

Supplementary Materials for

Size Distribution, Chemical Composition, and Emission Factors of Particulate Matter from Metallurgical Processes

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Table S0. Overview of Supplementary Materials

Block	Included item(s)	Content
Source information	Text S1; Tables S1–S2	Sites, APCDs, operation, products, and flue-gas conditions.
Dilution sampling	Text S2; Figure S1	FPS-4000 setup, DR control, size fractions, filter handling, and QA/QC.
Analytical methods	Text S3; Tables S3–S7	Element, ion, and OC/EC methods; parameters, detection limits, and QA/QC.
Mass closure and carbon	Text S4–S5; Figure S2; Table S8	Mass reconstruction, closure uncertainty, OC/EC notes, and carbon data.
WSII and acidity	Text S6–S7; Figures S3–S4	Precursor constraints, PM ₁ sulfate/nitrate relations, AE/CE, and C/A ratios.
Elemental/REE profiles	Figures S5–S7; Text S8	Element proportions, REE enrichment ratios, and REE mass fractions.
Sampling representativeness	Text S9	Representativeness, reliability, and limitations of field stack sampling.
Risk indicators	Table S9; References	PM ₁ toxic-metal metrics and supporting literature.

Text S1. Process overview of the sampled sources

Table S1 summarizes the nine fixed-source sampling sites investigated in this study, including the sampling location, primary air-pollution control devices (APCDs), fuel/energy type, operating load, sector, process/operation, and product. To help readers interpret the cross-sector comparisons, we further clarify the process units represented by each stack. ID1 corresponds to the combined environmental exhaust of a hydrometallurgical zinc line (roasting–leaching–purification–electrowinning) after ZnO-based desulfurization. ID2 represents the blast-furnace ironmaking stack in the steel sector, where iron-bearing burden materials and coke are reduced at high temperature to produce hot metal. The flue gas was treated by a circulating fluidized bed (CFB) system before discharge. ID3 is the acid plant outlet associated with copper off-gas utilization for sulfuric acid production via the double-conversion double-absorption (DCDA) process, where SO₂ is converted/absorbed to produce H₂SO₄ and the tail gas is released after particulate control. ID 4 is the centralized off-gas stack from pyrometallurgical copper smelting (collected furnace/converter off-gases) treated by a baghouse followed by wet flue-gas desulfurization (WFGD). ID5 is the centralized stack of primary aluminum electrolysis (Hall–Héroult), where potroom off-gases are collected and treated by adsorption-based dry scrubbing and filtration. ID6 corresponds to tin chemical production (SnCl₄) via chlorination of metallic tin, with emissions controlled by a cyclone pre-collector and lime-slurry wet scrubbing. ID7 represents the centralized stack of pyrometallurgical tin smelting (reduction smelting and refining) controlled by a baghouse. ID8 is the fuming furnace outlet in pyrometallurgical zinc processing (thermal volatilization and re-oxidation to ZnO fume), with coarse removal by settling/gravity collectors followed by a baghouse. ID9 corresponds to the blast-furnace stack in pyrometallurgical lead smelting (sintering–blast furnace reduction–bullion refining) with flue gas treated by WFGD. These descriptions align with the site information reported in Table S1 and provide the process background for the emissions characterization presented in the main text and supplementary figures.

Table S1. Summary of fixed-source sampling sites

ID	Sampling location	Primary air-pollution control devices (APCDs)	Fuel/energy	Operating load (%)	Sector	Process/operation	Product	Abbrev.
1	Environmental exhaust stack	ZnO-based desulfurization	Coal	85	Zinc smelting (hydrometallurgy)	Hydrometallurgical zinc production	Zn	Zn(Hydro)
2	Blast-furnace ironmaking stack	Flue-gas circulating fluidized bed (CFB) system	Coal	85	Iron and steel	Blast furnace (BF) ironmaking	Hot metal / iron	Fe Smelt
3	Acid plant outlet	Fabric filter (baghouse)	Coal	80	Copper smelting & sulfuric acid production	Double-conversion double-absorption (DCDA)	H ₂ SO ₄	Cu-Acid
4	Centralized off-gas stack	Baghouse + wet flue-gas desulfurization (WFGD)	Coal	85	Copper smelting	Pyrometallurgical copper smelting	Cu	Cu Smelt
5	Centralized off-gas stack	Baghouse + adsorption control	Electricity	90	Aluminum smelting	Primary aluminum electrolysis	Al	Al Smelt

6	Centralized off-gas stack	Cyclone pre-collector + wet scrubbing with lime slurry (water-scrubber)	Coal	90	Tin chemicals (SnCl ₄)	Chlorination of metallic tin	SnCl ₄	Tin-Chem
7	Centralized off-gas stack	Baghouse	Coal	100	Tin smelting	Pyrometallurgical tin smelting	Sn	Sn Smelt
8	Fuming furnace outlet	Baghouse + gravity settling/dust collector	Coal	95	Zinc smelting (pyrometallurgy)	Pyrometallurgical zinc smelting	Zn	Zn(Pyro)
9	Blast furnace stack	Wet flue-gas desulfurization (WFGD)	Coal	95	Lead smelting	Pyrometallurgical lead smelting	Pb	Pb Smelt

Table S2. Flue Gas Characteristics of Fixed Emission Sources

Sector / source	Mean flue-gas velocity (m/s)	O ₂ (vol.%)	Moisture (vol.%)	Temperature (°C)	SO ₂ (mg/m ³)	NO _x (mg/m ³)
Zn(Hydro)	12.7	11.6	13.2	56	38	118
Fe Smelt	3.8	18.4	3.09	117	21	209
Cu-Acid	13.8	6.6	7.2	21	2.0	37.3
Cu Smelt	9.1	19.5	7.2	25	1.5	159
Al Smelt	10.2	20.6	7.8	93	83	275
Tin-Chem	1.9	17.4	3.8	64	437	149
Sn Smelt	6.6	20.5	6.8	30	136	84
Zn(Pyro)	4.9	19.8	11.2	33	56	92
Pb Smelt	3.3	12.0	7.2	39	216	13

Text S2. Dilution sampling setup and quality control

Fixed-source particulate matter (PM) was collected using a Dekati FPS-4000 dilution sampling system equipped with a mixing/residence (aging) chamber (Fig. S1). The sampling concept was adapted from U.S. EPA OTM-37, i.e., hot stack gas is rapidly diluted with conditioned clean air to simulate near-ambient cooling and dilution after stack release, thereby enabling collection of both filterable PM and PM formed/condensed during post-dilution cooling (U.S. EPA, 2018). This approach is widely used for characterizing semivolatile/condensable contributions and generating chemically resolved source profiles under near-ambient conditions(Peng et al., 2024; Liu et al., 2022).

