New Insight into Atmospheric Mercury Emissions from Zinc Smelters Using Mass Flow Analysis

Qingru Wu,[†,‡] Shuxiao Wang,*,[†,‡] Mulin Hui,[†] Fengyang Wang,[†] Lei Zhang,[†,‡] Lei Duan,[†,‡] and Yao Luo[†]

[†]State Key Joint Laboratory of Environmental Simulation and Pollution Control, School of Environment, Tsinghua University, Beijing 100084, People's Republic of China

[‡]State Environmental Protection Key Laboratory of Sources and Control of Air Pollution Complex, Beijing 100084, People's Republic of China

S *Supporting Information*

ABSTRACT: The mercury (Hg) flow paths from three zinc (Zn) smelters indicated that a large quantity of Hg, approximately 38.0−57.0% of the total Hg input, was stored as acid slag in the landfill sites. Approximately 15.0−27.1% of the Hg input was emitted into water or stored as open-dumped slags, and 3.3−14.5% of the Hg input ended in sulfuric acid. Atmospheric Hg emissions, accounting for 1.4−9.6% of the total Hg input, were from both the Zn production and waste disposal processes. Atmospheric Hg emissions from the waste disposal processes accounted for 40.6, 89.6, and 94.6% of the total atmospheric Hg emissions of the three studied smelters, respectively. The Zn production process mainly contributed to oxidized Hg (Hg^{2+}) emissions, whereas the waste disposal process generated mostly elemental Hg (Hg^0) emissions. When the emissions from these two processes are considered together, the emission proportion of the Hg^{2+} mass was 51, 46, and 29% in smelters A, B, and C, respectively. These results indicated that approximately 10.8 ± 5.8 t of atmospheric Hg emissions from the waste disposal process were ignored in recent inventories. Therefore, the total atmospheric Hg emissions from the Zn industry of China should be approximately 50 t.
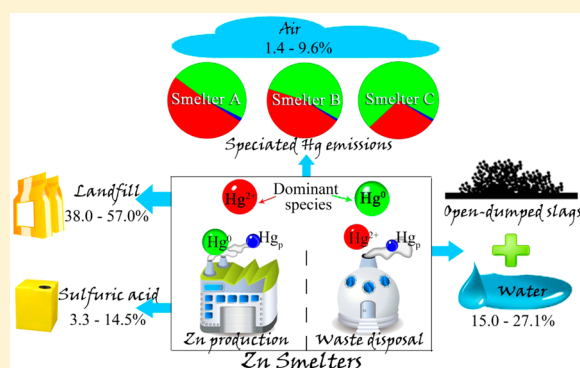
1. INTRODUCTION

As one of the largest anthropogenic Hg emitters, the Zn smelting industry is regulated for Hg emissions by the Minamata Convention on Mercury.[1−5] Previous studies indicated that ore concentrates were the dominant Hg source for the Zn industry.[6−9] Most Hg in the concentrates was released into the flue gas in the roaster. Various air pollution control devices (APCDs) had variable Hg removal efficiencies, from 2.4 to 99.3%.[6−9] In general, more than 95.0% Hg in the roasting flue gas was transferred into dust, waste acid, or sulfuric acid or was reclaimed by specific Hg removal techniques.[6−9] Without specific Hg removal techniques, Hg would mostly be found in the waste acid, accounting for 69.7−84.6% of the total Hg input.[9] Instead, approximately 58.0% Hg was reclaimed by specific Hg removal techniques.[6] Less than 1.0% Hg was emitted as atmospheric Hg in the exhaust roasting gas, and the main Hg speciation was Hg^{2+} (82−96%).[6,9]

Previous studies mainly focused on the emission characteristics of atmospheric Hg from the Zn production process.[6−9] However, there are unresolved questions in terms of Hg re-emissions from the thermal disposal of wastes in the tracking of the Hg flow in Zn smelters. Hg in the roasting flue gas was largely removed into Hg-containing wastes by APCDs, but the fate of Hg in these wastes has been unclear. For example, approximately 10% Hg in the flue gas was captured as dust.[6−10]

