Occupational Exposure to Polychlorinated Dibenzo-*p*-dioxins and Dibenzofurans, Dioxin-like Polychlorinated Biphenyls, and Polychlorinated Naphthalenes in Workplaces of Secondary Nonferrous Metallurgical Facilities in China

Jicheng Hu, Minghui Zheng,* Wenbin Liu, Changliang Li, Zhiqiang Nie, Guorui Liu, Ke Xiao, and Shujun Dong

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

S Supporting Information

ABSTRACT: The concentrations of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), dioxin-like polychlorinated biphenyls (dl-PCBs), and polychlorinated naphthalenes (PCNs) were determined in workplace air from eight secondary nonferrous metal processing plants to investigate occupational exposure to these toxic compounds. The total estimated daily intakes of PCDD/Fs and dl-PCBs for workers by inhalation in the workplace were in the range of 0.15–9.91 and 0.13–8.59 pg of WHO-TEQ/kg of body weight (bw) for moderate and light activities, respectively. The daily inhalation doses for workers in the workplaces of three investigated plants exceeded the tolerable daily intake recommended by the World Health Organization. These results indicate that the risk of occupational exposure to dioxins by inhalation in the workplace of plants investigated was considerably high. For PCNs, the daily inhalation doses for workers in the workplace were in the range of 0.005–4.46 and 0.004–3.87 pg of TEQ/kg of bw for moderate and light activities, respectively, which were lower than those of dioxins. To identify the source of PCDD/Fs, PCBs, and PCNs in workplace air, their homologue profiles were compared with those in stack gas from the plants investigated. It was found that significant dioxin contamination in workplace air was mainly attributed to the emission of fugitive gas from smelting furnaces during reclamation processes.

■ INTRODUCTION

Secondary metal smelters primarily engage in the recovery of nonferrous metals and alloys from new and used scrap and dross. Scrap metal and metal wastes may contain organic materials, such as plastics, paints, and solvents.¹ High emissions of unintentionally produced persistent organic pollutants (UP-POPs) have been determined in stack gas of secondary nonferrous metal processing plants, caused by the combustion of these impurities in the presence of various types of metals during reclamation processes.^{2–6} During the secondary nonferrous metal smelting process, the smelting furnace door would be open for feeding raw material, mixing, and other necessary operations. Therefore, fugitive UP-POP emissions can be directly released into the workplace air during the process. Several studies have been conducted to investigate polychlorinated dibenzo-*p*-dioxin and dibenzofuran (PCDD/F) concentrations in the workplace air of some industrial thermal processes, such as sinter plants, municipal solid waste incinerators (MSWIs), and secondary aluminum and copper smelters.^{7–10} Moreover, the results of these studies suggested that there was significant PCDD/F contamination in the workplace air of the industrial thermal process plants investigated. Shih et al.⁸ investigated PCDD/F levels in the

workplace atmosphere of a sinter plant, and their results indicated that PCDD/F concentrations in workplace air (0.55–2.14 pg of I-TEQ/m³) were obviously higher than that of the outside ambient environment (0.07 pg of I-TEQ/m³). In a secondary aluminum smelter, PCDD/F concentrations during operation were observed to be higher than that during periods of no operation in workplace air.⁷ Relatively high concentrations of PCDD/Fs were observed in the air samples collected near the furnace and casting department of a secondary copper smelter (1.41–34.8 pg of WHO-TEQ/m³) and a secondary aluminum smelter (0.49–12.6 pg of WHO-TEQ/m³).⁹ Shih et al.¹⁰ found that PCDD/F WHO-TEQ concentrations in the workplace air were 5–15 times higher than those in the surrounding environment of two MSWIs. However, there is a lack of information about the concentrations of dioxins in the workplace air compared with intensive studies of dioxin emissions via stack gas from industrial thermal processes.^{2–4,11–13}

