Research paper

Unintentional production of persistent chlorinated and brominated organic pollutants during iron ore sintering processes

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H I G H L I G H T S

- PBDD/F emission factors were derived for six iron ore sintering plants in China.
- These emission factors are important for compiling the global emission inventory.
- Significant correlations among POPs suggest the possibility of synergetic reduction.
- PCDD/Fs were dominant contributors to total toxic equivalents of multiple POPs.

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A B S T R A C T

Iron ore sintering (SNT) processes are major sources of unintentionally produced chlorinated persistent organic pollutants (POPs), including polychlorinated dibenzo-*p*-dioxins/dibenzofurans (PCDD/Fs), polychlorinated biphenyls (PCBs), and polychlorinated naphthalenes (PCNs). However, few studies of emissions of brominated POPs, such as polybrominated dibenzo-*p*-dioxins/dibenzofurans (PBDD/Fs) and polybrominated diphenyl ethers (PBDEs), during SNT have been performed. Stack gas and fly ash samples from six typical SNT plants in China were collected and analyzed to determine the concentrations and profiles of PCDD/Fs, PCBs, PCNs, PBDD/Fs, and PBDEs, as well as any correlations among these compounds. The PCDD/F, PCB, PCN, PBDD/F, and PBDE emission factors were 2.47, 0.61, 552, 0.32, and 107 $\mu\text{g t}^{-1}$, respectively (109, 4.07, 10.4, 4.41 and 0.02 ng toxic equivalents t^{-1} , respectively). PCBs were the most abundant compounds by mass, while PCNs were the next most abundant, contributing 51% and 42% to the total POP concentration, respectively. However, PCDD/Fs were the dominant contributors to the chlorinated and brominated POP toxic equivalent concentrations, contributing 89% to the total toxic equivalent concentration. The PCDD/F and other chlorinated and brominated POP concentrations were positively correlated, indicating that chlorinated and brominated POP emissions could be synergistically decreased using the best available technologies/best environmental practices already developed for PCDD/Fs.

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1. Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs), polychlorinated biphenyls (PCBs), polychlorinated naphthalenes (PCNs) and polybrominated diphenyl ethers (PBDEs) are persistent organic pollutants (POPs) covered under the Stockholm Convention on POPs. Polybrominated dibenzo-*p*-dioxins and dibenzofurans (PBDD/Fs) are the brominated analogs of PCDD/Fs

and display similar structures and toxicity [1]. Recent studies have found that new POPs, such as PCNs and PBDD/Fs, make appreciable contributions to the total 2,3,7,8-tetrachlorodibenzo-*p*-dioxin toxic equivalent (TEQ) concentrations in environmental matrices and human tissues, relative to the contributions made by PCDD/Fs [2–4]. However, the sources and emission profiles of these new POPs are not well understood. Intensive studies of PCDD/F formation and emissions from a number of industrial sources have been performed. Other unintentionally produced POPs are formed and emitted along with PCDD/Fs during combustion and metallurgical processes [5–11]. It is therefore important to consider these

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Table 1
Information on the iron ore sintering plants (listed as codes) sampled in this study.

	XH	HX	XJ	RC	TG	SG
Scales of sintering machine (m ²)	36	90	200	200	360	500
Air pollution control devices (APCD)	^a CC	^b EP	^b EP	^b EP	^b EP	^c GD and ^b EP
O ₂ (%)	17.3	17.5	14	17.6	19.1	17.9
Average flow rate of stack gas (Nm ³ h ⁻¹)	212368	391590	325234	327199	589385	1058736

^a CC, ceramic cyclone system.

^b EP, electrostatic precipitator.

^c GD, gas desulfurization system.

POPs together, when performing studies related to controlling POP emissions from industrial sources.

Iron ore sintering (SNT) processes have been found to be major sources of PCDD/Fs in China. According to the Chinese national implementation plan for the Stockholm Convention, SNT processes release about 30% of the total PCDD/F emissions to the atmosphere in stack gases [12]. Other chlorinated POPs, such as PCBs [13], PCNs [14], and other chemicals [15], can be released in stack gases and fly ash produced during SNT processes. Compared with the concentrations and profiles of chlorinated POPs, the concentrations and profiles of brominated POPs released during SNT processes have scarcely been studied. Du et al. [5] determined the concentrations and profiles of PBDD/Fs at one sintering plant, but did not include the more brominated congeners (hepta- and octa-brominated PBDD/Fs). Wang et al. [10] studied PBDE and PBDD/F emissions during metallurgical processes and found high PBDE and PBDD/F concentrations (geometric mean concentrations of 35.2 and 0.399 ng Nm⁻³, respectively) in stack gases produced during SNT processes. Drage et al. [16] found that the mean PBDD/F concentration based on 2005 World Health Organization (WHO) toxic equivalent factors was 0.14 ng WHO-TEQ/m³ (range: 0.03–0.39 ng WHO-TEQ/m³), which was approximately 10 times lower than their PCDD/F homologs. They also found that PBDD/F formation mechanisms via de novo synthesis were similar to that of PCDD/Fs [16]. Wang et al. [17] documented the emissions of PBDEs and PBDD/Fs from ferrous foundries. However, the relationships between the concentrations and profiles of different chlorinated and brominated POPs produced during SNT processes have not yet been identified.

A very large amount of SNT is performed in China. Case studies of typical Chinese sintering plants could help develop methods to control emissions of multiple POPs and to decrease the potential risks posed by these chemicals to environmental and human health. The aim of this study was to determine the concentrations, profiles, and relationships of PCDD/Fs, PCBs, PCNs, PBDD/Fs, and PBDEs produced during SNT processes. The results of correlation analyses for different POPs may improve our understanding of how emissions of new POPs can be controlled, along with PCDD/F emissions, using best available technologies and best environmental practices (BATs/BEPs) for PCDD/Fs.

