Characterization of polychlorinated dibenzo-*p*-dioxins and dibenzofurans, dioxin-like polychlorinated biphenyls, and polychlorinated naphthalenes in the environment surrounding secondary copper and aluminum metallurgical facilities in China

Jicheng Hu^{a, b}, Minghui Zheng^{a, *}, Wenbin Liu^a, Zhiqiang Nie^a, Changliang Li^a, Guorui Liu^a, Ke Xiao^a

^a 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

^b College of Life and Environmental Science, MinZu University of China, Beijing 100081, China

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ABSTRACT

Unintentionally produced persistent organic pollutants (UP-POPs) were determined in ambient air from around five secondary non-ferrous metal processing plants in China, to investigate the potential impacts of the emissions of these plants on their surrounding environments. The target compounds were polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), dioxin-like polychlorinated biphenyls (dl-PCBs), and polychlorinated naphthalenes (PCNs). The PCDD/F, dl-PCB, and PCN concentrations in the ambient air downwind of the plants were 4.70–178, 8.23–7520 and 152–4190 pg/m³, respectively, and the concentrations upwind of the plants were lower. Clear correlations were found between ambient air and stack gas concentrations of the PCDD/Fs, dl-PCBs, and PCNs among the five plants, respectively. Furthermore, the UP-POPs homolog and congener patterns in the ambient air were similar to the patterns in the stack gas samples. These results indicate that UP-POPs emissions from the plants investigated have obvious impacts on the environments surrounding the plants.

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1. Introduction

Persistent organic pollutants (POPs), such as polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), polychlorinated biphenyls (PCBs), and polychlorinated naphthalenes (PCNs), can be formed unintentionally during industrial thermal processes, including waste incineration (Ni et al., 2009; Hu et al., 2013b), iron ore sintering (Grochowalski et al., 2007; Liu et al., 2012a), and secondary non-ferrous metal smelting (Weber et al., 2008; Ba et al., 2009). Once emitted from a plant where industrial thermal processes are performed, these unintentionally produced POPs (UP-POPs) could potentially have great impacts on the ambient environment and human health because of their high toxicities, persistence, and abilities to bioaccumulate. Emissions of these UP-POPs from industrial thermal processes and their potential impacts

on the environments surrounding industrial plants have, therefore, attracted an increasing attention in recent years.

Intensive studies have been performed to investigate PCDD/F concentrations in environments surrounding municipal solid waste incinerators (MSWIs) (Oh et al., 2002; Shih et al., 2006; Liu et al., 2012b). Liu et al. (2012b) determined PCDD/F concentrations in a series of air and soil samples collected around a typical MSWI and found that the MSWI had potentially influenced the PCDD/F concentrations in the environment. Shih et al. (2006) found that the average PCDD/F concentration (0.0828 pg WHO-TEQ/Nm³; WHO = World Health Organization, TEQ = toxic equivalent) in air samples collected from around two MSWIs was 6.5 times higher than the concentration in air at a remote site (0.0132 pg WHO-TEQ/Nm³). Oh et al. (2002) found that characteristic PCDD/F homolog patterns in ambient air samples collected from near a MSWI were different to the patterns in background air samples but similar to the patterns in stack gases emitted from the plant. The results of these studies indicate that the MSWIs mentioned above had strong effects on the PCDD/F concentrations and homolog patterns in their

* Corresponding author.

E-mail address: zhengmh@rcees.ac.cn (M. Zheng).

surrounding environments. Compared with the intensive research on MSWIs described above, relatively few studies of the concentrations of UP-POPs in the environments surrounding secondary non-ferrous metal processing plants have been performed. Chen et al. (2004) found that PCDD/F concentrations in ambient air around a secondary aluminum smelter (SeAl) were higher when it was operating than when it was not operating. Colombo et al. (2011) found that PCDD/F concentrations in soil samples around a SeAl plant decreased with increasing distance from the plant, and that the most contaminated sites were less than 500 m from the plant. However, these two studies were each performed at only one plant, and intensive investigations, especially including different types and sizes of smelters, should be performed to characterize the concentrations of UP-POPs in the environments surrounding secondary non-ferrous metal processing plants.