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Although remarkably high levels of PCDD/F contamination have been observed in workplace air from secondary nonferrous metal processing plants in previous studies,^{7,9} few investigations of the assessment of occupational exposure to airborne PCDD/Fs at the workplaces have been conducted, not to mention polychlorinated biphenyls (PCBs) and polychlorinated naphthalenes (PCNs). Furthermore, PCNs have recently been proposed for inclusion in Annexes A, B, and/or C to the Stockholm Convention, 2011. Therefore, eight secondary nonferrous metal processing plants were investigated for the concentrations of UP-POPs (PCDD/Fs, dl-PCBs, and PCNs) in the workplace air in this study. The plants investigated include secondary copper smelters (SeCu), secondary aluminum smelters (SeAl), and secondary lead smelters (SePb). A preliminary assessment was performed on occupational exposure to PCDD/Fs, dl-PCBs, and PCNs by inhalation in the workplace. In addition, UP-POPs in stack gas from these secondary nonferrous metal processing plants were also determined. The homologue profiles of UP-POPs in workplace air were compared with those in stack gas to identify the source of UP-POPs in workplace air. The results of this study will be helpful for understanding occupational exposure to UP-POPs by inhalation in workplaces of secondary nonferrous metal-lurgical facilities.

MATERIALS AND METHODS

Sampling. Eight typical secondary nonferrous metal processing plants were investigated, including SeCu, SeAl, and SePb (see the basic information in Table 1). Air samples

Table 1. Basic Information about the Investigated Secondary Nonferrous Metal Processing Plants

	plant	capacity per year (thousand tons)	raw material ^a	fuel	air pollution control system
SeCu	TY	100	copper scrap, blister copper, and ACRE ^b	heavy oil	—
	CX	10	copper-bearing residues	heavy oil	bag filters
	YD	200	copper scrap, blister copper, and ACRE ^b	heavy oil	bag filters
SeAl	SC	26	aluminum scrap	natural gas	cyclone and bag filters
	QY	180	aluminum scrap	natural gas	electrostatic precipitators
	HY	100	aluminum scrap and aluminum ingot	natural gas	bag filters
	TF	15	aluminum scrap	natural gas	bag filters
SePb	JA	10	lead-bearing part in plumbic accumulator	natural gas	bag filters

^aThe raw material source was relatively stable, and there was no great variation in its composition. ^bAnode copper remains after electrolysis.

from workplaces were collected using high-volume samplers (Echo Hi-Vol, Tecora Co.) in accordance with U.S. Environmental Protection Agency (EPA) Method TO-9A. Sampling points were located near the smelting furnace and on the side of the worker's operating platform, such as in the feed and mixing. Particulates were collected onto cleaned glass fiber filters (GFFs) (102 mm in diameter), whereas the gas phase

was adsorbed onto polyurethane foam (PUF) (63 mm diameter and 76 mm length). Prior to the sampling, the GFFs were baked at 450 °C to remove organic contaminants, and the PUFs were Soxhlet-extracted with acetone for 12 h. The air sampling flowing rate was 0.22 m³/min, and each sample was collected continuously for approximately 24 h during the smelting process. The sampling period covered all smelting process and also covered all working hours over the three 8 h shifts. In addition, three stack gas samples were collected simultaneously from each plant by an automatic isokinetic sampling system, Isostack Basic (TCR Tecora), according to European Standard EN-1948. Once the stack gas and air sampling were completed, the samples were tightly wrapped in aluminum foil and packed in sealed polyethylene bags to prevent contamination and loss. They were then brought back to the laboratory and stored at −18 °C until they were analyzed.