If the dust was treated in a pyro process, Hg on the dust might be released again as a gaseous phase.[11] Without proper measures to control the emissions of these Hg sources, Hg might be re-emitted to air. Thus, tracking the flow of Hg in Zn smelters is necessary for a comprehensive estimation of atmospheric Hg emissions from all of the thermal processes in the Zn industry. Furthermore, the speciation of the emitted Hg is a significant factor in determining the behavior of Hg because of the very different physical−chemical characteristics of Hg^{2+}, Hg^0, and particulate Hg (Hg_p). Previous studies only provided limited information on the Hg speciation profiles in the exhaust roasting gas.[6,9] The Hg speciation profiles in the exhaust dehydration kiln gas, exhaust cooling cylinder gas, exhaust slag roasting/smelting gas, and exhaust volatilization kiln gas are unknown. It is important to analyze the Hg speciation profiles in these categories of gases considering that their emissions might account for a large proportion of the total emissions. An investigation in a Zn smelter indicated that atmospheric Hg emissions from roasting gas was only 22 g
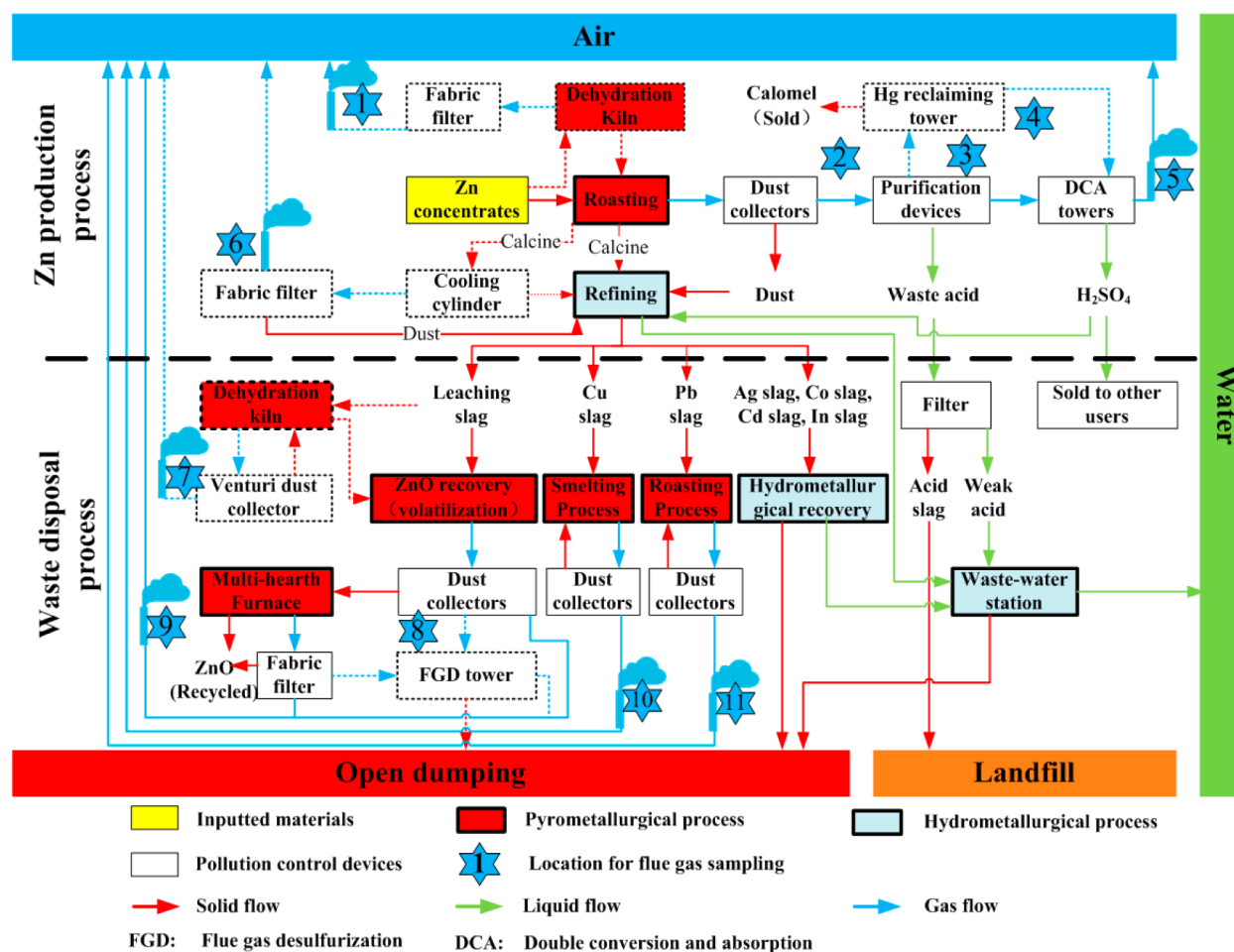
Figure 1. Zn production process and waste disposal process in the studied smelters (the dotted line represented that only one smelter using this process).

day^{-1}, whereas the emissions from exhaust volatilizing kiln gas in the zinc oxide (ZnO) recovery process reached 50 g day^{-1}.[6]

In this study, we investigate the Hg flow in three Zn smelters using an electrolytic process and focus on atmospheric Hg emission characteristics from the thermal processes in the flow. The contribution of waste disposal to atmospheric Hg emissions and its impact on Hg speciation profiles are discussed. These results will be helpful to improve the Hg emission inventory and provide further insight in the control of Hg emissions from Zn smelters.

2. METHODOLOGY

2.1. Characteristics of the Smelters Studied. We conducted field measurements in three Zn smelters (denoted as smelter A, smelter B, and smelter C). Both the Zn production and waste disposal processes were considered in this study. The detailed identities of the three smelters are listed in Table S1 of the Supporting Information.

2.1.1. Zn Production Process. All three smelters produce Zn with an electrolytic process. This process has been adopted to produce 79% of the refined Zn in China.[4] This process can be divided into the roasting process and the refining process (The refining process includes leaching, purification, and electrolysis.) (Figure 1). In the roasting process, the Zn concentrates (mainly zinc sulfide) are roasted into calcine (mainly ZnO) directly in smelters A and B, whereas the Zn concentrates are dried in an ore dehydration kiln before being roasted in smelter

C. In smelter A, calcine is additionally cooled in a cooling cylinder, where air pollutants are captured by a fabric filter (FF). The roasting flue gas is cleaned by a combination of APCDs, which include sequential dust collectors (waste heat boiler, cyclone separator, and electrostatic precipitator), purification devices, and double conversion and absorption (DCA) towers (Figure 1). Approximately 76% of the Chinese refined Zn has been produced in smelters using this type of flue gas cleaning process.[4] Dust, waste acid, and sulfuric acid are produced from the gas cleaning process. A Hg reclaiming tower is installed before DCA towers to recover flue gaseous Hg in smelter C. In the refining process, calcine, dust, and sulfuric acid are input into the leaching tank to dissolve ZnO in the dust and calcine. Metals, including silver (Ag), indium (In), cobalt (Co), copper (Cu), cadmium (Cd), and lead (Pb), are dissolved simultaneously and then separated as slags through leachate purification. The purified leachate is electrolyzed to produce refined Zn, and the insoluble materials in the leaching tank are emitted as leaching slag (Figure 1).

