

Discovery of Significant Emission of Halogenated Polycyclic Aromatic Hydrocarbons From Secondary Zinc Smelting

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Abstract

Chlorinated and brominated polycyclic aromatic hydrocarbons (Cl/Br-PAHs) are persistent organic pollutants, and controlling their adverse effects requires the identification of their sources. However, current knowledge on the formations of Cl/Br-PAHs is far insufficient for source control, much less on their formation mechanisms. In this field study, we firstly discovered secondary zinc smelting as a significant source of Cl/Br-PAHs. The mean concentration of Cl/Br-PAHs emitted in stack gas from secondary zinc smelting was 9,553 ng/m³, exceeding concentrations from other metal smelting sources by one or two orders of magnitude. Cl/Br-PAHs with fewer rings were the dominant congeners in stack gas from secondary zinc smelting and secondary copper smelting. However, emissions from secondary aluminum smelting were dominated by congeners with more rings. The differences in congener profiles were attributable to the catalytic effects of metal compounds during smelting activities. Zinc oxide and copper oxide dominantly catalyzed dehydrogenation reactions, contributing to the formation of intermediate radicals and subsequent dimerization to Cl/Br-PAHs with fewer rings. Aluminum oxide induced alkylation reactions and accelerated ring growth, resulting in the formation of Cl-PAHs with more rings. The newly proposed mechanisms can successfully explain the emission characteristics of Cl/Br-PAHs during smelting activities and the higher concentrations of Cl/Br-PAHs from secondary zinc smelting, which should be useful in targeted source control.

1. Introduction

Chlorine- or bromine-substituted polycyclic aromatic hydrocarbons (Cl/Br-PAHs) are emerging persistent organic pollutants, the congeners of which are considered much more toxic than those of their corresponding parent PAHs (dos Santos et al. 2020). In vitro aryl hydrocarbon receptor-mediated induction experiments in rat hepatoma cells have shown that some Cl/Br-PAHs exert dioxin-like toxicity (Horii et al. 2009). Moreover, the toxic equivalents of chlorinated PAHs have been estimated to be 30–50 times higher than those of dioxins. The ubiquitous incidence of Cl/Br-PAHs in air, soil, drinking water, and biota has been reported (Liu et al. 2020),(Xia et al. 2019). Cl/Br-PAHs have even been detected in environmental matrices in the remote and sparsely populated Tibetan plateau (Jin et al. 2020a), indicating the need to reduce their source emissions and corresponding ecological and health risks.

Identifying and quantifying the major emission sources of Cl/Br-PAHs is the first step in achieving source reduction and minimizing environmental risks. Cl/Br-PAHs are believed to be formed from natural processes and from incomplete combustion during anthropogenic activities, similarly to PAHs (Choi et al. 2012; Jin et al. 2020b; Ohura et al. 2018; Xu et al. 2018). However, unlike PAHs, knowledge of the sources and emissions of Cl/Br-PAHs is limited. Available information about Cl/Br-PAH sources is limited to a few industrial activities such as waste incineration and iron ore sintering smelting activities (Jin et al. 2018; Jin et al. 2017b; Xu et al. 2018). However, it is unclear whether there are other sources of Cl/Br-PAHs producing significantly higher emissions.

Organic radicals are important intermediates in the formation of persistent organic pollutants from precursors during thermal processes (Yang et al. 2017c; Zhao et al. 2020), and zinc oxide (ZnO) is known to catalyze the formation of those organic radical intermediates (Yang et al. 2017a). The catalytic capacity of ZnO during the formation of dioxins has been confirmed, and the emissions of dioxins from secondary zinc (SeZn) smelting activities have been shown to be comparable to those from SeCu and SeAl smelting and much higher than dioxin emissions from thermal processes such as municipal solid waste incineration and steelmaking (Liu et al. 2015). In addition, the main zinc-containing secondary raw materials used in the SeZn industries are scraps, sludge, and tailings from nonferrous metals and fly ash from other thermal industries, such as electric arc furnace steelmaking (Kaya et al. 2020). Those raw materials contain sufficient precursors and catalysts for the formation of Cl/Br-PAHs. Therefore, even SeZn industries that recycle raw materials from other steelmaking industries may be emission sources of pollutants (Kaya et al. 2020). However, to our knowledge, studies on Cl/Br-PAH formation and release from zinc compounds have not been conducted. The current emission status of Cl/Br-PAHs from SeZn industries is unknown. Dominant formation pathways of persistent organic pollutants such as dioxins and Cl/Br-PAHs catalyzed by ZnO have not been elucidated. We speculated that there might be high formation and release of Cl/Br-PAHs from zinc-related smelting industries under the proper conditions.