2. Materials and methods

2.1. Iron ore sintering plants and sample collection

Six typical sintering plants of different scales and with different air pollution control devices (APCDs) were selected within China. The concentrations and profiles of chlorinated and brominated POPs produced by these plants, as well as any correlations between these compounds were determined. The sintering machine sizes were between 36 and 500 m². The plants used three different types of APCDs. A ceramic-cyclone system was used at plant XH, electrostatic precipitators were used at plants HX, RC, TG, and XJ, and a gas desulfurization system with electrostatic precipitators was used at plant SG. Detailed information on these plants is given in Table 1.

Stack gas samples and fly ash samples were collected from the ventilation systems of the six SNT plants. Three stack gas samples and two fly ash samples were collected from each plant. The stack gas sampling point at each plant was downstream of the APCD. Each stack gas sample was collected using an automatic isokinetic sampling system (Isostack Basic; TCR TECORA, Milan, Italy), as described previously [18–20]. The three stack gas samples collected at each plant were used to determine the chlorinated and brominated POP emissions from the plant. The fly ash samples comprised the mixture of fly ash captured by the air pollution control devices (APCDs) during a 12-hr period of iron ore sintering. Samples were collected from outlets at the bottom of APCDs for gathering and storing fly ash, using a stainless-steel spoon. The fly ash samples were packed in aluminum foil and stored in PE (polyethylene) valve-sealed bags. These were transferred to the dioxin lab for POP analysis.

2.2. Sample analyses

The analytes were identified and quantified using isotope-dilution high-resolution gas chromatography (HGRC) and high-resolution mass spectrometry (HRMS) methods, which have been previously described in detail [18–22]. Each stack gas sample was spiked with ¹³C-labeled internal standards EDF-5408, EPA-1668 LCS, and ECN-5102 (Cambridge Isotope Laboratories, Andover, MA, USA), as well as EN-1948 ES and MBDE-MXFR (Wellington Laboratories, Guelph, Canada). Each stack gas sample underwent Soxhlet extraction for 20–24 h. Each extract was evaporated to a small volume (2–3 mL) using a rotary evaporator. A multilayer silica gel column was used to cleanup these extracts. After cleanup, the PCDD/Fs, PBDD/Fs PCBs, PCNs and PBDEs were separated by passing the extracts through an activated carbon column. The activated carbon column was eluted with 80 mL of dichloromethane/hexane (5/95, v/v) to elute PCBs, PCNs and PBDEs, followed by 250 mL of toluene to elute the PCDD/Fs and PBDD/Fs. Each fraction was evaporated to about 20 μ L using a rotary evaporator, and then evaporated under a gentle stream of N₂. As a final step, ¹³C-labeled injection solutions (EDF-5409, EPA-1668 IS, and ECN-5260 and EN-1948 IS and MBDE-MXFS) were added to determine the recoveries of internal standards. Each fly ash sample was spiked with ¹³C-labeled internal standards, digested in 1.0 mol L⁻¹ HCl, and then extracted and cleaned up using the protocol for stack gas samples.

The extracts were analyzed for PCDD/Fs, PCBs, PCNs, PBDD/Fs, and PBDEs (14 congeners, including BDE-17, BDE-28, BDE-47, BDE-66, BDE-71, BDE-85, BDE-99, BDE-100, BDE-138, BDE-153, BDE-154, BDE-1983, BDE-190, BDE-209) using a gas chromatograph coupled to a DFS mass spectrometer (Thermo Fisher Scientific, Waltham, MA, USA). The PCDD/F, PCB, and PCN congeners were separated using a DB-5MS fused silica column (60 m long, 0.25 mm i.d., 0.25 μ m film thickness; Agilent Technologies, Santa Clara, CA, USA). The PBDD/F and PBDE congeners were separated using a different DB-5MS fused silica column (15 m long, 0.25 mm i.d., 0.10 μ m film thickness; Agilent Technologies). Splitless/surge injection was used, while maintaining an injector temperature of 300 °C. The glass transfer line temperature was 280 °C. The mass

Table 2

Concentrations of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), dioxin-like polychlorinated biphenyls (dl-PCBs), polychlorinated naphthalenes (PCNs), polybrominated dibenzo-*p*-dioxins and dibenzofurans (PBDD/Fs), and polybrominated diphenyl ethers (PBDEs) in stack gases produced by the different iron ore sintering plants listed here as codes (n = 3 for each plant; TEQ = toxic equivalent concentration; WHO-TEQ = toxic equivalency, based on World Health Organization's toxic equivalent factors (2005)).

Compounds	XH	HX	XJ	RC	TG	SG
PCDD/Fs (ng Nm ⁻³)	1.84 ± 1.00	0.22 ± 0.07	2.98 ± 0.82	2.49 ± 0.89	1.19 ± 0.85	2.53 ± 1.46
dl-PCBs (ng Nm ⁻³)	0.46 ± 0.37	0.11 ± 0.08	0.42 ± 0.18	0.74 ± 0.46	0.15 ± 0.02	1.18 ± 0.38
PCNs (ng Nm ⁻³)	213 ± 34.6	526 ± 199	677 ± 112	383 ± 144	126 ± 25.7	528 ± 188
PBDD/Fs (ng Nm ⁻³)	0.14 ± 0.04	0.13 ± 0.004	0.37 ± 0.01	0.22 ± 0.05	0.14 ± 0.02	0.04 ± 0.01
PBDEs (ng Nm ⁻³)	23.4 ± 3.07	57.7 ± 13.3	115 ± 24.0	57.5 ± 19.7	78.5 ± 15.7	27.8 ± 21.6
PCDD/Fs _{WHO-TEQ} (pg WHO-TEQ Nm ⁻³)	150 ± 104	6.96 ± 4.08	174 ± 85.8	32.1 ± 9.18	32 ± 11.6	239 ± 146
dl-PCBs _{WHO-TEQ} (pg WHO-TEQ Nm ⁻³)	6.04 ± 4.32	0.19 ± 0.14	10.2 ± 7.39	1.21 ± 0.89	1.21 ± 0.17	11.2 ± 3.73
PCNs _{TEQ} (pg TEQ Nm ⁻³)	3.19 ± 0.81	6.92 ± 3.16	12.6 ± 2.30	6.24 ± 1.46	1.84 ± 0.41	6.71 ± 2.78
PBDD/Fs _{TEQ} (pg WHO-TEQ Nm ⁻³)	2.22 ± 0.61	1.60 ± 0.32	7.97 ± 0.78	2.44 ± 1.95	2.44 ± 0.55	0.82 ± 0.32
PBDEs _{TEQ} (pg TEQ Nm ⁻³)	0.025 ± 0.02	0.026 ± 0.003	0.006 ± 0.002	0.02 ± 0.02	0.005 ± 0.002	0.006 ± 0.002