2.1.2. Waste Disposal Process. The wastes produced from the Zn production process include waste acid, leaching slag, and metal slags. The waste acid is stored in a settler, and its precipitate (acid slag) is separated by filtration. The supernatant and filtrate are mixed, becoming a weak acid and are treated in a wastewater station. The slag produced from the wastewater station is open-dumped, and the drainage is allowed to flow to water. The leaching slag is roasted in a volatilization kiln in the

ZnO recovery process (Figure 1). The volatilization kiln gas goes through dust collectors (waste heat boiler and FF) for dust removal. The dust captured by the dust collectors is roasted in a multi-hearth furnace. The flue gas from this furnace is cleaned by FF before flowing into the same stack with the exhaust volatilization kiln gas. An additional flue gas desulfurization (FGD) tower is installed before the stack to remove SO$_2$ in smelter A. The water stream from the FGD tower is simply treated by a hydrocyclone and filter. The treated water is returned to the FGD tower, and the waste sludge (FGD gypsum) is open-dumped. In smelter A, the leaching slag is dried in a slag dehydration kiln before being roasted. Noble metals (including Ag, In, Cd, and Co) are retrieved from slags using hydrometallurgical recovery processes. Heavy metals (including Cu and Pb) are recovered by pyrometallurgical processes, and the dust collectors remove dust from the flue gases.

2.2. Hg Flow Analysis. The Hg flow in the Zn smelters examines the Hg input into the studied smelters, the stocks and flows in the smelters, and the outputs from the smelters to other systems. To finish the Hg flow, four major steps are required, including (1) goal and system definition, (2) data acquisition, (3) material balances, and (4) interpretation.[12,13] In this study, the target is to establish Hg flow in the studied smelters and to determine potential atmospheric Hg emission points. The studied systems are the whole smelters. The data used for Hg flow analysis include raw material consumption, waste and product production, and their Hg concentrations. The consumption/production data were obtained from the reports of smelters on production, sales, and purchases (see Table S2 of the Supporting Information). The Hg concentrations were tested using the method described in sections 2.2.1 and 2.2.2. Hg emissions from energy input are provided in S3 of the Supporting Information, which were beyond the borders of our flow analysis because these emissions were generally included as industrial/commercial uses in the emission sector of stationary combustion of fossil fuels (coal, oil, and natural gas).[1-3] Hg emissions from Pb slag roasting processes and the Cu slag smelting process were calculated on the basis of Hg in the metal slags and the Hg removal efficiency of the dust collectors.

2.2.1. Solid/Liquid Sampling and Analysis. The liquid samples were collected in polytetrafluoroethylene bottles according to the Chinese standard for wastewater sampling.[14] The solid samples were collected using the method of stockpile random sampling, which was described in detail in our previous paper.[15] The details on the number of samples collected are listed in Table S4 of the Supporting Information.

The liquid samples were analyzed immediately after sampling according to the United States Environmental Protection Agency (U.S. EPA) Method 7470A[16] with a F732-V intelligent mercury analyzer, which uses cold vapor atomic absorption spectrophotometry (CVAAS) and has a detection limit of 0.05 mg L^{-1}. The solid samples were dried and crushed to 100 mesh for subsequent analysis. Most of the solid samples were analyzed with U.S. EPA Method 7473[17] using a Lumex 915M + pyro attachment (with a detection limit of 0.5 mg t^{-1}). Samples with a Hg concentration exceeding its measuring range were digested with aqua regia at 95 °C in a water bath, and a suitable aliquot of digested solution was measured with F732-V (with a detection limit of 1.0 g t^{-1}).

2.2.2. Flue Gas Sampling and Analysis. The flue gas sampling locations are shown in Figure 1. The Ontario Hydro

method (OH method) was employed for sampling locations with the SO$_2$ concentration less than 1000 ppm.[18] For locations with the SO$_2$ concentration equal to or higher than 1000 ppm, the revised OH method[9] was used in smelters A and B, whereas the U.S. EPA Method 29[19] was adopted in smelter C. The revised OH method replaced 1 M KCl with 1 M KOH and increased the concentration of H$_2$O$_2$ from 1 to 3% (see S5 of the Supporting Information). The impinger solutions obtained from flue gas sampling were analyzed using the same method for liquid samples (see section 2.2.1).

2.2.3. Hg Removal Efficiency of APCDs. The synergic Hg removal effect of APCDs is one of the main factors determining the atmospheric Hg emissions from Zn smelters.[6-9] In this study, the Hg removal efficiency η (%) of APCD i, which is defined as the fraction of Hg captured by the device, can be calculated from the following equation:

$$
\begin{aligned}
\eta_i &= \left(1 - \frac{C_{outlet}P_{outlet}}{C_{inlet}P_{inlet}}\right) \times 100\% \\
&= \frac{C_{captured}P_{captured}}{C_{captured}P_{captured} + C_{outlet}P_{outlet}} \times 100\%
\end{aligned}
\tag{1}
$$

where C_{inlet} and C_{outlet} are the Hg concentrations in the flue gas at the inlet and outlet of APCDs, respectively (μg m^{-3}), P_{inlet} and P_{outlet} are the gas flow rates at the inlet and outlet of APCDs, respectively (km^3 year^{-1}), $C_{captured}$ and $P_{captured}$ are the Hg concentration and production of the materials produced by APCD i, respectively (g t^{-1} and t year^{-1}, respectively).

2.3. Quality Assurance (QA)/Quality Control (QC). Before sampling, all bottles were cleaned in the laboratory by immersion in a 10% HNO$_3$ (v/v) bath for 24 h, followed by repeated rinses in Milli-Q-grade water (18.2 MΩ cm). The flue gaseous Hg sampling system was calibrated after cleaning the sampling line thoroughly, and then, a leak test was performed. More than three parallel samplings under stable operating conditions were conducted to ensure the validity of the results.

Multiple dilutions of a 1000 μg mL^{-1} certified Hg standard solution (Hg standard solution, GSB04-1729-2004, supplied by the State Non-ferrous Metals and Electronic Materials Analysis and Testing Center) were used for the calibration of F732-V and the Lumex 915M + pyro attachment. The certified reference material of Zn/Pb ores (certified reference for the component analysis of rich Zn/Pb ores, GBW07165, supplied by the National Research Center for CRMs of China) was also used as the external standard. Each solid/liquid sample was analyzed 3 times, at least, to obtain parallel results, with a relative standard deviation of less than 10%.