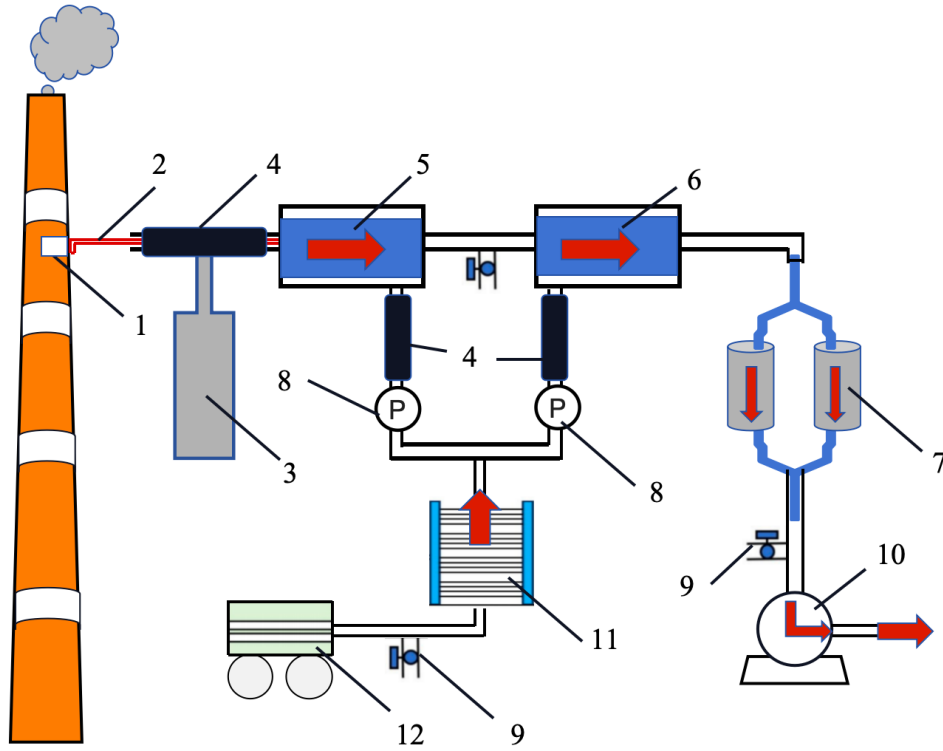


Fig. S1. Schematic diagram of the flue gas dilution tunnel sampling system. The numbered components are as follows: 1. Sampling port of the industrial stack; 2. Sampling probe; 3. Flue gas analyzer; 4. Heating jacket; 5. Primary dilution chamber; 6. Secondary dilution chamber; 7. Four-stage cascade impactor; 8. Pressure gauge; 9. Flow meter; 10. Sampling pump; 11. Filtration system; 12. Clean air generator.

S2.1 Dilution sampling configuration

Flue gas was extracted from the stack through a sampling probe. The transfer line upstream of dilution was heat-traced to minimize premature condensation and wall losses. Dilution air was produced by a clean-air supply unit and passed through filtration and drying/cooling modules prior to entering the dilution system. During field operation, dilution air was maintained at $< 29.4\text{ }^{\circ}\text{C}$ ($85\text{ }^{\circ}\text{F}$) and $\text{RH} < 50\%$, consistent with OTM-37 requirements for conditioned dilution air ([U.S. EPA, 2018](#)).

A two-stage dilution strategy was applied: an initial rapid quench/mixing stage followed by a secondary stage for fine adjustment and stabilization. Post-dilution conditions were controlled using temperature/RH feedback to keep the mixed-gas temperature at the filter location $\leq 29\text{ }^{\circ}\text{C}$ ($85\text{ }^{\circ}\text{F}$) while avoiding visible water condensation in the mixing section and residence chamber ([U.S. EPA, 2018](#)). Surface temperatures of key components were maintained above the diluted-sample dew point to minimize water condensation and associated artifacts ([U.S. EPA, 2018](#)).

S2.2 Dilution ratio (DR)

The dilution ratio (DR) was defined by flow rates:

$$DR = \frac{Q_{total}}{Q_{stack}}, \quad Q_{total} = Q_{dilution} + Q_{stack}$$

where Q_{stack} is the extracted stack gas flow and $Q_{dilution}$ is the dilution-air flow.

Following OTM-37 guidance, DR was selected to (i) cool the diluted sample to $\leq 29\text{ }^{\circ}\text{C}$, (ii) avoid water vapor condensation, and (iii) maintain adequate mass loading to meet analytical detection objectives. OTM-37 recommends using $DR \geq 10$ and ≤ 40 , selecting the lowest $DR \geq 10$ that avoids condensation and achieves detection limits, and not exceeding $DR \geq 40$ because excessive dilution may inhibit formation of condensable PM

that would otherwise occur under ambient dilution/cooling (U.S. EPA, 2018). Consistent with this framework, DR was maintained in the 10-15 range under stable operating conditions; DR stability was tracked continuously from measured flow rates and cross-checked using a CO₂ tracer dilution check (CO₂ before vs. after dilution) as an independent consistency assessment.

Because dilution conditions can influence measured fine PM mass and semivolatile partitioning, temperature/RH at the filter location was treated as the primary operational criterion, while keeping DR stable within the chosen range during each run (Lipsky and Robinson, 2006; England et al., 2007a,b).

S2.3 Size-segregated particle collection and particle bounce control

After stabilization in the residence chamber, the diluted aerosol was routed to a four-stage cascade impactor for aerodynamic size fractionation into four bins: >PM₁₀, PM_{2.5-10}, PM_{1-2.5}, and PM₁. The impactor operated at 30.0 L/min. Flow stability was verified before and after each run; data were accepted when the deviation was within $\pm 5\%$ of the target flow. To reduce particle bounce and re-entrainment on impaction surfaces, a thin layer of low-volatility silicone oil was applied to impaction substrates prior to sampling.

S2.4 Filter media assignment, sample number, and handling

Two filter media were used for different analytical targets. PTFE substrates were used for gravimetric mass and elemental analysis (ICP-MS), while pre-baked quartz-fiber substrates were used for OC/EC and water-soluble ion analyses. Nine representative industrial stacks were sampled once under stable operating conditions. Each sampling event produced four size-segregated samples (four aerodynamic bins) per analyte group. Therefore, the dataset includes $9 \times 4 = 36$ size-resolved samples for each filter medium used for the corresponding analyte group.

Given on-site operational constraints, parallel field duplicates were not conducted for each stack. Therefore, when mean values are reported for a given stack and size bin, they represent the single measurement. Uncertainty control relied on procedural QA/QC (flow/DR/temperature stability checks) and laboratory QA/QC (replicate weighing, blanks, and analytical replicates where applicable). Sampling duration (3-4 h) was adjusted to prevent filter overload based on pressure drop and loading.

S2.5 Gravimetric QA/QC and storage

Gravimetric conditioning was performed in a temperature- and humidity-controlled environment (20–23 °C; RH 30–40%) for ≥ 24 h before and after sampling. Each PTFE filter/substrate was weighed at least twice using a microbalance with 0.01 mg readability; replicate weights were required to agree within ≤ 0.02 mg, and the mean was used as the reported filter mass.

To minimize volatilization artifacts for semi-volatile (condensable-related) species, post-sampling filters were not oven-dried at elevated temperatures. All filters were sealed, protected from light, and stored at ≤ -20 °C until analysis.

S2.6 Blanks and data screening

Field blanks and laboratory blanks were included for background correction and quality assurance. Blank-corrected values were used in reporting. Data screening included checks on (i) stable dilution operation (temperature and DR), (ii) flow stability ($\pm 5\%$ acceptance), and (iii) gravimetric repeatability criteria. In addition, the dilution-based approach is widely used in stationary-source PM characterization specifically because it better mimics post-stack atmospheric cooling and improves characterization of semi-volatile contributions compared with conventional in-stack hot filtration or impinger-based approaches (England et al., 2007; U.S. EPA, 2018).

Text S3. Analytical method

S3.1 Elemental fraction analysis of particulate matter

For the analysis of inorganic elements, the element Fe was analyzed by inductively coupled plasma spectrometry (ICP-OES) alone; the remaining 38 inorganic elements were analyzed by inductively coupled plasma mass spectrometry (ICP-MS) using the "Determination of Lead and Other Metallic Elements in Air and Exhaust

Particulate Matter by Inductively Coupled Plasma Mass Spectrometry" as the reference standard, with the instrument model Agilent 7500a, inorganic elements including Li, Be, Na, P, K, Sc, As, Rb, Y, Mo, Cd, Sn, Sb, Cs, La, V, Cr, Mn, Co, Ni, Cu, Zn, Ce, Sm, W, Tl, Pb, Bi, Th, U, Zr, Al, Sr, Mg, Ti, Ca, Ba, Si.

(1) ICP-MS

I. Principle

In this study, ICP-MS was used to determine the specific elemental concentration of the sample particulate matter. Filter samples were digested with acids, and the resulting solution was nebulized and transported into the ICP torch, where analytes were ionized and introduced into the mass spectrometer for mass-to-charge separation.

