Atmospheric Emission of PCDD/Fs, PCBs, Hexachlorobenzene, and Pentachlorobenzene from the Coking Industry

GUORUI LIU, MINGHUI ZHENG,*
WENBIN LIU, CHENGZHI WANG,
BING ZHANG, LIRONG GAO, GUIJIN SU,
KE XIAO, AND PU LV

State Key Laboratory of Environmental Chemistry and
Ecotoxicology, Research Center for Eco-Environmental
Sciences, Chinese Academy of Sciences, P.O. Box 2871,
Beijing 100085, China

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The coking process is considered to be a potential source of unintentionally produced persistent organic pollutants (UP-POPs). However, intensive studies on the emission of UP-POPs from the coking industry are still very scarce. Emission of polychlorinated dibenzo-p-dioxins/dibenzofurans (PCDD/Fs), dioxin-like polychlorinated biphenyls (dl-PCBs), hexachlorobenzene (HxCBz), and pentachlorobenzene (PeCBz) covered under the Stockholm Convention were investigated for the coking process in this study. Stack gases from some typical coke plants in China were collected and analyzed to estimate the emission of UP-POPs from the coking industry. Emission factors of 28.9 ng WHO-TEQ tonne^{-1} for PCDD/Fs, 1.7 ng WHO-TEQ tonne^{-1} for dl-PCBs, 596 ng tonne^{-1} for HxCBz, and 680 ng tonne^{-1} for PeCBz were derived based on the investigated data. The annual emissions from the global coking industry were estimated to be 15.8 g WHO-TEQ for PCDD/Fs, 0.93 g WHO-TEQ for dl-PCBs, 333 g for HxCBz, and 379 g for PeCBz, respectively (reference year 2007). According to the distribution of PCDD/Fs, we argued for the de novo synthesis to be the major pathway of PCDD/F formation. With regard to the characteristics of dl-PCBs, the most abundant congener was CB-118, and the most dominant contributor to the total WHO-TEQ of dl-PCBs was CB-126.

Introduction

Persistent organic pollutants (POPs) are extremely harmful to human health and the environment because of their high toxicity, persistence in the environment, and bioaccumulation through the food web. Once released into the environment, they can be transported and distributed on a global scale by the grasshopper effect and global fractionation (1, 2). Minimizing environmental exposure to POPs is an important public goal for environmental protection, also with respect to sustainable development. As it is very difficult to eliminate POPs by photodegradation, chemical degradation, or biodegradation under environmental conditions due to their high stability and persistence (3), controlling and regulating the emission of unintentionally produced POPs

(UP-POPs) from key sources is one of the most effective measures for protecting our environment and human health from POPs (4–6).

Evaluating the emissions of UP-POPs from sources is important for applying the best available technology/best environmental practice (BAT/BEP) to priority sources and developing a POP inventory. Many sources for the emission of UP-POPs have been identified and quantified (7, 8), and the effects of various parameters on the formation of UP-POPs have been demonstrated in many studies (9–13). Sources of POPs and their relative importance have changed substantially over the past several decades. Municipal waste incineration was previously a major contributor of UP-POPs to the environment, but following the implementation of various regulations, and improvements in combustion technology and emission cleaning techniques, this is now generally considered to have a lower contribution to the total emissions to air. Thus, some other potential sources have recently received considerable attention. However, there are still uncertainties about the flux of UP-POPs into the environment for some potential sources.

The activity rate of coke production has been tremendous in recent years. In 2007, the global output reached about 558 million tonnes. China is the largest coke producing country, accounting for about 60% of global coke production in 2007, with many coke plants that use a variety of different scales and techniques. Although the coking process is a well-known source of polycyclic aromatic hydrocarbons (PAHs) (14), it is not yet widely recognized as a UP-POP source. Investigations into UP-POP emissions from coke plants in China are significant for evaluating release of UP-POPs from the global coking industry. Nevertheless, intensive investigations into the emission of UP-POPs, including polychlorinated dibenzo-p-dioxins/dibenzofurans (PCDD/Fs), dioxin-like polychlorinated biphenyls (dl-PCBs), hexachlorobenzene (HxCBz), and pentachlorobenzene (PeCBz), which are covered under the Stockholm Convention, have not been carried out for the coking process.

