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Characteristics of PCDD/Fs and metals in surface soil around an iron and steel plant in North China Plain

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HIGHLIGHTS

- PCDD/Fs pollution from iron and steel plants in north China is a serious problem.
- Soil heavy metals fingerprints indicated dioxin levels around iron and steel plants.
- High PCDD/Fs, Cd, Zn, and Pb levels were detected in downwind soil.

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ABSTRACT

In this study, the level of 18 species of metals and 17 species of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) were monitored in surface soil samples around an iron and steel plant in the North China Plain. The concentration of PCDD/Fs and metals in the soil ranged from 0.16 to 4.5 ng I-TEQ/kg and 1.2 to 24,182.2 mg/kg, respectively. Furthermore, the prevailing winds were confirmed to influence the spatial distribution of PCDD/Fs and metals concentrations. The highest concentration of PCDD/Fs was located in downwind soil sample 4 (S4), which showed more than 50% of PCDFs in the total PCDD/Fs, and high levels of lower chlorinated PCDFs. Moreover, the highest Cd and Zn concentrations of 18.1 and 2647.8 mg/kg, respectively, were observed in soil collected from S4, which were significantly above the government guidelines for metals in farmland soil. Our results show that a group of metals (Mg, Al, K, Fe, Cu, Zn, Se, Cd, Sb and Pb) was well correlated with all PCDD/Fs except three (OCDD, 1,2,3,4,6,7,8-HpCDD and 1,2,3,7,8,9-HxCDD), which likely originated from iron and steel processes. Additionally, Pb, Zn, Cd and all polychlorinated dibenzofurans showed a good correlation and grouped in one cluster, suggesting anthropogenic sources from sintering process. Therefore, the metallic characteristics in soil, especially the Pb, Zn and Cd tracers, implied evidence of the accumulation of PCDD/Fs from sinter plants.
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1. Introduction

The production of iron and steel in China currently accounts for one half of the amount produced globally, and it is generally over 0.8 billion tons per year. Moreover, China has been the largest iron and steel producing country in the world since 1996 (Dong et al., 2013; Zhang et al., 2014; Wang et al., 2016). The iron foundry industry is considered to be a major source of atmospheric emissions of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) and heavy metals (Wang et al., 2003; UNEP, 2005; Fang et al., 2011; Lv et al., 2011; Huang et al., 2015). Polychlorinated dibenzo-p-dioxins and dibenzofurans are a group of 210 chlorinated organic compounds, commonly known as dioxins, that are toxic chemicals that cause numerous adverse health effects.

Iron ore sintering results in the proper temperature, chlorinated precursors, metal catalysts and solid phase for formation of PCDD/Fs (Lv et al., 2011; Ooi and Lu, 2011). However, little is known about the emission of PCDD/Fs from such sintering processes or systems designed to control these emissions. The total PCDD/Fs emissions released to residue and air from iron foundries in China were found to be 0.484 and 24.8 g WHO-TEQ/year in 2008, respectively (Lv et al., 2011). Moreover, the iron and steel industry contributed more than 30% of the total PCDD/Fs emissions in China in 2004 (Wang et al., 2016), and this level reached 40–44% in Taiwan (Kao et al., 2011), which is greater than the amount released from

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municipal solid waste incinerators (MSWI). Moreover, the iron and steel industry has been recognized as one of the most important sources of PCDD/Fs based on investigations of the emission inventory in many countries (Quass et al., 2000; Caserini and Monguzzi, 2002; Ooi and Lu, 2011; Saral et al., 2014). Fu et al. (2012) demonstrated that acidic gaseous pollutants, incomplete combustion pollutants, particulate matter and toxic heavy metals were generated from exhaust gas during the production of iron and steel. Therefore, investigation of PCDD/Fs and heavy metals generated by the iron and steel industry is warranted.

In general, soil is regarded as a major reservoir of PCDD/Fs and metals because of its high sorption capacity for organic and metallic contaminants (Duarte-Davidson et al., 1997; Vilavert et al., 2009b). Atmospheric bulk deposition of pollutants in the vicinity of iron and steel plants was confirmed by Fang et al. (2011). Additionally, several studies have estimated the emission inventory of air pollutants or the characteristics of fly ash from iron and steel plants in China (Lv et al., 2011; Huang et al., 2015); however, the results of most of these were calculated based on limited data. Moreover, few studies have measured the levels of PCDD/Fs in soil around iron and steel plants in China, although a large number of studies have focused on the MSWI. Here, we evaluated the concentration of PCDD/Fs and metals in soil samples collected near an iron and steel plant in North China Plain to better understand their characteristics and spatial distribution. Using correlation and cluster analysis of PCDD/Fs and metals, we analyzed the possible groupings of similar emissions and identified abundant PCDD/Fs congeners and toxic heavy metals corresponding to potential soil pollution.

2. Materials and methods

2.1. Sampling

The iron and steel plant assessed in this study has been in operation for nearly 60 years and is located in Hebei Province, China. With a production capacity of 9,000,000 tons of steel per year, the facility consists of seven sinters (Fig. 1). Sinter 1 and 2, which were established in 2009 and 2015, respectively, each have an effective sintering area of 435 m^2. Sinter 3 has been used for 18 years and has an area of 400 m^2. Prior to their being taken out of service, sinters 4 and 5, which each have an area of 90 m^2, were in use for 25 years. Sinters 6 and 7, which each have an area of 360 m^2, have been used for nine years and.