Furthermore, previous studies have mainly been focused on PCDD/F contamination in the environments around secondary non-ferrous metal processing plants, and few investigations have been conducted on PCN contamination around such plants. Whereas PCNs have been proposed for inclusion in Annexes A, B, and/or C of the Stockholm Convention, in 2011. On the other hand, the UP-POPs concentrations in the environments surrounding secondary copper smelters (SeCu) have not been studied, to the best of our knowledge. Therefore, we determined the concentrations of UP-POPs (PCDD/Fs, dl-PCBs, and PCNs) in ambient air near five secondary non-ferrous metal processing plants. Three secondary copper smelters including TY, CX and YD plants and two secondary aluminum smelters including SC and QY plants were studied. Air samples were collected from downwind of each plant, and, at the same time, air samples were collected from upwind of each plant, to act as control samples. Additionally, the stack gas emitted from these investigated plants was also collected and analyzed during ambient air sampling period, which we have previously reported (Hu et al., 2013a). The concentrations and homolog profiles of the UP-POPs in the ambient air were compared with those found in stack gases emitted from the same plants. The results of this study will improve our understanding of characterization of UP-POPs in ambient environments surrounding secondary copper and aluminum smelters.

2. Materials and methods

2.1. Sample collection

Three SeCu and two SeAl plants, all located far from other possible pollution sources, were selected for the study, the aim of which was to assess the potential influence of UP-POPs emissions from secondary non-ferrous metal processing plants on the surrounding environments. Basic information about the five plants is given in Table 1. Ambient air samples were collected from three sampling sites near each plant. Two air samples were collected downwind of each plant (about 300 and 500 m from the stack, called A and B, respectively), and one sample was collected upwind of each plant (about 1000 m from the stack, called C), to act as a control sample. The air samples were collected using polyurethane foam (PUF) disk passive air samplers (PASSs). The samplers were left at the sampling sites for about two months, between April and October 2011 (Table 1). Before use, the PUF disks (14 cm diameter and 1.35 cm thick) were cleaned by washing them with water and then Soxhlet extracting them with acetone for 12 h. When the air sampling period was complete, each sample was tightly wrapped in aluminum foil and packed in a sealed

polyethylene bag, to avoid contamination or loss of analytes. The samples were taken to the laboratory and stored at -18°C until analysis.

2.2. Sample analysis

We have previously reported the details of the methods used to analyze the samples for UP-POPs (Guo et al., 2008; Hu et al., 2013a). Briefly, the samples were spiked with known amounts of $^{13}\text{C}_{12}$ -labeled PCDD/Fs, $^{13}\text{C}_{12}$ -labeled PCBs, and $^{13}\text{C}_{10}$ -labeled PCNs, for use as internal standards (Table S1), then they were Soxhlet extracted with toluene for approximately 24 h. Each sample extract was concentrated and then subjected to a series of adsorption chromatography clean-up procedures, which were an acidified silica gel column, a multilayer silica gel column (filled, from top to bottom, with anhydrous sodium sulfate, 1 g activated silica gel, 8 g silica gel containing 44% (w/w) of H_2SO_4 , 1 g activated silica gel, 5 g silica gel containing 33% (w/w) of 1 M NaOH, 1 g activated silica gel, 2 g of silica gel containing 10% (w/w) of AgNO_3 , and 1 g activated silica gel), and a basic alumina column. Finally, each extract was concentrated to approximately 20 μL by rotary evaporation and under a gentle stream of nitrogen. $^{13}\text{C}_{12}$ -labeled PCDD/F, $^{13}\text{C}_{12}$ -labeled PCB, and $^{13}\text{C}_{10}$ -labeled PCN standards (Table S1) were added to the extracts, to enable the recoveries of the internal standards to be estimated, before instrumental analysis. The PCDD/F and PCB analyses were performed using an Agilent 6890 gas chromatograph (Agilent Technologies, Santa Clara, CA, USA) coupled with an Autospec Ultima high-resolution mass spectrometer (Waters, Milford, MA, USA). A DB-5ms capillary column (60 m long, 0.25 mm id, 0.25 μm film thickness; Agilent Technologies) was used to separate the analytes. The mass spectrometer was equipped with a positive electron impact (EI+) source, selected ion monitoring mode was used, and the resolving power was 10,000. The electron energy was 35 eV and the source temperature was 250°C . The PCNs were analyzed using a Trace GC Ultra gas chromatograph coupled with a DFS mass spectrometer (Thermo Fisher Scientific, Waltham, MA, USA). The DFS mass spectrometer was fitted with an electron impact ion source and it was operated in selected ion monitoring mode, with a resolution of $>10,000$. A DB-5ms capillary column (60 m long, 0.25 mm id, 0.25 μm film thickness; Agilent Technologies) was used to separate the PCN congeners. The electron emission energy was 45 eV and the source temperature was 270°C .

