Mono- to Octachlorinated Polychlorinated Dibenzo-*p*-dioxin and Dibenzofuran Emissions from Sintering Plants Synergistically Controlled by the Desulfurization Process

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Supporting Information

ABSTRACT: The influence of desulfurization systems in sintering plants on polychlorinated dibenzo-*p*-dioxin and dibenzofuran (PCDD/F) concentrations, profiles, and emission factors was studied. Mono- to tri-CDD/Fs and tetra- to octa-CDD/F concentrations were 4.4 ± 2.3 and 10.5 ± 8.3 ng m⁻³, respectively, at the inlets and 0.87 ± 0.48 and 0.47 ± 0.22 ng m⁻³, respectively, after desulfurization. The toxic equivalents (TEQs) were 0.95 ± 0.093 and 0.51 ± 0.040 ng of I-TEQ m⁻³ at the inlets and after desulfurization, respectively. The congener profiles and homologue distributions were dominated by 2-MoCDF and MoCDF, respectively. The PCDD/F removal efficiencies achieved by desulfurization increased as the chlorination level increased. The PCDD/Fs became adsorbed to gypsum. Annual mono- to tri-CDD/Fs PCDD/F and TEQ (tetra- to octa-CDD/F) emission factors for flue gas and gypsum between 2003 and 2012 were determined. The total amounts of mono- to tri-CDD/Fs emitted in flue gas and gypsum between 2003 and 2012 were 10.7 and 10.2 kg, respectively. The total TEQs emitted in flue gas and gypsum between 2003 and 2012 were estimated to be 15486 and 1878 g of I-TEQ, respectively. PCDD/Fs adsorbed to gypsum are not effectively eliminated. The PCDD/F concentrations increased as the fly ash surface area increased moving through the electrostatic precipitator stages.

INTRODUCTION

Polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDDs and PCDFs, together called PCDD/Fs) pose risks to the environment and human health around the world because they are toxic and persistent and undergo long-range transport. PCDD/Fs are formed unintentionally during many thermal industrial activities, such as combustion processes and in processes in metallurgical and chemical plants.^{1–5} Identifying potential PCDD/F sources is an essential primary step when determining which sources should be prioritized when implementing emission controls. According to the most recent PCDD/F emission inventory, the contribution of PCDD/F emissions from Chinese sintering plants to the total Chinese industrial PCDD/F emissions to the atmosphere increased from 30.2% in 2003 to 34.8% in 2012.

Sintering is an important industry in China. Approximately 40% of the global iron ore sintering production currently occurs in China. Elaborate gas cleaning measures have been implemented to decrease PCDD/Fs emissions from sintering plants to meet emission legislation. These measures include not

only using selective catalytic reduction systems,⁶ using optimal sintering operating parameters,⁷ and installing urea addition plants⁸ but also using “clean” ores and selecting “clean” fuel (rather than coal). Different sintering plants are very different in size and use different techniques, so there are large differences between PCDD/Fs concentrations emitted by different plants.^{9,10} PCDD/F homologue distributions and congener profiles in the sintering flue gases were quite dissimilar to those in waste incinerator flue gases.^{11,12} The mechanisms involved in the formation of PCDD/Fs are not completely understood.¹³ In early studies, PCDD/F formation was attributed to de novo synthesis,¹³ but this may not be entirely the case in downdraft combustion processes.¹¹

Previous studies have focused on 17 2,3,7,8-chlorinated PCDD/F congeners. Only limited data on emissions of less

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chlorinated PCDD/Fs [the mono (Mo), di (Di), and tri (Tr) chlorodibenzo-*p*-dioxins and chlorodibenzofurans] from sintering plants are available.^{14,15} The formation pathways of less to more chlorinated PCDFs can explain the dominant congeners and explain the distribution of congener profiles and why 2,3,4,7,8-PeCDF is the largest contributor of TEQs in the main organic chemical industries.¹⁴ MoCDFs to TrCDFs contributed more than 95% of the total PCDF concentrations in serum samples from the operators of a municipal solid waste incinerator in Korea and people living near the incinerator.¹⁶ Some MoCDF congeners are mutagenic and embryotoxic.¹⁷ The less chlorinated PCDD/Fs contribute more than the 2,3,7,8-chlorinated PCDD/Fs to the total PCDD/F concentrations in the atmosphere.¹⁸ Therefore, less chlorinated PCDD/Fs could have significant effects on humans and the environment, but these effects have been almost ignored. It is therefore important to identify potential sources of and to characterize emissions of MoCDD/Fs to TrCDD/Fs.