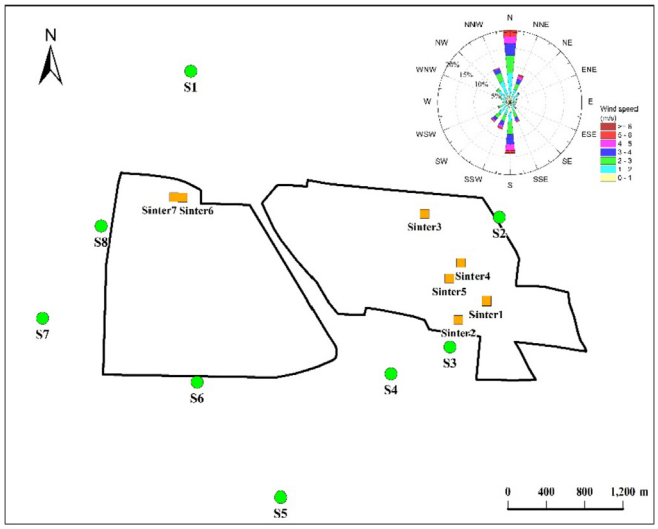


Fig. 1. Area of sampling.

In August of 2017, eight surface soil samples (S1–S8) were collected in the vicinity of the iron and steel plant in eight wind directions with S1 representing N and all others following in a clockwise direction. The soil samples were taken from the upper 20 cm and different distances from the seven sintering machines (0.3–3.3 km). Sample S1 was collected from a vegetable field, S2 consisted of backfill soil collected close to a highway, S3 was collected in the waste factory area, and S4–S7 came from agricultural fields used to cultivate corn and cotton. Finally, S8 was collected from a grove in the northwest. All samples were stored in polyethylene bags and transported to the laboratory for analysis.

2.2. Analytical procedure

The PCDD/Fs were analyzed according to the HJ 77.4–2008 method in China (MEP, 2008). Soil samples were dried and sieved through a 60-mesh sieve to remove gravel-sized materials, after which 20 g aliquots were spiked with $^{13}C_{12}$-labeled internal quantification standards and then Soxhlet extracted in 300 mL of toluene for 18 h. The extract was subsequently concentrated and transferred to n-hexane in separating funnels, after which it was treated with concentrated sulfuric acid to remove the fat and organic polymers. After shaking in the separating funnel, the n-hexane layer was concentrated and cleaned up with a multi-layer silica gel column. Following Soxhlet extraction, clean-up, evaporation and resuspension were done consecutively. PCDD/Fs eluted with 200 mL of n-hexane and further fractionated using a silica-gel dispersed carbon column. The PCDD/Fs were quantitatively measured using a 6890N gas chromatograph (Agilent, USA) coupled with a JEOL JMS-800D ultra high-resolution mass spectrometer. Quantification was achieved by the isotope dilution method and the RRF of calibration standards using a quartz capillary column (SGE, 60 m × 0.25 mm i.d. × 0.25 μm film thickness). The electron impact ionization energy was at 38 eV with a source temperature of 300 °C.

Quality assurance and quality control (QA/QC) were accomplished using a method blank, parallel samples and recoveries of $^{13}C_{12}$-labeled PCDD/Fs. The results of method blanks showed no interference and the relative deviation of parallel samples was 11%. The sampling recoveries were controlled in the range of 50–110% and the detection limits of the 17 toxic congeners of PCDD/Fs ranged from 0.05 to 0.2 ng/kg.

Determination of metals was accomplished according to the United States Environmental Protection Agency (USEPA) Method 6020A. Soil samples were dried and sieved through a 100-mesh sieve. Each sample was digested in a mixed acid solution containing nitric acid and hydrofluoric acid using a closed vessel microwave digestion system (MARS 5, CEM Corporation, Matthews, NC, USA) for 10 min until reaching 165 °C, and kept 20 min at this temperature. Following digestion, the solution was diluted to 100 mL with deionized water. The concentrations of Be, Na, Mg, Al, K, Ca, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Se, Cd, Sb, and Pb in soil were measured by Inductively Coupled Plasma Spectrometry with Mass Spectrometry (Thermo Scientific iCAP Qs ICP-MS, USA) using Rh as internal standard. For quality assurance/quality control (QA/QC), reference standards (soil, GBW07049-GBW07411, National Iron & Steel Research Institute) and blanks were analyzed to ensure good stability and avoid potential interference. Similarly, duplicate samples were determined and the result error was found to be less than 10%.

2.3. Statistical treatment

For statistical analyses, concentrations below the limit of detection (LOD) were set to one half of the LOD. To assess

toxicologically relevant information regarding PCDD/Fs, the toxic equivalents (I-TEQ) were calculated according to the I-TEF using the International Toxic Equivalent System (NATO I-TEQ) (NATO/CCMS, 1988).

Correlation and cluster analysis were conducted using R. The statistical treatment for the concentration of samples was as follows: (1) the dataset describing the 17 PCDD/Fs and 18 metals was prepared in csv file format, then loaded into the R environment; (2) correlation matrix and cluster analysis was conducted using Pearson's correlation coefficient, kmeans and hierarchical cluster analysis. For analysis and visualizations, this study used the following R packages: ggplot2, dplyr, ggcorrplot, FactomineR, factoExtra and cluster (Irawan and Putranto, 2016; Kassambara and Mundt, 2017; Le et al., 2008). A $p < 0.05$ was considered significant.