Few investigations on PCDD/F emissions from the coking industry have been carried out to date. Bremmer et al. (15) reported the monitoring results of PCDD/F emissions from a coke plant. The emission concentration in the exit gas and the annual emission of the plant were 0.15 ng I-TEQ m^{-3} and 0.2 g I-TEQ year^{-1} , respectively. An emission factor of 0.3 μg I-TEQ per tonne of coke produced (equal to 0.23 μg I-TEQ per tonne of feedstock) was derived and comprehensively used for evaluation of PCDD/F emissions from coke production in some inventories (16). The PCDD/F emissions from a coke plant located in an industrial park were investigated by Wang et al. (17), and the mean concentration of PCDD/Fs in stack gas was 8.7 pg I-TEQ Nm^{-3} . The derived emission factor was 13.4 ng I-TEQ per tonne of feedstock, and the estimated annual PCDD/F emission was 89 mg I-TEQ yr^{-1} for this plant. Compared with PCDD/Fs, investigations on dl-PCB emissions from coke plants are even more scarce. With regard to HxCBz and PeCBz, no intensive studies on HxCBz and PeCBz emissions during the coking process have been reported to our knowledge. Since large discrepancies in scales and techniques exist for the global coking industry, large uncertainties would be present when estimating the PCDD/F release from the global coking industry based on the current two case studies. Thus, a preliminary investigation that aimed to identify the potential sources of PCDD/Fs and dl-PCBs was carried out, and the levels emitted from three coke plants were reported (18). The primary aim of the present

* Corresponding author phone: 8610-6284-9172; fax: 8610-6292-3563; e-mail: zhengmh@rcees.ac.cn.

TABLE 1. Basic Information of the Investigated Coke Plants

	CP-1	CP-2	CP-3	CP-4	CP-5	CP-6	CP-7	CP-8
annual capacity (million tonne)	1	2.2	2.4	1	1	0.96	0.6	0.7
technique of coal charging	TC ^a	TC	TC	SC ^b	TC	SC	TC	TC
height of ovens (m)	4.3	7.3	4.3	4.3	6	4.3	4.3	4.3
coke quenching method	water	nitrogen	water	water	water	water	water	water
air pollution control device	BFs ^c	BFs	BFs	BFs	BFs	BFs	BFs	BFs
average flow rate (Nm ³ h ⁻¹)	60000	245800	87100	89000(PC) 46900(CC)	81000	105900	70800	78500
operating time per year (h)	8760	8760	8760	8760	8760	8760	8760	8760
output rate (T h ⁻¹)	114	251	75	114	114	75	52	80
sampling point	B ^d	B	B	A ^e , B	B	B	A	A

^a Top charging. ^b Stamp charging. ^c Baghouse filters. ^d Termed as waste gas emitted during pushing of coke. ^e Termed as waste gas emitted during charging of coal.

study was to derive the emission factors and evaluate the emission amounts of these selected UP-POPs from coking industry.

In this study, the coking process was identified as a source of these selected UP-POPs, and their emissions were quantified. Emission levels and characteristics are presented and discussed for different units (pushing of coke and charging of coal) in the coking process. Emission factors of these UP-POPs were also derived and used to estimate the emissions of these UP-POPs from the coking industry. These data are helpful for understanding the contribution of UP-POPs from the coking industry and developing an emission inventory of POPs.

Experimental Section

Sampling. Coke is produced by carbonization of coal in coke ovens. Coal is charged into the ovens and they are then subjected to external heating to approximately 1000 °C in the absence of air. Coke is then removed and quenched with water or dry inert gas. Formation and emission of UP-POPs might occur during charging of coal (CC) and pushing of coke (PC) in the coking process. To evaluate the emission of UP-POPs from the coking industry, eight typical coke plants in China were selected. For these coke plants, two separate dust arrestors (baghouse filters, BFs) were used for the treatment of gas released from CC and PC. For a few coke plants in China, such as the CP-1 and CP-2 plants, special techniques are used for the CC, and hardly any waste gas is released when the coal is charged into the ovens. Therefore, no stack was built for conducting the released gas. Although there are hundreds of coke plants in China, many plants are not suitable for field sampling of both CC and PC. To determine the release of UP-POPs during CC and PC, stack gases emitted during CC were collected for CP-7 and CP-8 plants, and those emitted during PC were collected for CP-3, CP-5, and CP-6 plants. To estimate the emission contribution during CC and PC, the stack gas samples from CC and PC were simultaneously collected and analyzed for CP-4. The basic information of the eight coke plants is described in Table 1. The stack gas samples released during CC and PC were termed as sampling point A and B, respectively. The schematics of basic coking process and air pollution control system for CC and PC are shown in Figures S1 and S2, respectively.

The stack gas samples were collected by an automatic isokinetic sampling system Isostack Basic (TCR TECORA, Italy) according to U.S. EPA Method 23. The sampling train was mainly composed of a heated probe, a filter box equipped with a quartz fiber filter, and a water-cooled XAD-2 adsorbent trap. A schematic of the sampling system is shown in Figure S3. Five surrogate ¹³C₁₂-PCDD/Fs (³⁷Cl₄-PCDD/Fs) target compounds (Wellington Laboratories, Guelph, Canada) were added into the XAD-2 resin in the adsorbent sampling

cartridge before sampling. All samples were tightly wrapped in aluminum foil to minimize contamination and loss. At the end of the sampling trip, the samples were immediately transferred to a refrigerator where they were stored until analysis.