3. RESULTS AND DISCUSSION

3.1. Hg Concentration in the Solid and Liquid Samples. The Hg concentrations in different samples are shown in Table S5 of the Supporting Information. The average Hg concentrations in the consumed Zn concentrates were 30.7 ± 12.7, 47.6 ± 12.5, and 24.7 ± 10.8 g t^{-1} (weighted geometric mean ± standard deviation) for smelters A, B, and C, respectively. The Hg concentration in the coke powder for the ZnO recovery process was 0.2 ± 0.1 g t^{-1} in smelter A and 0.3 ± 0.1 g t^{-1} in smelter B, which were much lower than the Hg concentration in the Zn concentrates.

The main intermediate materials were the dusts from the roasting process and the slags from the thermal process (including leaching slag, Cu slag, and Pb slag). The Hg

Table 1. Hg Concentrations in the Flue Gas

sampling location		Hg concentration in the flue gas ($\mu g\ m^{-3}$)		
number	description	smelter A	smelter B	smelter C
location 1	exhaust ore dehydration kiln gas			567.1 ± 58.1
location 2	roasting flue gas after dust collectors	11436.5 ± 1670.4	15134.4 ± 1760.4	11837.1 ± 2769.0
location 3	roasting flue gas after purification devices	3277.2 ± 3028.1	3591.1 ± 699.1	6833.3 ± 827.0
location 4	roasting flue gas after Hg reclaiming tower			877.5 ± 223.2
location 5	exhaust roasting gas	564.8 ± 485.6	34.5 ± 9.2	11.3 ± 1.7
location 6	exhaust cooling cylinder gas	408.7 ± 303.9		
location 7	exhaust slag dehydration kiln gas	8.3 ± 4.1		
location 8	volatilization kiln gas before FGD tower	43.0 ± 2.4		
location 9	exhaust volatilization kiln gas	170.9 ± 127.2	274.2 ± 10.7	238.1 ± 32.1
location 10	exhaust Cu slag smelting gas	399.8 ± 66.1	683.2 ± 83.2	185.2 ± 71.0
location 11	exhaust Pb slag smelting gas	77.5 ± 11.3	48.0 ± 7.5	35.9 ± 9.1
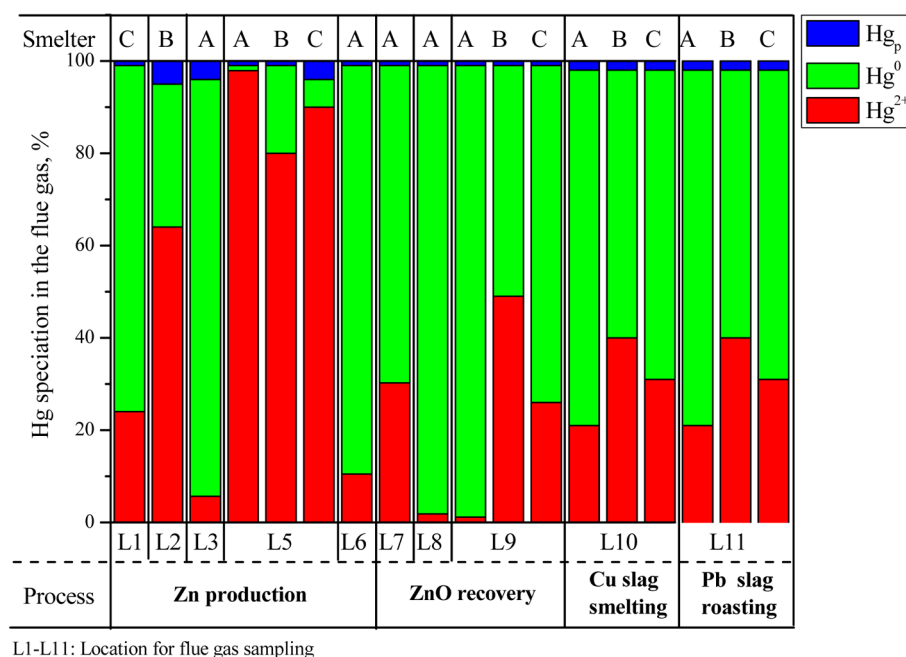
Figure 2. Hg speciation in the flue gas of different sampling locations.

concentrations in the dusts varied from 0.2 ± 0.2 to 33.1 ± 3.1 g t^{-1} in different smelters. In smelter A, the dust collected by the electrostatic precipitator was approximately 21.9 ± 11.4 g t^{-1} but only 0.4 ± 0.3 g t^{-1} for the dust collected by the cyclone separator. This Hg concentration variation might correlate with the particle diameter. Smaller sized particles might provide a larger specific surface area for the Hg interaction in the flue gas. The Hg concentrations in the leaching slag, Cu slag, and Pb slag were lower than that in the Zn concentrates. The main output Hg-containing material was acid slag, which contained the highest Hg concentration in all of the samples from the three smelters. The Hg concentration in the sulfuric acid was well below 10 g t^{-1}, the requirement for the best class of sulfuric acid for industrial use in China.[20]

3.2. Hg Concentration and Speciation in the Flue Gas.
3.2.1. Hg Concentration in the Flue Gas. Hg concentrations in different sampling locations are shown in Table 1. In the Zn production process, Hg in the Zn concentrates is released to the flue gas of the roaster. In the flue gas from the roaster, even after dust collection, the Hg concentration reached as high as $11\ 436.5 \pm 1670.4\ \mu g\ m^{-3}$ in smelter A, $15\ 134.4 \pm 1760.4\ \mu g\ m^{-3}$ in smelter B, and $11\ 837.1 \pm 2769.0\ \mu g\ m^{-3}$ in smelter C.