Clustering methods were used for classifying the results into groups of similar objects. Each species was assigned a score using the k-means clustering for measuring the Euclidean distance and allowing the phylogenic tree to be further plotted. Computed the distance matrix to identified the analogous groups based on the Principal Component Analysis (PCA). All calculation and phylogenic tree plot were executed via R (Maechle et al., 2012; Galili, 2015).

3. Results and discussion

3.1. PCDD/Fs in soils

The levels of PCDD/Fs in soil collected in the vicinity of the investigated plant are presented in Table 1. The means of the total PCDD/Fs and total I-TEQ contents in surface soil were 114 ± 91 ng/kg and 1.16 ± 1.30 ng I-TEQ/kg, respectively, with a range of 0.16 ng I-TEQ/kg to 4.5 ng I-TEQ/kg (13–320 ng/kg). The highest PCDD/Fs concentration was found at S4, while the second highest was found at sampling point S5, which were both located south of the facility. The lowest PCDD/Fs level was found at site S2, which was located northwest of the site. The unusually high concentration observed around S4 compared with the other sampling points can be attributed to the direction of wind and proximity to sinters 1 to 3. In China, no PCDD/Fs guidelines for agricultural land have been established; however, S4 exceeded the Canadian soil guideline value (4 pg TEQ/kg) of PCDD/Fs for agricultural land (CCME, 2002).

As shown in Fig. 2, comparison of the homologue profiles of PCDD/Fs of the sampling points revealed significant differences ($p > 0.05$). However, different distribution patterns among the high and low concentrations were evident. For high levels, more than 50% of the PCDFs dominated the total PCDD/Fs, and an increasing trend of TeCDFs with higher PCDD/Fs was observed. Nevertheless, about 60% of the OCDD and 20% of the HpCDDs accounted for the total PCDD/Fs related to the lower concentration soil samples. It should be noted that the fingerprint from the high PCDD/Fs has similar characteristics to the combustion pattern of the fly ash samples from iron sintering (Rotatori et al., 2006; Lv et al., 2011; Ooi and Lu, 2011). This distribution indicated that PCDFs more easily accumulate in soil influenced by the iron sintering process, suggesting that the low chlorinated PCDFs may have undergone continued effects. This is likely because less chlorinated homologues degrade much more rapidly than highly chlorinated ones in soil (Zhang et al., 2009), which may be a result of formation, accumulation and mixing of congeners at different positions in the sources of the pollution. Comparison with the soil samples from MSWI, PCDFs predominated was similar to the iron and streel plant, but the PeCDFs was the highest among MSWI samples (Jin et al., 2012). A common feature of soil samples around the steel manufacturing plant and uncontrolled electronic waste burning was that TeCDFs was the dominant homologue (Xu et al., 2013).

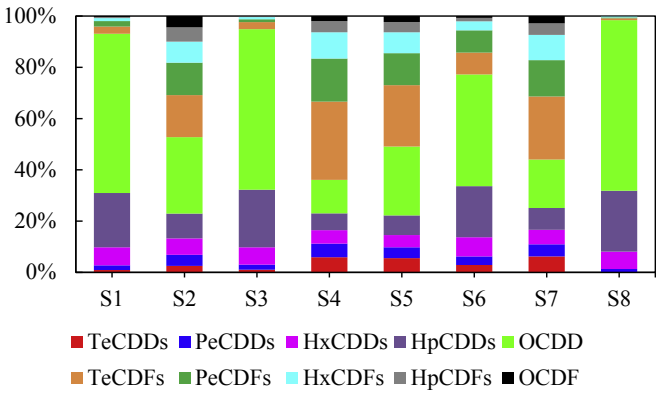


Fig. 2. PCDD/Fs homologue profile for soil samples.

Table 1
Concentration of PCDD/Fs (ng/kg dw) in soil samples collected from around the iron and steel plant.