In this study, we characterized 38 Cl/Br-PAHs emitted from full-scale SeZn smelting plants and compared the emissions with those from various secondary metal smelting plants. We first derived the Cl/Br-PAH emission factors in terms of mass and toxic equivalents and then used those to estimate the annual quantities of emissions. These congener profiles can provide diagnostic information on their source apportionment in the environment and their dominant formation pathways during the smelting process. This study is important for prioritizing the emission sources of Cl/Br-PAHs and can be useful in formulating strategies for target source control.

2. Experimental

2.1 Stack Gas Collection from SeZn Smelting Plants

Cl/Br-PAH emission status was compared between SeZn smelting industries and some other secondary nonferrous smelting industries. In total, seven stack gas samples from SeZn smelting, SeCu smelting, and SePb smelting plants were collected according to the EU standard EN-1948-1 sampling method (Xu et al. 2018; Yang et al. 2017b). The emission levels of Cl/Br-PAHs from SeAl smelting plants recorded in our previous studies were also compared (Jin et al. 2017a; Xu et al. 2018). We focused on two full-scale SeZn plants; Fig. 1 illustrates production processes at these plants. Hot galvanizing scrap, zinc-containing leaching residues, and the ashes and slags from shaft furnace steelmaking processes were always used as the raw materials for SeZn smelting. Rotary kilns were the dominant smelting equipment.

2.2 Cl/Br-PAH Analysis in Stack Gas Samples from SeZn Plants

We analyzed Cl/Br-PAHs using a method modified from our previous studies.(Jin et al. 2020a; Jin et al. 2017a; Xu et al. 2018) 38 Cl/Br-PAH congeners in the stack gas samples were analyzed by isotope dilution gas chromatography combined with high-resolution mass spectrometry (Thermo Fisher Scientific, Waltham, MA, USA). Detailed purification and instrumental analysis methods were shown in the Supplementary Materials. The recoveries of the isotopic internal standards of Cl/Br-PAHs added before sample collection and purification exhibited the reliability of the sampling and pretreatment processes, which were 30–115% in this study and can meet the trace analysis requirements of Cl/Br-PAHs. One laboratory blank was run to ensure that there was no significant contamination during sample analysis.

3. Results And Discussion

3.1 Considerably Higher Concentrations of Cl/Br-PAHs are Emitted from SeZn Plants than from Other Secondary Nonferrous Smelting Industries

We first studied the emission levels of Cl/Br-PAHs from SeZn smelting plants. The average mass concentrations of $\sum_{19}\text{Cl-PAHs}$ and $\sum_{19}\text{Br-PAHs}$ in the stack gas from SeZn industries were 9,388.15 and 164.88 ng/Nm³, respectively. Average toxic equivalency (TEQ) concentrations of $\sum_{19}\text{Cl-PAHs}$ were 11,141.86 pg TEQ/Nm³, more than two orders of magnitude higher than that of the $\sum_{19}\text{Br-PAHs}$ (36.83 pg TEQ/Nm³). The Cl/Br-PAH mass concentrations (Fig. 2) and TEQ concentrations (Figure S1) from SeZn plants were the highest compared to that from other secondary nonferrous industries, approximately 40 times higher than those from SeCu plants (means: 101.24 and 16.57 ng/Nm³ for $\sum_{19}\text{Cl-PAHs}$ and $\sum_{19}\text{Br-PAHs}$, respectively), 58 times higher than those from SePb plants (means: 101.24 and 16.57 ng/Nm³ for $\sum_{19}\text{Cl-PAHs}$ and $\sum_{19}\text{Br-PAHs}$, respectively), and two orders of magnitude higher than those from SeAl plants (means: 101.24 and 16.57 ng/Nm³ for $\sum_{19}\text{Cl-PAHs}$ and $\sum_{19}\text{Br-PAHs}$, respectively). This differs considerably from the findings of our previous overall survey on the emission levels of dioxins from 14 industrial sources, where the highest dioxin levels originated in SeCu industries (Liu et al. 2015). This indicates differing formation efficiencies of dioxins and the dioxin-like Cl/Br-PAHs during thermal industrial processes. As for the emerging Cl/Br-PAHs, SeZn smelting is therefore a critical source of Cl/Br-PAHs and requires research attention.

