



Concentrations, profiles, and emission factors of unintentionally produced persistent organic pollutants in fly ash from coking processes



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HIGHLIGHTS

- Fly ash was identified as a route of POPs release from the coking industry.
- Emission factors were derived for unintentionally produced POPs in coking ash.
- The data obtained were useful for developing an integrated source inventory.
- Congener profiles for the unintentionally produced POPs in coking ash are presented.

GRAPHICAL ABSTRACT



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ABSTRACT

The coking process has been found to be an important source of unintentionally produced persistent organic pollutants (UP-POPs). However, the concentrations, profiles, and emission factors of UP-POPs in fly ash from coke plants have not been studied. In this study, six UP-POPs (polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), polychlorinated biphenyls (PCBs), polychlorinated naphthalenes (PCNs), hexachlorobenzene (HxCBz), and pentachlorobenzene (PeCBz)) were identified and quantified in fly ash from eight coke plants. The average concentrations of the PCDDs, PCDFs, and “dioxin-like” PCBs were 1.5, 2.26, and 0.26 pg TEQ g⁻¹, respectively, and the average concentrations of the PCNs, HxCBz, and PeCBz were 256, 290, and 146 pg g⁻¹, respectively. The proportion each homolog contributed to the total concentration of the PCDFs, PCBs, and PCNs decreased with increasing chlorination level. The PCDFs contributed the biggest proportion of the total UP-POPs toxic equivalents (TEQs), and the average emission factors in fly ash were 10.5, 17.3, and 1.82 ng TEQ t⁻¹ for the PCDDs, PCDFs, and “dioxin-like” PCBs, respectively, and 1792, 2028, and 1025 ng t⁻¹ for the PCNs, HxCBz, and PeCBz, respectively. These data are essential for establishing an integrated UP-POP release inventory.

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1. Introduction

Since the discovery of polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) in flue gases and fly ash from municipal solid waste incinerators in 1977 [1],

the formation and emission of PCDDs and PCDFs (PCDD/Fs) and other “dioxin-like” (dl-) compounds has attracted increasing concern because of their adverse effects on the environment and human health [2–6]. Other dl-compounds, such as polychlorinated biphenyls (PCBs), polychlorinated naphthalenes (PCNs), hexachlorobenzene (HxCBz), and pentachlorobenzene (PeCBz), can also be unintentionally produced and released during thermal processes [7,8], and these chemicals (including the PCDD/Fs) are called unintentionally produced persistent organic pollutants

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Table 1
Basic information on the coke plants studied.

Site name	P1	P2	P3	P4	P5	P6	P7	P8
Height of ovens (m)	6	6	7.3	4.3	4.3	6	4.3	4.3
Annual capacity (million ton)	0.5	1.8	2.2	0.6	1	1	0.96	0.7
Coal charging technique	TC ^a	TC	TC	TC	SC ^b	TC	SC	TC
Coke quenching method	Water	Nitrogen	Nitrogen	Water	Water	Water	Water	Water
APCD ^c	BFs ^d	BFs	BFs	BFs	BFs	BFs	BFs	BFs
Origin of fly ash	PC ^e ; CC	PC ^f ; CC; QC ^g	PC;	PC	PC; CC	PC; CC	PC	CC; PC
Amount of fly ash produced for per ton of coke production (kg t ⁻¹)	7	6	5	9	9	6	10	7

^a Top charging.

^b Stamp charging.

^c Air pollution control device.

^d Bag filters.

^e The ash was collected during the pushing of the coke.

^f The ash was collected during the charging of the coal.

^g The ash was collected during the quenching of the coke.

(UP-POPs) [9]. Identifying and quantifying UP-POPs in various anthropogenic sources is the primary step in controlling their emission and reducing the environmental burden of, and human exposure to, these compounds [10,11].

Stack gas and residue emissions are the two main ways UP-POPs are released from industries that have major thermal processes. Heterogeneous reactions during thermal processes are the dominant UP-POP formation mechanisms [12], and fly ash is considered to be an important matrix for catalyzing these heterogeneous reactions because it contains relatively large amounts of carbon and catalytic elements [13–16]. High UP-POPs concentrations have been found in fly ash samples from various thermal industries, so fly ash is considered to be one of the most important sources of UP-POPs to the environment [17].