When the flue gas went through the purification devices, the Hg concentration was reduced to $3277.2 \pm 3028.1\ \mu g\ m^{-3}$ in smelter A, $3591.1 \pm 699.1\ \mu g\ m^{-3}$ in smelter B, and $6833.3 \pm 827.0\ \mu g\ m^{-3}$ in smelter C. A Hg reclaiming tower installed after the purification devices further reduced the Hg concentration in the flue gas to $877.5 \pm 223.2\ \mu g\ m^{-3}$ in smelter C. When the flue gas went through the DCA towers, the Hg concentration in the exhaust gas was $564.8 \pm 485.6\ \mu g\ m^{-3}$ in smelter A, $34.5 \pm 9.2\ \mu g\ m^{-3}$ in smelter B, and $11.3 \pm 1.7\ \mu g\ m^{-3}$ in smelter C. In smelter A, some Hg in the roasting flue gas leaked out into the cooling cylinder and the Hg concentration in the exhaust gas was diluted by air to $408.7 \pm 303.9\ \mu g\ m^{-3}$. In smelter C, the Hg concentration in the exhaust ore dehydration kiln gas was $567.1 \pm 58.1\ \mu g\ m^{-3}$.

In the ZnO recovery process of the waste disposal process, the Hg concentration was only $8.3 \pm 4.1\ \mu g\ m^{-3}$ in the exhaust gas from the slag dehydration kiln of smelter A. Most Hg was released into the volatilization kiln flue gas. In smelter A, the Hg concentration after dust collectors for the volatilization kiln flue gas was $43.0 \pm 2.4\ \mu g\ m^{-3}$. However, because of the recycling of the collected dust in the multi-hearth furnace, Hg captured by the dust collectors was released into the multi-

hearth furnace flue gas. In smelter A, these two streams of gases were desulfurized in a FGD tower, and the Hg concentration after the FGD tower (also as exhaust volatilization kiln gas) was 170.9 ± 127.2 μg m^{-3}. In smelters B and C, the two streams of gases emitted directly, and the Hg concentrations were 274.2 ± 10.7 and 238.1 ± 32.1 μg m^{-3}, respectively. In the Cu slag smelting process, the Hg concentrations in the exhaust gas were 399.8 ± 66.1, 683.2 ± 83.2, and 185.2 ± 71.0 μg m^{-3} in smelters A, B, and C, respectively. In the Pb slag roasting process, the Hg concentration in the exhaust gas was 77.5 ± 11.3 μg m^{-3} in smelter A, 48.0 ± 7.5 μg m^{-3} in smelter B, and 35.9 ± 9.1 μg m^{-3} in smelter C.

Although the roaster was the largest Hg emitter in the Zn smelters, most Hg in the flue gas was removed after passing through a series of APCDs and only a small proportion of Hg in this gas was emitted into the air. The Hg concentration in the exhaust roasting gas was reduced to the same level as or was much less than the Hg concentration in other exhaust gases (including exhaust ore dehydration kiln gas, exhaust cooling cylinder gas, exhaust volatilization kiln gas, exhaust Cu slag smelting gas, and exhaust Pb slag roasting gas).

3.2.2. Hg Speciation in the Flue Gas. Overall, the Hg$_p$ proportion was less than 5% at all of the sampling locations (see Figure 2). In the roaster, Hg in Zn concentrates was released to flue gas as Hg^0 at the roasting temperature of 900−1000 °C.[10] Then, part of Hg^0 was oxidized to Hg^{2+} with the existence of gaseous oxidants (e.g., Cl) or catalytic oxidants (e.g., dust) in the flue gas.[21,22] The flue gas temperature declined when the flue gas went through dust collectors. Hg^0 and Hg^{2+} in the gas phase either condensed on or were adsorbed by dust, and most Hg$_p$ was removed. Hg^{2+} was the primary form after dust collectors in smelter B, the proportion of which reached 64%. It can be estimated that most Hg^{2+} and Hg$_p$ would be removed by purification devices.[6] Thus, Hg^0 was the dominant Hg species in the flue gas after the purification devices. However, when the flue gas went through the DCA towers, the share of Hg^{2+} increased significantly, i.e., 98% in smelter A, 80% in smelter B, and 90% in smelter C. This was mainly caused by the oxidation effect of both the V$_2$O$_5$ catalyst and concentrated sulfuric acid in the tower.[6,9]

In the waste disposal process, Hg^0 was the dominant speciation at all sampling locations. In the ZnO recovery process, the Hg^0 proportion was 68% in the exhaust slag dehydration kiln gas of smelter A. The Hg^0 proportion in the exhaust volatilization kiln gas comprised 98% in smelter A, 52% in smelter B, and 69% in smelter C. In the Cu slag smelting and Pb slag roasting processes, the Hg^0 proportion accounted for 58−78% in the three smelters.

Overall, the main Hg speciation in the exhaust roasting gas was Hg^{2+}, which was consistent with previous studies.[6,9] However, previous studies neglected that exhaust gases (e.g., exhaust dehydration kiln gas, exhaust cooling cylinder gas, exhaust volatilization kiln gas, and exhaust slag smelting gas) have a tendency to share a higher Hg^0 proportion. The final Hg speciation profile for a Zn smelter should comprehensively consider the mass emissions of different Hg forms in all exhaust gases, which will be discussed in the following section.

3.2.3. Hg Removal Efficiency of APCDs. The Hg removal efficiencies of different APCDs are shown in Table S6 of the Supporting Information. The dust collectors showed 8.7−11.9% efficiencies for Hg removal. The Hg removal efficiencies of purification devices were 55.6−83.1%, which were impacted by the Hg^{2+} proportion in the inlet flue gas.[9] The Hg removal

efficiencies for DCA towers were 82.7% in smelter A, 99.0% in smelter B, and 96.5% in smelter C. The efficiency of DCA towers in smelter A was much lower because there was only one layer of catalytic bed in the second conversion tower, whereas two layers of catalytic bed were used in smelters B and C. The Hg removal efficiency of the Hg-reclaiming tower in smelter C was 91.5%. It could be concluded that the combined efficiencies of APCDs for the roasting flue gas were 96.6, 99.8, and 99.9% for smelters A, B, and C, respectively.