II. Pre-treatment of samples

PTFE filter substrates were used for elemental analysis. For each sample, a known fraction of the PTFE filter (1/4 of the deposit area) was cut into small pieces and placed in an acid-cleaned fluoropolymer (PFA/PTFE) digestion vessel. A total of 5.0 mL concentrated HNO₃ (68%, MOS grade) was added, followed by HF to aid dissolution of refractory components. The vessel was tightly capped and heated on a digestion block/hotplate at ~220 °C for 2.5 h. After cooling to room temperature, 5.0 mL dilute HCl (2% v/v) was added to stabilize the matrix. The digest was quantitatively transferred and diluted to 10.0 mL with 18.2 MΩ ultrapure water, mixed thoroughly, and analyzed by ICP-MS (Agilent 7500a). Method blanks and field blanks were processed in parallel, and routine QC included calibration checks and standard recoveries (80–120%) as described in Section V.

III. Instrument operating conditions

Reagents required for the method: MOS grade 68% pure nitric acid; high-purity hydrofluoric acid; superior pure grade hydrochloric acid; multi-element standard solution; 18.2 MΩ ultra-pure water.

Table S3. ICP-MS instrument operating parameters

Parameter	Setting	Parameter	Setting
Power (kW)	1.3	Number of repetitions (times)	3
Sampling depth (mm)	6.9	Measurement method	Peak jump
Carrier gas flow (L/min)	1.15	Sampling cone type	Ni cone
Sample Lifting Speed (rps)	0.1	Nebulizer type	High salt atomizer
Single element integration time (s)	0.5	Mist cooling water temperature (°C)	18
Nebulizer chamber temperature (°C)	2	Resolution (μm)	100

IV. Detection limit

Table S4. Detection limits of ICP-MS method

Element	Average (n=12)	Detection limit (3s)
V	0.0309	0.003
Cr	0.0964	0.0168
Mn	0.0155	0.0094
Co	0.0004	0.0004
Ni	0.0083	0.0091
Cu	0.0437	0.0260
Zn	0.1159	0.1144
As	0.1018	0.0143
Cd	0.0002	0.0003
Pb	0.0118	0.0054

V. Quality Control

For the analysis of field blanks: 1 blank sample is prepared for each batch of samples and the resulting assay value must be less than 2 times the blank sample. For the analysis of method blanks: 1 blank must be prepared for

each batch of samples to ensure that the results are reliable. The detection limit is more than 2 times higher than the blank value. Quality control of the standard sample: The standard sample is quality controlled according to the principle of at least 1 per 10 draws, with a recovery rate between 80% and 120%. Repeat samples for quality control, and the standard sample extraction rate requirements are the same, and should ensure that the relative error between the analytical results is less than 20%.

(2) ICP-OES

I. Principle

Elemental Fe in particulate matter was analyzed using inductively coupled plasma spectrometry (ICP-OES). The ICP light is collimated through the slit, spectroscopically, and then detected by the detector to complete the qualitative and quantitative analysis of the sample.

II. Pre-treatment of samples

A quarter of each PTFE (Teflon) filter was cut using ceramic scissors and placed in a pre-cleaned crucible . The sample was pre-ashed at 300 °C for 40 min, followed by ashing at 530-550 °C for 2h. After cooling to room temperature in a desiccator, the ash was wetted with anhydrous ethanol to improve reagent contact. An alkali fusion step was then performed by adding 0.10-0.20 g NaOH (solid) and heating at 500 °C for 10 min. After cooling, the melt was dissolved in 5.0 mL hot ultrapure water and heated to near boiling to facilitate extraction. The solution was quantitatively transferred, acidified by adding 2.0 mL HCl (2% v/v), and the crucible was rinsed with additional dilute HCl . The final volume was adjusted to 10.0 mL with ultrapure water, mixed thoroughly, and analyzed by ICP-OES together with calibration standards.

III. Instrument operating conditions

Reagents required for the method: sodium hydroxide (solid); pure hydrochloric acid; preparation of standard solution for elemental Fe according to GB602-88.

Table S5. ICP-OES instrument operating parameters

Parameter	Setting	Parameter	Setting
Power (kW)	1.2	Observation height (mm)	10
Plasma gas flow (L/min)	15	Cleaning time (s)	15
Auxiliary gas flow (L/min)	1.5	Points time (s)	10
Nebulizer pressure (kPa)	200	Number of readings (s)	3

IV. Detection limit

Table S6. Detection limit of ICP-OES method

Element	Fe
Detection limit (µg/ml)	0.181

V. Quality Control

For the analysis of field blanks: 1 blank sample is prepared for each batch of samples and the resulting assay value must be less than 2 times the blank sample. For the analysis of method blanks: 1 blank must be prepared for each batch of samples to ensure that the results are reliable. The detection limit is more than 2 times higher than the blank value. Quality control of the standard sample: The standard sample is quality controlled according to the principle of at least 1 per 10 draws, with a recovery rate between 80% and 120%. Repeat samples for quality control, and the standard sample extraction rate requirements are the same, and should ensure that the relative error between the analytical results is less than 20%.

S3.2 Analysis of ionic components in particulate matter

Water-soluble inorganic ions in particulate matter were quantified using an ion chromatograph (Dionex Aquion, Thermo Scientific, USA). Ten ionic species were measured, including PO_4^{3-} , F^- , Cl^- , Na^+ , NH_4^+ , SO_4^{2-} , Mg^{2+} , Ca^{2+} , K^+ and NO_3^- . A quarter of each quartz-fiber filter was cut and transferred into a 25 mL polypropylene

tube, extracted with ultrapure water by ultrasonication for 20 min, and then filtered. The filtrate was directly analyzed by IC via an autosampler (AS-DV).

Anions were separated on an IonPac AS22 analytical column (4×250 mm) with an AG22 guard column (4×50 mm), while cations were separated on an IonPac CS12A analytical column (4×250 mm) with a CG12A guard column (4×50 mm). For anion analysis, a $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$ eluent (4.5/1.4 mmol/L) was used at a flow rate of 1.00 mL/min; an anion suppressor (AERS, 4 mm) was operated at 26 mA, and the column pressure was maintained at 1400–1600 psi. For cation analysis, the eluent was sulfuric acid at 13.6 mmol/L delivered at 1.00 mL/min; a cation suppressor (CERS, 4 mm) was operated at 80 mA, and the column pressure was 1400–1600 psi. Ion identification and quantification were performed using external calibration.

Quality assurance and quality control (QA/QC) included laboratory blanks, procedural blanks, duplicate analyses, and spiked recoveries. For each batch of samples, at least two laboratory blanks were analyzed and the blank results were required to be below the method quantification limit; the relative deviation of blank duplicates was required to be $\leq 20\%$. At least one full procedural blank per batch was also included and was required to be below the method quantification limit; otherwise, the cause was investigated and the batch was reprocessed. Calibration curves were accepted when the correlation coefficient (R^2) was ≥ 0.995 . A mid-level calibration check standard was analyzed for each batch, and the relative error was required to be $\leq 10\%$; otherwise, the calibration was renewed. At least 10% of samples were analyzed in duplicate (or at least one duplicate when the batch size was < 10), with relative deviation $\leq 20\%$. Spiked recoveries were performed at least once per batch, and recoveries were required to be within 80%–120%. Method detection limits and quantification limits are summarized in Table S7.