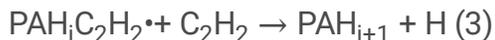
The data from this field study can be used to estimate the annual emission factors of Cl/Br-PAHs from secondary nonferrous metal smelting in China (Liu et al. 2014; Yang et al. 2020). The compiling of Cl/Br-PAH emission inventories would identify important emission sources, enabling a targeted implementation of strategies to control Cl/Br-PAHs from priority sources. The emission factors of Cl-PAHs and Br-PAHs from SeZn smelting were estimated at 178.79 and 3.58 mg/t, respectively. The average emission factors of Cl-PAHs and Br-PAHs in TEQ from SeZn smelting are 211.58 and 0.80 µg TEQ/t, respectively, approximately two orders of magnitude higher than those of Cl-PAHs from the other secondary nonferrous industries (Table S1). From the emission factors and the activity levels derived (Yang et al. 2020; Yang et al. 2021), it could be estimated that the annual emissions of Cl/Br-PAHs from SeZn

smelting plants are 40.3 g TEQ in China. Figure 2c shows detailed annual emission amounts, indicating that SeZn smelting is a significant source of Cl/Br-PAH emissions.

3.2 Congener Profiles of Cl/Br-PAHs from SeZn Smelting Plants and Implications for the Dominant Formation Mechanisms

Cl/Br-PAH congener profiles assist in understanding their emission characteristics and dominant emission pathways during various secondary nonferrous smelting processes. Considering the much higher concentrations of Cl-PAHs than Br-PAHs (>82% of total Cl/Br-PAH concentrations), we focused on congener distributions and formation mechanisms of Cl-PAHs (Table 1). The congener characteristics of Cl-PAHs from SeZn industries were similar to those of congeners from SeCu industries but differed from those of congeners from SeAl industries (Table 1). The similarity between Cl-PAH concentrations from SeZn and SeCu industries was 90% and that of SeZn and SeAl industries was 48%. Cl-PAHs with relatively fewer rings, including 9-chloronephenanthrene/2-chloronephenanthrene, 1-chlorineanthracene, 3-chlorinephenanthrene, and 3-chlorinefluoranthene were dominant congeners and accounted for 72% and 59% of the total \sum_{19} Cl-PAHs in stack gas from the SeZn and SeCu industries, respectively. In contrast, Cl-PAHs from SeAl industries exhibited a higher proportion of congeners with more rings. 1-chlorinepyrene, 9-chlorinephenanthrene/2-chlorinephenanthrene, and 6-chlorinebenzo[a]pyrene were the dominant congeners. This indicates differing formation pathways of Cl-PAHs by metal-specific catalysis in the SeZn, SeCu and SeAl industries.

The catalytic effects of metal compounds dominated different reactions and contributed to the discrepant congener profiles. Table 1 shows that under ZnO and CuO catalysis, hydrogenation and dehydrogenation reactions can be induced in the precursors. Therefore, the intermediate radicals can be easily formed by hydrogen abstraction from precursors such as phenols and benzenes. In addition, ZnO is an intrinsic semiconductor and can produce intrinsic defectivity at higher temperatures (D'Arienzo et al. 2019; Özgür et al. 2005). We detected the hole of ZnO by electron paramagnetic resonance (Table 1); this hole can result in electron transfer to the precursors, accelerating the formation and stabilization of the intermediate radicals (D'Arienzo et al. 2019; Yang et al. 2017a), which can further dimerize to form Cl-PAHs. Therefore, the concentrations of intermediate radicals catalyzed by ZnO were relatively higher than those of radicals catalyzed by CuO, contributing to the relatively higher concentrations of Cl-PAHs, polychlorinated naphthalenes (Liu et al. 2014), and polychlorinated biphenyls (Liu et al. 2013) on the surface of ZnO particles. However, oxidization reactions can easily occur under catalysis by CuO, resulting in preferable formation of polychlorinated dibenzo-*p*-dioxins and furans containing one or two para-oxygens (Liu et al. 2015). The highest levels of emitted polychlorinated dibenzo-*p*-dioxins and furans have been shown to occur in SeCu smelting (Liu et al. 2015). Unlike ZnO and CuO, Al₂O₃ dominantly catalyzes alkylation reactions, which promote Cl-PAH ring growth. The main kinetic PAH ring growth has been represented by the following reactions (Frenklach, 1990):