Sample Preparation and Analysis. Analysis of PCDD/Fs and dl-PCBs was carried out based on U.S. EPA Methods 23 and 1668A modifications. Briefly, when analyzed, the samples were spiked with known amounts of ¹³C₁₂-PCDD/F internal standards and a ¹³C₁₂-PCB mixture (Wellington Laboratories, Guelph, Canada). They were then Soxhlet extracted with 250 mL of toluene for about 24 h, and the extracts were concentrated with a rotary evaporator. The concentrated sample extract was then subjected to a series of cleanup by adsorption chromatography, including a 44% sulfuric acid-treated silica column and a multilayer silica gel column. PCDD/Fs and PCBs were fractionated by basic alumina column. Finally, all fractions were reduced to about 20 µL by rotary evaporator and a gentle stream of nitrogen. Prior to injection, ¹³C₁₂-labeled PCDD/F and ¹³C₁₂-labeled PCB injection standards were added into the corresponding fractions for calculation of the recoveries.

The PCDD/F and dl-PCB analyses were performed by an Agilent 6890 gas chromatograph coupled with a Waters Autospec Ultima high-resolution mass spectrometer (MS) by tracing the M⁺, (M + 2)⁺, or the most intensive ions of the isotope cluster. A DB-5 ms fused-silica column (60 m × 0.25 mm i.d. × 0.25 µm) was used for the separation of congeners. The mass range of the MS was calibrated by perfluorokerosene, and the MS was tuned and operated at ≥10 000 resolution with 38 eV EI energy. Selected ion monitoring (SIM) mode was used for data acquisition. For the analysis of HxCBz and PeCBz, the samples were spiked with known amounts of ¹³C₆-HxCBz before extraction. The extraction and cleanup of HxCBz and PeCBz in stack gas samples followed the same procedure as that for the dl-PCBs. The analysis of HxCBz and PeCBz was carried out by an Agilent 6890 gas chromatograph equipped with a HP-5MS capillary column (30 m × 0.32 mm i.d. × 0.25 µm) and interfaced to an Agilent 5973N MS. The data were acquired in SIM mode by tracing the two most abundant ions of the molecular ion clusters, and ¹³C₆-HxCBz was used as an isotope internal standard for quantitative determination of HxCBz and PeCBz.

The sampling recoveries of five ¹³C₁₂-PCDD/F surrogate standards were measured relative to the ¹³C₁₂-PCDD/F internal standards and are a measure of the collection efficiency. In this study, the recoveries were in the range 71–95% for the five surrogate ¹³C₁₂-labeled PCDD/F sampling standards. The recoveries of nine ¹³C₁₂-labeled PCDD/F internal standards were from 40 to 95%, and the recoveries of ¹³C₁₂-labeled PCB standards were in the range 56%–116%. The recoveries of ¹³C₆-HxCBz were in the range 44%–72%.

TABLE 2. Average Concentrations (pg Nm⁻³ or pg TEQ Nm⁻³, *n* = 3) of the Selected POPs in Samples

	Σ2378-PCDD/Fs	ΣWHO-TEQ (PCDD/Fs)	ΣI-TEQ (PCDD/Fs)	Σdl-PCBs	ΣWHO-TEQ (dl-PCBs)	HxCBz	PeCBz
CP-1	388	25.6	24.1	329	1.02	439	463
CP-2	156	11.2	9.6	1245	0.74	351	661
CP-3	97.3	11.1	7.2	1021	0.51	312	480
CP-4 (PC)	159	13.7	10.9	2549	1.41	816	356
CP-4 (CC)	1023	89.3	79.4	4648	4.79	491	402
CP-5	173	11.6	9.7	406	0.49	322	405
CP-6	73.9	4.9	4.2	396	0.27	182	209
CP-7	126	5.5	5.0	98.7	0.30	183	274
CP-8	106	11.1	8.1	2016	0.77	313	353

Blank experiments were carried out for every batch of samples. Detailed information on the sample collection, preparation, analysis, and quality control can be found in the Supporting Information.

Results and Discussion

Emission Levels. The concentrations of the UP-POPs in the stack gas samples converted to dry standard conditions (273 K and 101.3 kPa) are shown in Table 2. WHO-TEF values by Van den Berg et al. (19) were adopted for calculating the TEQs of PCDD/Fs and dl-PCBs. For congeners with concentrations below the LOD, a value of LOD/2 was assigned for calculating the total concentration.