spectrometer was tuned and operated at a resolution of around 10,000. Electron impact ionization mode was used, with an electron energy of 45 eV. The mass spectrometer was operated in selected ion monitoring mode. The instrumental analysis method is described in detail in previous publications [18–22].

2.3. Quality control and assurance

The recoveries of the ¹³C-labeled PCDD/F internal standards were 45%–118%, while the recoveries of the PCB and PCN internal standards were 42%–103% and 39%–109%, respectively. The recoveries of the ¹³C-labeled tetra- to hepta-brominated PBDD/F standards were 35%–102% for stack gas samples, and 30%–84% for fly ash samples. The recoveries of the ¹³C-labeled octa-brominated standards (OBDD/F) were 25%–64% for stack gas samples and 10%–20% for fly ash samples. The recoveries of ¹³C-labeled PBDE standards were 65%–116%.

In spite of the low recovery values obtained in this study, we consider the recoveries of ¹³C-labeled OBDD/Fs to be acceptable, supported by the following reasons. First, addition of ¹³C-labeled congeners to the samples before pretreatment allowed them to be used to calibrate the loss of corresponding native congeners during the extraction and cleanup procedure. This ensured accurate results, despite multiple extraction, cleanup, and concentration steps prior to instrumental detection. Second, there is no standard method for PBDD/F analysis. Recoveries of the ¹³C₁₂-labeled octa-chlorinated homolog (¹³C₁₂-OCDD) are required to be within 17%–157%, according to the US Environmental Protection Agency (US EPA) method 1613 B for PCDD/F analysis. Using equivalent guidelines, the recoveries of ¹³C₁₂-OBDD/F in this study are acceptable for trace analysis of PBDD/Fs, using the isotopic dilution HRGC/HRMS method. The recoveries of ¹³C-labeled PCDD/F and ¹³C-labeled PCB internal standards met the requirements for trace analyses of POPs, using isotope-dilution HRGC/HRMS methods, defined in standards US EPA 1613 B (17%–185%) and US EPA 1668A (14%–127%). Three quality control criteria were used for identifying the peaks of target compounds: (1) matching GC retention times to the corresponding ¹³C₁₂-labeled standard compounds; (2) isotopic ratios between quantified and identified ions having values within ± 15% of their theoretical values; and (3) a signal-to-noise ratio of greater than 3:1. In addition, one blank sample was included in each batch of samples analyzed. No obvious contamination was found in the blank samples.

3. Results and discussion

3.1. Chlorinated and brominated persistent organic pollutant concentrations in the stack gases and fly ash produced during sintering

The chlorinated and brominated POP concentrations in the stack gas samples from the six SNT plants are shown in Table 2.

Their 2005 WHO toxic equivalence factors were used to calculate PCDD/F and PCB TEQs. The PCN TEQ was defined as the sum of the products of each PCN congener concentration analyzed, and its relative potency factor (RPF) relative to 2,3,7,8-tetrachlorodibenzo-*p*-dioxin [23–25]. The PBDD/F TEQs were calculated using interim toxic equivalence factors, similar to the toxic equivalence factors for their chlorinated analogs, as suggested by the WHO scheme [26]. The PBDE TEQs were estimated using the relative potencies shown in Table S1 [27].

The mass and TEQ concentrations of the 2,3,7,8-chlorinated PCDD/Fs in the stack gas samples were 0.14–5.18 ng Nm⁻³ and 3.65–408 pg TEQ Nm⁻³, respectively. These concentrations were lower than in stack gases produced in other SNT plants [13,28]. Likewise, dioxin-like (dl) PCB concentrations were 0.07–18.8 pg TEQ Nm⁻³ (0.04–1.70 ng Nm⁻³), which were lower than those reported by Tian et al. (0.23–0.37 ng WHO-TEQ Nm⁻³) for China [15], Aries et al. (0.042–0.111 ng WHO-TEQ Nm⁻³) for the UK [13] and Esposito et al. (0.004–0.52 ng WHO-TEQ Nm⁻³) for Italy [29].

The contributions of PCNs and PBDD/Fs (new POPs) to the total TEQ concentrations in environmental matrices and human tissues have increased in recent years [2–4]. However, little information on PCN and PBDD/F emissions from industrial plants is available. The PCN mass and TEQ concentrations in our stack gas samples were 58–885 ng Nm⁻³ and 1.80–14.9 pg TEQ Nm⁻³, respectively. The PBDD/F concentrations in the stack gas samples were 0.59–8.52 pg TEQ Nm⁻³ (0.034–0.52 ng Nm⁻³). These values were slightly lower than PBDD/F concentrations of 0.00252–0.0263 ng TEQ Nm⁻³ (0.125–3.01 ng Nm⁻³) measured in stack gases produced by SNT plants in a study by Wang et al. [10]. However, they were comparable to concentrations in stack gases produced by municipal solid waste incinerators of 0.997–6.04 pg TEQ Nm⁻³ (31.1–138.8 pg Nm⁻³) [30] and by electric arc furnaces of 0.00252–0.0263 ng TEQ Nm⁻³ (0.0198–2.78 ng Nm⁻³) [10]. A number of studies of PBDE concentrations and profiles in various environmental matrices have been carried out, although few studies have dealt with the sources and emission profiles of unintentionally produced PBDEs [10]. The PBDE concentrations in the stack gas samples in this study were 0.004–0.045 pg TEQ Nm⁻³ (13.8–138 ng Nm⁻³), which were comparable to concentrations for 30 congeners of 12.8–62.3 ng Nm⁻³ in the stack gas of SNT processes in previous studies [10]. This indicates that unintentional emissions are important current sources of PBDEs, in addition to the historical manufacture and use of PBDEs [31].