3.3. Hg Flow in the Studied Smelter. The recovery rate for the Hg flow was $103 \pm 9\%$ in smelter A, $93 \pm 12\%$ in smelter B, and $111 \pm 7\%$ in smelter C, which were within acceptable accuracies.[6,9,21] The difference between the Hg input and output was mainly caused by the fluctuations of Hg in the ore concentrates.

In all three smelters, Hg in the Zn concentrates comprised more than 99.5% of the total Hg input. As for the outputs, a large proportion of Hg was stored in the acid slags, approximately 55.7, 57.0, and 38.0% of total input in smelters A, B and C, respectively (see Table 2). The acid slags were

Table 2. Hg Outputs in the Studied Smelters

environment and product	Hg outputs (%)		
	smelter A	smelter B	smelter C
air (Zn production process)	5.7	0.1	0.3
air (waste disposal process)	3.9	1.3	5.2
landfill	55.7	57.0	38.0
recycled Hg	0.0	0.0	38.2
sulfuric acid	13.7	14.5	3.3
water and open-dumped slags	21.0	27.1	15.0

sealed up in the landfill sites. In smelter C, approximately 38.2% Hg was released into calomel. Calomel was sent to a qualified company for Hg recovery. Hg in sulfuric acid accounted for 13.7, 14.5, and 3.3% of total Hg input for smelters A, B, and C, respectively. The sulfuric acid produced from smelter A was used as a dressing solvent by a vanadium ore dressing plant. The sulfuric acid from smelters B and C was sold to various types of users, such as chemical and fertilizer plants. Sulfuric acid was generally used as acid solvent. Thus, instead of being emitted to air, it was quite possible that Hg in sulfuric acid might be emitted into wastewater, captured into slag, or remained in the products (e.g., pesticide). Total Hg in the noble metal slags (e.g., Ag slag, Cd slag, Co slag, and In slag) comprised 5.3, 1.9, and 2.9% for smelters A, B, and C, respectively. Hg in these slags tended to emit into wastewater or remained in the waste slags.[23] Hg emitted as water station slag accounted for 15.2% in smelter A, 25.0% in smelter B, and 12.0% in smelter C. In smelter A, approximately 0.3% of Hg was emitted into FGD slag. It should be noted that the waste slags, FGD slag, and water station slag were open-dumped. Total Hg emitted into water and open-dumped slags accounted for 15.0−27.1%.

In addition to the amount of Hg mentioned above, the rest of Hg was emitted into air, approximately 9.6% in smelter A, 1.4% in smelter B, and 5.5% in smelter C. In the three smelters, about $2.0 \pm 3.2\%$ Hg was emitted from the Zn production process; meanwhile, atmospheric Hg emissions from the waste disposal process accounted for $3.5 \pm 2.0\%$ of total Hg input. In particular, dust played a significant role for atmospheric Hg emissions from the waste disposal process. Hg in the dust accounted for more than 85% of the total Hg input to the
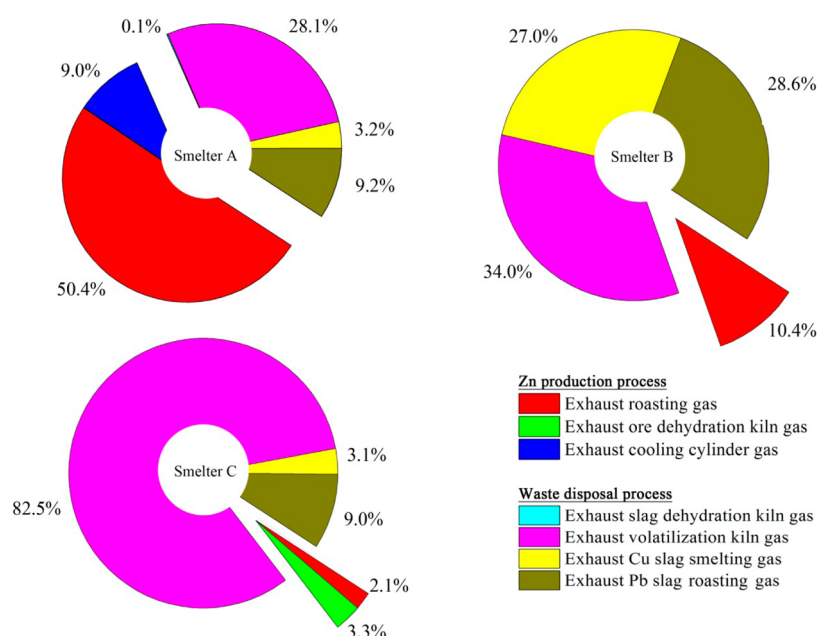
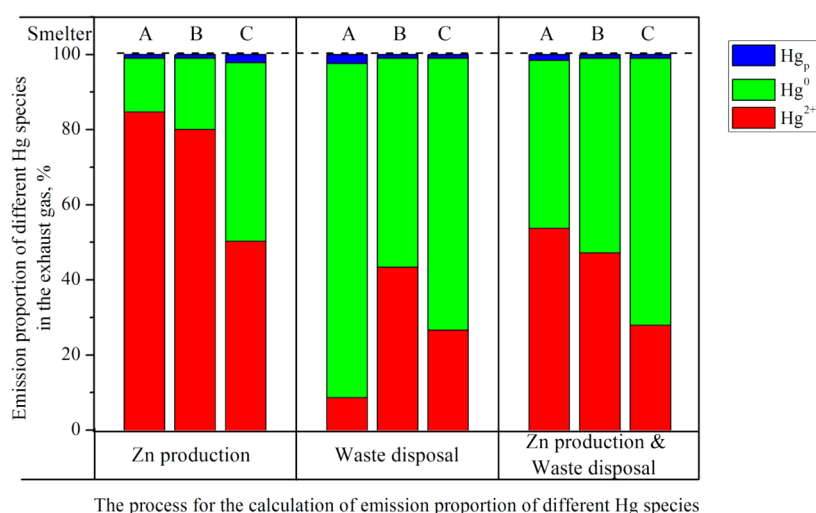**Figure 3.** Mass proportion of atmospheric Hg emitted from different exhaust gas sources.