where i denotes the aromatic ring number of the PAHs, $\text{PAH}_i\cdot$ is a PAH radical formed by dehydrogenation, and $\text{PAH}_i\text{C}_2\text{H}_2\cdot$ is a radical formed by alkylation via the addition of C_2H_2 to PAH_i . Considering alkylation catalyzed by Al_2O_3 , reaction step 3 can be achieved and result in the formation of Cl-PAHs of higher ring numbers. The reaction rate of step 3 would be lowered under catalysis by ZnO and CuO , thereby contributing to the dominance of Cl-PAHs with fewer rings. These catalytic effects of metal compounds can successfully explain the emission characteristics of Cl/Br-PAHs during smelting processes and the higher levels of Cl/Br-PAHs emitted from SeZn smelting. The mechanisms proposed in this study can be useful in targeted source control of Cl/Br-PAHs.

Table 1 Chlorinated polycyclic aromatic hydrocarbon (Cl-PAH) congener profiles and their potential formation mechanisms under catalysis by various metal compounds abundant in smelting processes. Ant: anthracene; Fle: fluorene; Pyr: pyrene; Flu: fluoranthene; Bap: benzo[a]pyrene; Phe: phenanthrene; BaA: benz[a]anthracene; Any: acenaphthylene; Triph: triphenylene; Ana: acenaphthene.

Catalysts	Catalytic reactions	POP species easily formed	Dominant mechanisms	Cl-PAH congener patterns
ZnO	<ol style="list-style-type: none"> 1. Hydrogenation reaction 2. Dehydrogenation reaction (Raynes and Taylor, 2021) 	Cl-PAHs of lower rings including PCNs.		
CuO	<ol style="list-style-type: none"> 1. Hydrogenation reaction 2. Dehydrogenation reaction 3. Oxidation reaction (Jia et al. 2021) 	Dioxins (oxidation products) and Cl-PAHs of lower rings.		
Al ₂ O ₃	<ol style="list-style-type: none"> 1. Alkylation reaction (Dubé et al. 2005; Xu et al. 2020) 	Cl-PAHs of higher rings.		

4. Conclusion

Current knowledge on the emissions and formation mechanisms of the emerging pollutants - Cl/Br-PAHs is lacking. This study firstly discovered significant emissions of Cl/Br-PAHs from SeZn smelting. Emission factors of Cl/Br-PAHs from SeZn smelting were also derived. Cl/Br-PAHs with fewer rings were the dominant congeners in stack gas from SeZn and SeCu smelting, different with that from SeAl smelting, which were attributable to the catalytic effects of metal compounds during smelting activities.

Therefore, this study systematically proposed the formation mechanisms and characteristics of Cl/Br-PAHs from various secondary smelting industries. The newly proposed mechanisms can successfully explain the emission characteristics of Cl/Br-PAHs during smelting activities and the higher concentrations of Cl/Br-PAHs from secondary zinc smelting.

Declarations

Authors' contributions

LY and GL contributed to general planning of the research. YY, QY, LY and GL collected the samples. SL performed the ESR detection. YY and LY performed data analysis, wrote the draft and draw the photos and figures. MZ and LY critically revised the manuscript.

Conflict of interest

This is to certify that the authors of this manuscript have no affiliations with or involvement in any organization or entity with any financial interest, or non-financial interest in the subject matter or materials discussed in this manuscript.