The PCDD/F, dl-PCB, PCN, and PBDE concentrations in the fly ash samples from heads and tails of the SNT machines sampled in this study, as well as values from the literature are shown in Table S2. The PCDD/F TEQ concentrations in the fly ash sampled at the heads and tails of the sintering machines were 2.00–63.1 and 0.25–1.41 ng g⁻¹, which were slightly higher than values of 0.17–0.88 ng g⁻¹ reported by Wang et al. [32]. The dl-PCB concen-

trations in the fly ash sampled from the heads and tails of the sintering machines were 1.20–5.49 and 0.10–5.12 ng g⁻¹, which were comparable to values of 0.49–1.47 ng g⁻¹ reported by Wang et al. [33]. The PBDE concentrations in the fly ash sampled from the heads and tails of the sintering machines were 2.61–9.60 and 1.32–5.98 ng g⁻¹, respectively. The PCN concentrations in the fly ash sampled from the heads and tails of the sintering machines were 7.76–28.4 and 10.3–51.5 ng g⁻¹, which were comparable to values of 4.95–64.2 ng g⁻¹ reported by Wang et al. [11]. For comparison, the PCDD/F, dl-PCB, and PBDE concentrations in the fly ash captured by the APCDs are shown in Fig. S1. At all plants, the concentrations of these POPs in the fly ash samples from the heads of the sintering machines were much higher than their concentrations in the fly ash samples from the tails of the sintering machines. This indicates that mitigation of the formation and emission of PCDD/Fs, dl-PCBs, and PBDEs should be focused on the heads of sintering machines.

3.2. Chlorinated and brominated persistent organic pollutant contributions to the total mass concentrations and toxic equivalency in stack gases and fly ash produced during sintering

The contributions of the different groups of POPs to the total TEQ concentrations were calculated and compared to determine the relative importance of their emissions during SNT. The contributions of the different POPs to the total mass concentrations and TEQ concentration are shown in Fig. 1. The PCBs had the highest mass concentrations in the stack gas samples, contributing about 51% to the total mass concentrations. The next most abundant groups were PCNs and PBDEs, which contributed 42% and 7% to the total mass concentrations, respectively. The PCDD/Fs and PBDD/Fs made very small contributions of 0.17% and 0.02% to the total mass concentrations. However, because PCDD/Fs have higher toxic equivalence factors than other compounds, they contributed about 89% to the total TEQ concentrations. Meanwhile, PCNs and PCBs contributed 5% and 4% to the total TEQ concentrations. Thus, PCDD/Fs (traditional POPs) are still the dominant contributors to the total chlorinated and brominated POP TEQ concentrations in stack gases emitted during SNT processes.

3.3. Congener profiles of the chlorinated and brominated persistent organic pollutants produced during the sintering processes

The congener profiles for PCDD/Fs, dl-PCBs, dl-PCNs, PBDD/Fs, and PBDEs in stack gases can be used to identify the specific sources of chlorinated and brominated POPs in environmental matrices. The chlorinated and brominated POP congener profiles for the stack gas samples from the SNT plants are presented in Fig. 2. The results presented in this study were from experiments on an industrial scale. However, it is very difficult to correlate various operating techniques and parameters with POP emission levels at industrial scale, given the complexity of industrial operations and the limited number of investigated plants in this study. Here, higher chlorinated/brominated congeners, such as OCDD/Fs, 1,2,3,4,6,7,8-HpCDD, OBDF, 1,2,3,4,6,7,8-HpBDD/Fs, and BDE-209, were the most abundant PCDD/F, PBDD/F, and PBDE congeners. However, less chlorinated aromatics, such as CB-118, CB-77, CB-105, CN-1, and CN-2, were the most abundant dl-PCB and PCN congeners. Similar characteristics have been observed in stack gas from iron ore sintering plants in the UK and China in profiles of PCDD/Fs [13,15], PCBs [13,15], PCNs [14], PBDD/Fs and PBDEs [10]. However, the underlying reasons for these common characteristics are yet to be clarified.

Here, we propose explanations for the various POP profiles observed in this study. In the case of PCNs, we speculate that

Fig. 1. Contributions of the polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), polybrominated dibenzo-*p*-dioxins and dibenzofurans (PBDD/Fs), dioxin-like polychlorinated biphenyls (dl-PCBs), polychlorinated naphthalenes (PCNs), and polybrominated diphenyl ethers (PBDEs) to the mean (a) mass concentrations and (b) toxic equivalent concentrations in the stack gases produced during iron ore sintering processes.

chlorination of naphthalene is important during industrial thermal processes. Therefore, less chlorinated naphthalenes, such as CN-1 and CN-2, are easily formed by direct chlorination of naphthalene. It is likely that further chlorination reactions are more difficult to activate, making less chlorinated congeners dominant. A similar formation pathway may also explain our observations for PCBs. However, we surmise that the formation mechanism for PCDD/Fs is more complex than for PCBs and PCNs. Possibly, *de novo* synthesis is important for PCDD/F formation during metallurgical processes. In this way, higher chlorinated congeners could be formed, making them the dominant congeners of PCDD/Fs. A similar synthesis pathway may also explain our observations for PBDD/Fs.