Sample Analysis. In this study, analysis of 17 2,3,7,8-PCDD/F and 12 dl-PCB congeners was conducted on the basis of modifications of U.S. EPA Methods 1613 and 1668A, respectively. Tri- to octachlorinated naphthalenes were analyzed by the isotope dilution high-resolution gas chromatography–high-resolution mass spectrometry (HRGC–HRMS) method as described in our previous study.¹⁴ The samples were spiked with known amounts of ¹³C₁₂-labeled PCDD/F, ¹³C₁₂-labeled PCB, and ¹³C₁₀-labeled PCN internal standards (Table S1 of the Supporting Information) and then were Soxhlet-extracted with toluene for approximately 24 h. Subsequently, the sample extracts were concentrated and subjected to a series of cleanups by adsorption chromatography, including an acid silica gel column, a multilayer silica gel column [from top to bottom, anhydrous sodium sulfate, 1 g of activated silica gel, 8 g of silica/H₂SO₄ 44% (w/w) gel, 1 g of activated silica gel, 5 g of silica/NaOH (1 M) 33% (w/w) gel, 1 g of activated silica gel, 2 g of silica/AgNO₃ 10% (w/w) gel, and 1 g of activated silica gel], and a basic alumina column. Finally, the extracts were concentrated to approximately 20 μL by rotary evaporation and a gentle nitrogen gas stream. Prior to injection, ¹³C₁₂-labeled PCDD/F, ¹³C₁₂-labeled PCB, and ¹³C₁₀-labeled PCN recovery standards (Table S1 of the Supporting Information) were added to the extracts. PCDD/F and PCB analyses were performed by HRGC–HRMS with an Agilent 6890 gas chromatograph coupled to a Waters Autospec Ultima high-resolution mass spectrometer. A DB-5 ms capillary column (60 m × 0.25 mm × 0.25 μm, Agilent) was used. The high-resolution mass spectrometer was equipped with a positive electron impact (EI+) source. The selected ion monitoring analyzer mode was used with a resolving power of 10000. The electron energy and source temperature were specified at 35 eV and 250 °C, respectively. PCNs were analyzed using a Trace GC Ultra gas chromatograph coupled with a DFS mass spectrometer (Thermo Fisher Scientific) with an electron impact ion source. The high-resolution mass spectrometer was operated in selected ion monitoring mode with a resolution greater than 10000. A DB-5 ms capillary column (60 m × 0.25 mm × 0.25 μm, Agilent) was also used for the separation of PCN congeners. The electron emission energy was set to 45 eV. The source temperature was 270 °C.

The recoveries of PCDD/F, PCB, and PCN internal standards were in the range of 50–120, 40–111, and 46–112% in the workplace air samples, respectively, and the recoveries were in the range of 40–117, 50–110, and 43–115% in stack gas samples, respectively (Table S1 of the Supporting

Table 2. Concentrations of UP-POPs in Workplace Air of the Plants Investigated (picograms per cubic meter)

		PCDD/Fs		PCBs		ΣTEQ^a (PCDD/Fs and dl-PCBs)	PCNs ^b	
		$\Sigma 2378\text{-PCDD/Fs}$	ΣTEQ^a	$\Sigma\text{dl-PCBs}$	ΣTEQ^a		ΣPCNs	ΣTEQ
SeCu	TY	800	44.5	279	5.07	49.6	4630	1.30
	CX	1400	32.1	128	1.50	33.6	4530	1.13
	YD	20.9	0.86	31.0	0.12	0.98	293	0.065
SeAl	SC	556	26.0	726	0.96	27.0	31900	22.3
	QY	5.28	0.52	569	0.21	0.73	1710	0.37
	HY	13.3	1.75	32.5	0.21	1.96	640	0.26
	TF	58.0	5.94	770	0.76	6.71	2510	0.081
SePb	JA	12.7	0.78	15.5	0.070	0.85	252	0.026

^aTEQs were calculated using WHO1998-TEF. ^bIncluding tri- to octa-chlorinated PCNs.

Information). In the identification of the target compounds, the following quality control criteria were used. (a) GC retention times were matched to the corresponding standard compounds. (b) A signal-to-noise ratio of >3:1 was used. (c) The isotopic ratios between the quantitative and confirmation ions were within $\pm 15\%$ of the theoretical values. One method blank was included in each batch of samples, which had been spiked with the same amount of internal standard as the samples. No target compounds were detected in the blank samples.