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Figures

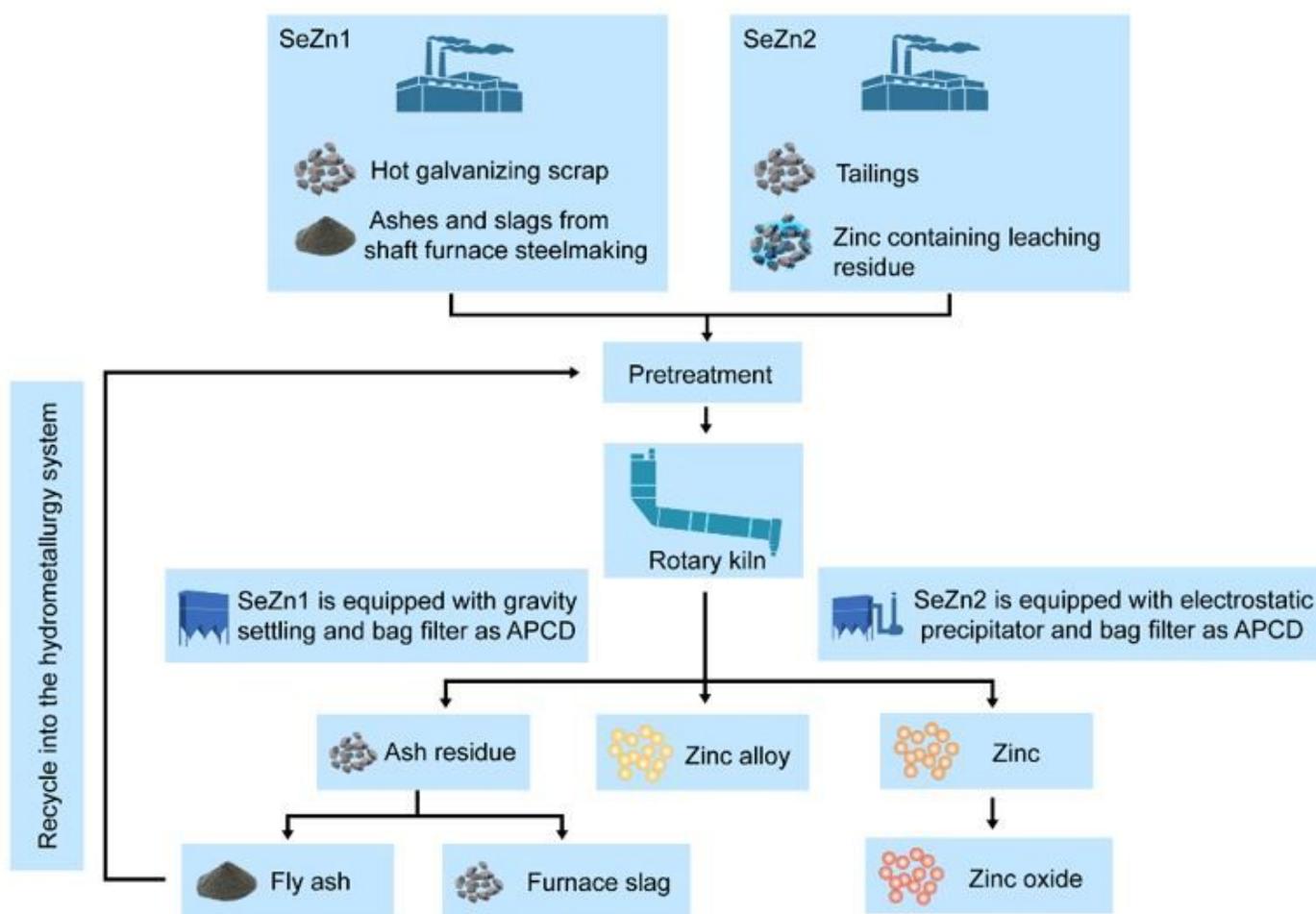


Figure 1

Basic information and process flow chart for the two secondary zinc smelting plants sampled in the study (SeZn1 and SeZn2). APCD, air pollution control device.