	S1	S2	S3	S4	S5	S6	S7	S8	Range	Mean	Std
2,3,7,8-TeCDD	0.025[a]	0.025 [a]	0.081	0.22	0.025 [a]	0.025 [a]	0.025 [a]	0.025 [a]	0.025–0.22	0.056	0.065
1,2,3,7,8-PeCDD	0.17	0.045 [a]	0.38	0.81	0.21	0.19	0.12	0.22	0.045–0.82	0.27	0.22
1,2,3,4,7,8-HxCDD	0.20	0.05 [a]	0.50	0.84	0.17	0.19	0.05 [a]	0.29	0.05–0.84	0.29	0.25
1,2,3,6,7,8-HxCDD	0.41	0.05 [a]	1.1	1.1	0.43	0.46	0.20	0.60	0.05–1.1	0.54	0.36
1,2,3,7,8,9-HxCDD	0.86	0.05 [a]	1.7	1.0	0.52	0.68	0.18	1.1	0.05–1.7	0.76	0.50
1,2,3,4,6,7,8-HpCDD	5.2	0.52	15	8.1	3.3	4.2	1.6	6.9	0.52–15	5.6	4.3
OCDD	44	4.0	120	42	28	35	10	56	4.0–120	42	34
2,3,7,8-TeCDF	0.15	0.11	0.61	3.5	1.0	0.25	0.51	0.025 [a]	0.025–3.5	0.77	1.07
1,2,3,7,8-PeCDF	0.13	0.16	0.29	3.0	0.83	0.26	0.44	0.04 [a]	0.04–3.0	0.64	0.92
2,3,4,7,8-PeCDF	0.092	0.045 [a]	0.21	3.7	0.91	0.30	0.54	0.045 [a]	0.045–3.7	0.73	1.16
1,2,3,4,7,8-HxCDF	0.05 [a]	0.21	0.18	3.5	0.99	0.28	0.85	0.05 [a]	0.05–3.5	0.76	1.09
1,2,3,6,7,8-HxCDF	0.23	0.15	0.38	3.4	0.94	0.39	0.51	0.17	0.15–3.4	0.77	1.02
1,2,3,7,8,9-HxCDF	0.05 [a]	0.05 [a]	0.21	0.86	0.27	0.17	0.18	0.05 [a]	0.05–0.86	0.23	0.25
2,3,4,6,7,8-HxCDF	0.05 [a]	0.05 [a]	0.05 [a]	2.0	0.53	0.17	0.30	0.05 [a]	0.05–2.0	0.40	0.63
1,2,3,4,6,7,8-HpCDF	0.20	0.47	0.30	10	2.8	0.77	1.6	0.045 [a]	0.045–10	2.02	3.13
1,2,3,4,7,8,9-HpCDF	0.05 [a]	0.05 [a]	0.05 [a]	0.99	0.38	0.05 [a]	0.25	0.05 [a]	0.05–0.99	0.23	0.31
OCDF	0.24	0.59	0.22	6.3	2.4	0.56	1.5	0.1 [a]	0.1–6.3	1.49	1.96
∑PCDDs	66	7.0	180	120	51	62	23	83	7.0–180	74	52
∑PCDFs	4.8	6.4	9.9	200	53	18	30	1.5	9.9–200	40	62
Ratio of F/D	0.07	0.91	0.06	1.67	1.04	0.29	1.30	0.02	0.02–1.67	0.67	0.60
∑PCDD/Fs	71	13	190	320	100	81	53	84	13–320	114	91
∑PCDD/Fs (ng I-TEQ/kg)	0.46	0.16	1.1	4.5	1.2	0.63	0.70	0.51	0.16–4.5	1.16	1.30

[a] The concentration of samples for which values were below the LOD (limit of detection) was set to 1/2 LOD.

For better comparison with the available data, we summarized the I-TEQ values of PCDD/Fs in soil collected from around various sources in Table 2, along with the ratio of F/D values. As shown in Table 2, the PCDD/Fs levels around the iron and steel plant, MSWI, cement plant, and hospital waste incinerator were far lower than those in the vicinity of electronic wastes (EWs) disposal and recycling facilities and pentachlorophenol (PCP) manufacturing plants in some areas of South China (Leung et al., 2007; Xu et al., 2013; Jin et al., 2012; Li et al., 2012; Zhang et al., 2009). In this study, the ratio of PCDFs/PCDDs (F/D) ranged from 0.02 to 1.67, with an average value of 0.67, which is far less than the level of EWs recycling facilities and EWs plants in Guiyu, China (Table 2) (Leung et al., 2007; Chakraborty et al., 2017), but higher than those of soils in south China investigated by Zhang et al. (2009). The highest ratio of F/D was 1.67 from S4, indicating abundant enrichment of polychlorinated dibenzofurans in this area and that the characteristics of high PCDFs in downwind soil is similar to the homologue profiles of PCDD/Fs. These discrepancies might be the de novo mechanism as the main source of PCDD/Fs formation and more PCDFs being formed because of the long-term deposition of pollutants in the vicinity of the iron and steel making plant (Nganai et al., 2014).

3.2. Metals in soils

The concentration of eighteen primary metals in the soil around the iron and steel plant is shown in Fig. 3. The highest mean concentrations in soil corresponded to Al and Fe (24,182.2 and 21,049.0 mg/kg, respectively), whereas Sb, Be and Cd presented the lowest values (1.2, 2.0 and 2.4 mg/kg, respectively). The mean concentrations of the metals in soil were as follows: Sb < Be < Cd < Mg < Na < As < K < Ni < Se < Cu < Pb < Ca < Cr < V < Zn < Mn < Fe < Al. Moreover, the Cd and Zn levels of S4 were 18.1 and 2647.8 mg/kg, which were well above the limits of 0.60 and 300 mg/kg, respectively, set for agricultural soils by the Chinese MEP (Ministry of Environmental Protection) (CEPA, 1995).

To better view the spatial distribution of pollutants in soil samples, the metals and dioxins from S1 to S8 were visualized in Fig. 3. The results revealed a clear tendency in which the target compounds were divided into three groups. The first group contained Mg, Al, K, Fe, Cu, Zn, Se, Cd, Sb and Pb, and dioxins, with the highest concentrations being in S4. The maximum concentrations of heavy metals, including Zn, Cd and Pb, were 175, 108 and 11 times higher than the minimum, respectively. The areas surrounding smelters are vulnerable to the atmospheric deposition of fly ash with heavy metals; therefore, sinter emissions may contribute significantly to