RESULTS AND DISCUSSION

Concentrations of UP-POPs in Workplace Air. The concentrations of PCDD/Fs and dl-PCBs were determined in air samples collected from the workplaces of the eight secondary nonferrous metal processing plants investigated. TEQs of PCDD/Fs and dl-PCBs were calculated using World Health Organization (WHO) 1998 TEF¹⁵ and are listed in Table 2. There was a large variation in PCDD/F and dl-PCB concentrations among different metallurgy processes and among different plants in the same metal category. The concentrations of PCDD/Fs ranged from 0.52 to 44.5 pg of WHO-TEQ/m³ among secondary nonferrous metal processing plants. Several studies have investigated PCDD/F levels in the workplace air of SeCu, SeAl, and other industrial thermal processes (Table 3). It can be seen that the PCDD/F concentrations of SeCu and SeAl in this study were in agreement with those found in SeCu and SeAl reported by Lee et al.⁹ and aluminum recyclers reported by Sweetman et al.,¹⁶ but higher than those of other industrial thermal processes listed in Table 3.^{8–10,17,18} PCDD/F concentrations of SePb in this study were in agreement with those of iron ore sinter,⁸ a basic oxygen steelmaking plant,¹⁸ electric arc furnaces,⁹ and MSWIs.¹⁰ For dl-PCBs, the concentrations were in the range of 0.070–5.07 pg of WHO-TEQ/m³ in workplace air among secondary nonferrous metal processing plants. PCB levels have seldom been reported in workplace air of secondary nonferrous metal processing plants, to the best of our knowledge, although some studies have investigated atmospheric levels of PCBs in the surrounding environment of industrial thermal processes.^{19,20} With regard to PCNs, the total concentrations (tri- to octachlorinated naphthalenes) were in the range of 252–31900 pg/m³ in workplace air among secondary nonferrous metal processing plants (Table 2). The dioxin-like toxicity of PCNs has been investigated in previous studies.^{21–23} The relative potency factors (RPFs) of individual PCN congeners to 2378-TCDD estimated in these studies have been used to evaluate the toxicity of PCNs.^{14,24,25} In this study, the TEQs of PCNs were defined by the sum of the products of the concentration of each congener multiplied by its RPF

Table 3. PCDD/F Concentrations in Workplace Air of Various Industrial Processes

industrial thermal process	$\Sigma 2378\text{-PCDD/Fs}$ (pg/m ³)		ΣTEQs (pg/m ³)	
	range	mean	range	mean
iron ore sinter ⁸	7.61–23.2	16.6	0.55–2.14 ^a	1.48 ^a
iron ore sinter ¹⁸	– ^b	– ^b	0.12–5.93 ^{c,d}	1.21 ^{c,d}
basic oxygen steelmaking plant ¹⁸	– ^b	– ^b	0.13–2.03 ^{c,d}	0.71 ^{c,d}
electric arc furnace ⁹	– ^b	– ^b	1.61–2.01 ^c	1.81 ^c
electric arc furnace ¹⁷	2.6–69.5	24.5	0.26–8.34 ^c	2.46 ^c
MSWIs ¹⁰	0.541–77.6	14.9	0.0307–4.73 ^c	0.822 ^c
SeAl ⁷	– ^b	5.50	– ^b	0.571 ^a
SeAl ⁹	– ^b	– ^b	0.49–12.6 ^c	7.16 ^c
aluminum recyclers ¹⁶	– ^b	– ^b	2.0–72.7	17.7
SeCu ⁹	– ^b	– ^b	1.41–34.8 ^c	12.4 ^c
SeAl (this study)	5.28–556	158	0.52–26.0 ^c	8.55 ^c
SeCu (this study)	20.9–1400	741	0.86–44.5 ^c	25.8 ^c
SePb (this study)	12.7		0.78 ^c	

^aData were reported using I-TEF. ^bData were not reported. ^cData were reported using WHO1998-TEF. ^dData include WHO-12 PCB.

reported by Noma et al.²⁴ (Table S2 of the Supporting Information). The dioxin-like PCNs (dl-PCNs) were defined as those congeners whose toxic equivalent factors have been calculated (Table S2 of the Supporting Information). The TEQ concentrations of PCNs were in the range of 0.026–22.3 pg/m³ in workplace air among secondary nonferrous metal processing plants. There are no reports concerning PCN levels in workplace air from secondary nonferrous metal processing to the best of our knowledge.