Emissions of SO₂ from Chinese sintering plants exceeded 140×10^6 tons (7.3% of total industrial SO₂ emissions) in 2012. Desulfurization systems have recently been introduced to control air pollution by removing SO₂ from sintering plant flue gases. Desulfurization systems have been found to remove various pollutants, including dust and NO_x, at the same time they remove SO₂.¹⁹ However, no systematic research into the possibility of synergistically controlling PCDD/Fs emissions in sintering flue gas using desulfurization systems has previously been described.

Four typical sintering plants were used in this study. Flue gas samples were collected at the desulfurization system inlets and outlets to investigate the influences the systems had on the concentrations and profiles of the MoCDD/Fs to octa (O) CDD/Fs emitted and used to derive the emission factors. Fly ash and gypsum samples were also collected to improve our understanding of the release of MoCDD/F to OCDD/F from sintering plants.

MATERIALS AND METHODS

Sampling. Sintering flue gases are at high temperatures and contain large amounts of particles, so a baghouse cannot be used. An electrostatic precipitator therefore has to be used to decrease the amounts of particles emitted. Electrostatic precipitators significantly increase the amounts of PCDD/Fs that form during the sintering process, but this was ignored.

Sintering plants in China currently most commonly use wet or semidry desulfurization systems, the schematics of which are shown in Figure 1. In a wet desulfurization system, the flue gas is treated with a sorbent slurry in an aqueous medium before

being emitted to the atmosphere. In a semidry desulfurization system, an aqueous sorbent slurry similar to that used in a wet system but at a higher sorbent concentration is used. The waste products are collected using a standard particulate matter collection device, such as a baghouse.

Four sintering plants, DH, TS, SK, and ST, with sintering areas of 90, 180, 360, and 500 m², respectively, were studied. In China, small sintering plants (area of <90 m²) are mostly equipped with wet desulfurization systems, whereas medium (90–180 m²) and large (>180 m²) plants tend to be equipped with semidry systems. Plant DH had a wet desulfurization system, and plants TS, SK, and ST had semidry systems. Operational information for plants DH, TS, SK, and ST is given in Table S1.

Six flue gas samples were collected from each plant, three at the inlet and three at the outlet. The samples were collected using an automatic isokinetic sampling system (Tecora Corp., Milan, Italy). The sample collection methods have previously been described in detail.¹⁴ Briefly, the sampling train included a heated probe, a filter box with a quartz-fiber filter, and a water-cooled XAD-2 adsorbent trap. The quartz-fiber filter collected particulate-bound pollutants, and the XAD-2 adsorbent resin trapped vapor-phase contaminants. A gypsum sample was collected from the desulfurization system at each plant. Four fly ash samples were collected from different stages of the electrostatic precipitators that were connected in series in plants DH and TS. One fly ash sample (a mixture of fly ash from all of the stages) was collected from the electrostatic precipitator in SK and ST because it was not practical to collect a sample from each stage of the precipitators.

MoCDD/F to OCDD/F Analysis. The 2,3,7,8-chlorinated PCDD/Fs were analyzed following standard method EN-1948, which has been described previously.^{20–22} Briefly, each sample was spiked with ¹³C-labeled PCDD/F internal standards (EN-1948 ES; Cambridge Isotope Laboratories, Andover, MA) and then Soxhlet extracted with 250 mL of toluene for ~24 h. Before extraction, the fly ash and gypsum samples were treated with 1 M HCl. Each extract was purified by being passed through a multilayer silica gel column and a basic alumina column. The extract was then spiked with ¹³C₁₂-labeled PCDD/Fs (EN-1948 IS; Cambridge Isotope Laboratories) to allow the native PCDD/Fs and labeled internal standards to be quantified.

The MoCDD/Fs to TrCDD/Fs in each sample were qualitatively and quantitatively analyzed. A ¹³C-labeled internal standard (EDF-4955; Cambridge Isotope Laboratories) containing 2-MoCDD, 2,3-DiCDD, 2,3,7-TrCDD, 2-MoCDF, 2,8-DiCDF, and 2,4,8-TrCDF was added before the sample was extracted, and an aliquot of the extract was concentrated and then passed through a multilayer silica gel column eluted with 100 mL of hexane. The extract was evaporated and passed through a column containing 8 g of basic alumina, which was eluted with 80 mL of 2% dichloromethane in hexane and then 150 mL of 12% dichloromethane in hexane. The second fraction, containing the MoCDD/Fs to TrCDD/Fs, was concentrated to 40 μL of nonane under a gentle stream of nitrogen.