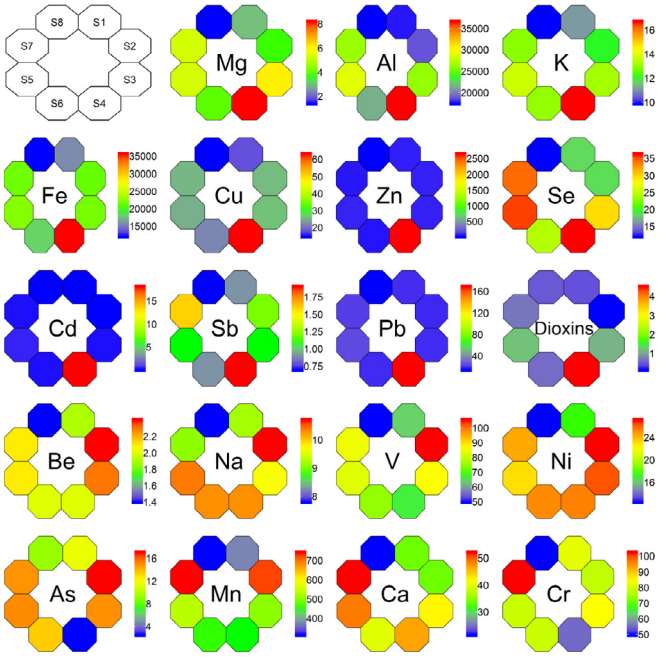


Fig. 3. Metals and dioxins concentration in different samples (unit: ng/kg).

the enrichment of Cd, Zn and Pb over time (Wang et al., 2003). In contrast, the other group contained Be, Na, V, Mn, Ni and As, with the highest levels being observed in S2, whereas dioxins were lowest at this sample point. Furthermore, V and Ni were associated with the refinement and burning of oil, as well as traffic (Rovira et al., 2015), suggesting that the types of metals found in S2 originated from diesel vehicles. The rest of Mn, Ca and Cr belongs to the last group, shown a highest level in S7. The three metals suggested different sources from both natural and anthropogenic emissions, Ca is the tracer of soil and construction materials, while Mn and Cr indicated that combustion sources (Pan et al., 2015). These findings indicated that the iron and steel plant has become a potential contributor of dioxins and metals from the first group to surrounding soil. Overall, the results of factor analysis imply a difference in the contamination sources contributing to soil.

The main sources of heavy metals include various waste incinerators, steelmaking, fuel combustion, industries, and so on. Researches has found that Cd, Zn and Pb could be used as indicators for source identification of the steel manufacturing plants (Al-

Table 2
Levels of PCDD/Fs in soil from around different sources.

Location	Source	Mean(Min – Max) (ng I-TEQ/kg)	Ratio of F/D	Reference
Northern China	Iron and steel plant	1.16(0.16–4.5)	0.67(0.02–1.67)	This study
Guiyu, China	EWs disposal	20(5.7–57)	0.11–0.26	(Xu et al., 2013)
Guiyu, China	EWs from the acid leaching site	489(203–1100) (WHO TEQ)	11.89	(Leung et al., 2007)
India	EWs recycling	31(8–99) (WHO TEQ)	2.4	(Chakraborty et al., 2017)
Catalonia, Spain	Cement plant	1.01(0.40–2012)		(Schuhmacher et al., 2009)
Catalonia, Spain	MSWI	0.64(0.13–2.41)		(Vilavert et al., 2009a)
Shanghai, China	MSWI	1.218(0.972–1.464)		(Jin et al., 2012)
Hangzhou, China	MSWI	2.274(1.324–5.188)		(Jin et al., 2012)
Taiwan	MSWI	2.11(0.524–5.02)		(Cheng et al., 2003)
Zhejiang, China	Hospital waste incinerator	1.09(0.46–2.63)		(Li et al., 2012)
North China	Iron and steel plant	1.81(0.82–2.4)		(Sun et al., 2017)
South China	Residential/commercial area	4.36(0.30–8.22)	0.072(0.001–0.31)	(Zhang et al., 2009)
	Industrial area	5.14(1.44–8.23)	0.11(0.013–0.24)	
	Suburban	5.47(1.19–15.9)	0.056(0.003–0.47)	
	Remote mountains	2.21(0.36–2.87)	0.021(0.004–0.056)	
Tainan, Taiwan	Pentachlorophenol (PCP) manufacturing plant	1400 ± 1740	0.30	(Lee et al., 2006)

Khashman and Shawabkeh, 2009; Wang et al., 2003). The highest concentrations of Cd, Zn and Pb were detected in downwind soil in this study, in contrast the concentration of Cr was lowest in the same soil sample. Comparison of the source of MSWI, there was poor contribution from atmospheric deposition since the possible sources from natural geological occurrences or agricultural activities (Capuano et al., 2005; Vilavert et al., 2009a).

3.3. Correlation and cluster analysis

The results of correlation analysis of 17 PCDD/Fs and 18 metals within the soil are depicted in Fig. 4. Individual PCDD/Fs components showed positive correlation to a group of metals, suggesting that some metals could be the indicators for PCDD/Fs from the iron and steel plant. Pearson correlations for all species were discussed below.

The pattern of PCDD/Fs and metals, displayed three groups to correlation, dependently on the difference of colors. OCDD, 1,2,3,4,6,7,8-HpCDD and 1,2,3,7,8,9-HxCDD were positively correlated with each other, but showed different patterns from other PCDD/Fs and metals with a Pearson's correlation coefficient close to zero. The correlation of metals was related to the two groups described above. Specifically, the first group (Mg, Al, K, Fe, Cu, Zn, Se, Cd, Sb and Pb), which likely originated from the iron and steel process, was well correlated with all PCDD/Fs except three (OCDD, 1,2,3,4,6,7,8-HpCDD and 1,2,3,7,8,9-HxCDD). The good correlation between those PCDD/Fs and the first group of metals suggests that they originated from the same source. However, another group (Be, Na, V, Mn, Ni and As) showed poor correlation compared with the first group. Interestingly, As behaves somewhat differently than Se and Pb, which have all been found to be good tracers of coal combustion processes (Tian et al., 2015). These findings suggest that As was probably removed or washed out of soil in the form of arsenious oxide. Additionally, fuel combustion, past mining activities, road traffic and agricultural activities might be sources of As (Hamzah et al., 2011). These findings showed that the soil concentration was obviously influenced by its location relative to the sinters as a result of atmospheric deposition.