To improve our understanding of UP-POP levels in workplace air from the plants investigated, UP-POP concentrations in this study were compared with those in ambient air reported in previous studies. Intensive studies of the atmospheric levels of PCDD/Fs in local environments all over the world have been conducted. A review of PCDD/F concentrations in ambient air was presented by Lohmann and Jones;²⁶ the general trend in TEQs is as follows: <10 fg/m³ at remote sites, 20–50 fg/m³ at rural sites, and 100–400 fg/m³ at urban and industrial sites. Atmospheric levels of PCBs and PCNs have also been reported in many countries and regions, with concentrations in the range of 0.5–148 fg of WHO-TEQ/m³ for PCBs and 2–160 pg/m³ for PCNs.^{27–32} The concentrations of PCDD/Fs, PCBs, and PCNs in this study were obviously higher than the values mentioned above

reported for ambient air. In addition, the total WHO-TEQ concentrations of PCDD/Fs and dl-PCBs (0.73–49.6 pg of TEQ/m³) in workplace air in this study were all higher than the ambient air quality limitations for dioxins (0.6 pg of TEQ/m³) in Japan.³³ Furthermore, the TEQ concentrations of PCNs in workplace air from the TY, CX, and SC plants (1.30, 1.13, and 22.3 pg of TEQ/m³, respectively) were also higher than the concentration limits mentioned above. Therefore, workers were exposed to high concentrations of airborne PCDD/Fs, dl-PCBs, and PCNs in the secondary nonferrous metal smelting processing plants investigated. It is essential that occupational exposure to these compounds be assessed to understand the potential exposure risk of workers in these workplaces.

Occupational Exposure to UP-POPs in the Workplace.

Currently, occupational exposure to UP-POPs in the workplace is considered only in terms of inhalation via air; occupational exposure in managing highly contaminated fly ashes was ignored. Inhalation exposure to PCDD/Fs, dl-PCBs, and PCNs in the workplace was roughly estimated by assuming inhalation rates of 1.5 and 1.3 m³/h for moderate and light activities, respectively,¹⁷ and an 8 h work shift. The inhalation dose was calculated by the following equation:

$$ID = (C_{\text{air}} I_{\text{rate}} T_w f_r) / BW \quad (1)$$

where ID is inhalation dose for workers in the workplace in picograms of TEQ per kilogram of body weight per day, C_{air} is air concentration expressed in picograms of TEQ per cubic meter, I_{rate} is the inhalation rate of a worker in cubic meters per hour, T_w is the exposure time in the workplace (hours), f_r is inhalation absorption factor (1 was used assuming 100% absorption),^{16–18} and BW is the body weight of workers (60 kg).

Table 4 lists the estimated daily intakes of PCDD/Fs, dl-PCBs, and PCNs for workers by inhalation in the workplace. The total estimated daily intakes of PCDD/Fs and dl-PCBs for workers by inhalation in the workplace were in the range of 0.15–9.91 and 0.13–8.59 pg of WHO-TEQ/kg of body weight for moderate and light activities, respectively. Preliminary health risk assessments were performed by comparison with the recommended tolerable daily intake (TDI). The WHO European Centre for Environment and Health recommended a TDI of 1–4 pg of WHO-TEQ/kg of body weight (including the WHO-12 PCBs) in 1998,³⁴ while a TDI of 2 pg of WHO-TEQ/kg of body weight per day was recommended by the UK Committee on the Toxicity of Chemicals in Food, Consumer Products and the Environment (COT), based upon effects on the developing male reproductive system mediated via the maternal body burden.³⁵ It can be observed that the estimated inhalation dose of dioxins (PCDD/Fs and dl-PCBs) in the workplace of TY, CX, and SC plants exceeded the TDI recommended by WHO and COT, although dietary intakes are not considered for workers. In previous studies, it was estimated that >90% of exposure of the general population to these compounds occurs through diet, with food from animal origin being the predominant source.^{17,34,36} However, the daily intakes by inhalation for workers in the workplace in this study were already comparable with the TDI. Therefore, the results indicated that the risk of occupational exposure to PCDD/Fs and dl-PCBs by inhalation in the workplace of the secondary nonferrous metal processing plants investigated was considerably high.