The MoCDD/Fs to OCDD/Fs were analyzed using an Agilent 6890 high-resolution gas chromatograph (Agilent Technologies, Santa Clara, CA) coupled to an Autospec Ultima high-resolution mass spectrometer (Waters, Milford, MA). The gas chromatograph was equipped with a DB-5MS column (60 m × 0.25 mm × 0.25 μm, Agilent Technologies).

Figure 1. Schematics of a wet desulfurization system (left) and a semidry desulfurization system (right).

Table 1. PCDD/F Concentrations in the Samples

			MoCDD/Fs to TrCDD/Fs	2,3,7,8-chlorinated PCDD/Fs	I-TEQ
flue gas (ng m ⁻³ and ng of I-TEQ m ⁻³)	inlet	DH	7.3 ± 1.8	21.9 ± 6.8	2.3 ± 0.56
		TS	4.0 ± 1.1	4.5 ± 2.3	0.44 ± 0.12
		SK	3.2 ± 1.1	7.2 ± 2.4	0.32 ± 0.22
		ST	3.1 ± 0.71	8.4 ± 1.7	0.69 ± 0.14
	outlet	DH	1.5 ± 0.10	0.40 ± 0.11	0.99 ± 0.53
		TS	0.58 ± 0.041	0.25 ± 0.063	0.20 ± 0.0087
		SK	0.95 ± 0.069	0.51 ± 0.11	0.022 ± 0.0018
		ST	1.2 ± 0.029	0.73 ± 0.13	0.062 ± 0.0045
gypsum (ng kg ⁻¹ and ng of I-TEQ kg ⁻¹)		DH	1836	6589	525
		TS	940	1200	120
		SK	653	1900	78.7
		ST	394	2141	106.7
fly ash (ng kg ⁻¹ and ng of I-TEQ kg ⁻¹)	DH	D1	3363	8353	352
		D2	8670	8554	369
		D3	38535	10772	495
		D4	95787	14157	642
	TS	T1	2044	2932	231
		T2	9709	10811	662
		T3	35723	14496	725
		T4	52464	18425	880
		SK (mixed)	46200	16380	515
		ST (mixed)	34500	9652	472

The mass spectrometer was operated at a resolution of at least 10000 in selected ion monitoring mode. Two ions among $M+$, $M+2$, and $M+4$ were monitored. The PCDD/Fs congeners as well as the total for the homologues were identified and quantified on the basis of the retention time and the isotope ratios. The concentrations of the 27 MoCDD/F to OCDD/F congeners (including 1-MoCDD, 2-MoCDD, 2,3-DiCDD, 2,3,7-TrCDD, 1-MoCDF, 2-MoCDF, 3-MoCDF, 4-MoCDF, 2,8-DiCDF, 2,4,8-TrCDF, and 17 2,3,7,8-chlorinated PCDD/Fs) in the samples were analyzed. Six less chlorinated PCDD/Fs (2-MoCDF, 2,8-DiCDF, 2,4,8-TrCDF, 2-MoCDD, 2,3-DiCDD, and 2,3,7-TrCDD included in EDF-4955) and 13 2,3,7,8-chlorinated PCDD/Fs (2,3,7,8-TCDF, 2,3,4,7,8-PeCDF, 1,2,3,4,7,8-HxCDF, 1,2,3,6,7,8-HxCDF, 2,3,4,6,7,8-HxCDF, 1,2,3,4,6,7,8-HpCDF, OCDF, 2,3,7,8-TCDD, 1,2,3,7,8-PeCDD, 1,2,3,4,7,8-HxCDD, 1,2,3,6,7,8-HxCDD, 1,2,3,4,6,7,8-HpCDD, and OCDD included in EN-1948 ES) were identified and quantified by corresponding ¹³C₁₂-labeled internal standards. For the congeners without, corresponding ¹³C₁₂-labeled internal standards (including 1-MoCDF, 3-MoCDF, 4-MoCDF, 1,2,3,7,8-PeCDF, 1,2,3,7,8,9-HxCDF, 1,2,3,4,7,8,9-HpCDF, 1-MoCDD, and 1,2,3,7,8,9-HxCDD) were identified and quantified by ¹³C₁₂-labeled internal standards of the similar congeners. The levels of the mono- to octachlorinated homologues were estimated by the average of ¹³C₁₂-labeled internal standards of the similar congeners. The 2,3,7,8-chlorinated PCDD/Fs congener recoveries were 43–126%, while the less chlorinated PCDD/Fs congener recoveries were 42–97%.