Cluster analysis provides a phylogenic tree plot to categorize the species and identified analogous groups. Fig. 5 shows the PCDD/Fs and metals diagram of cluster analysis based on the mean species within soil samples. PCDD/Fs and metals were grouped into four clusters or eight groups, which reveals the same conclusion as shown in correlation analysis. In terms of the species between four different clusters, Cluster 1 and 4 all were composed of metals. It implies that the anthropogenic metallic emissions or traffic-related emissions could be the important source of soil. Cluster 2 consisted of 1,2,3,4,6,7,8-HpCDD, 1,2,3,6,7,8 -HxCDD, 1,2,3,7,8,9-HxCDD and OCDD, which were different to another PCDD/Fs. This means that the formation or transform of the four PCDDs were relatively independent (Li et al., 2012). The remaining species were joined together in the Cluster 4, with the largest cluster, Pb, Zn, Cd and all PCDFs combined together, which indicated that they might have had the same origin. Al-Khashman and Shawabkeh (2009) found that the highest concentrations of Pb, Zn, Cd close to the site of the steel plants, which is consistent with the results of this study (Fig. 3). Meanwhile, there are significant correlation between those heavy metals in all sampling points ($p > 0.05$), with Pb vs. Zn and Cd are well correlated ($R^2 = 0.998$). Since heavy metals of Pb, Zn and Cd are indicators of steel manufacturing plants, and there are significant correlations between those three heavy metals and PCDFs in all soil samples, the PCDFs might have originated from metals smelting too. In addition, the results of cluster and correlation analysis confirmed the levels of anthropogenic heavy metals and PCDFs in soil from similar sources around the sintering plant.

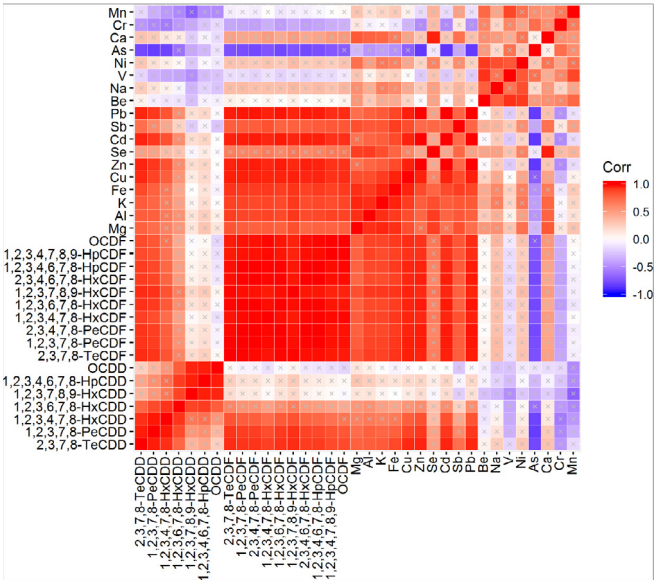


Fig. 4. Pearson correlation of PCDD/Fs and metals (x: $p > 0.05$).

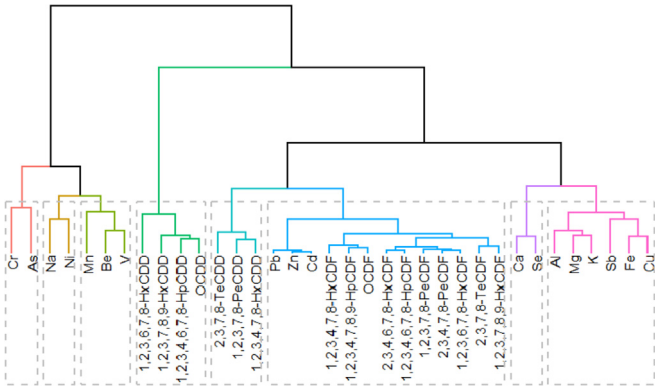


Fig. 5. Phylogenic tree plot of cluster analysis of PCDD/Fs and metals.

4. Conclusions

China is the largest producer of iron and steel in the world, and the iron industry is considered a potential source of PCDD/Fs. In the present study, S4, which was located in the prevailing downwind direction from the studied iron and steel plant, showed a high value of PCDD/Fs. These results show that special attention should be paid to Cd and Zn contamination in soils around iron and steel plants because a high amount of PCDD/Fs may be present. The soil around the iron and steel plant was characteristic of the high contribution of PCDFs and an increasing trend of low chlorinated dibenzo-*p*-dioxins, while a group of metals (Mg, Al, K, Fe, Cu, Zn, Se, Cd, Sb and Pb) was closely correlated with the contaminated surface soil. The indicative metals of the iron and steel plants was Pb, Zn and Cd in the soil samples, and the good correlation and same cluster of these metals and PCDFs were found to be related to sintering process. Hence, it is possible to better characterize the sources of PCDD/Fs by using metallic tracers in soil, which will be helpful in identification of contamination originating from incinerators and other sources. As more information will become available in the future, analyzing more soil samples around the iron

and steel plant in China is necessary to confirm the contribution of dioxins and human health risk assessment, and to ensure better making for actions to reduce dioxins from the steel processing plant.