Bremmer et al. (15) reported that the level of PCDD/Fs in exit gas from a coke plant was 150 pg I-TEQ Nm⁻³. Wang et al. (17) investigated a coke plant and determined the concentration of PCDD/Fs to be 8.7 pg I-TEQ Nm⁻³. From Table 2, it can be seen that the concentrations of PCDD/Fs ranged from 4.9 to 89.3 pg WHO-TEQ Nm⁻³ among the Chinese coke plants. The concentrations of PCDD/Fs for the coke plants investigated in this study were lower than that reported by Bremmer et al. (15), but comparable with that reported by Wang et al. (17). The concentrations of dl-PCBs ranged from 0.27 to 4.79 pg WHO-TEQ Nm⁻³ for the investigated plants. These values are lower than the dl-PCB emissions from the iron ore sintering plants with coke as fuel in the UK, which had a range of 42–111 pg WHO-TEQ Nm⁻³ (20). As for HxCBz, investigations on HxCBz emissions during the coking process have not been reported to our knowledge, existing studies on unintentional release of HxCBz from stationary sources have mainly focused on waste and coal combustion, metals production, chemicals manufacture, and so on (6, 21–23). To explore the priority sources for applying BAT/BEP to reduce the release of UP-POPs, the emission levels of UP-POPs during the coking process were compared with those from other industrial sources. For example, Grochowalski and Konieczny (24) reported that the HxCBz concentrations in flue gas from coal-fired circulated fluidized bed (CFB) boilers ranged from 11.5 to 42.0 ng Nm⁻³. Aittola et al. (25) investigated the HxCBz emission from an aluminum smelter plant with baghouse filters as air pollution control device (APCD), and the concentration of HxCBz was 2.66 μg m⁻³. In this study, the concentrations of HxCBz ranged from 182 to 816 pg Nm⁻³, which are far lower than that of the CFB boilers and the aluminum smelter plant. Due to the inclusion of PeCBz in the UN-ECE POP protocol (26) and Stockholm Convention, public attention to the sources and environmental levels of PeCBz has recently been aroused. Although the environmental levels of PeCBz have been reported in some work (27, 28), investigations into unintentional emission of PeCBz from industrial sources are rare. Existing studies on unintentional release of PeCBz have mainly focused on chemicals manufacture, waste incineration, and so on, and the reported emission levels of PeCBz from waste incineration were in the range 0.42–39 μg Nm⁻³ (27). In this study, the concen-

trations of PeCBz in stack gas samples from the coking process ranged from 209 to 661 pg Nm⁻³, these values are far lower than that of waste incineration reported by Bailey et al. (27). It can be seen that the concentration of PCDD/Fs and dl-PCBs from CC was slightly higher than that from PC. The difference between CC and PC for HxCBz and PeCBz concentrations was not very obvious.

Routine measurement of dioxins is currently complicated and expensive. Correlation among the related chlorinated organic compounds exists for some sources (29, 30), and efforts have been made to identify surrogates for the determination of PCDD/F concentrations in flue gas (31, 32). For example, öberg and Bergström (33) suggested that HxCBz is a suitable surrogate for PCDD/F formation from the combustion of hazardous and municipal wastes on an industrial scale. In this study, to explore the possible indicators for dioxins emitted from the coking industry, the correlation among PCDD/Fs, dl-PCBs, HxCBz, and PeCBz in the samples from the eight coke plants was also analyzed by linear fitting. These correlations are shown in Figure S4. The correlations between the PCDD/Fs and HxCBz, PCDD/Fs and PeCBz, dl-PCBs and HxCBz, dl-PCBs and PeCBz were not strong for the coking process in this study. Although the linear correlation between the concentrations of PCDD/Fs and dl-PCBs was not very strong (*R* was around 0.63; *p* < 0.01), a very good linear relation ([WHO-TEQ of PCDD/Fs] = 17.7 × [WHO-TEQ of dl-PCBs] – 0.66; *R* = 0.94; *p* < 0.01) was observed between the WHO-TEQs of PCDD/Fs and the WHO-TEQ of dl-PCBs. The WHO-TEQs of PCDD/Fs were about 18 times of those of dl-PCBs, thus the WHO-TEQs of PCDD/Fs might be inferred from the WHO-TEQs of dl-PCBs, which could save the cost of PCDD/F analysis.

Emission Characteristics. The congener profiles of seventeen 2378-substituted PCDD/Fs and twelve dl-PCBs were selected as the fingerprints of PCDD/F and dl-PCB emissions from the coke plants. To evaluate the distribution of PCDD/F and dl-PCB patterns in stack gases from the coke plants, the concentrations of PCDD/F and dl-PCB congeners were normalized to the percent of the sum of 2378-substituted PCDD/Fs and the sum of dl-PCBs, respectively. Figure 1 demonstrates the emission patterns for CC and PC. A strong resemblance between the patterns might indicate similar formation mechanisms for PCDD/Fs and dl-PCBs during CC and PC. The PCDD/F congener pattern was very similar to that obtained by Bremmer et al. (15) and Wang et al. (17).