RESULTS AND DISCUSSION

MoCDD/F to OCDD/F Concentrations in the Flue Gas and Gypsum Samples. The concentrations of the 27 MoCDD/F to OCDD/F congeners in the flue gas, gypsum, and fly ash samples are listed in Table 1. The 2,3,7,8-chlorinated PCDD/F TEQs were calculated using internationally accepted toxic equivalence factors.²³

The MoCDD/F to TrCDD/F concentrations were 2.1–9.2 ng m⁻³ (mean of 4.4 ± 2.3 ng m⁻³) in the inlet flue gas samples and 0.38–1.67 ng m⁻³ (mean of 0.87 ± 0.48 ng m⁻³) in the outlet flue gas samples, so the removal efficiencies were 69.9–87.2%. The 2,3,7,8-chlorinated PCDD/F concentrations were 2.2–28.7 ng m⁻³ (mean of 10.5 ± 8.3 ng m⁻³) in the inlet flue gas samples and 0.29–0.87 ng m⁻³ (mean of 0.47 ± 0.22 ng m⁻³) in the outlet flue gas samples, so the removal efficiencies were 91.2–98.2%. The TEQ concentrations were 0.094–2.9 ng of I-TEQ m⁻³ (mean of 0.95 ± 0.093 ng of I-TEQ m⁻³) in the inlet flue gas samples and 0.012–0.15 ng of I-TEQ m⁻³ (mean of 0.051 ± 0.040 ng of I-TEQ m⁻³) in the outlet flue gas samples, so the removal efficiencies were 91.0–95.8%.

The MoCDD/F to TrCDD/F, 2,3,7,8-chlorinated PCDD/F, and TEQ concentrations in the gypsum samples were 394–1836, 1200–6589, and 78.7–525 ng of I-TEQ kg⁻¹, respectively. The dioxin mass balance in the desulfurization process was analyzed and is presented in Table S2, among the inlet and outlet flue gas as well as gypsum. The concentrations of MoCDD/F to TrCDD/F in the gypsum and outlet flue gas accounted for 73.0–88.2% of those in the inlet flue gas, and the concentrations of 2,3,7,8-chlorinated PCDD/F in the gypsum and outlet flue gas accounted for 77.3–84.5% of those in the inlet flue gas. The compounds that were thought to be removed from the flue gases were adsorbed by the gypsum, causing the gypsum to be classified as toxic waste. In China, gypsum is treated in three main ways, by being recycled, discarded, or reused (as an important raw material in the construction industry).

To the best of our knowledge, this was the first intensive investigation of MoCDD/F to TrCDD/F concentrations in flue gases and gypsum samples from sintering plants, and no previously published data on MoCDD/F to TrCDD/F concentrations in samples collected in sintering plants are available to compare with our concentrations. Our data provide some clues about the pathways through which the PCDD/Fs formed and the mechanisms involved in transformations

Figure 2. PCDD/F congener profiles in the inlet and outlet flue gas samples and the gypsum samples.

between nontoxic PCDD/F congeners and toxic 2,3,7,8-chlorinated PCDD/F congeners.

It should be noted that the TEQ concentrations in the inlet gases were higher than the Chinese standard (GB 28662-2012) of 0.5 ng of I-TEQ m^{-3} and that the desulfurization systems decreased the concentrations to <0.1 ng of I-TEQ m^{-3} . The desulfurization installations operated at <200 °C, so the formation of PCDD/Fs during desulfurization was avoided.²⁴ The TEQ concentrations were higher in the gypsum samples than those that have been found in soil samples^{25–27} and in fly ash collected in primary magnesium smelting and coking plants.^{28,29} The pollution of PCDD/Fs in gypsum cannot be ignored.