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References

Al-Khashman, O.A., Shawabkeh, R.A., 2009. Metal distribution in urban soil around steel industry beside Queen Alia Airport, Jordan. Environ. Geochem. Health 31 (6), 717–726.
Capuano, F., Cavalchi, B., Martinelli, G., Pecchini, G., Renna, E., Scaroni, I., Bertacchi, M., Bigliardi, G., 2005. Environmental prospection for PCDD/PCDF, PAH, PCB and heavy metals around the incinerator power plant of Reggio Emilia town (Northern Italy) and surrounding main roads. Chemosphere 58, 1563–1569.
Caserini, S., Monguzzi, A.M., 2002. PCDD/Fs emissions inventory in the Lombardy Region: results and uncertainties. Chemosphere 48, 779–786.
CCME(Canadian Council of Ministers of the Environment), 2002. Canadian Environmental Quality Guidelines.
CEPA, 1995. Environmental quality standards for soil (GB15618-1995). In: Chinese Environmental Protection Adminstration (Beijing).
Chakraborty, P., Selvaraj, S., Nakamura, M., Prithiviraj, B., Cincinelli, A., Bang, J.J., 2017. PCBs and PCDD/Fs in soil from informal e-waste recycling sites and open dumpsites in India: levels, congener profiles and health risk assessment. Sci. Total Environ. 621, 930–938.
Cheng, P.S., Hsu, M.S., Ma, E., Chou, U., Ling, Y.C., 2003. Levels of PCDD/FS in ambient air and soil in the vicinity of a municipal solid waste incinerator in Hsinchu. Chemosphere 52, 1389–1396.
Dong, L., Zhang, H., Fujita, T., Ohnishi, S., Li, H., Fujii, M., Dong, H., 2013. Environmental and economic gains of industrial symbiosis for Chinese iron/steel industry: Kawasaki's experience and practice in Liuzhou and Jinan. J. Clean. Prod. 59, 226–238.
Duarte-Davidson, R., Sewart, A., Alcock, R.E., Cousins, I.T., Jones, K.C., 1997. Exploring the balance between sources, deposition, and the environmental burden of PCDD/Fs in the U.K. terrestrial environment : an aid to identifying uncertainties and research needs. Environ. Sci. Technol. 31, 1–11.
Fang, M., Choi, S.D., Baek, S.Y., Park, H., Chang, Y.S., 2011. Atmospheric bulk deposition of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) in the vicinity of an iron and steel making plant. Chemosphere 84, 894–899.
Fu, B.Q., Huang, J.Y., Zhang, L., Wang, L.N., Liu, P., 2012. Research on wastes emission standard and development trend in iron and steel industry in China. Wisco Technol. 50 (6), 56–61.
Galili, T., 2015. dendextend: an R package for visualizing, adjusting, and comparing trees of hierarchical clustering. Bioinformatics 31 (22), 3718–3720.
Hamzah, Z., Saat, A., Wood, A.K., Bakar, Z.A., 2011. Sedimentation, heavy metals profiles and cluster Analysis of a former Tin mining lake. Int. J. Environ. Sustain Dev. 2 (6), 448–453.
Huang, T., Tian, C., Zhang, K., Gao, H., Li, Y.F., Ma, J., 2015. Gridded atmospheric emission inventory of 2,3,7,8-TCDD in China. Atmos. Environ. 108, 41–48.
Irawan, D.E., Putranto, T.T., 2016. Hydrochemical Assessment of Semarang Area Using Multivariate Statistics: a Sample Based Dataset, pp. 1–11.
Jin, Y.Q., Liu, H.M., Li, X.D., Ma, X.J., Lu, S.Y., Chen, T., Yan, J.H., 2012. Health risk assessment of PCDD/F emissions from municipal solid waste incinerators (MSWIs) in China. Environ. Technol. 33, 2539–2545.
Kao, W.Y., Ma, H.W., Chang-Chien, G.P., 2011. Evaluation of incremental population and individual carcinogenic risks of PCDD/Fs from steel and iron industry in Taiwan by a site-specific health risk assessment method. Aerosol Air Qual. Res. 11, 716–731.
Kassambara, A., Mundt, F., 2017. Factoextra: Extract and Visualize the Results of Multivariate Data Analyses. R package version 1.0.5.
Lee, C.-C., Guo, Y.L., Kuei, C.-H., Chang, H.-Y., Hsu, J.-F., Wang, S.-T., Liao, P.-C., 2006. Human PCDD/PCDF levels near a pentachlorophenol contamination site in Tainan, Taiwan. Chemosphere 65, 436–448.
Le, S., Josse, J., Husson, F., 2008. FactoMineR: an R package for multivariate analysis. J. Stat. Software 25 (1), 1–18.
Leung, A.O.W., Luksemburg, W.J., Wong, A.S., Wong, M.H., 2007. Spatial distribution of polybrominated diphenyl ethers and polychlorinated dibenzo-p-dioxins and dibenzofurans in soil and combusted residue at Guiyu, an electronic waste recycling site in southeast China. Environ. Sci. Technol. 41, 2730–2737.
Li, X.D., Yan, M., Yang, J., Chen, T., Lu, S.Y., Yan, J.H., 2012. PCDD/Fs in soil around a hospital waste incinerator: comparison after three years of operation. J. Environ. Sci. 24, 699–703.