It was found that more highly chlorinated congeners were the dominant species for 2378-substituted PCDD/Fs. Four congeners, comprising OCDD, 1234678-HpCDD, 1234678-HpCDF, and OCDF were the dominant species, which together took up around 65% of the total seventeen 2378-substituted PCDD/Fs. Many other studies (31, 34, 35) have also confirmed that OCDD, HpCDD, HpCDF, and OCDF are major contributors to the total 2378-substituted congeners for thermal-related sources. Homologue profiles of PCDD/Fs are normally correlated with different pathways of dioxin formation. In this study, the homologue profiles of PCDD/Fs

FIGURE 1. Fingerprints of 2378-PCDD/Fs and dl-PCBs from the coking process.

FIGURE 2. Homologue profiles of PCDD/Fs from the coking process.

are presented in Figure 2. A strong resemblance was observed between the coking process and other thermal sources (36–38).

Different ratios of PCDFs to PCDDs ($R_{DF/DD}$) normally indicate different mechanisms of PCDD/F formation. For precursor formation of PCDD/Fs, some research has shown that $R_{DF/DD}$ was much lower than 1 (39–42). On the other hand, de novo synthesis normally requires an $R_{DF/DD}$ of greater than 1 (36, 39). The degree of chlorination is normally used to indicate the distribution of different chlorinated homologues. It is the sum of the percentages of the homologues multiplied by the numbers of substituted chlorines on the homologues (36). The $R_{DF/DD}$ values and the degree of chlorination are given in Table 3, and it can be seen that the ratio of PCDFs to PCDDs is greater than 1. Finally, de novo synthesis was assumed to be the main formation mechanism of PCDD/Fs during the coking process according to the characteristics and distribution of PCDD/Fs ($R_{DF/DD} > 1$).

With respect to dl-PCBs, CB-118 contributed over 40% of the total dl-PCBs in terms of concentration, followed by CB-105 and CB-77. These three dl-PCB congeners together accounted for about 80% of the total concentration of the

TABLE 3. Ratios of PCDFs to PCDDs, and Degree of Chlorination of PCDDs and PCDFs

	ratio of PCDFs to PCDDs						degree of chlorination	
	tetra	penta	hexa	hepta	octa	total	PCDDs	PCDFs
CP-1	2.4	1.2	2.5	0.9	0.6	1.5	6.0	5.7
CP-2	3.5	1.5	2.5	1.2	0.7	1.8	6.1	5.6
CP-3	4.1	1.3	4.0	1.4	0.5	1.5	6.7	6.0
CP-4(PC)	4.3	3.9	4.5	1.6	0.4	2.3	6.4	5.2
CP-4(CC)	5.0	2.8	3.8	2.1	0.6	2.7	6.2	5.7
CP-5	3.0	3.3	4.8	1.6	0.3	1.8	6.6	5.5
CP-6	4.3	2.4	4.0	1.7	0.3	1.6	6.7	5.5
CP-7	3.4	1.6	2.4	1.9	0.6	1.3	6.9	6.0
CP-8	1.8	2.4	3.1	1.2	0.3	1.1	6.7	5.7
average	3.5	2.3	3.5	1.5	0.5	1.7	6.5	5.7

twelve dl-PCBs. Although the percentage of CB-126 in the total dl-PCBs was less than 5% in terms of concentration, CB-126 was the most predominant toxic contributor, contributing around 80% of the total dl-PCB TEQ, due to its high WHO-TEF compared with the other dl-PCB

FIGURE 3. Distribution of the selected UP-POPs from the coking process.

congeners. This hints that the total toxicity of PCDD/Fs and dl-PCBs might be inferred from CB-126 by combining the linear correlation obtained in Figure S4. Aries et al. (20) reported the pattern of the twelve dl-PCB congeners obtained for iron ore sintering with coke as fuel, and a similar emission pattern between the iron ore sintering and the coking process was observed. Finally, the distributions of PCDFs, PCDDs, dl-PCBs, HxCBz, and PeCBz are given in Figure 3, and it can be seen that the trends of these UP-POPs for the coking process were dl-PCBs > PCDFs $\approx$ PeCBz $\approx$ HxCBz > PCDDs, which is a distribution similar to that of the iron and steel industry (34).

Emission Factors and Estimation of Annual Emission.

An emission factor can be defined as the average emission rate of a given pollutant relative to the intensity of a specific activity for a given source. An emission amount could be estimated from an emission factor by assuming a linear relation between the intensity of the activity and the emission resulting from this activity. The emission factor and emission amount are normally calculated by the following equations:

$$\text{Emission factor} = \frac{(\text{flow rate} \times \text{concentration})}{\text{output rate (or feeding rate)}}$$

$$\text{Emission}_{\text{pollutant}} = \text{Activity level} \times \text{Emission factor}_{\text{pollutant}}$$

In this study, emission factors of investigated UP-POPs were derived based on the investigated data. The derived emission factors are listed in Table S3.