2.3. Quality assurance and quality control

The recoveries of the PCDD/F, PCB, and PCN internal standards in the ambient air samples were in the ranges of 42–118%, 42–119%, and 45–115%, respectively (Table S1). The following quality control criteria were used when identifying a target compound: (a) the chromatographic retention time matched that of the corresponding standard compound; (b) the signal-to-noise ratio was greater than 3:1; and (c) the isotopic ratio between the quantitation and confirmation ions was within $\pm 15\%$ of the theoretical value. One method blank was included in each batch of samples, and the blanks were spiked with the same amounts of internal standard as were the samples. No target compounds were detected in any of the blank samples.

3. Results and discussion

3.1. Atmospheric UP-POPs concentrations in the ambient air from around the plants

The UP-POPs concentrations in the ambient air around the five plants were estimated from the concentrations found in the PUF samplers by applying a typical sampling rate of $3.5\text{ m}^3/\text{day}$ (Mari et al., 2008; Hogarth et al., 2012b; Zhang et al., 2013). The TEQ concentrations for the PCDD/Fs and dl-PCBs were calculated using the WHO 2005 toxic equivalence factors (TEFs) (Van den Berg et al., 2006). The PCDD/F and dl-PCB concentrations in the ambient air samples from near the secondary copper and aluminum smelters were $4.70\text{--}178\text{ pg/m}^3$ (mean $41.8 \pm 60.2\text{ pg/m}^3$) and $8.23\text{--}7520\text{ pg/m}^3$ (mean $1560 \pm 2600\text{ pg/m}^3$), respectively, and the WHO-TEQ concentrations were $0.37\text{--}15.5\text{ pg/m}^3$ (mean $4.45 \pm 5.76\text{ pg/m}^3$)

Table 1
Sampling dates and basic information on the SeCu and SeAl plants investigated.

	Plant	Date of PAS deployment	Date of PAS harvest	Capacity/year (1000 t)	Fuel	Air pollution control system	Stack height (m)
SeCu	TY	23-Aug-2011	25-Oct-2011	100	Heavy oil	—	20
	CX	27-Apr-2011	28-Jun-2011	10	Heavy oil	Bag filters	15
	YD	25-Aug-2011	28-Oct-2011	200	Heavy oil	Bag filters	30
SeAl	SC	21-Apr-2011	22-Jun-2011	26	Natural gas	Cyclone + bag filters	10
	QY	25-Apr-2011	24-Jun-2011	180	Natural gas	Electrostatic precipitators	25

PAS = passive air sampler.

(Table 2). The total PCN (the sum of the tri- to octa-chlorinated naphthalene) concentrations were $152\text{--}4190\text{ pg/m}^3$ (mean $1940 \pm 1510\text{ pg/m}^3$) (Table 2). The dioxin-like toxicities of the PCNs have been investigated in previous studies (Hanberg et al., 1990; Blankenship et al., 2000; Villeneuve et al., 2000), and relative potency factors (RPFs) for individual PCN congeners relative to the toxicity of 2,3,7,8-TCDD estimated in those studies have been used to evaluate the toxicities of PCN mixtures found in other studies (Noma et al., 2004; Guo et al., 2008; Liu et al., 2009). We defined the PCN TEQ as the sum of the products of the concentration of each congener and its RPF reported by Noma et al. (2004) (Table S2). The dioxin-like PCNs (dl-PCNs) were defined as the congeners for which TEFs have been calculated (Table S2). The PCN TEQ concentrations in the ambient air samples from near the secondary non-ferrous metal processing plants were $0.01\text{--}0.63\text{ pg/m}^3$ (mean $0.19 \pm 0.21\text{ pg/m}^3$). It can be seen that the UP-POPs concentrations in the ambient air around the different plants varied considerably (Table 2). Relatively high PCDD/F concentrations were found in the air samples from near plants CX and TY, and relatively high PCB concentrations were found near plants QY and SC. The UP-POPs concentrations were higher in all of the air samples collected downwind of the plants than in the samples collected upwind (Table 2). This suggests that UP-POPs concentrations in ambient air may be influenced by emissions from secondary copper and aluminum smelters.