Table S7. Method detection limit and lower limit of determination for filter membrane samples

Serial number	Ionic name	detection limits	Lower limit of measurement
		($\mu\text{g}/\text{m}^3$)	($\mu\text{g}/\text{m}^3$)
1	F^-	0.010	0.040
2	Cl^-	0.012	0.048
3	NO_3^-	0.027	0.108
4	SO_4^{2-}	0.030	0.120
5	PO_4^{3-}	0.029	0.176
6	Na^+	0.019	0.076
7	Ca^{2+}	0.037	0.148
8	Mg^{2+}	0.020	0.080
9	NH_4^+	0.020	0.080
10	K^+	0.017	0.208

S3.3 Analysis of carbon fraction in particulate matter

OC and EC were quantified using a DRI thermal/optical carbon analyzer (Model 2015, DRI, USA) following the IMPROVE protocol. Carbon evolved during the programmed thermal steps was oxidized to CO_2 , converted to CH_4 , and then quantified using a flame ionization detector. The optical signal was monitored to correct for pyrolyzed organic carbon. A circular punch of 0.526 cm^2 was taken from each quartz-fiber filter using a clean stainless-steel punch. The samples were heated at 140°C (OC1) 280°C (OC2), 480°C (OC3), and 580°C (OC4) in an oxygen-free pure helium environment to convert organic carbon to CO_2 and CH_4 . The samples were then heated progressively at 580°C (EC1) 740°C (EC2) and 840°C (EC3) in an oxygen-containing 2% environment to convert elemental carbon to CO_2 , and CH_4 . During the heating of the sample, some of the organic carbon can be carbonized to form black carbon, which makes it difficult to distinguish organic carbon from elemental carbon. Therefore, during the measurement process, the reflectance of the filter paper was monitored by a 633 nm He-Ne

laser, and the change of light intensity was used to clearly indicate the onset of oxidation of elemental carbon to distinguish OC and EC. The OC and EC mass concentrations were obtained according to the IMPROVE protocol: $OC = OC1 + OC2 + OC3 + OC4 + OPC$, $EC = EC1 + EC2 + EC3 + OPC$. The detection limits of the instrument were OC ($0.304 \mu\text{g}/\text{m}^3$) and EC ($0.085 \mu\text{g}/\text{m}^3$).

The quality control measures throughout the analysis process were: (1) The instrument should be calibrated using a standard gas of CH_4/CO_2 before and after the sample is analyzed. (2) Weekly measurements of blank samples from the laboratory and instrument system should be ensured. (3) Parallel analysis should also be performed at a random rate of 1 in 10, and the number of measurements for the standard samples should be twice a week to ensure a stable recovery of 98%-102%.

Text S4. Chemical mass reconstruction and mass-closure assessment

Chemical mass reconstruction was performed to summarize size-resolved PM composition and to facilitate inter-process comparison of “chemical fingerprints”. For each size fraction, the reconstructed mass (M_{recon}) was defined as the sum of organic matter (OM), elemental carbon (EC), water-soluble ions (WSI), mineral matter (MIN), and trace elements (TE):

$$M_{\text{recon}} = \text{OM} + \text{EC} + \text{WSI} + \text{MIN} + \text{TE}$$

The mass-closure ratio (Closure) was calculated as:

$$\text{Closure}(\%) = 100 \times M_{\text{recon}} / \text{PM}_{\text{grav}}$$

where PM_{grav} is the gravimetric mass concentration for each size fraction.

S4.1 Definition of reconstructed components

(1) OM and EC.

OC and EC were measured on pre-baked quartz filters using a thermal–optical carbon analyzer. OM was estimated as $\text{OM} = 1.6 \times \text{OC}$, a commonly used conversion factor for atmospheric/combustion-related aerosols (Vecchi et al., 2009). EC was directly taken from the thermal–optical measurement.

(2) WSI (water-soluble ions).

WSI was calculated as the sum of ten quantified ions (F^- , Cl^- , NO_3^- , SO_4^{2-} , PO_4^{3-} , Na^+ , NH_4^+ , K^+ , Mg^{2+} , Ca^{2+}) measured by ion chromatography on quartz filters. Note that this definition of WSI includes the major secondary inorganic aerosol (SIA) ions (SO_4^{2-} , NO_3^- , NH_4^+).

(3) MIN (mineral matter).

Mineral matter was estimated using crustal/structural elements and oxide conversion factors:

$$\text{MIN} = 1.89 \times \text{Al} + 2.14 \times \text{Si} + 1.40 \times \text{Ca} + 1.43 \times \text{Fe} + 1.67 \times \text{Ti} + 1.20 \times \text{K} + 1.66 \times \text{Mg}$$

(4) TE (trace elements).

TE represents the sum of measured trace elements that are not accounted for in the MIN calculation, expressed as elemental mass concentrations. TE primarily includes metal(loid)s typically associated with high-temperature processes and/or volatilization–condensation behaviors (e.g., As, Cd, Pb, Zn, Cu, Sb, Sn, etc.). As with most reconstruction schemes, TE is treated as elemental mass; associated anions/oxygen (e.g., oxides, sulfates, chlorides) are not explicitly added and may contribute to unresolved mass.

S4.2 Mass closure and unresolved fraction

Across all processes and size fractions, the closure ratio varied substantially from 52.18% to 110.33%, with a mean of $78.9 \pm 23.0\%$ (mean $\pm$ SD), indicating that the reconstruction captures the dominant measured components but does not fully close the PM mass in all cases. To visualize only the “unresolved” portion, we calculated:

$$\text{Unresolved}(\%) = \max(0, 100 - \text{Closure}(\%))$$

This quantity was plotted in Figure S2. Cases with $\text{Closure} > 100\%$ are therefore shown as 0% unresolved in Figure S2 but are discussed below as potential overestimation due to reconstruction assumptions. The largest

unresolved fractions were generally observed in the PM_{2.5-10} and some fine-mode samples, consistent with the presence of unquantified mass components and/or methodological uncertainties (e.g., particle-bound water, salt/oxide-associated mass not explicitly accounted for, and parallel-filter differences) (Tishmack and Burns, 2004).

S4.3 Major sources of uncertainty

The observed under- or over-closure can be attributed to several factors:

Parallel-filter representativeness. Gravimetric PM and elemental composition were derived from PTFE filters, whereas carbon fractions and WSI were measured on quartz filters sampled in parallel. Small differences in loading and semi-volatile losses between filters may affect closure.

OM/OC conversion factor. A fixed factor (1.6) introduces uncertainty because OM composition can vary by process and size fraction. OM can be overestimated or underestimated depending on the true organic aerosol oxidation state and molecular composition. Individual organic acids were not separately quantified. Their carbon may be partly represented by the measured OC; however, the fixed OM/OC factor may not fully account for the molecular mass of highly oxygenated organic compounds, which could contribute to the observed under-closure.

Unaccounted particle-bound water and hydration. Hygroscopic salts (e.g., sulfates) and acidic aerosols may retain bound water that contributes to gravimetric mass but is not explicitly included in reconstructed dry-ion mass. This contribution may be particularly relevant for processes equipped with wet flue gas desulfurization or wet scrubbing, where entrained sulfate-rich droplets and particles may retain bound water or form hydrated sulfate salts. The associated particle-bound and crystallization water contributes to gravimetric mass but is not represented by the sum of measured dry ionic species. Because mineral phases and individual organic compounds were not directly characterized, their respective contributions to the unresolved mass cannot be quantified from the present dataset.

Boundary between WSI and MIN for alkaline/earth ions. In coarse particles, Ca/Mg/K can exist in both soluble and insoluble forms. When WSI is treated as the direct sum of measured ions while MIN is estimated from total elemental Ca/Mg/K, partial double counting may occur, potentially contributing to closures slightly above 100% in some samples (e.g., submicron WSI-dominant cases).

Speciation of trace metals and associated anions/oxygen. TE is treated as elemental mass only. If metals are present as oxides, sulfates, or chlorides, the associated non-metal mass is not explicitly accounted for, contributing to unresolved mass.

S4.4 Implications for interpretation

Given the moderate and variable closure, the reconstruction is primarily used here for relative comparison and fingerprint identification across processes and size fractions rather than for exact mass accounting. Importantly, the strongest conclusions in the main text rely on high-contrast patterns (e.g., WSI-dominant versus OM-dominant submicron profiles), which are robust to reasonable uncertainties in reconstruction assumptions.