Stack gases collected from CP-4(CC), CP-7, and CP-8 plants were classified as CC, and it was calculated that the average emission factors during CC were 18.4 ng WHO-TEQ tonne^{-1} (15.8 ng I-TEQ tonne^{-1}), 1.05 ng WHO-TEQ tonne^{-1} , 253 ng tonne^{-1} , and 295 ng tonne^{-1} for PCDD/Fs, dl-PCBs, HxCBz, and PeCBz, respectively. From the data of CP-1, CP-2, CP-3, CP-4(PC), CP-5, and CP-6 plants, the average emission factors during PC were derived to be 10.6 ng WHO-TEQ tonne^{-1} (8.6 ng I-TEQ tonne^{-1}), 0.61 ng WHO-TEQ tonne^{-1} , 343 ng tonne^{-1} , and 385 ng tonne^{-1} for PCDD/Fs, dl-PCBs, HxCBz, and PeCBz, respectively. Thus, the average emission factors for the sums of CC and PC were 28.9 ng WHO-TEQ tonne^{-1} (24.4 ng I-TEQ tonne^{-1}), 1.7 ng WHO-TEQ tonne^{-1} , 596 ng tonne^{-1} , and 680 ng tonne^{-1} for PCDD/Fs, dl-PCBs, HxCBz, and PeCBz, respectively.

The emission factor of PCDD/Fs derived in this study was about 1 order of magnitude lower than that (0.3 μg I-TEQ tonne^{-1}) suggested by the UNEP PCDD/PCDF Toolkit in 2005. From the emission factor of dl-PCBs, it

can be seen that the toxic contribution of dl-PCBs accounted for about 5% of PCDD/F toxicity during coke production, and the emission factor of dl-PCBs was lower than that (averaging 0.13 μg I-TEQ tonne^{-1} sinter) of iron ore sintering plants with coke as fuel in the UK (20). With regard to HxCBz and PeCBz, the derived emission factor for coke production was relatively low compared with other sources, such as waste incineration, secondary copper production, cement production, and so on (6, 27). Taking the output of coke in 2007 as an example, the global output of coke reached about 558 million tonnes. The emission amounts of PCDD/Fs, dl-PCBs, HxCBz, and PeCBz were estimated to be 15.8 g WHO-TEQ (13.3 g I-TEQ), 0.93 g WHO-TEQ, 333 and 379 g, respectively, based on the emission factors derived in this study. These data might be helpful for understanding the levels of UP-POPs produced by the coking industry and in developing a POP inventory.

Acknowledgments

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Supporting Information Available

The basic coking process, air pollution control system for CC and PC, sample collection, preparation and analysis, the emission factors for the investigated coke plants, and the correlation among 2378-PCDD/Fs, dl-PCBs, HxCBz, and PeCBz. This material is available free of charge via the Internet at <http://pubs.acs.org>.

Literature Cited

- Wania, F. Assessing the potential of persistent organic chemicals for long-range transport and accumulation in polar regions. *Environ. Sci. Technol.* **2003**, *37*, 1344–1351.
- Gouin, T.; Mackay, D.; Jones, K. C.; Harner, T.; Meijer, S. N. Evidence for the “grasshopper” effect and fractionation during long-range atmospheric transport of organic contaminants. *Environ. Pollut.* **2004**, *128*, 139–148.
- Weber, R. Relevance of PCDD/PCDF formation for the evaluation of POPs destruction technologies - Review on current status and assessment gaps. *Chemosphere* **2007**, *67*, S109–S117.
- Weber, R.; Gaus, C.; Tysklind, M.; Johnston, P.; Forter, M.; Hollert, H.; Heinisch, E.; Holoubek, I.; Lloyd-Smith, M.; Masunaga, S.; Moccarelli, P.; Santillo, D.; Seike, N.; Symons, R.; Torres, J. P. M.; Verta, M.; Varbelow, G.; Vijgen, J.; Watson, A.; Costner, P.; Woelz,