3.2. Influence of UP-POPs emissions from the plants on the surrounding environment

The stack gas emitted from the investigated plants was also collected and analyzed during ambient air sampling period, which we have previously reported (Hu et al., 2013a). The concentrations and homolog profiles of the UP-POPs in the ambient air were compared with those in the stack gases emitted from the same plants to determine if UP-POPs emissions from each plant affected their surrounding environment.

3.2.1. The relationship between UP-POPs concentrations in the ambient air and stack gases

Although there were also large variation in the UP-POPs concentrations in the stack gases emitted from different plants (Hu et al., 2013a), we found that there were clear correlations between the ambient air and the stack gas concentrations of the

Table 2
PCDD/F, dl-PCB, and PCN concentrations in ambient air from near the SeCu and SeAl plants (pg/m^3).

		$\Sigma 2378\text{-PCDD/Fs}$	$\Sigma \text{dl-PCBs}$	$\Sigma \text{WHO-TEQ}$	PCNs^a	
					ΣPCNs	ΣTEQ
Downwind	TYA ^b	9.72	125	0.80	720	0.05
	TYB ^b	66.6	86.3	5.77	2620	0.36
	CXA	178	204	15.5	4020	0.63
	CXB	116	178	14.4	3340	0.45
	YDA	4.70	8.23	0.37	152	0.01
	YDB	9.41	14.1	0.69	244	0.03
	SCA	7.80	1180	1.15	1340	0.10
	SCB	8.11	1240	1.14	1640	0.07
	QYA	7.06	5040	1.88	1180	0.06
	QYB	10.6	7520	2.82	4190	0.10
Upwind	TYC ^b	1.71	4.72	0.18	238	0.009
	CXC	57.5	116	9.20	1180	0.23
	YDC	1.53	6.07	0.08	85.4	0.01
	SCC	3.51	1050	0.64	413	0.03
	QYC	2.51	1230	0.55	739	0.02

^a Including tri- to octa-chlorinated naphthalenes.

^b XXA, XXB, and XXC are the air samples collected from downwind (A and B) and upwind (C) of the plants.

PCDD/Fs, dl-PCBs and PCNs among the five investigated plants, respectively (Fig. 1). For instance, if relatively high UP-POPs concentrations were found in the stack gas emitted from an investigated plant, the corresponding levels in its ambient air were also found to be higher than those of other plants. When the UP-POPs concentrations in the stack gases emitted from an investigated plant were relatively low, the corresponding levels in its ambient air were also lower than those of other plants. The result indicated that the secondary copper and aluminum smelters investigated may be a major UP-POPs source in their ambient air.

3.2.2. Comparison of UP-POPs patterns in the ambient air and stack gases

The tetra- to octa-chlorinated PCDD/F, tetra- to deca-chlorinated PCB, and tri- to octa-chlorinated PCN homolog profiles in the ambient air samples were analyzed. As is shown in Fig. 2, the less chlorinated PCDD/Fs were the main homologs in the ambient air from near plants TY, CX, and SC, while the more chlorinated PCDD/F

Fig. 1. PCDD/F, PCB, and PCN concentrations in ambient air at sites A, B, and C around SeCu and SeAl plants and in stack gases from the plants.

Fig. 2. Homolog profiles of PCDD/Fs in ambient air around SeCu and SeAl plants and in stack gases from the plants.