Meanwhile, it is noteworthy that the estimated inhalation dose of PCNs in the workplace of SC plants had reached a

Table 4. Estimated Daily Intakes of UP-POPs for Workers in the Workplaces of Secondary Nonferrous Metal Processing Plants (picograms of TEQ per kilogram of body weight)

		PCDD/Fs ^a	dl-PCBs ^a	sum of PCDD/Fs and dl-PCBs ^a	PCNs ^b
TY	light activity	7.71	0.88	8.59	0.23
	moderate activity	8.90	1.01	9.91	0.26
CX	light activity	5.56	0.26	5.82	0.20
	moderate activity	6.42	0.30	6.72	0.23
YD	light activity	0.15	0.021	0.17	0.011
	moderate activity	0.17	0.024	0.20	0.013
SC	light activity	4.51	0.17	4.67	3.87
	moderate activity	5.20	0.19	5.39	4.46
QY	light activity	0.090	0.036	0.13	0.064
	moderate activity	0.10	0.042	0.15	0.074
HY	light activity	0.30	0.036	0.34	0.045
	moderate activity	0.35	0.042	0.39	0.052
TF	light activity	1.03	0.13	1.16	0.014
	moderate activity	1.19	0.15	1.34	0.016
JA	light activity	0.14	0.012	0.15	0.004
	moderate activity	0.16	0.014	0.17	0.005

^aData were calculated using WHO1998-TEQ. ^bData were calculated using TEQ of PCNs listed in Table 2.

relatively high level (4.46 and 3.87 pg of TEQ/kg of body weight for moderate and light activities, respectively). The estimated daily intakes by inhalation of PCNs were in the range of 0.005–0.26 and 0.004–0.23 pg of TEQ/kg of body weight for moderate and light activities, respectively, in the workplaces of the other plants investigated. The assessment of inhalation exposure to PCNs for workers has not been reported in workplaces of secondary nonferrous metal processing plants to the best of our knowledge. These results suggested that more attention should be paid to the health risks of PCNs by inhalation in the workplace of secondary nonferrous metal processing plants.

To improve our understanding of the relative importance of PCNs compared with dioxins, the contribution of each compound (PCDD/Fs, dl-PCBs, and PCNs) to total UP-POP intake by inhalation was calculated for workers in the workplaces of plants investigated (Figure 1). The contribution of PCNs accounted for 45, 34, and 12% of the total UP-POP intake by inhalation in SC, QY, and HY plants, respectively. Moreover, the contribution of PCNs was comparable with that of PCDD/Fs in SC and QY plants (53 and 47%, respectively). Park et al.³⁷ found similar results among TEQ contributions of PCDD/Fs, PCBs, and PCNs in the serum of individuals working at MSWIs. In their study, the PCN contribution to total TEQ in the serum (26.8%) was found to be slightly greater than that of the PCDDs (23.8%), PCDFs (25.0%), and PCBs (24.3%).³⁷ Nevertheless, the contributions of PCNs to total UP-POP intake by inhalation in TY, CX, YD, TF, and JA plants were relatively small (1.2–6.2%). A possible difference in raw materials or operating conditions among different plants may be responsible for this difference and requires further research. With regard to the dl-PCBs, a relatively large contribution to total UP-POP intake by inhalation was found

Figure 1. Contribution (percent) of each compound (PCDD/Fs, dl-PCBs, and PCNs) to total UP-POP intake by inhalation in the workplace of the plants investigated.

in TY, YD, QY, and TF plants (10, 11, 19, and 11%, respectively). The TEQ contribution from dl-PCBs formed via *de novo* synthesis usually accounted for approximately 3–7.5% of the total TEQ in the incineration processes.^{38,39} Therefore, other sources besides *de novo* formation may exist for the dl-PCBs, such as industrial PCBs input via raw materials.