Figure 4. Speciated Hg emissions from different processes.

refining process. This Hg was emitted to waste liquid, leaching slags, or metal slags. During the thermal processes of leaching slag, Pb and Cu slags, most Hg was re-emitted into the air. Overall, the Hg emission from waste disposal processes accounted for 40.6, 89.6, and 94.6% of the total atmospheric Hg emissions for smelters A, B, and C, respectively (see Figure 3). In smelters B and C, the atmospheric Hg emissions from exhaust volatilization kiln gas shared the largest proportion of approximately 34.0 and 82.5%, respectively, of the total atmospheric Hg emissions.

3.4. Implications for National Hg Emissions. In the recent studies on atmospheric Hg emissions from the primary Zn industry, emissions were calculated mainly based on Hg released from ore concentrates and the Hg reductions by APCDs in the Zn production process.[1,4,10] Hylander and Herbert estimated that 5% Hg was emitted to air by smelters with installed DCAs but without specific Hg removal devices, leaving 95% Hg in the wastes or byproducts unresolved.[10] Our investigation on the Hg flows in Zn smelters indicated that Hg

emissions from the waste disposal process accounted for 40.6, 89.6, and 94.6% of total atmospheric Hg emissions for smelters A, B, and C, respectively (see Figure 4). In China, the total Hg input into the Zn industry with the electrolytic process reached 287.9 t in 2010 (excluding the 17.6 t of the Hg input to smelters with dust collectors and smelters without APCDs).[4] If the proportion of 3.5 ± 2.0% was used for estimating the atmospheric Hg emission from the waste disposal process, there was an additional 10.8 ± 5.8 t of atmospheric Hg emissions caused by waste disposal. In the recent studies, the atmospheric Hg emission from zinc smelters of China was about 40 t,[1,4] which indicated that about 27% of total emissions was ignored in the current inventories. In the coming years, the backward Chinese Zn smelters will be phased out and result in approximately 30 t of Hg reduction. This meant that the emissions from the waste disposal process (10.8 t) would be as significant as that from the Zn production process in the future.

The disposal of wastes would also impact the atmospheric Hg speciation profiles for the Zn industry. If only considering

the Zn production process, the Hg^{2+} emission proportion was 85% in smelter A, 80% in smelter B, and 50% in smelter C (see Figure 4). However, when considering both the Zn production and the waste disposal processes, we find that the Hg^{2+} emission proportion decreased to 51% in smelter A, 46% in smelter B, and 29% in smelter C. The waste disposal process mainly contributed to Hg^0 emissions. It should be noted that smelter C, which installed a Hg reclaiming tower for its roasting flue gas, showed the lowest proportion of Hg^{2+}. As mentioned before, the high Hg^{2+} emission was mainly found in the exhaust roasting gas because the DCA towers would oxidize Hg^0 into Hg^{2+}. Because the Hg reclaiming tower was installed before the DCA towers, the Hg amount into and out of the DCA towers would decrease, which was the major reason leading to the lower share of Hg^{2+} in the total atmospheric Hg emissions for the whole smelter. In other words, the installation of specific Hg removal devices in the roasting flue gas would reduce the Hg^{2+} proportion in the Hg speciation profile for the Zn industry. A FGD tower installed after the DCA towers would also reduce the Hg^{2+} proportion as a result of the same reason. With the tightening of emission restriction for air pollutants in China,[24] additional FGD tower or specific Hg removal devices would be installed for the roasting flue gas cleaning. From this point of view, the Hg^{2+} proportion emitted from the Zn industry would decrease.

The challenges of applying these results to other Zn smelters include the uncertainty of the Hg removal efficiencies of APCDs and the disposal pattern of wastes/byproducts. The Hg removal efficiencies of APCDs mainly affect the Hg distribution among dust, waste acid, sulfuric acid, calomel, and air in the roasting process. The amount of Hg in the dust would further impact the atmospheric Hg emissions from the waste disposal process. The disposal pattern of dust and slags would also affect the atmospheric Hg emissions. In the imperial smelting process (ISP) to produce both Zn and lead (Pb), dust was re-roasted in the roaster with Zn concentrates. Thus, the waste disposal process had limited atmospheric Hg emissions. In some smelters, the Pb/Cu slags might be landfilled instead of smelted. In addition, if the Pb and Cu slags were smelted in other smelters, Hg might be stored in these slags for several years before being emitted to the atmosphere. This would increase the difficulty in determining the temporal and spatial distribution of atmospheric Hg emissions from the Zn industry.

The field measurements in the studied smelters were conducted at a short-term interval. In the future studies, long-term measurements are required to check the stability of the synergic Hg removal effect of APCDs and analyze Hg emission trends.

ASSOCIATED CONTENT

Ⓢ Supporting Information

S1, identities of the three tested smelters (Table S1); S2, consumption of materials used for Zn production and the production of wastes/byproducts produced (Table S2); S3, Hg emissions from energy input (Table S3); S4, number of collected samples (Table S4); S5, description of the OH method and the revised OH method; S6, Hg concentration in the solid/liquid samples (Table S5); and S7, Hg removal efficiency of APCDs in the roasting process. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*Telephone: +86-1062771466. Fax: +86-1062773597. E-mail: shxwang@tsinghua.edu.cn.

Notes

The authors declare no competing financial interest.

REFERENCES

(1) United Nations Environment Programme (UNEP). *Technical Background Report for the Global Mercury Assessment*; UNEP: Geneva, Switzerland, 2013.