Lv, P., Zheng, M., Liu, G., Liu, W., Xiao, K., 2011. Estimation and characterization of PCDD/Fs and dioxin-like PCBs from Chinese iron foundries. Chemosphere 82, 759–763.
Maechle, R.M., Rousseeuw, P., Struyf, A., Hubert, M., Hornik, K., Studer, M., Roudier, P., Gonzalez, J., 2012. Cluster: Cluster Analysis Basics and Extensions. R package version 2.0.1.
MEP, 2008. National Environmental Protection Standard of the People's Republic of China. HJ 77.4-2008. Soil and Sediment Determination of Polychlorinated Dibenzo-p-Dioxin (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) Isotope Dilution HRGC-HRMS.
NATO/CCMS, 1988. Scientific Basis Fot the Development of the International Toxicity Equivalency Fatcor (I-TEQ) Method of Risk Assessment for Complex Mixtures of Dioxins and Related Compounds. Report No. 178.
Nganai, S., Dellinger, B., Lomnicki, S., 2014. PCDD/PCDF ratio in the precursor formation model over CuO surface. Environ. Sci. Technol. 48, 13864–13870.
Ooi, T.C., Lu, L., 2011. Formation and mitigation of PCDD/Fs in iron ore sintering. Chemosphere 85, 291–299.
Pan, Y.P., Tian, S.L., Li, X.R., Sun, Y., Li, Y., Wentworth, G.R., Wang, Y.S., 2015. Trace elements in particulate matter from metropolitan regions of Northern China: sources, concentrations and size distributions. Sci. Total Environ. 537, 9–22.
Quass, U., Fermann, M., Bröker, G., 2000. The European Dioxin Emission Inventory Stage II, vol. 1.
Rotatori, M., Guerriero, E., Bianchini, M., Gigliucci, P., Guarnieri, A., Lutri, A., Mosca, S., Rossetti, G., Vardè, M., 2006. PCDD/F profiles of an iron ore sintering plant. Organohalogen Compd. 68, 2248–2251.
Rovira, J., Flores, J., Schuhmacher, M., Nadal, M., Domingo, J.L., 2015. Long-term environmental surveillance and health risks of metals and PCDD/Fs around a cement plant in Catalonia, Spain. Hum. Ecol. Risk Assess. 21, 514–532.
Saral, A., Gunes, G., Demir, S., 2014. Atmospheric PCDD/PCDF emission inventory for Turkey. Atmos. Pollut. Res. 5, 24–33.
Schuhmacher, M., Nadal, M., Domingo, J.L., 2009. Environmental monitoring of PCDD/Fs and metals in the vicinity of a cement plant after using sewage sludge as a secondary fuel. Chemosphere 74, 1502–1508.
Sun, B.F., Bo, X., Zhang, S.X., Diao, X.J., Kan, H., Cheng, J., Liu, M., Wu, P.C., T. Z, Hu, X.B., 2017. Effect of exhaust gas from sintering machines on the concentration of dioxin in soil around a steel plant. China Envrion. Sci. 37, 4222–4229.
Tian, H.Z., Zhu, C.Y., Gao, J.J., Cheng, K., Hao, J.M., Wang, K., Hua, S.B., Wang, Y., Zhou, J.R., 2015. Quantitative assessment of atmospheric emissions of toxic heavy metals from anthropogenic sources in China: historical trend, spatial variation distribution, uncertainties and control policies. Atmos. Chem. Phys. 15, 12107–12166.
UNEP, 2005. Standardized Toolkit for Identification and Quantification of Dioxin and Furan Release, second ed. UNEP Chemicals, Geneva.
Vilavert, L., Nadal, M., Mari, M., Schuhmacher, M., Domingo, J.L., 2009a. Modification of an environmental surveillance program to monitor PCDD/Fs and metals around a municipal solid waste incinerator. J. Environ. Sci. Health Part A 44, 1343–1352.
Vilavert, L., Nadal, M., Mari, M., Schuhmacher, M., Domingo, J.L., 2009b. Modification of an environmental surveillance program to monitor PCDD/Fs and metals around a municipal solid waste incinerator. Environ. Lett. 44, 1343–1352.
Wang, K., Tian, H., Hua, S., Zhu, C., Gao, J., Xue, Y., Hao, J., Wang, Y., Zhou, J., 2016. A comprehensive emission inventory of multiple air pollutants from iron and steel industry in China: temporal trends and spatial variation characteristics. Sci. Total Environ. 559, 7–14.
Wang, Q.-R., Cui, Y.-S., Liu, X.-M., Dong, Y.-T., Christie, P., 2003. Soil contamination and plant uptake of heavy metals at polluted sites in China. Environ. Lett. 38, 823.
Xu, P., Tao, B., Li, N., Qi, L., Ren, Y., Zhou, Z., Zhang, L., 2013. Levels, profiles and source identification of PCDD/Fs in farmland soils of Guiyu, China. Chemosphere 91, 824–831.
Zhang, F.M., Meng, X.L., Cao, C.Z., Li, L., 2014. Construction of circulating economy development model for new generation iron and steel plant. Adv. Mater. Res. 875–877, 1133–1137.
Zhang, S.K., Peng, P.A., Huang, W.L., Li, X.M., Zhang, G., 2009. PCDD/PCDF pollution in soils and sediments from the Pearl River Delta of China. Chemosphere 75, 1186–1195.