The removal efficiency was calculated using the formula $\text{RE}_{\%} = (C_{\text{IN}} - C_{\text{OUT}})/C_{\text{IN}} \times 100\%$. According to the results presented in this study, the TEQ concentrations after the electrostatic precipitators (i.e., before the desulfurization systems) did not exceed 1.0 ng of I-TEQ m^{-3} (except in plant DH). Therefore, a further decrease of 91.0–95.8% achieved using desulfurization systems would guarantee that PCDD/F emissions would be lower than 0.5 ng of I-TEQ m^{-3} .

The desulfurization systems were originally designed to decrease SO_2 emissions, so the conditions under which the systems were operated were not optimized for eliminating PCDD/Fs. The TEQ removal efficiencies achieved by the desulfurization systems were excellent and were higher than TEQ removal efficiencies that have been found using electrostatic precipitators (41.4%),²⁴ wet fine scrubbers (68.4%),²⁴ and selective catalytic reduction systems (69.0%).⁶ In addition, the PCDD/F homologue removal efficiencies increased as the number of chlorine substituents increased, as shown in Figure S1. This would mainly have been caused by the PCDD/Fs partitioning between the solid and vapor phases.³⁰ Generally, less chlorinated PCDD/F homologues have vapor pressures higher than those of more chlorinated homologues, so larger proportions of less chlorinated than more chlorinated PCDD/Fs will be found in the gaseous phase at a specific temperature. More chlorinated homologues are more likely than less chlorinated homologues to condense onto particulate matter.³¹ A desulfurization system will intercept solid particles in sintering flue gas, so a desulfurization system will effectively remove solid-phase PCDD/Fs but will be

ineffective at removing gas-phase PCDD/Fs. The more chlorinated PCDD/F congeners will therefore be removed more efficiently than the less chlorinated congeners.

The PCDD/F concentrations in the samples from the different plants varied considerably. The MoCDD/F to OCDD/F concentrations were higher in the flue gases emitted from plant DH than in the flue gases emitted from the other plants. Plant DH had outdated facilities,³² and the proportion of recycled material added to raw materials was much higher (>20%) than at the other plants. This could explain why the PCDD/F concentrations were higher at plant DH than at the other plants.³³

MoCDD/F to OCDD/F congener profiles in the flue gas and gypsum samples were studied. The MoCDD/F to TrCDD/F and 2,3,7,8-chlorinated PCDD/F congener profiles found in the inlet and outlet flue gas samples and the gypsum samples are shown in Figure 2. The congener concentrations were normalized to the sum of the 27 congeners to minimize the influence of the concentrations of particular congeners.

The overall PCDD/F congener profiles in the inlet flue gases were similar for all of the sintering plants, indicating that similar PCDD/F formation mechanisms occurred in all of the plants and that the characteristics of the emissions were not strongly affected by the operating conditions or the sinter mixture used. The less chlorinated PCDF congeners were found at concentrations higher than those of the less chlorinated PCDD congeners in the inlet flue gases. The dominant congener, 2-MoCDDF, contributed 3.0–8.5% of the total PCDD/Fs concentrations, and the next most abundant congeners, 2,4,8-TrCDDF and 2,8-DiCDDF, contributed 2.5–10.7 and 3.7–7.4%, respectively. These congeners have also been found to be very dominant in samples collected in waste incineration and organic chemical plants.^{14,18} This was attributed to positions 2, 4, and 8 of the PCDF ring having relatively low bond dissociation energies.¹⁷ 2,3-DiCDD and 1-MoCDD contributed 1.5–3.6 and 1.3–4.3%, respectively, of the total PCDD/Fs concentrations. 2,3,7,8-Tetra (T) CDF was the predominant 2,3,7,8-chlorinated PCDF congener, and it contributed 4.4–12.6% of the total PCDD/F concentrations. 2,3,4,7,8-PeCDDF was the main contributor to the total TEQs, contributing 37.3–50.8%.

The desulfurization systems achieved excellent removal efficiencies for the 27 PCDD/F congeners. The removal efficiencies were higher for the more chlorinated PCDD/F congeners than for the less chlorinated congeners. The contributions of the less chlorinated PCDD/F congeners to the total PCDD/F concentrations were generally increased by the desulfurization systems, but the contributions of the 2,3,7,8-chlorinated PCDD/F congeners were generally decreased. The mean contribution of 2,8-DiCDDF (the dominant PCDD/F congener) to the total PCDD/F concentrations was increased from 5.1 to 21.7% by the desulfurization systems. The mean contribution of 2,3,7,8-TCDF (the predominant 2,3,7,8-chlorinated PCDD/F congener) to the total PCDD/F concentrations was decreased from 8.6 to 2.4% by the desulfurization systems. The mean contribution of 2,3,4,7,8-PeCDDF (the main contributor to the TEQ) to the total TEQs was also decreased from 43.2 to 38.0% by the desulfurization systems.