- J.; Wycisk, P.; Zennegg, M. Dioxin- and POP-contaminated sites-contemporary and future relevance and challenges. *Environ. Sci. Pollut. Res.* **2008**, *15*, 363–393.
- (5) Breivik, K.; Alcock, R.; Li, Y. F.; Bailey, R. E.; Fiedler, H.; Pacyna, J. M. Primary sources of selected POPs: regional and global scale emission inventories. *Environ. Pollut.* **2004**, *128*, 3–16.
 - (6) Bailey, R. E. Global hexachlorobenzene emissions. *Chemosphere* **2001**, *43*, 167–182.
 - (7) Gullett, B. K.; Touati, A.; Hays, M. D. PCDD/F, PCB, HxCBz, PAH, and PM emission factors for fireplace and woodstove combustion in the San Francisco Bay region. *Environ. Sci. Technol.* **2003**, *37*, 1758–1765.
 - (8) Gullett, B. K.; Touati, A. PCDD/F emissions from forest fire simulations. *Atmos. Environ.* **2003**, *37*, 803–813.
 - (9) Gullett, B. K.; Lemieux, P. M. Role of combustion and sorbent parameters in prevention of polychlorinated dibenzo-p-dioxin and polychlorinated dibenzofuran formation during waste combustion. *Environ. Sci. Technol.* **1994**, *28*, 107–118.
 - (10) Gullett, B. K.; Raghunathan, K. Observations on the effect of process parameters on dioxin/furan yield in municipal waste and coal systems. *Chemosphere* **1997**, *34*, 1027–1032.
 - (11) Pandelova, M. E.; Lenoir, D.; Kettrup, A.; Schramm, K. W. Primary measures for reduction of PCDD/F in co-combustion of lignite coal and waste: Effect of various inhibitors. *Environ. Sci. Technol.* **2005**, *39*, 3345–3350.
 - (12) Wikström, E.; Ryan, S.; Touati, A.; Gullett, B. K. Key parameters for de novo formation of polychlorinated dibenzo-p-dioxins and dibenzofurans. *Environ. Sci. Technol.* **2003**, *37*, 1962–1970.
 - (13) Wikström, E.; Ryan, S.; Touati, A.; Telfer, M.; Tabor, D.; Gullett, B. K. Importance of chlorine speciation on de Novo formation of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans. *Environ. Sci. Technol.* **2003**, *37*, 1108–1113.
 - (14) Yang, H. H.; Lee, W. J.; Chen, S. J.; Lai, S. O. PAH emission from various industrial stacks. *J. Hazard. Mater.* **1998**, *60*, 159–174.
 - (15) Bremmer, H. J.; Troost, L. M.; de Kuipers, G.; Koning, J. Sein, A. A. In *Emissions of Dioxins in the Netherlands*; Report No. 770501018; RIVM; Bilthoven, Netherlands, 1994.
 - (16) Eduljee, G. H.; Dyke, P. An updated inventory of potential PCDD and PCDF emission sources in the UK. *Sci. Total Environ.* **1996**, *177*, 303–321.
 - (17) Wang, J. B.; Hung, C. H.; Hung, C. H.; Chang-Chien, G. P. Polychlorinated dibenzo-p-dioxin and dibenzofuran emissions from an industrial park clustered with metallurgical industries. *J. Hazard. Mater.* **2009**, *161*, 800–807.
 - (18) Liu, G.; Zheng, M.; Ba, T.; Liu, W.; Guo, L. A preliminary investigation on emission of polychlorinated dibenzo-p-dioxins/dibenzofurans and dioxin-like polychlorinated biphenyls from coke plants in China. *Chemosphere* **2009**, *75*, 692–695.
 - (19) Van den Berg, M.; Birnbaum, L.; Bosveld, A. T. C.; Brunstrom, B.; Cook, P.; Feeley, M.; Giesy, J. P.; Hanberg, A.; Hasegawa, R.; Kennedy, S. W.; Kubiak, T.; Larsen, J. C.; van Leeuwen, F. X. R.; Liem, A. K. D.; Nolt, C.; Peterson, R. E.; Poellinger, L.; Safe, S.; Schrenk, D.; Tillitt, D.; Tysklind, M.; Younes, M.; Waern, F.; Zacharewski, T. Toxic equivalency factors (TEFs) for PCBs, PCDDs, PCDFs for humans and wildlife. *Environ. Health Perspect.* **1998**, *106*, 775–792.
 - (20) Aries, E.; Anderson, D. R.; Fisher, R.; Fray, T. A. T.; Hemfrey, D. PCDD/F and “dioxin-like” PCB emissions from iron ore sintering plants in the UK. *Chemosphere* **2006**, *65*, 1470–1480.
 - (21) Meijer, S. N.; Ockenden, W. A.; Sweetman, A.; Breivik, K.; Grimalt, J. O.; Jones, K. C. Global distribution and budget of PCBs and HCB in background surface soils: Implications for sources and environmental processes. *Environ. Sci. Technol.* **2003**, *37*, 667–672.
 - (22) Grochowalski, A.; Lassen, C.; Holtzer, M.; Sadowski, M.; Hudyma, T. Determination of PCDDs, PCDFs, PCBs and HCB emissions from the metallurgical sector in Poland. *Environ. Sci. Pollut. Res.* **2007**, *14*, 326–332.