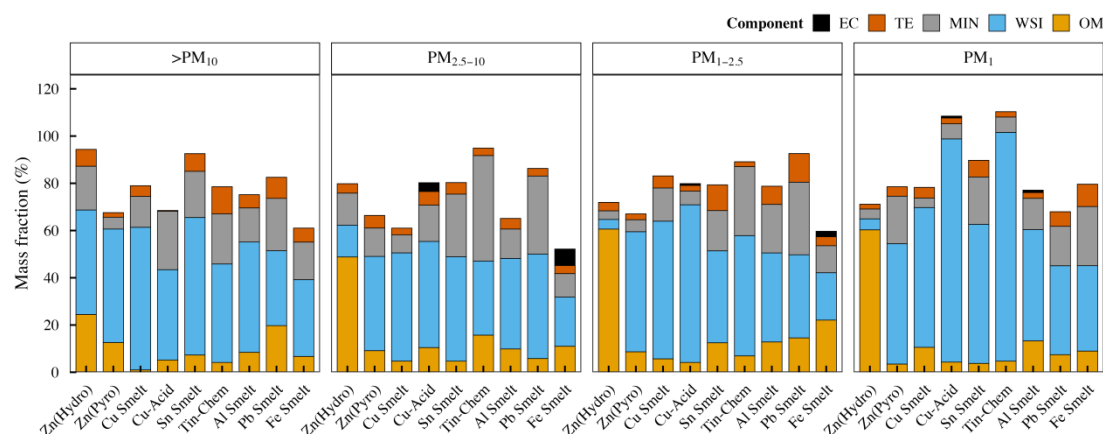


Figure S2. Chemical mass reconstruction of size-resolved PM from different metallurgical processes.

The unresolved fraction was calculated as $\text{Unresolved (\%)} = \max\left\{\frac{\text{Mrecon} - \text{PMgravand}}{\text{PMgravand}}, 0, 100 - \text{Closure(\%)}\right\}$, where $\text{Closure(\%)} = 100 \times \text{Mrecon} / \text{PMgravand}$ and $\text{Mrecon} = \text{OM} + \text{EC} + \text{WSI} + \text{MIN} + \text{TE}$. Values with closure >100% are shown as 0% unresolved in this figure and are attributed to reconstruction assumptions (e.g., OM/OC factor and potential overlap between WSI and MIN for Ca/Mg/K).

Text S5. Additional notes on carbonaceous components (OC and EC).

A fraction of EC measurements was below the method detection limit (DL); these values were substituted with 1/2 DL to enable statistical summaries and visualization (Table S8). To avoid attributing OC/EC variability to a single factor, OC–EC features were further compared with stack O₂ levels (operating parameters in Table S2). Zn(Hydro) exhibited lower O₂ (11.6%) than Zn(Pyro) (19.8%) and showed an opposite OC size-distribution pattern (fine-mode enrichment vs. coarse-mode dominance), suggesting that oxidative conditions may be associated with the release/partitioning of condensable organic precursors. However, Cu-Acid showed low O₂ (6.6%) but consistently low OC (<16 µg/m³), indicating that O₂ alone cannot explain OC enhancement and that process-specific organic precursor availability remains a key constraint. Therefore, O₂ is treated here as a boundary indicator rather than a causal driver, and its influence should be interpreted in the context of each process.

Table S8. Size-segregated concentrations of organic carbon (OC) and elemental carbon (EC) in stack PM emitted from different metallurgical processes.

Sector / Process	Size	EC (µg/m ³)	OC (µg/m ³)	TC (µg/m ³)	EC/PM (%)	OC/PM (%)	OC/EC
Zinc smelting (hydrometallurgy)	>PM ₁₀	4.92	172.49	176.59	0.28	9.79	35.06
	PM _{2.5-10}	12.24	677.42	681.52	0.35	19.53	55.34
	PM _{1-2.5}	9.4	2669.78	2673.88	0.09	24.24	284.02
	PM ₁	80.55	2468.72	2472.82	0.79	24.11	30.65
Zinc smelting (pyrometallurgy)	>PM ₁₀	11.36	821.21	822.44	0.16	9.22	74.63
	PM _{2.5-10}	11.36	266.34	277.7	0.16	3.65	23.45
	PM _{1-2.5}	11.36	242.6	253.96	0.16	3.47	21.36
	PM ₁	11.36	48	59.36	0.33	1.39	4.23
Iron & steel (Fe Smelt)	>PM ₁₀	12.01	72.02	84.03	0.45	2.68	6
	PM _{2.5-10}	203.46	200.28	403.74	4.48	4.41	0.98
	PM _{1-2.5}	68.12	407.04	475.16	1.48	8.83	5.98
	PM ₁	12.01	155.31	167.31	0.28	3.59	12.93
Copper smelting	>PM ₁₀	5.08	3.76	8.83	0.54	0.4	0.74
	PM _{2.5-10}	5.08	20.42	25.49	0.47	1.89	4.02
	PM _{1-2.5}	5.08	24.5	29.58	0.34	1.66	4.82
	PM ₁	11.46	78.7	90.16	0.61	4.22	6.87
Copper smelting – acid plant (DCDA)	>PM ₁₀	0.85	4.17	5.02	0.42	2.07	4.91
	PM _{2.5-10}	7.3	12.76	20.06	2.39	4.18	1.75
	PM _{1-2.5}	1.38	6.22	7.6	0.51	2.27	4.51
	PM ₁	4.69	15.49	20.18	0.52	1.72	3.3
Tin chemicals (SnCl ₄ production)	>PM ₁₀	1.74	11.68	13.42	0.25	1.66	6.71

Tin smelting (pyrometallurgy)	PM _{2.5-10}	2.15	46.21	48.36	0.29	6.29	21.49
	PM _{1-2.5}	1.74	22.43	24.17	0.21	2.77	12.89
	PM ₁	15.77	70.75	86.51	0.42	1.88	4.49
	>PM ₁₀	11.75	128.67	140.43	0.27	2.92	10.95
	PM _{2.5-10}	11.75	86.57	98.32	0.26	1.88	7.37
	PM _{1-2.5}	11.75	234.78	246.54	0.25	4.99	19.98
	PM ₁	11.75	59.12	70.88	0.3	1.5	5.03
	>PM ₁₀	1.37	13.92	15.29	0.33	3.38	10.16
Aluminum smelting (primary electrolysis)	PM _{2.5-10}	1.37	16.27	17.64	0.33	3.94	11.88
	PM _{1-2.5}	1.37	20.82	22.19	0.34	5.13	15.2
	PM ₁	3.45	28.01	31.46	0.65	5.32	8.12
	>PM ₁₀	14.56	174	188.56	0.66	7.89	11.95
Lead smelting (pyrometallurgy)	PM _{2.5-10}	14.56	43.31	57.87	0.78	2.33	2.97
	PM _{1-2.5}	14.56	128.95	143.5	0.66	5.82	8.86
	PM ₁	14.56	74.43	88.98	0.58	2.97	5.11

Notes:

(1) PM mass used to calculate EC/PM and OC/PM was obtained from the parallel quartz-filter samples used for carbon analysis.

(2) For values below the method detection limit (DL), concentrations were substituted with 1/2 DL.

Text S6. Process conditions as background constraints on WSII profile variability

In conventional atmospheric chemistry, secondary inorganic aerosol (SIA) is commonly defined as particulate sulfate, nitrate, and ammonium produced from oxidation of gaseous precursors (e.g., SO₂ and NO_x) and subsequent gas–particle partitioning involving NH₃ (Huang et al., 2024; Jones et al., 2021). For emissions from stationary stacks, however, SIA-like inorganic salts may also arise on much shorter timescales immediately after release, because hot flue gas undergoes rapid cooling and dilution and can generate condensable particulate matter (CPM) and associated inorganic salts near the source (Wang et al., 2022; Su et al., 2025). Under rapid cooling and dilution, acidic or semi-volatile precursors may reach supersaturation upon mixing with dilution air, triggering condensation, homogeneous nucleation, and subsequent particle growth—processes that can resemble CPM formation pathways. Such near-source partitioning can transfer species originally present in the gas phase or semi-volatile form into the particle phase within seconds to tens of seconds, depending on the cooling–dilution rate and moisture conditions (Wang et al., 2022; Liu et al., 2023).