The PBDD/F to PCDD/F mass concentration ratio (B/C ratio) has been used to trace industrial sources [5]. We calculated the B/C ratios for stack gas samples and compared them with the B/C ratios for various thermal industrial processes, including electric arc furnaces, SNT plants, municipal solid waste incinerators, and converter steelmaking processes, as is shown in Fig. S2 [10,30,34,35]. We surmise that B/C ratios vary with different sources. For example, concentrations of PCDD/Fs and PBDD/Fs in Guangzhou and Shanghai [36,37] yield B/C ratios in the range of 0.02–0.2. However, it is impossible to obtain a B/C ratio of 0.2 derived only from municipal solid waste incinerations and electric arc furnaces (their B/C ratios were both below 0.1). We speculate that converter steel making

Fig. 2. Congener profiles of (a) polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) and dioxin-like polychlorinated biphenyls (dl-PCBs), (b) polychlorinated naphthalenes (PCNs), (c) polybrominated dibenzo-*p*-dioxins and dibenzofurans (PBDD/Fs), and (d) polybrominated diphenyl ethers (PBDEs) produced during the iron ore sintering processes at six different plants (the codes for the different sintering plants are shown in the legend).

(with higher B/C ratios) may be an important source of PBDD/Fs in these cities. Conversely, low B/C ratios for environmental matrices likely reflect sources with higher chlorine concentrations in their raw materials. In this case, electric arc furnaces and waste incinerators may be sources of their PCDD/Fs.

Currently, data for PBDD/Fs (tera- to octa-PBDD/Fs) and PCDD/Fs are lacking for environmental matrices, and an inventory of B/C ratios for more varied sources is needed. This makes it challenging to carry out source apportionment using this approach at present. The B/C ratio reported in this study is an important contribution towards this goal.

3.4. Chlorinated and brominated persistent organic pollutant emission factors during sintering processes

It is important to derive emission factors from case studies to determine the total emissions of multiple POPs from the SNT industry at the national or even global scale. Such calculations are important because of China's important contribution to global iron production. However, an accurate emission inventory requires emission factors to be derived from many more SNT plants than have currently been inventoried [38]. PCDD/F and PCB emission factors for SNT processes have been derived in some previous studies [39–42], while PCN and brominated POP emission factors have not been sufficiently studied. Here, we derive emission factors for these POPs and calculate their amounts emitted from SNT plants, following methods described previously [14,15,34].

In our study, the emission factors for PCDD/Fs, dl-PCBs, PCNs, PBDD/Fs, and PBDEs were 2.97–679 ng TEQ t⁻¹ (0.16–27.8 μg t⁻¹), 0.06–25.7 ng TEQ t⁻¹ (0.03–3.97 μg t⁻¹), 2.27–48.9 ng TEQ t⁻¹ (117–2910 μg t⁻¹), 0.98–30.9 ng TEQ t⁻¹ (0.06–3.42 μg t⁻¹), and 0.01–0.26 ng TEQ t⁻¹ (23.0–485 μg t⁻¹), respectively, as shown in Table S3. Using the geometric mean of a relatively large dataset can decrease the uncertainty involved in estimating amounts emitted based on emission factors [38]. Here, we used the geometric means of our data, combined with data from previous publica-

tions to determine emission factors to estimate the amounts of the different POPs emitted by the SNT industry [38]. The geometric means for PCDD/F, dl-PCB, PCN, PBDD/F, and PBDE emission factors were 109 ng WHO-TEQ t⁻¹ (2.47 μg t⁻¹), 4.07 ng WHO-TEQ t⁻¹ (0.61 μg t⁻¹), 10.4 ng TEQ t⁻¹ (552 μg t⁻¹), 4.41 ng TEQ t⁻¹ (0.32 μg t⁻¹), and 0.02 ng TEQ t⁻¹ (107 μg t⁻¹), respectively. The PCDD/F emission factor was similar to emission factors reported by Cieplik et al. and Wang et al. [43,44], but was lower than the value of 2.97–3.68 μg WHO-TEQ t⁻¹ from a previous study in China [15], and the value of 2.05–2.35 μg WHO-TEQ t⁻¹ reported for the UK [13]. The dl-PCB emission factor was higher than the emission factors reported by Aries et al. (0.12–0.15 μg WHO-TEQ t⁻¹) [13] and Tian et al. [15]. The PCN emission factor was comparable to the emission factor (0.5–41.5 ng TEQ t⁻¹, 14–1749 μg t⁻¹) determined by Liu et al. [14]. The PBDD/F and PBDE emission factors were comparable to values for PBDD/Fs (0.00235–0.0713 μg WHO-TEQ t⁻¹, 0.222–8.15 μg t⁻¹) and PBDE (32.1–169 μg t⁻¹) reported by Wang et al. [10].

We used the annual sintered ore output of China [45,46] to estimate the amounts of chlorinated and brominated POPs released during SNT processes each year; these results are shown in Table S3. The amounts of PCDD/Fs, dl-PCBs, PCNs, PBDD/Fs, and PBDEs released during SNT processes in 2014, based on these calculations, were 113 g TEQ y⁻¹ (2.57 kg y⁻¹), 4.23 g TEQ y⁻¹ (0.63 kg y⁻¹), 10.8 g TEQ y⁻¹ (574 kg y⁻¹), 10.8 g TEQ y⁻¹ (0.33 kg y⁻¹), and 0.02 g TEQ y⁻¹ (111 kg y⁻¹), respectively. These data are important contributions to the emission inventory for multiple POPs for the Chinese SNT industry.