 - (23) Barber, J. L.; Sweetman, A. J.; van Wijk, D.; Jones, K. C. Hexachlorobenzene in the global environment: Emissions, levels, distribution, trends and processes. *Sci. Total Environ.* **2005**, *349*, 1–44.
 - (24) Grochowalski, A.; Konieczynski, J. PCDDs/PCDFs, dl-PCBs and HCB in the flue gas from coal fired CFB boilers. *Chemosphere* **2008**, *73*, 97–103.
 - (25) Aittola, J. P.; Paasivirta, J.; Vattulainen, A.; Sinkkonen, S.; Koistinen, J.; Tarhanen, J. Formation of chloroaromatics at a metal reclamation plant and efficiency of stack filter in their removal from emission. *Chemosphere* **1996**, *32*, 99–108.
 - (26) Lerche, D.; van de Plassche, E.; Schwegler, A.; Balk, F. Selecting chemical substances for the UN-ECE POP protocol. *Chemosphere* **2002**, *47*, 617–630.
 - (27) Bailey, R. E.; van Wijk, D.; Thomas, P. C. Sources and prevalence of pentachlorobenzene in the environment. *Chemosphere* **2009**, *75*, 555–564.
 - (28) Dvorska, A.; Lammel, G.; Klanova, J.; Holoubek, I.; Kosetice, Czech Republic - ten years of air pollution monitoring and four years of evaluating the origin of persistent organic pollutants. *Environ. Pollut.* **2008**, *156*, 403–408.
 - (29) Weber, R.; Iino, F.; Imagawa, T.; Takeuchi, M.; Sakurai, T.; Sadakata, M. Formation of PCDF, PCDD, PCB, and PCN in de novo synthesis from PAH: Mechanistic aspects and correlation to fluidized bed incinerators. *Chemosphere* **2001**, *44*, 1429–1438.
 - (30) Pandelova, M.; Lenoir, D.; Schramm, K. W. Correlation between PCDD/F, PCB and PCBz in coal/waste combustion. Influence of various inhibitors. *Chemosphere* **2006**, *62*, 1196–1205.
 - (31) Fiedler, H.; Lau, C.; Eduljee, G. Statistical analysis of patterns of PCDDs and PCDFs in stack emission samples and identification of a marker congener. *Waste Manage. Res.* **2000**, *18*, 283–292.
 - (32) Oh, J. E.; Touati, A.; Gullett, B. K.; Mulholland, J. A. PCDD/F TEQ indicators and their mechanistic implications. *Environ. Sci. Technol.* **2004**, *38*, 4694–4700.
 - (33) Öberg, T.; Bergström, J. G. T. Hexachlorobenzene as an indicator of dioxin production from combustion. *Chemosphere* **1985**, *14*, 1081–1086.
 - (34) Buekens, A.; Stieglitz, L.; Hell, K.; Huang, H.; Segers, P. Dioxins from thermal and metallurgical processes: recent studies for the iron and steel industry. *Chemosphere* **2001**, *42*, 729–735.
 - (35) Chang, M. B.; Huang, H. C.; Tsai, S. S.; Chi, K. H.; Chang-Chien, G. P. Evaluation of the emission characteristics of PCDD/Fs from electric arc furnaces. *Chemosphere* **2006**, *62*, 1761–1773.
 - (36) Everaert, K.; Baeyens, J. The formation and emission of dioxins in large scale thermal processes. *Chemosphere* **2002**, *46*, 439–448.
 - (37) Suzuki, K.; Kasai, E.; Aono, T.; Yamazaki, H.; Kawamoto, K. De novo formation characteristics of dioxins in the dry zone of an iron ore sintering bed. *Chemosphere* **2004**, *54*, 97–104.
 - (38) Xhrouet, C.; Pirard, C.; De Pauw, E. De novo synthesis of polychlorinated dibenzo-p-dioxins and dibenzofurans on fly ash from a sintering process. *Environ. Sci. Technol.* **2001**, *35*, 1616–1623.
 - (39) Altwicker, E. R. Formation of PCDD/F in municipal solid waste incinerators: Laboratory and modeling studies. *J. Hazard. Mater.* **1996**, *47*, 137–161.
 - (40) Altwicker, E.; Milligan, M. S. Dioxin formation from tetrachlorophenol over fly ash under breakthrough conditions. *Organohalogen Compd.* **1993**, *11*, 269–272.
 - (41) Huang, H.; Buekens, A. On the Mechanisms of Dioxin Formation in Combustion Processes. *Chemosphere* **1995**, *31*, 4099–4117.
 - (42) Luijk, R.; Akkerman, D. M.; Slot, P.; Olie, K.; Kapteijn, F. Mechanism of Formation of Polychlorinated Dibenzo-p-Dioxins and Dibenzofurans in the Catalyzed Combustion of Carbon. *Environ. Sci. Technol.* **1994**, *28*, 312–321.

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