It has been speculated that the coking process is a potential source of UP-POPs, because it has conditions that are essential for UP-POP formation, including macromolecular materials in coal (the carbon source), chlorine (inorganic or organic), catalytic metal elements in the raw materials, and suitable temperature ranges. We have confirmed that the coking process is a potential source of UP-POPs by characterizing stack gas emissions from coking plants in previous studies [9,10]. However, concentrations, profiles, and emission factors of UP-POPs in fly ash from coking plants have not been reported up to now, and these are essential for developing an integrated UP-POP release inventory for the coking industry.

In this study, we collected fly ash samples from eight coke plants in China, and determined six types of UP-POPs in the samples using isotope dilution gas chromatography-mass spectrometry. The primary aims of the study were: (1) to quantify the concentrations of UP-POPs in fly ash samples from coking processes, to understand the release of UP-POPs in coking ash; (2) to assess the UP-POP profiles in fly ash, which could help understand the UP-POP formation mechanisms and identify specific sources; and (3) to derive emission factors for UP-POPs in fly ash, so that an integrated UP-POP release inventory for the coking industry can be developed. To the best of our knowledge, this is the first intensive investigation of the concentrations, profiles, and emission factors of UP-POPs in fly ash from the coking industry. Because of the scale of industrial activity in China, the UP-POP emission data for typical Chinese coke plants produced from this study might have significant implications for evaluating UP-POP emissions from the global coking industry.

2. Experimental

2.1. Sampling and information on the coke plants studied

Coke is produced by carbonizing coal in an oven that is externally heated to approximately 1000 °C in the absence of air. The

coke is removed from the oven and quenched with water or dry inert gas. The formation and emission of UP-POPs can occur during three different stages of the process, including charging the coal (CC), pushing the coke (PC), and quenching the coke (QC). The coke production process has been described in detail previously [9], and a schematic of the coking process is presented in the Supplementary Material (Fig. S1). In this study, UP-POPs were analyzed in fly ash emitted from eight coke plants that were of different sizes and that used different operational techniques. The height of the coke ovens in the plants ranged from 4.3 to 7.3 m, and the coke plants used either top charging or stamp charging of coal, and either water quenching or inert gas quenching of the coke. Samples of the fly ash produced during the CC, PC, and QC processes were collected separately, from the fabric bag filters used to clean the emissions. The origins (CC, PC, or QC) of the fly ash collected are given in Table 1. The fly ash samples were collected using a stainless steel spoon. Each composite fly ash sample comprised 3–6 sub-samples from the chosen sampling points. The fly ash samples were tightly wrapped in aluminum foil and sealed in polyethylene (PE) bags to avoid contamination and loss. The samples were stored in a refrigerator until analysis. Detailed information on the coke plants studied and on the fly ash samples collected is given in Table 1.

2.2. Chemical analysis

PCDDs, PCDFs, and PCBs were analyzed by isotope dilution high resolution gas chromatography-high resolution mass spectrometry (HRGC/HRMS), using modified US Environmental Protection Agency (EPA) methods 8290 (PCDD/Fs) and 1668A (PCBs). The detailed sample extraction, cleanup, and instrumental analysis procedures for the PCDD/Fs and dl-PCBs have been described in detail by Ba et al. [17]. Briefly, the fly ash samples were spiked with known amounts of ¹³C₁₂-labeled PCDD, PCDF, and PCB internal standards, treated with 1 mol L⁻¹ HCl, then Soxhlet extracted with 250 mL of toluene for about 24 h. The extracts were concentrated in a rotary evaporator, then subjected to a series of cleanup steps, including columns containing silica gel treated with 44% (by weight) sulfuric acid and multilayer silica gel columns. PCDDs, PCDFs, and PCBs were then fractionated using basic alumina columns, each of the fractions was reduced to about 20 μL by rotary evaporation and under a gentle stream of nitrogen, and ¹³C₁₂-labeled PCDD, PCDF, and PCB injection standards were added.

PCNs were analyzed using an isotope dilution HRGC/HRMS method that has been described previously [10,18]. Briefly, the samples were spiked with known amounts of ¹³C₁₀-labeled PCN internal standards (catalog no. ECN-5102, containing ¹³C₁₀-PCNs-27, -42, -52, -67, -73, and -75; Cambridge Isotope Laboratories, Andover, MA, USA). The samples were Soxhlet extracted and the

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