3.5. Correlations between chlorinated and brominated persistent organic pollutant concentrations

It has been found in previous studies that other chlorinated POPs are formed and released along with PCDD/Fs during industrial thermal processes [47]. Significant correlations among different compounds may indicate that conditions favoring their forma-

A principal component analysis (PCA) of the homologs of different chlorinated and brominated aromatics was carried out in this study. Our PCA results are shown in Fig. 3. Most of the PCB and PCN homologs were correlated, as were PCDD/F and PBDD/F homologs. This indicates that PCBs and PCNs, as well as PCDD/Fs and PBDD/Fs, may have similar formation pathways during sintering processes. For example, correlations were observed between tetrachlorinated biphenyls (TeCB) and tetrachlorinated naphthalenes (TeCN), as well as hexachlorinated biphenyls (HxCB) and hexachlorinated naphthalenes (HxCN). Correlations also were found among heptabrominated diphenyl ethers (HpBDE), tetrabrominated dibenzofurans (TeBDF), pentabrominated dibenzofurans (PeBDF), hexabrominated dibenzofurans (HxBDF) and heptabrominated dibenzofurans (HpBDF). Fig. S3 displays the linear correlations of these homologs. The linear correlation coefficient (R^2) for concentrations of TeCB and TeCN was 0.55. Meanwhile, HpBDE correlated well with TeBDF ($R^2 = 0.47$), PeBDF ($R^2 = 0.57$), HxBDF ($R^2 = 0.56$), and HpBDF ($R^2 = 0.65$). Fig. 4 shows that correlations also were found between the total concentrations of PCBs and polychlorinated dibenzofurans ($R^2 = 0.54$), the total concentrations of PBDEs and PBDD/Fs ($R^2 = 0.43$), and the total concentrations of PCDD/Fs and PBDD/Fs ($R^2 = 0.34$). In general, the

PCDD/Fs were included in the initial group of 12 POPs covered by the Stockholm Convention on POPs, signed in 2004. The aim of the Stockholm Convention was to decrease intentional and unintentional POP emissions, as well as their environmental burdens. BATs/BEPs for decreasing PCDD/F emissions from SNT plants have been developed and suggested [47]. Our positive correlations between concentrations of PCDD/Fs and other chlorinated and brominated POPs suggest that emissions of chlorinated and brominated POPs could be synergistically decreased, along with emissions of PCDD/Fs, using BATs/BEPs that have already been developed for PCDD/Fs.

Emissions of chlorinated and brominated POPs, including PCDD/Fs, during SNT processes were studied. Correlations between the concentrations of the different POPs also were identified. The PCBs were the most abundant compounds by mass concentration, contributing about 51% to the total mass concentrations of POPs in stack gas samples. The PCNs were the next most abundant POPs, contributing 42% to this total. However, PCDD/Fs were the dominant contributors to the total chlorinated and brominated POP TEQ concentrations in stack gases emitted during the SNT processes, contributing 89% to the total TEQ concentrations. The B/C ratios in stack gases emitted during the SNT processes were calculated and compared with B/C ratios for other industrial thermal sources. The B/C ratios appear to reflect the sources of chlorinated and brominated POPs in environmental matrices. Positive correlations

Fig. 4. Correlations between the concentrations of (a) dioxin-like polychlorinated biphenyls (dl-PCBs) and polychlorinated dibenzofurans (PCDFs), (b) dioxin-like polychlorinated naphthalenes (dl-PCNs) and polychlorinated dibenzo-p-dioxins (PCDDs), (c) polybrominated dibenzo-p-dioxins and dibenzofurans (PBDD/Fs) and polybrominated diphenyl ethers (PBDEs), and (d) polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) and PBDD/Fs. Slope and correlation coefficients (R^2) for each linear correlation are shown on plots.

were found between concentrations of PCDD/Fs and other chlorinated and brominated POPs in samples collected during the SNT processes. This suggests that emissions of multiple POPs could be synergistically decreased, along with emissions of PCDD/Fs, using BATs/BEPs developed to decrease PCDD/F emissions.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jhazmat.2017.02.027>.