Fs were more abundant near plants YD and QY. Interestingly, at 44%, the pentachlorodibenzo-*p*-dioxin homolog contribution to the total PCDD/F concentration was relatively high near plant SC. For PCBs and PCNs, the less chlorinated PCBs and PCNs were the dominant homologs, and the contributions to the total PCB and PCN concentrations decreased with increasing degree of chlorination (Figs. 3 and 4). When comparison of UP-POPs homolog profiles between ambient air and stack gas, it can be seen that there were clear differences in the PCDD/F homolog profiles between ambient

air and stack gas of SC plant, which is a result of the abundant PeCDD in the ambient air samples. In addition, the samples from plant TY also had unusual UP-POPs homolog profiles. Raw stack gases were sampled from plant TY because it did not have an air pollution control system, and, because of this, more particles were collected in the stack gas samples than in the stack gas samples from the other plants. Therefore, the more chlorinated PCDD/F, PCB, and PCN homologs, which are more likely to bind to particles, were more abundant in the stack gas samples from plant TY than from

Fig. 3. Homolog profiles of PCBs in ambient air around SeCu and SeAl plants and in stack gases from the plants.

Fig. 4. Homolog profiles of PCNs in ambient air around SeCu and SeAl plants and in stack gases from the plants.

the other plants. But it is relatively difficult for particles to be transported freely in ambient air around a plant, and many particles will be deposited close to their emission source. As a result, the more chlorinated PCDD/F, PCB, and PCN homologs appeared to be more abundant in the stack gas from plant TY than in the ambient air near the plant. However, the PCDD/F homolog profiles in the ambient air and stack gas samples were similar for plants CX, YD, and QY, as were (again, except for plant TY) the PCB and PCN homolog profiles (Figs. 2–4). These results indicate that UP-POPs emissions from the plants investigated may also have impacts on the UP-POPs homolog distributions in the ambient air.

The 2,3,7,8-chlorinated PCDD/F, dl-PCB, and dl-PCN congeners have received much attention because of their high toxicities, so it was important to assess the influence of the emissions of these dioxin-like congeners from the plants investigated on the surrounding environments. We investigated the relationships between the dioxin-like congener concentrations in the ambient air and stack gases using principal component analysis (PCA). In the PCA, the SeCu stack gas samples (called SGCu), the SeAl stack gas samples (called SGAl), and the ambient air samples were treated as cases, and the percentages the dioxin-like congeners contributed to the total concentrations were treated as variables. Two groups were identified using the PCA, one group containing all of the SeCu plant ambient air samples except for sample TYA (sample A from plant TY), and the other group containing all of the SeAl plant ambient air samples (Fig. 5). What is more, the “SGCu” and “SGAl” cases were included in the group containing the appropriate ambient air samples, which shows that the dioxin-like congener profiles in the ambient air samples from near the SeCu and SeAl plants were different from each other but similar to the respective stack gas profile. This indicates that the UP-POPs congener patterns in the ambient air near the plants were influenced by emissions from the plants. Furthermore, it suggests that the influence of UP-POPs emissions from secondary copper and aluminum smelters on the environment surrounding the plants is quite significant. Proper control strategies should, therefore, be applied, to decrease the influence of UP-POPs emissions from

secondary copper and aluminum smelters on the environment around the smelters.

3.3. Comparison of atmospheric UP-POPs concentrations with some industrial thermal processes

The PCDD/F concentrations in ambient air around SeAl plant and plants performing other industrial thermal processes have been studied previously, and the results are summarized in Table 3 (Oh et al., 2002; Wang et al., 2003; Chen et al., 2004; Shih et al., 2006; Xu et al., 2009; Liu et al., 2012b). It can be seen that the PCDD/F concentrations in ambient air near the SeAl plants in our

Fig. 5. Component plot for the PCA of the percentage contributions of 2,3,7,8-PCDD/Fs, dl-PCBs, and dl-PCNs to the total concentrations (The first two letters of the labels indicate the plant studied and the third letter indicates the sample location).

Table 3

PCDD/F concentrations in the ambient air around plants performing various industrial processes (pg/m³).