Source of UP-POPs in Workplace Air. UP-POP concentrations in stack gas also varied greatly among different metallurgies and among different plants in the same metal category (Table S3 of the Supporting Information). Upon comparison of UP-POP concentrations in workplace air with that in stack gas, similar trends were found for PCDD/Fs and dl-PCBs among the plants investigated (Figure 2). When a high concentration of UP-POPs was detected in stack gas, a relatively high concentration was also found in corresponding workplace air. For PCNs, a relatively high concentration was

found in the workplace air sample of the SC plant. The trend of PCN concentrations between workplace air and stack gas was more similar when the SC plant was not included (Figure 2). UP-POP concentrations in stack gas can be affected by many factors, such as the raw materials, operating conditions, and air pollution control system (APCS).^{13,40} Fugitive gas is directly released into workplace air from a smelting furnace and was not influenced by an APCS. This may be why a relatively higher target compound concentration was detected among workplace air samples, whereas the concentrations were relatively low among stack gas samples in some plants. However, the similar trends of UP-POP concentrations suggested that the mechanism of formation of UP-POPs in the workplace air and stack gas should be similar.

To identify the source of UP-POPs in workplace air, homologue profiles were analyzed for tetra- to octa-CDD/Fs, tetra- to deca-CBs, and tri- to octa-CN for PCDD/Fs, PCBs, and PCNs, respectively. As shown in Figure S1 of the Supporting Information, higher chlorinated PCDFs were the main homologues in the TY, CX, YD, and SC plants, while lower chlorinated PCDFs were more abundant in the QY, HY, TF, and JA plants. For PCBs and PCNs, the main homologues were observed as lower chlorinated CBs and CNs, and the weight distribution of PCB and PCN homologues decreased with an increasing degree of chlorination (Figures S2 and S3 of the Supporting Information). Furthermore, the UP-POP homologue profiles in workplace air were compared with those in stack gas (Figures S1–S3 of the Supporting Information). Although similar trends of UP-POP concentrations were found between workplace air and stack gas, it appears that there were certain differences for UP-POP homologue profiles. Overall, contributions of the higher chlorinated PCDD/Fs, PCBs, and PCNs in workplace air were higher than those in stack gas except for the TY plant.

Figure 2. Comparison of UP-POP concentration trends between workplace air and stack gas from the plants investigated. PCNs(A) and PCNs(B) were the trends including and excluding the SC plant, respectively.

Raw stack gas was sampled in the TY plant because no APCs was present. However, the particles in the stack gas, where the higher chlorinated homologues of PCDD/Fs, PCBs, and PCNs were more likely to bind, were removed effectively by APCs in other plants (sampling points were set downstream of all APCs). Moreover, as mentioned above, the fugitive gas was directly released into the workplace air from a smelting furnace and was not influenced by an APCs. As a result, the higher chlorinated homologues of PCDD/Fs, PCBs, and PCNs in workplace air appeared to be more abundant compared with that in stack gas. Obviously, this indicated that the significant UP-POP contamination in workplace air was mainly attributed to fugitive gas emission from smelting furnaces during the reclamation process. Therefore, secondary nonferrous metallurgical facilities should pay more attention to preventing the unintentional release of fugitive UP-POP emissions into workplace air from furnaces during the smelting process, along with effective control of their emissions via stack gas.

■ ASSOCIATED CONTENT

■ Supporting Information

Additional information about recoveries of labeled standards for PCDD/Fs, PCBs, and PCNs; relative potency factors (RPFs) of the dl-PCN; UP-POP concentrations in stack gas of the plants investigated; PCDD/F and dl-PCB concentrations in workplace air of the plants investigated; and homologue profiles of UP-POPs in workplace air and stack gas from the plants investigated. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*Phone: +86 10 62849172. Fax: +86 10 62923563. E-mail: zhengmh@rcees.ac.cn.

Notes

The authors declare no competing financial interest.

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