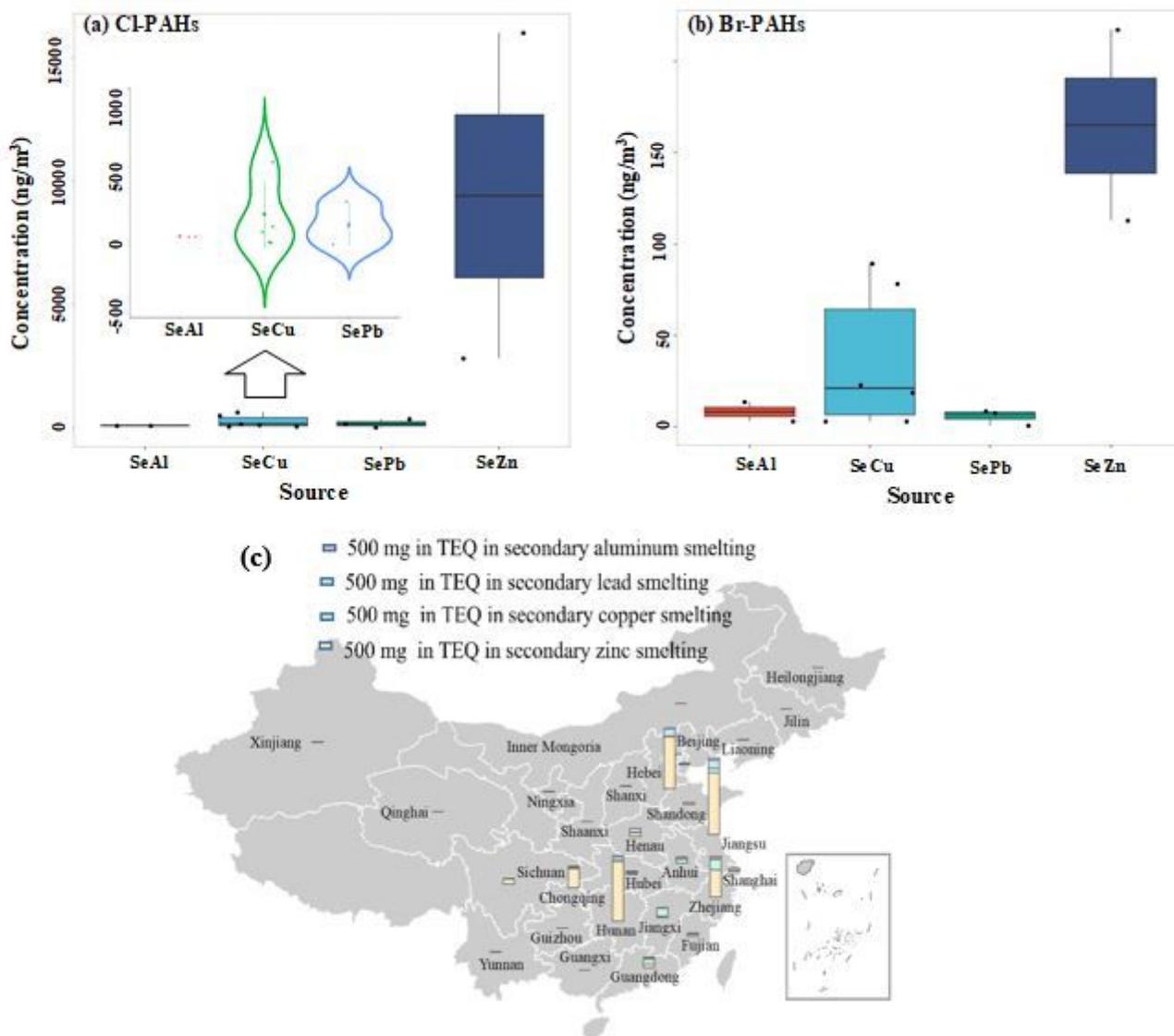


Figure 2

Emissions of (a) chlorinated polycyclic aromatic hydrocarbons (Cl-PAHs) and (b) brominated polycyclic aromatic hydrocarbons (Br-PAHs) by mass from four secondary nonferrous metal smelting processes. (c) Annual emissions in China. SeAl, secondary aluminum; SeCu, secondary copper; SePb, secondary lead; SeZn, secondary zinc; TEQ, toxic equivalency.

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