% difference of the 24 samples, with ten homologues as the variables, were identified by PCA. The score plot for the PCA of PC1 and PC2 is exhibited in Fig. 4. The experimental data for the atmospheric deposition samples in vicinity of the MSWI appeared to agglomerate into two groups. Group I was aggregated closer to MSWI in the score plot, indicating that the samples of this group were more influenced by the MSWI than by other sources. And it should also be noticed that, for the period of July, with the remarkably higher atmospheric bulk deposition fluxes of PCDD/Fs, the MSWI obviously influenced the atmospheric bulk deposition flux of PCDD/Fs in vicinity of the MSWI. The score plot indicated that the majority of the atmospheric deposition samples were in group II, which displayed similar characters to the ULGV and DV sources. It demonstrated that both the MSWI and vehicle emission acted as indispensable PCDD/Fs sources in vicinity of the MSWI, especially for the urban areas.

3.4. Positive matrix factorization (PMF) analysis

By comparing the decrease in Q value while increased the number of factor by 1, the PMF method apportioned 5 source categories. These apportioned 5 source categories were MSWI, diesel vehicles (DV), atmosphere background (AB), industrial combustion (IC) and un-leaded gas vehicles (ULGV), accounting for 43.3%, 38.1%, 6.89%, 6.19% and 5.50% in average, respectively of PCDD/Fs in atmospheric deposition in the Vicinity of the MSWI in Shanghai.

As shown in Fig. 5, for factor 1, PCDFs showed a little higher contribution than those of PCDDs, indicating limited influence of industrial activities and other combustion processes (Hao et al., 2018). Factor 1 contribution was also presented seasonal change of higher in winter and summer, lower in autumn and spring. And the profile of Factor 1 was very similar with the profile of atmosphere from background area in Shanghai (Tian et al., 2015). So Factor 1 was assigned to atmosphere background in Shanghai.

Factor 2 was heavily loaded with OCDD, 1234678-HpCDD, 1234689-HpCDF and OCDF. Researches showed that 1234678-HpCDF, 1234678-HpCDD and OCDD were the most abundant PCDD/F congeners in vehicle emissions (Turrio-Baldassarri et al., 2005; Aristizabal et al., 2011). Factor 5, which was similar to factor 2, was distinguished by 1234678-HpCDF, OCDF and OCDD, also highly in accordance with the dominant 2378-substituted congeners reported in vehicle emissions and air from high traffic areas (Li et al., 2014; Chang et al., 2004). By comparing the profile of the diesel vehicle emission and un-leaded gas vehicle emission (USEPA, 2001), the contributions of 1234678-HpCDF and OCDF in un-leaded gas vehicle emission is higher than that in diesel vehicle emission; and the contributions of OCDD in un-leaded gas vehicle emission is lower than that in diesel vehicle emission. So the factor 2 was assigned to diesel vehicle emissions, while factor 5 was assigned to un-leaded gas vehicles.

Factor 3 was heavily loaded with 1234789-HpCDF, OCDF and 123 678-HxCDF, and included a wide range of PCDFs. 1234678-HpCDD and OCDD were also dominant in PCDDs. High abundances of PCDFs are linked to thermal processes, e.g., emissions from MSWIs (Uchimiya et al., 2007). OCDF was suggested to be indicated of MSWIs (Xuan et al., 2017). Zhu et al. (2018) did a research about emission characteristics of PCDD/Fs in stack gas from municipal solid waste incineration plants in Northern China. The results showed that 1234678-HpCDD, OCDD, OCDF and 1234789-HpCDF were the largest contributors for the emission concentrations of PCDD/Fs. And another research of 15 waste incinerators in China suggesting 1234678-HpCDF, OCDF and 1234678-HpCDD were dominant PCDD/Fs congeners in stack gas from MSWI (Li et al., 2017). Therefore, factor 3 was selected to represent MSWI.

Factor 4 has been significantly associated with lower chlorinated PCDFs (2378-TCDF, 12378-PeCDF, 23478-PeCDF, 123478-HxCDF),