To aid interpretation of cross-sector variability in water-soluble inorganic ion (WSII) profiles, flue-gas operating parameters (SO₂ and NO_x) during sampling were compared against the ionic composition in PM₁ (Figure S3). Importantly, gas-phase SO₂/NO_x concentrations do not linearly determine particulate sulfate/nitrate burdens, because formation and retention depend on both precursor availability and multiphase partitioning/kinetics (Huang et al., 2024; Jones et al., 2021). In addition, near-source inorganic salt formation can be strongly modulated by post-emission cooling–dilution dynamics and moisture content (Wang et al., 2022; Liu et al., 2023). Ammonia availability may be further influenced by process-related NH₃ slip (e.g., from denitrification), which can promote formation of ammonium salts under suitable acidity and temperature conditions (Cheng et al., 2020; Jones et al., 2021). Moreover, APCD-related process features (e.g., droplet carryover and acid mist downstream of wet control devices) can directly introduce sulfate-rich fine particles or enhance apparent sulfate dominance in submicron fractions (Wang et al., 2023; Zhou et al., 2024).

As shown in Figure S3a, PM₁ sulfate was significantly and positively correlated with flue-gas SO₂ ($r = 0.69$, $p < 0.05$), suggesting that higher SO₂ levels are generally associated with higher fine-mode sulfate. Meanwhile, several process points exhibited relatively high sulfate despite low SO₂, indicating that fine sulfate can be jointly influenced by precursor load and rapid near-source condensation/nucleation as well as process-form emissions. For instance, Tin-Chem showed elevated SO₂ (Table S2: 437 mg/m³), consistent with a pronounced WSII-dominated fine fraction and a sulfate-enhanced profile. In contrast, Cu-Acid exhibited low SO₂ during sampling (Table S2: 2 mg/m³) but still displayed a sulfate-dominated PM₁ fraction (SO₄²⁻ share = 59.67%), implying a combined effect of process-form emissions (e.g., acid mist/sulfate-rich particles) and rapid near-source formation rather than being solely controlled by regional-scale oxidation of SO₂ (Zhou et al., 2024; Tang et al., 2025).

By comparison, PM₁ nitrate showed no significant relationship with flue-gas NO_x ($r = -0.14$, $p = 0.72$), indicating that NO_x alone is not predictive of particulate NO₃⁻ (Jones et al., 2021; Ward et al., 2025). Nitrate formation and partitioning are more strongly constrained by thermal stability, ammonia availability, and particle acidity/neutralization conditions. Notably, under high-temperature flue-gas conditions, NO_x is not directly equivalent to particulate nitrate; formation of particle-phase nitrate typically requires lower temperatures and suitable acid-base environments, often involving HNO₃ as the proximate precursor to particulate nitrate. Therefore, in this study NO_x is better interpreted as a background indicator of operating conditions and control configurations rather than a direct predictor of NO₃⁻ abundance.

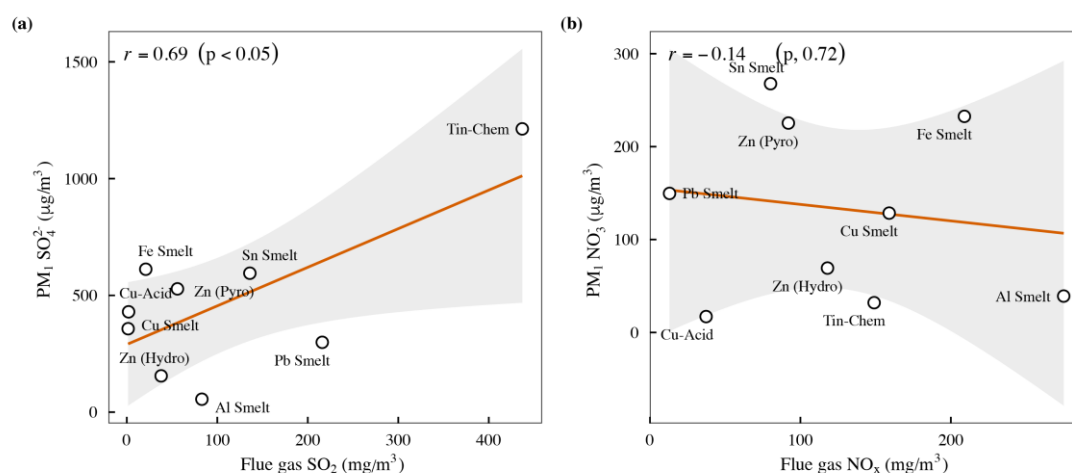


Figure S3. Relationships between gaseous precursors and ionic components in PM₁ from different industrial sources. (a) Linear regression between PM₁ sulfate and flue-gas SO₂; (b) linear regression between PM₁ nitrate and flue-gas NO_x. Solid lines denote linear fits and shaded areas represent 95% confidence intervals. Pearson correlation coefficients (r) and p -values are reported.

Text S7. Definition of WSIs, charge-balance calculation, and uncertainty notes

Water-soluble inorganic ions (WSIs) were defined as the sum of mass concentrations of ten ions: F⁻, Cl⁻, NO₃⁻, SO₄²⁻, PO₄³⁻, Na⁺, NH₄⁺, K⁺, Mg²⁺, Ca²⁺. Ion concentrations were measured by ion chromatography and were used to construct size-resolved ionic profiles for cross-sector fingerprinting.

To characterize the acid-base balance of the soluble ionic system, the charge-balance approach was applied by calculating the total anion equivalents (AE) and cation equivalents (CE), and using the cation-to-anion equivalent ratio (C/A) as an indicator. Ion concentrations are in μg/m³, and equivalents are calculated using equivalent weights (molecular weight divided by charge):

$$\begin{aligned}
 AE &= \frac{F^-}{19} + \frac{Cl^-}{35.5} + \frac{NO_3^-}{62} + \frac{SO_4^{2-}}{48} + \frac{PO_4^{3-}}{31.7} \\
 CE &= \frac{Na^+}{23} + \frac{NH_4^+}{18} + \frac{K^+}{39} + \frac{Mg^{2+}}{12} + \frac{Ca^{2+}}{20} \\
 C/A &= \frac{CE}{AE}
 \end{aligned}$$

AE and CE are thus reported in $\mu\text{eq}/\text{m}^3$. A ratio of $C/A \approx 1$ indicates near electroneutrality and a relatively neutral ionic system; $C/A < 1$ suggests an excess of anion equivalents and potentially more acidic particles; and $C/A > 1$ indicates an excess of cation equivalents, which may reflect enhanced contributions from ammonium salts and/or alkali/alkaline-earth salts. It should be noted that this charge-balance approach reflects the relative acidity of the measured soluble ionic system only. Unmeasured H^+ , organic anions, complexed/bound ionic species, and particle-bound water can also affect the actual acidity. Therefore, C/A is best used for profile comparison and relative trend assessment rather than as a direct surrogate for particle pH.

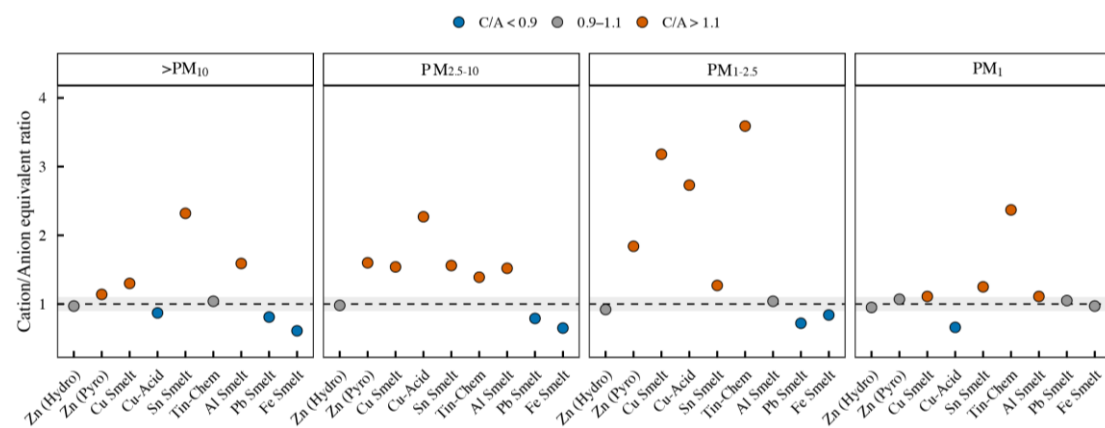


Figure S4. Molar ratio of cation to anion equivalents (C/A) in size-resolved flue-gas particulate matter.