References

- [1] Environmental Health Criteria 205: Polybrominated Dibenzop-dioxins and Dibenzofurans, WHO, Geneva, 1998 <http://www.inchem.org/documents/ehc/ehc/ehc152.htm>.
- [2] K. Kannan, J.L. Kober, Y.S. Kang, S. Masunaga, J. Nakanishi, A. Ostaszewski, J.P. Giesy, Polychlorinated naphthalenes, biphenyls, dibenzo-p-dioxins, and dibenzofurans as well as polycyclic aromatic hydrocarbons and alkylphenols in sediment from the Detroit and Rouge Rivers, Michigan, USA, *Environ. Toxicol. Chem.* 20 (2001) 1878–1889.
- [3] H. Park, J.H. Kang, S.Y. Baek, Y.S. Chang, Relative importance of polychlorinated naphthalenes compared to dioxins, and polychlorinated biphenyls in human serum from Korea: contribution to TEQs and potential sources, *Environ. Pollut.* 158 (2010) 1420–1427.
- [4] J.W. Choi, S. Fujimaki, K. Kitamura, S. Hashimoto, H. Ito, N. Suzuki, S. Sakai, M. Morita, Polybrominated dibenzo-p-dioxins, dibenzofurans, and diphenyl ethers in Japanese human adipose tissue, *Environ. Sci. Technol.* 37 (2003) 817–821.
- [5] B. Du, M. Zheng, H. Tian, A. Liu, Y. Huang, L. Li, T. Ba, N. Li, Y. Ren, Y. Li, S. Dong, G. Su, Occurrence and characteristics of polybrominated dibenzo-p-dioxins and dibenzofurans in stack gas emissions from industrial thermal processes, *Chemosphere* 80 (2010) 1227–1233.
- [6] J.B. Wang, C.H. Hung, C.H. Hung, G.P. Chang-Chien, Polychlorinated dibenzo-p-dioxin and dibenzofuran emissions from an industrial park clustered with metallurgical industries, *J. Hazard. Mater.* 161 (2009) 800–807.
- [7] J.B. Wang, M.-S. Wang, E.M.-Y. Wu, G.-P. Chang-Chien, Y.-C. Lai, Approaches adopted to assess environmental impacts of PCDD/F emissions from a municipal solid waste incinerator, *J. Hazard. Mater.* 152 (2008) 968–975.
- [8] J.B. Wang, C.-H. Hung, C.-H. Hung, G.-P. Chang-Chien, Polychlorinated dibenzo-p-dioxin and dibenzofuran emissions from an industrial park clustered with metallurgical industries, *J. Hazard. Mater.* 161 (2009) 800–807.
- [9] M.-S. Wang, S.-J. Chen, K.-L. Huang, Y.-C. Lai, G.-P. Chang-Chien, J.-H. Tsai, W.-Y. Lin, K.-C. Chang, J.-T. Lee, Determination of levels of persistent organic pollutants (PCDD/Fs, PBDD/Fs, PBDEs, PCBs, and PBBs) in atmosphere near a municipal solid waste incinerator, *Chemosphere* 80 (2010) 1220–1226.
- [10] L.-C. Wang, Y.-F. Wang, H.-C. Hsi, G.-P. Chang-Chien, Characterizing the emissions of polybrominated diphenyl ethers (PBDEs) and polybrominated dibenzo-p-dioxins and dibenzofurans (PBDD/Fs) from metallurgical processes, *Environ. Sci. Technol.* 44 (2010) 1240–1246.
- [11] M. Wang, W. Liu, M. Hou, Q. Li, Y. Han, G. Liu, H. Li, X. Liao, X. Chen, M. Zheng, Removal of polychlorinated naphthalenes by desulfurization and emissions of polychlorinated naphthalenes from sintering plant, *Sci. Rep.* 6 (2016).
- [12] T.P.s.R.o. China, National Implementation Plan for the Stockholm Convention on Persistent Organic Pollutants, (2007) 54–56.
- [13] E. Aries, D.R. Anderson, R. Fisher, T.A.T. Fray, D. Hemfrey, PCDD/F and dioxin-like PCB emissions from iron ore sintering plants in the UK, *Chemosphere* 65 (2006) 1470–1480.
- [14] G. Liu, M. Zheng, B. Du, Z. Nie, B. Zhang, W. Liu, C. Li, J. Hu, Atmospheric emission of polychlorinated naphthalenes from iron ore sintering processes, *Chemosphere* 89 (2012) 467–472.
- [15] B. Tian, J. Huang, B. Wang, S. Deng, G. Yu, Emission characterization of unintentionally produced persistent organic pollutants from iron ore sintering process in China, *Chemosphere* 89 (2012) 409–415.
- [16] D.S. Drage, E. Aries, S. Harrad, Studies into the formation of PBDEs and PBDD/Fs in the iron ore sintering process, *Sci. Total Environ.* 485–486 (2014) 497–507.
- [17] L.C. Wang, Y.F. Wang, C.H. Tsai, G.P. Chang-Chien, Emissions of polybrominated diphenyl ethers (PBDEs) and polybrominated dibenzo-p-dioxins and dibenzofurans (PBDD/Fs) from ferrous foundries, *European Aerosol Conference in Karlsruhe* (2009).
- [18] G.R. Liu, M.H. Zheng, W.B. Liu, C.Z. Wang, B. Zhang, L.R. Gao, G.J. Su, K. Xiao, P. Lv, Atmospheric emission of PCDD/Fs, PCBs, hexachlorobenzene, and pentachlorobenzene from the coking industry, *Environ. Sci. Technol.* 43 (2009) 9196–9201.
- [19] M. Wang, G. Liu, X. Jiang, S. Li, W. Liu, M. Zheng, Formation and emission of brominated dioxins and furans during secondary aluminum smelting processes, *Chemosphere* 146 (2016) 60–67.
- [20] G.R. Liu, M.H. Zheng, P. Lv, W.B. Liu, C.Z. Wang, B. Zhang, K. Xiao, Estimation and characterization of polychlorinated naphthalene emission from coking industries, *Environ. Sci. Technol.* 44 (2010) 8156–8161.
- [21] S.M. Li, G.R. Liu, M.H. Zheng, W.B. Liu, M. Wang, K. Xiao, C.L. Li, Y.W. Wang, Comparison of the contributions of polychlorinated dibenzo-p-dioxins and