Industrial thermal process	Σ 2378-PCDD/Fs		Σ TEQ		Reference
	Range	Mean	Range	Mean	
Crematory	— ^a	6.57	— ^a	0.521 ^b	Wang et al., 2003
MSWI	3.08–30.4	12.1	0.23–1.66 ^b	0.82 ^b	Liu et al., 2012b
MSWI	0.250–4.27	1.40	0.02–0.22 ^c	0.08 ^c	Shih et al., 2006
MSWI	3.96–164	31.9	0.06–3.03 ^b	0.495 ^b	Xu et al., 2009
MSWI	21.2–75.2	38.3	0.38–1.16 ^b	0.71 ^b	Oh et al., 2002
SeAl	1.45–7.40	4.25	0.14–0.67 ^b	0.36 ^b	Chen et al., 2004
SeAl	7.06–10.6	8.39	0.31–0.84 ^d	0.61 ^d	This study
SeCu	4.70–178	64.1	0.32–13.6 ^d	5.26 ^d	This study

^a Date were not reported.

^b Date were reported using I-TEF.

^c Date were reported using WHO 1998 TEFs.

^d Date were reported using WHO 2005 TEFs.

study were similar to those found near a crematory by Wang et al. (2003), near a SeAl plant by Chen et al. (2004), and near MSWIs (Oh et al., 2002; Xu et al., 2009; Liu et al., 2012b). However, the PCDD/F concentrations in ambient air near the SeCu smelters in our study were higher than those of industrial thermal processes listed in Table 3, so it is essential that intensive studies are performed to investigate the potential impacts of SeCu plants on their surrounding environments.

Concentrations of dl-PCB in ambient air around secondary non-ferrous metal processing plants have seldom been studied, to the best of our knowledge, although there have been several studies of PCB concentrations in ambient air around MSWIs and steel plants. Wang et al. (2010) found PCB concentrations in the air near a MSWI of 4.66–8.81 fg WHO-TEQ/m³ (mean 6.74 fg WHO-TEQ/m³). Li et al. (2011) studied PCB concentrations around a steel industry complex using passive air samplers, and found concentrations of 0.3–23.0 fg WHO-TEQ/m³, with an average of 12.0 fg WHO-TEQ/m³. The dl-PCBs concentrations we found were clearly higher than those reported by Wang et al. (2010) and Li et al. (2011). To the best of our knowledge, there are no reports of PCN concentrations in ambient air around secondary non-ferrous metal processing plants, but PCN concentrations have been determined in ambient air un-associated with specific potential sources in a number of areas, such as Ghana (total tri- to octa-chlorinated naphthalene concentrations of 27–95 pg/m³, mean 49 pg/m³) (Hogarh et al., 2012b), North China (total tetra- to octa-chlorinated naphthalene concentrations of 10–2460 pg/m³, median 48 pg/m³) (Lin et al., 2013), and East Asia (total tri- to octa-chlorinated naphthalene concentrations of 2–160 pg/m³, mean 31.6 pg/m³) (Hogarh et al., 2012a). The PCN concentrations we found in ambient air around the secondary copper and aluminum smelters investigated were significantly higher than the concentrations in the studies mentioned above. It can be seen that both the PCB and PCN concentrations in the ambient air around the plants we studied were relatively high. Nevertheless, this study only included a small number of air sampling sites near to five secondary non-ferrous metal processing plants, so it is essential that more intensive studies are performed to further investigate UP-POPs concentrations in environments surrounding secondary non-ferrous metals processing plants, particularly SeCu plants.

4. Conclusions

The concentrations of UP-POPs, including PCDD/F, dl-PCB, and PCN, in ambient air near three secondary copper and two aluminum smelters were simultaneously reported in this study. The influence of UP-POPs emissions from the plants on their

surrounding environment was assessed by comparing the UP-POPs concentrations and homolog patterns in the ambient air with those in stack gases from the same plants. It was found that there were a clear correlation between ambient air and stack gas concentrations of UP-POPs among five investigated plants, respectively. What is more, UP-POPs patterns in the ambient air were similar to those of in the stack gases. The results suggest that the UP-POPs concentrations and distributions in the ambient air were affected by UP-POPs emissions from the plants. In addition, markedly high PCDD/F concentrations were found in ambient air near a secondary copper smelter, so it is essential that intensive studies are performed to further investigate the potential impact of SeCu plants on their surrounding environments.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.envpol.2014.06.007>.

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