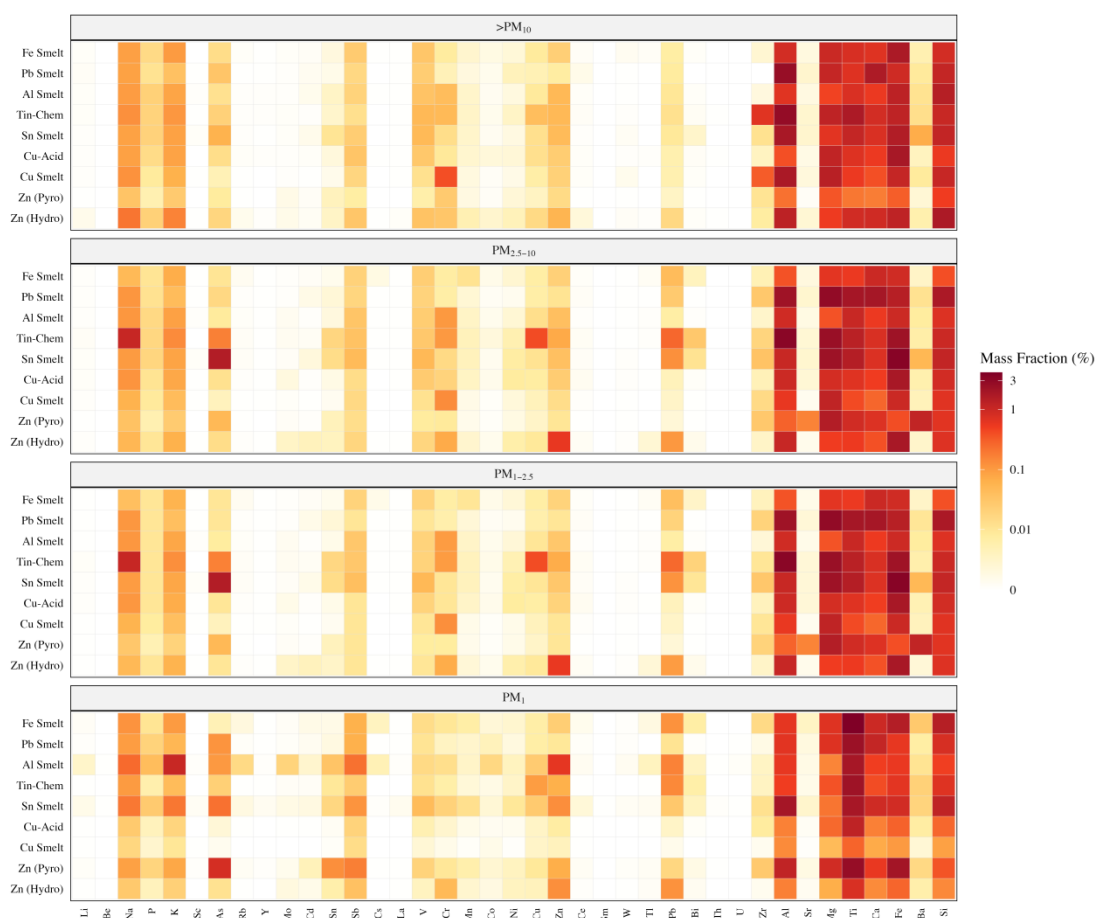


Figure S5. Mass fractions of inorganic elements in size-resolved particulate matter emitted from different metallurgical processes. Mass fractions are expressed as percentages of particle mass, where 1% corresponds to 10,000 mg/kg PM.

Text S8. Size-dependent distribution of rare earth-related elements

In addition to conventionally concerned metals/metalloids, the size distribution characteristics of Sc, Y, La, and Ce were quantified as supplementary process fingerprints. The mass fractions of these elements were generally in the range of 10^{-4} – 10^{-3} , with Ce showing the highest relative abundance among the measured rare earth-related elements. Sc, Y, La, and Ce exhibited systematic enrichment in the PM₁ fraction of Sn Smelt, whereas Ce, La, and Y from Zn(Hydro) showed higher relative contributions in the >PM₁₀ fraction and lower contributions in PM₁. Zn(Pyro) showed enrichment of Ce in PM₁. These results indicate process-dependent REE partitioning, potentially reflecting differences in raw material composition, process chemistry, and by-product formation characteristics. Because of their low mass fractions, these elements are interpreted here as supplementary process fingerprints rather than primary contributors to PM₁-bound risk-related metal burdens. These contrasting size-dependent REE patterns may provide supplementary tracers for distinguishing metallurgical processes in future receptor modeling, particularly when interpreted jointly with major- and trace-element source profiles. Their source specificity, cross-facility consistency, and stability during atmospheric transport require further validation using repeated source measurements, ambient samples, and comparisons with non-metallurgical sources before they can be considered unique source markers.

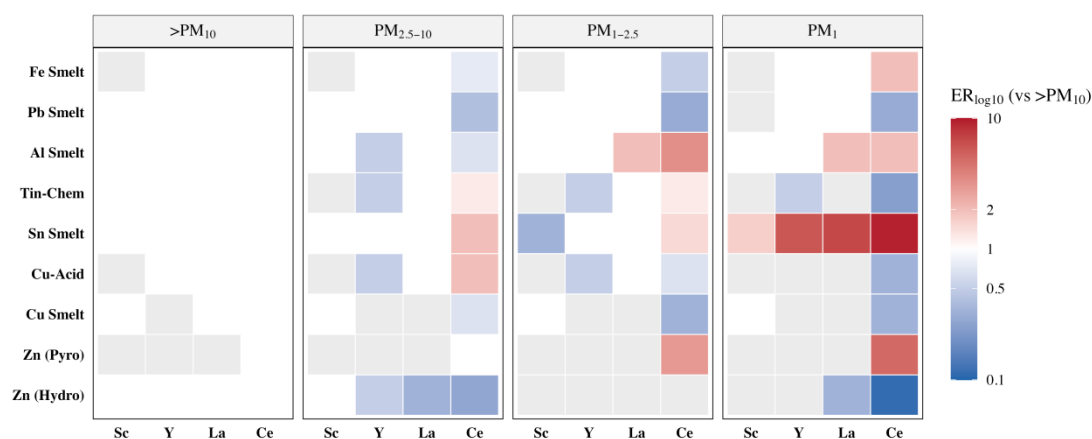


Figure S6. Size-dependent enrichment ratios (ER, fraction-based) of key rare earth elements.

ER is defined as the ratio of an element's mass fraction in a given size bin to its mass fraction in the coarse fraction (>PM₁₀): $ER = \text{Fraction}(\text{size}) / \text{Fraction}(>PM_{10})$. Heatmap colors are shown on a logarithmic scale ($\log_{10}(ER)$), where white indicates $ER \approx 1$ (comparable to >PM₁₀), blue indicates $ER < 1$ (depletion relative to the coarse fraction), and red indicates $ER > 1$ (enrichment relative to the coarse fraction). Because ER is calculated from mass fractions, variations in ER reflect shifts in relative composition across size bins, and should not be interpreted as direct increases or decreases in absolute concentrations.