The contributions of the 2,3,7,8-chlorinated PCDD/Fs to the total PCDD/F concentrations (mean of 66.0%) were higher than the contributions of the less chlorinated congeners in the gypsum samples. This is evidence that the PCDD/Fs that were

removed during the desulfurization process were transferred to the gypsum. 2,3,4,6,7,8-Hexa (Hx) CDF (which contributed a mean of 9.3% of the total PCDD/F concentrations) was the dominant PCDD/F congener. 3-MoCDDF (which contributed a mean of 5.6% of the total PCDD/F concentrations) was the dominant less chlorinated congener.

MoCDD/F to OCDD/F Homologue Distributions in the Flue Gas and Gypsum Samples. The PCDD/F homologue distributions found in the inlet and outlet flue gas samples and the gypsum samples are shown in Figure 3.

Figure 3. PCDD/F homologue distributions in the inlet and outlet flue gas samples and the gypsum samples.

The MoCDD/F to TrCDD/F homologues were found at concentrations lower than those of the TCDD/F to OCDD/F homologues in the inlet flue gas samples. The MoCDD/F to TrCDD/F homologues contributed 25.1–47.3% of the total PCDD/F concentrations. The contributions of the MoCDD/F to TrCDD/F homologue groups to the total PCDD/F concentrations decreased as the chlorination level increased, whereas the contributions of the TCDD/F to OCDD/F homologues varied. The homologue patterns were rather different from the patterns that have been found in samples from waste incineration plants.¹⁸ The MoCDDFs (which contributed 12.2–26.0% of the total PCDD/F concentrations) were the most abundant homologue group in the inlet flue gas samples. The MoCDDs and DiCDDs were also relatively abundant less chlorinated homologues, contributing 5.3–7.4 and 1.9–6.7%, respectively, of the total PCDD/F concen-

trations. The HxCDFs (which contributed 11.7–19.8% of the total PCDD/F concentrations) were the dominant 2,3,7,8-chlorinated homologue group.

The TCDD/F to OCDD/F homologue contributions to the total PCDD/F concentrations were smaller and the MoCDD/F to TrCDD/F homologue contributions larger in the outlet flue gas samples than in the inlet flue gas samples. The MoCDFs were the most abundant PCDD/F homologue group in the outlet flue gases, the mean contribution to the total PCDD/F concentrations being 29.8%. The DiCDFs were the next most abundant homologue group, contributing a mean of 14.8% of the total PCDD/F concentrations. The HxCDFs were the dominant 2,3,7,8-chlorinated PCDD/F homologue group, the mean contribution to the total PCDD/F concentrations being 8.9%.

We compared the influences of the wet and semidry desulfurization systems on the MoCDD/F to OCDD/F homologues in the flue gas samples. The MoCDF and DiCDF contributions to the total PCDD/F concentrations were increased by 24.7 and 17.2%, respectively, by the wet desulfurization system and were increased by a further 9.3 and 5.8%, respectively, by the semidry desulfurization systems. The TCDF, PeCDF, and HxCDF contributions were decreased by 10.4, 12.0, and 12.0%, respectively, by the wet desulfurization system and were decreased further by 1.3, 1.9, and 4.2%, respectively, by the semidry desulfurization systems.

The TCDD/F to OCDD/F homologues were found at concentrations much higher than those of the MoCDD/F to TrCDD/F homologues in the gypsum samples. The TCDD/F to OCDD/F homologues contributed 60.5–83.8% of the total PCDD/F concentrations. These results were in agreement with the desulfurization processes removing the TCDD/Fs to OCDD/Fs from flue gas more efficiently than they removed the MoCDD/Fs to TrCDD/Fs. The PeCDFs dominated the homologue patterns in the gypsum samples, contributing a mean of 24.3% of the total PCDD/F concentrations. The MoCDFs were relatively abundant and contributed a mean of 4.2% of the total PCDD/F concentrations.