(2) Streets, D. G.; Hao, J. M.; Wu, Y.; Jiang, J. K.; Chan, M.; Tian, H. Z.; Feng, X. B. Anthropogenic mercury emissions in China. *Atmos. Environ.* **2005**, *39*, 7789−7806.

(3) Wu, Y.; Wang, S. X.; Streets, D. G.; Hao, J. M.; Chan, M.; Jiang, J. K. Trends in anthropogenic mercury emissions in China from 1995 to 2003. *Environ. Sci. Technol.* **2006**, *40*, 5312−5318.

(4) Wu, Q. R.; Wang, S. X.; Zhang, L.; Song, J. X.; Yang, H.; Meng, Y. Update of mercury emissions from China's primary zinc, lead and copper smelters, 2000−2010. *Atmos. Chem. Phys.* **2012**, *12*, 11153−11163.

(5) Wang, S. X.; Zhang, L.; Wang, L.; Wu, Q. R.; Wang, F. Y.; Hao, J. M. A review of atmospheric mercury emissions, pollution and control in China. *Front. Environ. Sci. Eng.* **2014**, *8* (5), 631−649.

(6) Wang, S. X.; Song, J. X.; Li, G. H.; Wu, Y.; Zhang, L.; Wan, Q.; Streets, D. G.; Chin, C. K. Estimating mercury emissions from a zinc smelter in relation to China's mercury control policies. *Environ. Pollut.* **2010**, *158*, 3347−3353.

(7) Li, G. H.; Feng, X. B.; Li, Z. G.; Qiu, G. L.; Shang, L. H.; Liang, P.; Wang, D. Y.; Yang, Y. K. Mercury emission to atmosphere from primary Zn production in China. *Sci. Total Environ.* **2010**, *408*, 4607−4612.

(8) Park, J. M.; Lee, S. B.; Kim, H. C.; Song, D. J.; Kim, M. S.; Kim, M. J.; Kim, Y. H.; Lee, S. H.; Kim, J. C.; Lee, S. J. Emission characteristics of mercury in Zn smelting process. *J. Korea Soc. Atmos. Environ.* **2010**, *26* (5), 507−516.

(9) Zhang, L.; Wang, S. X.; Wu, Q. R.; Meng, Y.; Yang, H.; Wang, F. Y.; Hao, J. M. Were mercury emission factors for Chinese non-ferrous metal smelters overestimated? Evidence from onsite measurements in six smelters. *Environ. Pollut.* **2012**, *171C*, 109−117.

(10) Hylander, L. D.; Herbert, R. B. Global emission and production of mercury during the pyrometallurgical extraction of nonferrous sulfide ores. *Environ. Sci. Technol.* **2008**, *42* (16), 5971−5977.

(11) Sikkema, J. K.; Alleman, J. E.; Ong, K. S.; Wheelock, T. D. Mercury regulation, fate, transport, transformation, and abatement within cement manufacturing facilities: Review. *Sci. Total Environ.* **2011**, *409* (20), 4167−4178.

(12) Chakraborty, L. B.; Qureshi, A.; Vadenbo, C.; Hellweg, S. Anthropogenic mercury flows in India and impacts of emission controls. *Environ. Sci. Technol.* **2013**, *47*, 8105−8113.

(13) Chang, T. C.; You, S. J.; Yu, B. S.; Kong, H. W. The fate and management of high mercury-containing lamps from high technology industry. *J. Hazard. Mater.* **2007**, *141* (3), 784−792.

(14) Ministry of Environment Protection (MEP). *Technical Specifications Requirements for Monitoring of Surface Water and Waste Water (HJ/T 91-2002)*; MEP: Beijing, China, 2002.

(15) Zhang, L.; Wang, S. X.; Meng, Y.; Hao, J. M. Influence of mercury and chlorine content of coal on mercury emissions from coal-

fired power plants in China. *Environ. Sci. Technol.* **2012**, *46* (11), 6385−6392.

(16) United States Environmental Protection Agency (U.S. EPA). *Method 7470A: Hg in Liquid Waste (Manual Cold-Vapor Technique)*; U.S. EPA: Washington, D.C., 1994.

(17) United States Environmental Protection Agency (U.S. EPA). *Method 7473: Hg in Solids and Solutions by Thermal Decomposition Amalgamation and Atomic Absorption Spectrophotometry*: U.S. EPA: Washington, D.C., 1998.

(18) ASTM International. *Standard Test Method for Elemental, Oxidized, Particle-Bound, and Total Mercury in Flue Gas Generated from Coal-Fired Stationary Sources (Ontario-Hydro Method)*; ASTM International: West Conshohocken, PA, 2002.

(19) United States Environmental Protection Agency (U.S. EPA). *Method 29: Determination of Metals Emissions from Stationary Sources*; U.S. EPA: Washington, D.C., 1998.

(20) Ministry of Environment Protection (MEP). *Sulfuric Acid for Industrial Use (GB 234-2002)*; MEP: Beijing, China, 2010.

(21) Wang, S. X.; Zhang, L.; Li, G. H.; Wu, Y.; Hao, J. M.; Pirrone, N.; Sprovieri, F.; Ancora, M. P. Mercury emission and speciation of coal-fired power plants in China. *Atmos. Chem. Phys.* **2010**, *10* (3), 1183−1192.

(22) Galbreath, K. C.; Zygarlicke, C. J. Mercury transformations in coal combustion flue gas. *Fuel Process. Technol.* **2000**, *65*, 289−310.

(23) Nriagu, J. O.; Pacyna, J. M. Quantitative assessment of worldwide contamination of air, water and soils by trace-metals. *Nature* **1988**, *333* (6169), 134−139.

(24) Ministry of Environment Protection (MEP). *Emission Standard of Pollutants for Lead and Zinc Industry (GB25466-2010)*; MEP: Beijing, China, 2010.