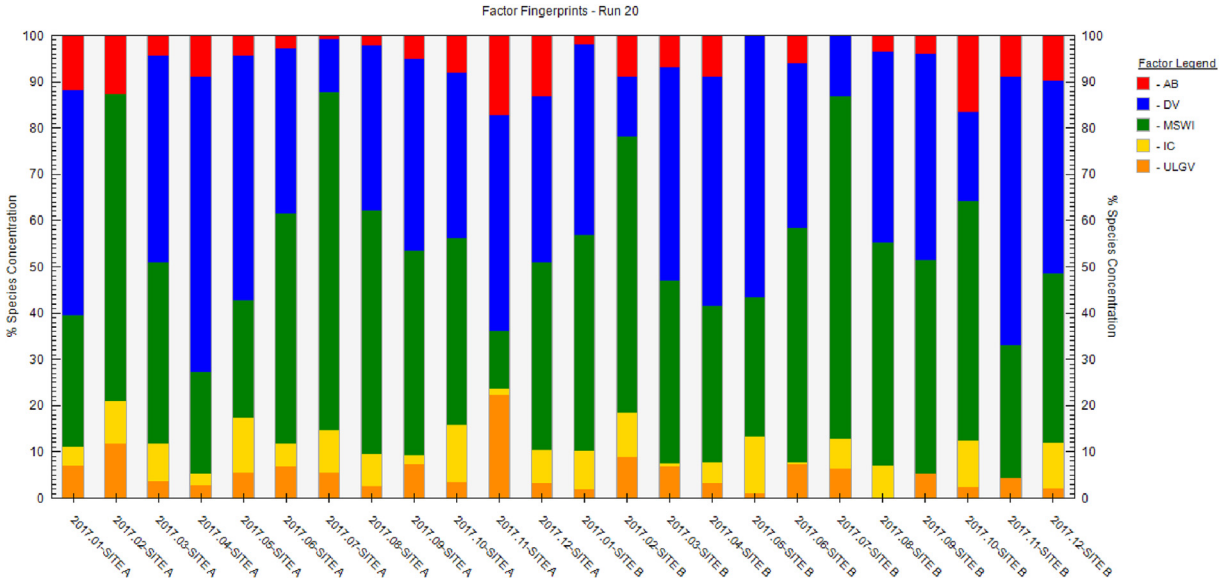
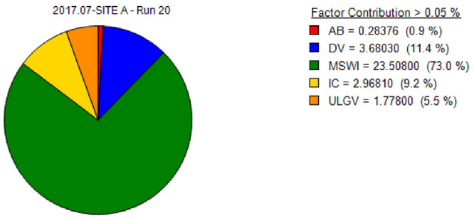


Fig. 6. The contributions of five distinct factors apportioned by PMF in all specimens.



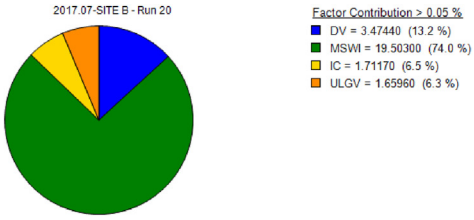


Fig. 7. The contributions of five distinct factors apportioned by PMF in July.

OCDF and 123789-HxCDD, 1234678-HpCDD. High abundances of PCDFs are linked to thermal processes (Uchimiya et al., 2007). But it lacked of 1234678-HpCDF and OCDF as the indicator of MSWI. To conclude, this source was assigned to other industrial combustion, related to thermal emissions associated with industrial combustion.

Fig. 6 shows site-specific sources and their contributions to PCDD/Fs in atmospheric deposition samples in vicinity of the MSWI in Shanghai, based on data sets consisting of 17 PCDD/F congeners. The nearly equal contributions to the sum of PCDD/Fs were seen to come from vehicle emissions (including diesel vehicle emissions and unleaded gas vehicle emissions) and MSWI, accounting for 43.6% and 43.3%, respectively of PCDD/Fs in atmospheric deposition in the Vicinity of the MSWI in Shanghai. A significant contribution to PCDD/F levels from the traffic-related sources was also seen in Korea (Jang et al., 2020), explained by larger road transportation volume in big cities.

In some special period, like in July (see in Fig. 7), the significant higher contribution to the sum of PCDD/Fs was MSWI, compared to vehicle emissions. Considering the elevated PCDD/Fs concentration of atmospheric deposition in July, the consistent conclusion can be drew with the PCA method, that MSWI may not be the only major source for PCDD/Fs in atmospheric deposition in vicinity of the MSWI in Shanghai. But MSWI did influence the PCDD/Fs in atmospheric deposition in vicinity of the MSWI in Shanghai, especially for the higher contaminated period.

4. Conclusions

An investigation of long-term atmospheric bulk deposition fluxes of PCDD/Fs was firstly performed in the vicinity of a MSWI in Shanghai. The atmospheric bulk deposition fluxes of PCDD/Fs in the vicinity of a MSWI in Shanghai were consistent with those near an iron and steel making plant in Korea, MSWIs in Taiwan, and other areas in China, such as Guangzhou and Harbin. Seasonal atmospheric bulk deposition fluxes of PCDD/Fs exhibited high levels in summer, moderate levels in winter, and low levels in spring and autumn. The PCA method indicated the MSWI was not the only emission source in vicinity of the MSWI and the vehicle emission was also an indispensable PCDD/Fs source in vicinity of the MSWI, especially for the urban areas. Moreover, PMF method apportioned 5 source categories: MSWI, diesel vehicles, atmosphere background, industrial combustion and un-leaded gas vehicles, accounting for 43.3%, 38.1%, 6.89%, 6.19% and 5.50% in average, respectively of PCDD/Fs in atmospheric deposition in the Vicinity of MSWI in Shanghai, China.

CRediT authorship contribution statement

Yunyun Deng: Conceptualization, Methodology, Software, Writing - original draft. **Pingan Peng:** Supervision, Writing - review & editing. **Lijuan Jia:** Investigation, Formal analysis. **Haowen Yin:** Conceptualization. **Jianfang Hu:** Validation, Data curation. **Wanlian Mao:** Investigation.

Declaration of competing interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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