The total PCDD to total PCDF concentration ratio and the average degree of chlorination (the average number of chlorine atoms in each molecule) have previously been used to “fingerprint” samples.³ The total PCDD to total PCDF concentration ratios are listed in Table S3. The ratios for the MoCDD/Fs to TrCDD/Fs in the inlet and outlet flue gas samples were higher than the ratios for the TCDD/Fs to OCDD/Fs. The PCDD average degrees of chlorination (4.3–6.2) and the PCDF average degrees of chlorination (3.7–5.1) showed that the PCDD/Fs were more chlorinated in the inlet flue gas samples than in the outlet flue gas samples (for which the PCDD and PCDF average degrees of chlorination were 2.4–4.4 and 2.3–4.2, respectively). This would have been the case because the less chlorinated PCDD/Fs made larger contributions to the total PCDD/F concentrations after the flue gases had been desulfurized. Considering the congener profiles and homologue distributions from this study and our previous studies and quantum chemical investigation of formation of PCDD/Fs,^{14,34} we concluded that the less chlorinated PCDD/Fs are precursors that are chlorinated to form the 2,3,7,8-chlorinated PCDD/Fs during the sintering process.

MoCDD/F to OCDD/F Emissions and Characteristics in Fly Ash Samples. Fly ash collected in the first, second, and third stages of the electrostatic precipitators in the sintering

plants was recycled to allow residual metals in the ash to be recovered. Fly ash collected in the fourth stage of each electrostatic precipitator was discarded and would be classified as waste treated by landfill. The PCDD/F concentrations in the fly ash samples are listed in Table 1. The concentrations clearly increased from the first to the fourth stages of the electrostatic precipitators in plants DH and TS. The MoCDD/F to TrCDD/F concentrations in the fly ash samples were 2044–95787 ng kg⁻¹. This is the first intensive investigation of MoCDD/F to TrCDD/F concentrations in fly ash samples produced in sintering plants, so no MoCDD/F to TrCDD/F concentration data for other sintering plants are available to compare with our data. The 2,3,7,8-chlorinated PCDD/F concentrations were 2638–18425 ng kg⁻¹ (172–880 ng of I-TEQ kg⁻¹). These concentrations were higher than those that have been found in fly ash from primary magnesium smelting plants³⁵ and coking plants³⁵ and similar to concentrations that have been found in municipal solid waste incineration fly ash.²¹ The MoCDD/F to TrCDD/F concentrations in the fly ash samples were almost 2.3 times higher than the 2,3,7,8-chlorinated PCDD/F concentrations. The MoCDD/F to TrCDD/F concentrations increased by 223%, on average, from the first to the fourth stages of the precipitators in plants DH and TS, whereas the TCDD/F to OCDD/F concentrations and TEQs increased by only 66.4 and 47.7%, respectively.

More fine particles are produced during the sintering process than during the waste incineration process. This would mean that more MoCDD/Fs to TrCDD/Fs would be adsorbed in sintering plants than in waste incinerators when the flue gases are passed through an electrostatic precipitator. The proportions of the MoCDD/Fs to TrCDD/Fs found in the flue gases were not much higher in our samples than those that have been found in waste incineration flue gases.

The particle size clearly decreased and the Brunauer–Emmett–Teller surface areas increased moving from the first to the fourth stages of the precipitators in plants DH and TS (Table S4). This shows that the finer fly ash had a larger specific surface area, which would favor the adsorption of PCDD/Fs. The MoCDD/Fs to TrCDD/Fs have vapor pressures higher than those of the 2,3,7,8-chlorinated PCDD/Fs and larger proportions of the MoCDD/Fs to TrCDD/Fs than 2,3,7,8-chlorinated PCDD/Fs will therefore be in the gaseous phase. The MoCDD/Fs to TrCDD/Fs will therefore more easily adsorb onto finer particles than will the 2,3,7,8-chlorinated PCDD/Fs because of the high surface area/volume ratios of the fine particles. The PCDD/F homologue distributions in the fly ash samples, shown in Figure S2, indicated that the fraction of the MoCDD/Fs to TrCDD/Fs present in the fly ash increased moving along the electrostatic precipitators.