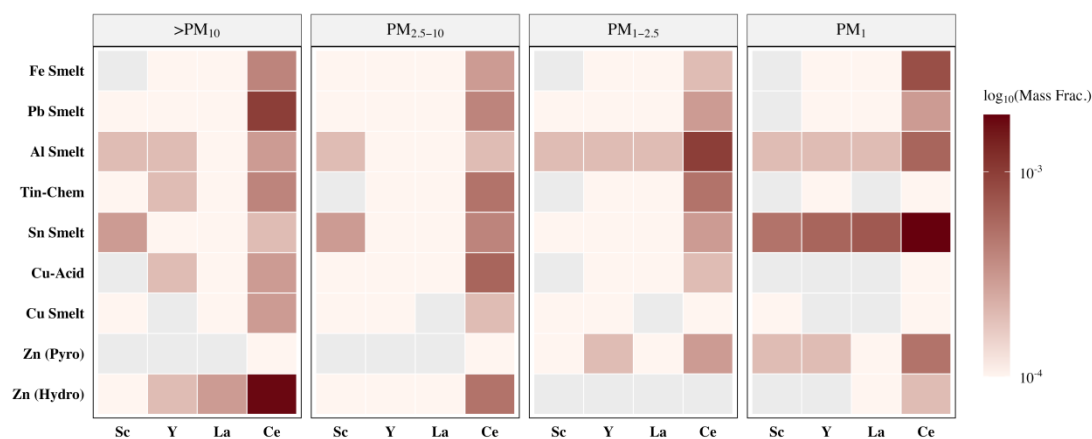


Figure S7. Mass-fraction (percentage) distributions of key rare earth elements in size-segregated particulate matter.

The heatmap shows the mass fractions (as % of particle mass) of La, Ce, Y, and Sc across four size bins ($>PM_{10}$, $PM_{2.5-10}$, $PM_{1-2.5}$, and $<PM_1$). Colors are mapped on a logarithmic scale ($\log_{10}$) to enhance visualization of low-abundance elements. Metallurgical sectors are arranged along the x-axis and elements along the y-axis. This figure is intended to compare differences in the relative contributions of rare earth elements among sectors and size bins, rather than differences in absolute concentrations.

Table S9. Risk-oriented indicators for PM_1 -bound toxic metals across industrial processes ($\Omega = As + Cd + Sb + Pb + Cr$).

Process (abbrev.)	ΣEF_{PM_1} ($\mu g/t$ product)	ΣEF_{total} ($\mu g/t$ product)	Share $_{PM_1}$ (%)
Zn (Hydro)	2257.12	5201.91	43.4
Zn (Pyro)	2087.50	9331.03	22.4
Tin-Chem	141.13	438.83	32.2
Sn Smelt	2559.63	6283.76	40.7
Cu Smelt	755.52	2489.27	30.4
Cu-Acid	24.96	63.39	39.4
Pb Smelt	996.15	1932.25	51.6
Fe Smelt	174.55	978.08	17.8
Al Smelt	271.61	409.91	66.3

Text S9. Representativeness, reliability, and limitations of field stack sampling

Field measurements of size-resolved particulate matter from metallurgical stacks are substantially more challenging than ambient sampling because the sampling process must be conducted under real industrial operating conditions while simultaneously maintaining stable extraction, dilution, temperature, humidity, pressure drop, and aerodynamic size separation. In the present study, one successful size-resolved sampling event was obtained for each of the nine representative metallurgical process stacks under stable operation. Each sampling event lasted 3–4 h and generated four size-segregated particle fractions for each filter medium. These valid field samples were collected from the main exhaust channels of mainstream metallurgical production units after the corresponding air pollution control devices, and therefore provide direct process-level information on particulate emissions under actual industrial conditions.

Repeated sampling for each stack was not completed because of practical and technical constraints during field stack testing, including limited access to sampling ports, high-temperature and high-moisture flue gas, condensation control, pressure-drop increases, and the risk of filter overloading. Several trials failed to meet the required sampling stability or filter-loading conditions, and only valid runs satisfying the operational and QA/QC requirements were retained. Therefore, the reported values for a given stack and size fraction represent one successful field measurement under stable operating conditions. This sampling design mainly limits the quantification of short-term intra-stack variability and repeated-run reproducibility. Accordingly, the emission factors should be interpreted as process-specific field references under the sampled stable conditions, while annual plant-level averages or regulatory compliance values would require additional repeated tests across different operating loads, feed compositions, and APCD states.

Importantly, the lack of repeated field runs does not preclude the use of these data for process fingerprinting, source characterization, and control-priority identification. The reliability of the chemical profiles is supported by several lines of evidence. First, the selected stacks covered representative metallurgical processes, including hydrometallurgical zinc production, pyrometallurgical zinc smelting, copper smelting, sulfuric acid production, tin

smelting, tin chemical production, aluminum electrolysis, lead smelting, and iron/steel smelting. Second, sampling was conducted only during stable industrial operation, and operating loads, flue-gas temperature, moisture, oxygen content, SO₂, and NO_x were recorded to support interpretation. Third, the dilution sampling system followed the conceptual framework of U.S. EPA OTM-37, in which hot stack gas is diluted and cooled to near-ambient conditions to better characterize primary particulate matter, including particles formed through post-dilution condensation (U.S. EPA, 2018; England et al., 2007a,b; Lipsky and Robinson, 2006). The dilution ratio, post-dilution temperature, flow stability, blanks, filter handling, gravimetric measurements, and laboratory chemical analyses were controlled through the QA/QC procedures described in Text S2 and Text S3.

The representativeness of the obtained chemical profiles is further supported by their strong agreement with metallurgical process chemistry. The sulfate-dominated and acidic PM₁ profiles observed in Cu-Acid and Tin-Chem are consistent with sulfur-rich flue-gas chemistry, SO₂/SO₃ conversion, acid mist, and condensable sulfate formation in stationary-source emissions (Yang et al., 2015; Wu et al., 2019; Le et al., 2025a,b). The organic-rich fine particles in Zn(Hydro) are consistent with the use of organic additives and acid-mist suppression processes during hydrometallurgical zinc production. The enrichment of volatile and semi-volatile metals in fine particles from pyrometallurgical processes is also consistent with high-temperature volatilization, oxidation, homogeneous nucleation, heterogeneous condensation, and APCD-dependent partitioning mechanisms reported for metallurgical and combustion sources (Kan et al., 2015; Wang et al., 2017; Wang et al., 2018; Zhang et al., 2022; Zhang et al., 2024). These internally consistent patterns indicate that the measured chemical profiles reflect process-driven emission characteristics rather than random sampling artifacts.

The comparability of the results with previous field measurements further supports their use as source-profile and emission-factor references. Field studies on iron/steel production, cement plants, copper smelting, and lead/zinc smelting have shown that size-segregated emission factors and chemically resolved particulate profiles are valuable for source characterization, emission-inventory refinement, and process-specific control assessment, although direct numerical comparison can be affected by process configuration, sampling method, production load, feed composition, and APCD performance (Jia et al., 2018; Guo et al., 2022; Zhang et al., 2022; Zhang et al., 2024). In this study, the measured emission factors generally fall within comparable ranges or show explainable deviations relative to previous reports, while the observed size-resolved chemical features are consistent with known process mechanisms. This agreement strengthens the interpretation that the dataset captures representative process fingerprints under the sampled industrial conditions.

Therefore, the present dataset is particularly suitable for identifying process-specific size distributions, chemical fingerprints, and PM₁-bound metal-burden patterns across metallurgical processes. The strongest conclusions of this study are based on high-contrast and mechanism-consistent features, including sulfate-dominated PM₁ in Cu-Acid and Tin-Chem, organic-rich fine particles in Zn(Hydro), and process-dependent enrichment of risk-related metals in PM₁. These chemical and size-resolved patterns are less sensitive to single-run variability than exact emission-factor magnitudes and provide a robust basis for source-oriented comparison and control-priority screening. Future studies should expand repeated stack tests across multiple plants, production loads, feed materials, and APCD operating states to further quantify intra-process variability and reduce emission-factor uncertainty.

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