**Supplementary Materials**

**Discovery of significant emission of halogenated polycyclic aromatic hydrocarbons from secondary zinc smelting**

Yuanping Yang a,b, Lili Yang a,b,\*, Guorui Liu a,b,c, Minghui Zheng a,b,c, Qiuting Yang a,b, Shuting Liu a,b

a State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing, 100085, China

b College of Resources and Environment, University of Chinese Academy of Sciences, Beijing, 100049, China

c School of Environment, Hangzhou Institute for Advanced Study, UCAS, Hangzhou 310000, China

\* Corresponding author: Tel: +86-10-6284-9356

E-mail: llyang@rcees.ac.cn

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**Contents:**

**Analysis Methods of Cl/Br-PAH in Stack Gas Samples from SeZn Plants.**

**Table S1**. Emission factors of Cl-PAHs and Br-PAHs in stack gas samples from various secondary nonferrous metal smelting processes

**Figure S1**. (a) Cl-PAHs TEQ concentration and (b) Br-PAHs concentrations in the stack gas from different secondary nonferrous metal smelting processes including secondary aluminum smelting (SeAl), secondary copper smelting (SeCu), secondary lead smelting (SePb) and secondary zinc smelting (SeZn).

**Analysis Methods of Cl/Br-PAH in Stack Gas Samples from SeZn Plants**

Before sampling, isotopic internal standards of Cl/Br-PAHs including 13C6-1-chloropyrene, 13C6-7-chlorobenz[a]anthracene, 13C6-7-bromobenz[a]anthracene (Cambridge Isotope Laboratories, Tewksbury, MA, USA), 13C6-9-chlorophenanthrene, 13C6-2-choroanthracene, and 9-bromophenanthrene-d9 (Toronto Research Chemicals, North York, ON, Canada) were added to an adsorbent agent (XAD-2 resin) as sampling markers to evaluate the recovery during sampling. The stack gas collected was wrapped in aluminum foil and sealed in valve bags. Samples were stored in a refrigerator until sample purification and instrumental analysis.

During purification of samples from SeZn industries that contain more organic impurities, using only activated silica gel column cannot achieve the purification required for analyzing Cl/Br-PAHs at trace levels. A gel permeation chromatography column and an inverted activated carbon column were added for sample purification. For gel permeation chromatography column purification, 70 mL N-hexane/dichloromethane (1/1, v/v) were used for pre-leaching, and 130 mL N-hexane/dichloromethane (1/1, v/v) were then used as the eluent after loading the samples. The eluent was then concentrated and passed through the activated carbon column for further purification. N-hexane/dichloromethane (60 mL, 4/1, V/V) solution and 100 mL of toluene were used for pre-leaching. After sample loading, 60 mL of N-hexane/dichloromethane (4/1, V/V) solution were used for leaching and the leachate was discarded. Next, the activated carbon column was reversed and eluted with 100 mL toluene. The eluent was then concentrated to approximately 20 µL by rotary evaporator and nitrogen blower, and 13C6-7,12-diClBenz[a]anthracene (Cambridge Isotope Laboratories) was added as an injection standard for the calculation of recoveries. The determination was conducted on a DB-5MS capillary column (60.0 m × 0.25 mm ID × 0.25 µm, Agilent Technologies, Santa Clara, CA, USA). The gas chromatography inlet temperature was 280°C and the carrier gas was high-purity helium (≥99.999%). The programmed temperature of the column was as follows: initial temperature 50°C, then increase to 175°C at 25°C/min, increase to 200°C at 5°C/min for 28 min, then increase to 300°C at 8°C/min for 10 min. The ionization mode was electron impact and the electron energy was set to 45 eV.

**Table S1**. Emission factors of Cl-PAHs and Br-PAHs in stack gas samples from various secondary nonferrous metal smelting processes

|  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  | | In this study | | | | | | | | SecCu1 | SecPb2 | SecAl2 |
| SecCu1 | SecCu2 | SecCu3 | SecCu4 | SecPb1 | SecPb2 | SecZn1 | SecZn2 |
| Emission factor in Mass | Cl-PAHs(mg t-1) | 0.11 | 2.35 | 2.38 | 0.60 | 0.23 | 14.59 | 85.55 | 272.03 | 0.3 | 0.5 | 0.2-1.1 |
| Br-PAHs(mg t-1) | 0.29 | 0.09 | 1.14 | 0.016 | 0.018 | 0.33 | 3.47 | 3.69 | 0.05 | 0.03 | 0.04 |
| Emission factor in TEQ | Cl-PAHs (μg TEQ t-1) | 0.15 | 1.52 | 7.09 | 0.35 | 0.24 | 6.49 | 98.84 | 324.34 | 1.1 | 0.5 | 0.9-1.8 |
| Br-PAHs (μg TEQ t-1) | 0.05 | 0.02 | 1.34 | 0.005 | 0.0044 | 0.041 | 0.78 | 0.82 | 0.01 | 0.01 | 0.05-0.06 |

SecCu: Secondary copper smelting process; SecPb: Secondary lead smelting process; SecZn: Secondary zinc smelting process; SecAl: Secondary aluminum smelting process.



**Figure S1.** a) Cl-PAHs mass concentration, (b) Br-PAHs mass concentration, (c) Cl-PAHs TEQ concentration and (d) Br-PAHs concentrations in the stack gas from different secondary nonferrous metal smelting processes including secondary aluminum smelting (SeAl), secondary copper smelting (SeCu), secondary lead smelting (SePb) and secondary zinc smelting (SeZn).

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