Emission Inventory of MoCDD/Fs to OCDD/Fs in China from 2003 to 2012. The emission factor of a contaminant is typically used to estimate the total amount of that contaminant that is emitted each year, to establish an inventory. The MoCDD/F to TrCDD/F emission factors for the inlet and outlet flue gases and gypsum were 17.6, 4.2, and 10.6 μg t⁻¹, respectively. The TEQ emission factors for the gypsum were very different for different sized sintering plants (<90 and >90 m²). Therefore, we divided the emission factors into two classes to allow the emissions to be estimated accurately. The emission factor for <90 m² sintering plants was 5.9 μg of I-TEQ t⁻¹, and the emission factor for >90 m²

sintering plants was $1.1 \mu\text{g}$ of I-TEQ t^{-1} . The TEQ emission factors for the inlet and outlet flue gases were 3.3 and $0.18 \mu\text{g}$ of I-TEQ t^{-1} , respectively.

We combined the sintering outputs (shown in Figure S3) and the percentage of plants that had desulfurization systems (shown in Figure 4) between 2003 and 2012. The total MoCDD/F to TrDD/F emissions were preliminarily estimated to be $\sim 10.7 \text{ kg}$ in flue gas and 10.2 kg in gypsum from 2003 to 2012.

Figure 4. Annual I-TEQ emissions in flue gases and gypsum from sintering plants in China and the percentage of plants with desulfurization systems between 2003 and 2012.

The annual TEQ emissions released in flue gas and gypsum by the sintering industry from 2003 to 2012 were estimated, and the results are shown in Figure 4. Annual TEQ emissions to the atmosphere from Chinese sintering plants gradually decreased as the percentage of plants with desulfurization systems increased. In contrast, TEQ emissions in gypsum increased. The total TEQ emitted in gypsum between 2003 and 2012 was found to be 1878 g of I-TEQ, which accounted for 12.1% of the total PCDD/F TEQs emitted to the atmosphere (15486 g of I-TEQ). It is noteworthy that PCDD/Fs in gypsum are not effectively eliminated and will probably reenter the environment and become a new source of PCDD/Fs. Therefore, the risks posed by PCDD/Fs in gypsum are important and should be managed more effectively than they are currently. We speculate that desulfurization might play a key role in controlling PCDD/F emissions. All sintering plants

will have to be fitted with desulfurization systems by the end of 2015 to meet Chinese legislation, and we estimate that only 735 g of PCDD/Fs will be emitted annually by Chinese sintering plants from that time.

It is important to identify key regions in which sintering plants emit PCDD/Fs, and this is an essential primary step when developing and implementing emission controls. The spatial distributions of PCDD/Fs emitted by the Chinese sintering industry in 2003 and 2012 are shown in Figure 5. Five provinces in North China (Hebei, Shanxi, Tianjin, Inner Mongolia, and Beijing) are the main areas in which PCDD/Fs are emitted by the sintering industry. PCDD/F emissions in this region accounted for 40.0% of all industrial emissions of PCDD/Fs in 2003, but this had decreased to 35.9% in 2012. The decrease may have been caused by the percentage of plants with desulfurization systems increasing to 47.9% by 2012. The same region also suffers from serious air pollution that causes toxic effects. It is possible that these pollutants may exist in symbiotic relationships, which will be a reference for future research into synergistic decreases in emissions. Sintering flue gas contains not only PCDD/Fs but also brominated dibenzo-*p*-dioxins and dibenzofurans, halogenated polycyclic aromatic hydrocarbons, polychlorinated biphenyls, and polychlorinated naphthalenes. Using desulfurization systems could lead to synergistic decreases in emissions of these unintentionally produced persistent organic pollutants (UP-POPs) that have properties similar to those of PCDD/Fs. Moreover, appropriate emphasis should be placed on controlling UP-POPs in gypsum as these compounds are not effectively eliminated.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.est.5b06095](https://doi.org/10.1021/acs.est.5b06095).

Operational information about sintering plants (Table S1), PCDD/F mass balances (Table S2), total PCDD to total PCDF concentration ratios and average degrees of chlorination in flue gas samples (Table S3), particle sizes and Brunauer–Emmett–Teller surface areas of fly ashes from the first to the fourth stages of the precipitators in plants DH and TS (particle size = mean volume) (Table S4), removal efficiencies of PCDD/Fs homologues (Figure S1), PCDD/F homologue distributions in the

Figure 5. Spatial distributions of PCDD/F emissions (kilograms of I-TEQ) from sintering plants in 2003 (left) and 2012 (right). The percentage of plants with desulfurization systems in the region of interest in 2012 is shown in the pie chart.

fly ash samples (Figure S2), and annual production of sintering ore in China (Figure S3) ([PDF](#))

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Notes

The authors declare no competing financial interest.

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