- dibenzofurans and other unintentionally produced persistent organic pollutants to the total toxic equivalents in air of steel plant areas, *Chemosphere* 126 (2015) 73–77.
- [22] M. Wang, G.R. Liu, X.X. Jiang, W.B. Liu, L. Li, S.M. Li, M.H. Zheng, J.Y. Zhan, Brominated dioxin and furan stack gas emissions during different stages of the secondary copper smelting process, *Atmos. Pollut. Res.* 6 (2015) 464–468.
- [23] Y. Noma, T. Yamamoto, S.-i. Sakai, Congener-specific composition of polychlorinated naphthalenes, coplanar PCBs, dibenzo-p-dioxins, and dibenzofurans in the Halowax Series, *Environ. Sci. Technol.* 38 (2004).
- [24] J. Falandysz, A. Fernandes, E. Gregoraszcuk, M. Rose, The toxicological effects of halogenated naphthalenes: a review of Aryl hydrocarbon receptor-mediated (dioxin-like) relative potency factors, *J. Environ. Sci. Health Part C* 32 (2014) 239–272.
- [25] J. Falandysz, A. Fernandes, E. Gregoraszcuk, R. Martin, Aryl hydrocarbon receptor mediated (dioxin-like) relative potency factors for chlornaphthalenes, *Organohalogen Compd.* 75 (2013) 336–338.
- [26] M.S. Berg, L.S. Denison, M.J. Birnbaum, H. DeVito, J. Fiedle, M. Falandysz, D. Rose, S. Schrenk, C. Safe, A. Tohyama, M. Tritscher, R.E. Tysklind, Polybrominated dibenzo-p-dioxins, dibenzofurans, and biphenyls: inclusion in the toxicity equivalency factor concept for dioxin-like compounds, *Toxicol. Sci.* 133 (2013) 197–208.
- [27] E. Eljarrat, D. Barcelo, Priority lists for persistent organic pollutants and emerging contaminants based on their relative toxic potency in environmental samples, *Trac-Trend Anal. Chem.* 22 (2003) 655–665.
- [28] C. Zou, J. Han, H. Fu, Emissions of PCDD/Fs from steel and secondary nonferrous productions, *Procedia Environ. Sci.* 16 (2012) 279–288.
- [29] V. Esposito, A. Maffei, D. Bruno, B. Varvaglione, S. Ficocelli, C. Capoccia, M. Spartera, R. Giua, M. Blonda, G. Assennato, POP emissions from a large sinter plant in Taranto (Italy) over a five-year period following enforcement of new legislation, *Sci. Total Environ.* 491–492 (2014) 118–122.
- [30] L.-C. Wang, H.-C. Hsi, Y.-F. Wang, S.-L. Lin, G.-P. Chang-Chien, Distribution of polybrominated diphenyl ethers (PBDEs) and polybrominated dibenzo-p-dioxins and dibenzofurans (PBDD/Fs) in municipal solid waste incinerators, *Environ. Pollut.* 158 (2010) 1595–1602.
- [31] R.A. Hites, Polybrominated diphenyl ethers in the environment and in people: a meta-analysis of concentrations, *Environ. Sci. Technol.* 38 (2004) 945–956.
- [32] M. Wang, W. Liu, M. Hou, Q. Li, Y. Han, H. Li, N. Yan, M. Zheng, Mono- to octachlorinated polychlorinated dibenzo-p-dioxin and dibenzofuran emissions from sintering plants synergistically controlled by the desulfurization process, *Environ. Sci. Technol.* 50 (2016) 5207–5215.
- [33] M. Wang, M. Hou, K. Zhao, H. Li, Y. Han, X. Liao, X. Chen, W. Liu, Removal of polychlorinated biphenyls by desulfurization and emissions of polychlorinated biphenyls from sintering plants, *Environ. Sci. Pollut. Res.* 23 (2016) 7369–7375.
- [34] S. Li, M. Zheng, W. Liu, G. Liu, K. Xiao, C. Li, Estimation and characterization of unintentionally produced persistent organic pollutant emission from converter steelmaking processes, *Environ. Sci. Pollut. Res.* 21 (2014) 7361–7368.
- [35] Sumei Li, Guorui Liu, Mei Wang, Changliang Li, Minghui Zheng, Atmospheric emission of polybrominated dibenzo-p-dioxins and dibenzofurans from converter steelmaking processes, *Aerosol Air Qual. Res.* 15 (2015) 1118–1124.
- [36] H.R. Li, L.P. Yu, G.Y. Sheng, J.M. Fu, P.A. Peng, Severe PCDD/F and PBDDQ/F pollution in air around an electronic waste dismantling area in China, *Environ. Sci. Technol.* 41 (2007) 5641–5646.
- [37] H.R. Li, H.L. Feng, G.Y. Sheng, S.L. Lu, J.M. Fu, P.A. Peng, R. Man, The PCDD/F and PBDD/F pollution in the ambient atmosphere of Shanghai, China, *Chemosphere* 70 (2008) 576–583.
- [38] R.R. Black, C.P. Meyer, A. Touati, B.K. Gullett, H. Fiedler, J.F. Mueller, Emission factors for PCDD/PCDF and dl-PCB from open burning of biomass, *Environ. Int.* 38 (2012) 62–66.
- [39] G.R. Liu, Z.W. Cai, M.H. Zheng, Sources of unintentionally produced polychlorinated naphthalenes, *Chemosphere* 94 (2014) 1–12.
- [40] G.R. Liu, M.H. Zheng, M.W. Cai, Z.Q. Nie, B. Zhang, W.B. Liu, B. Du, S.J. Dong, J.C. Hu, K. Xiao, Atmospheric emission of polychlorinated biphenyls from multiple industrial thermal processes, *Chemosphere* 90 (2013) 2453–2460.
- [41] E. Aries, D.R. Anderson, R. Fisher, T.A.T. Fray, D. Hemfrey, PCDD/F and dioxin-like PCB emissions from iron ore sintering plants in the UK, *Chemosphere* 65 (2006) 1470–1480.
- [42] B. Tian, J. Huang, B. Wang, S.B. Deng, G. Yu, Emission characterization of unintentionally produced persistent organic pollutants from iron ore sintering process in China, *Chemosphere* 89 (2012) 409–415.
- [43] M.K. Cieplik, J.P. Carbonell, C. Muñoz, S. Baker, S. Krüger, P. Liljelind, S. Marklund, R. Louw, On dioxin formation in iron ore sintering, *Environ. Sci. Technol.* 37 (2003) 3323–3331.
- [44] L.-C. Wang, W.-J. Lee, P.-J. Tsai, W.-S. Lee, G.-P. Chang-Chien, Emissions of polychlorinated dibenzo-p-dioxins and dibenzofurans from stack flue gases of sinter plants, *Chemosphere* 50 (2003) 1123–1129.
- [45] C.S.I. Association, China Steel Yearbook, The Editorial Board of China Steel Yearbook, Beijing, (2014).
- [46] C.S.I. Association, China Steel Yearbook, The Editorial Board of China Steel Yearbook, Beijing, (2015).
- [47] G. Liu, M. Zheng, Perspective on the inclusion of polychlorinated naphthalenes as a candidate POP in Annex C of the Stockholm Convention, *Environ. Sci. Technol.* 47 (2013) 8093–8094.