Resolving Systematic Errors in Sulfate Source Apportionment: A Field-Validated Kinetic Isotope Fractionation Framework

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Text S1.Estimation of primary sulfate and secondary sulfate

The primary sulfate (calculated by 0.18 × Ca^{2+} +0.25 × Na^{+}) [1]contributed (2.65± 2.11%) to total sulfate mass.

$$T_{PS} = T_{ss} + T_{ts} \quad (1)$$

$$T_{SS} = T_{bbus} + T_{cc} + T_{VS} + T_{os} \quad (2)$$

where T_{PS}、T_{ss}、T_{ts}、T_{SS}、T_{bbus}、T_{cc}、T_{vs}、T_{os} are the primary sulfate (ps), sea salt sulfate (ss), terrestrial sulfate (ts), secondary sulfate(SS),biomass burning sulfate (bbus), coal combustion(cc), vehich sulfate(vs),oil sulfate(os).

Text S2. Calculation of ^{34}S Fractionation.

Theoretical δ^{34}S-SO_4^{2-} values can be calculated using the following equation according to previous studies[2-4]:

$$\delta^{34}S - SO_4^{2-}{}_{theoretical} = \sum \partial^{34}S - \varepsilon_i \times ln(1 - SOR) \times (1 - SOR)/SOR \quad (3)$$

where $\sum \delta^{34}S$ is calculated using eq 4; ε_i is the δ^{34}S fractionation factor between gas-phase SO_2 and particulate SO_4^{2-} generatedthrough different SO_4^{2-} formation pathways ; and SOR is the ratio of SO_4^{2-} to (SO_4^{2-} + SO_2), which ranges from 0 to 1.

$$\sum \partial^{34}S = \frac{[SO_2] \times \delta^{34}S - SO_2 + [SO_4^{2-}] \times \delta^{34}S - SO_4^{2-}}{[SO_2] + [SO_4^{2-}]} \quad (4)$$

where [SO_2] and [SO_4^{2-}] are the concentrations of gas-phase SO_2 and particulate SO_4^{2-} in the atmosphere, respectively; δ^{34}S-SO_2 is the gas-phase SO_2 value, and δ^{34}S-SO_4^{2-} is the δ^{34}S-SO_4^{2-} value in $PM_{2.5}$ in Nanjing.

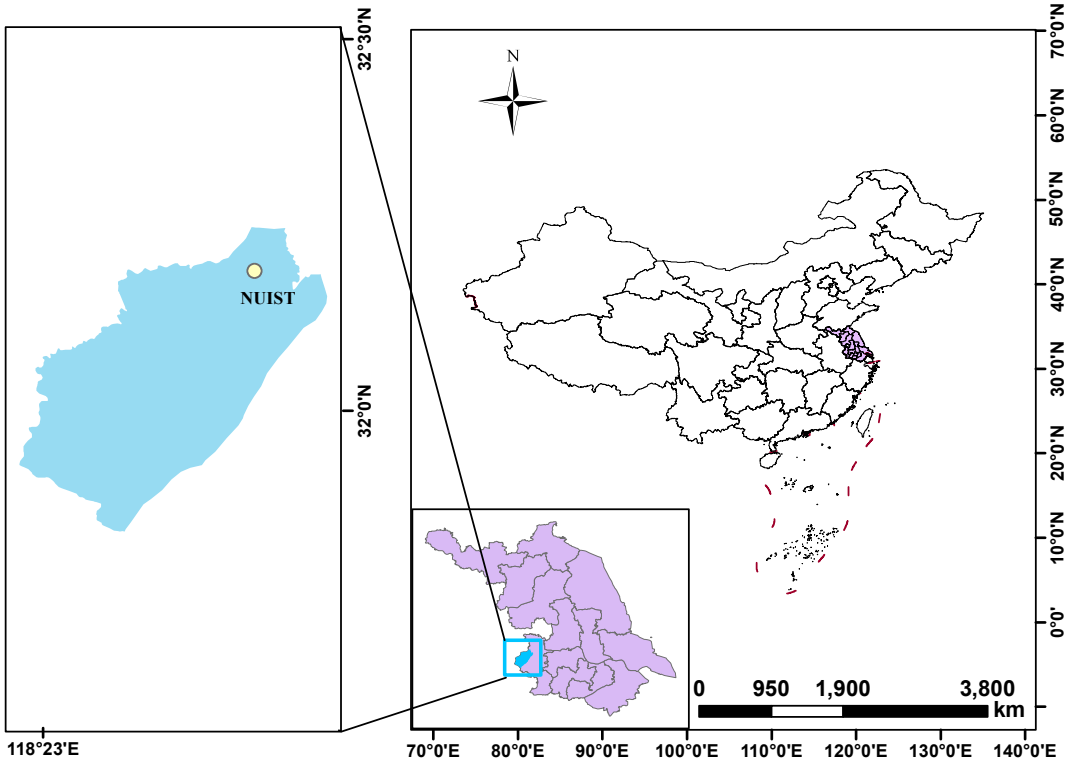

Figure S1. Map of atmospheric $PM_{2.5}$ sampling site in Nanjing City.

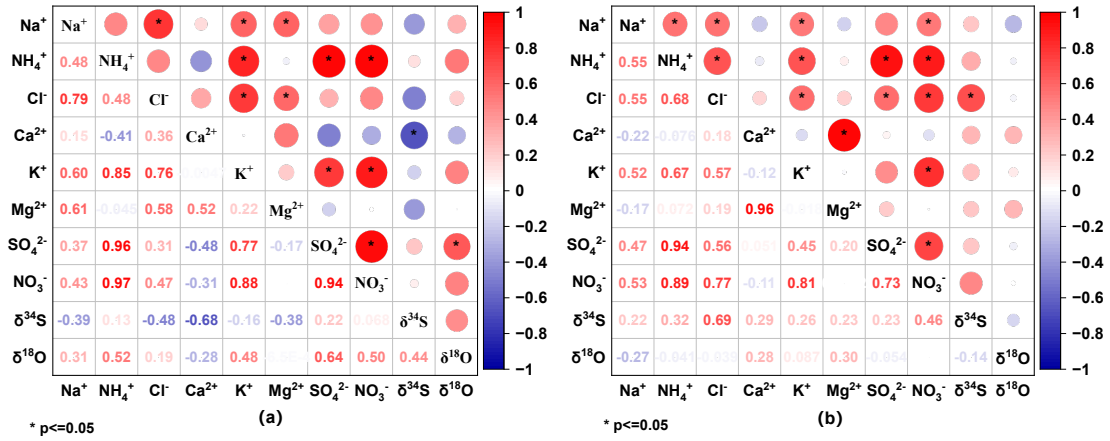

Figure S2. Correlation coefficients of water-soluble ions and stable isotopes in PM2.5 in Nanjing (a: winter b: Summer).

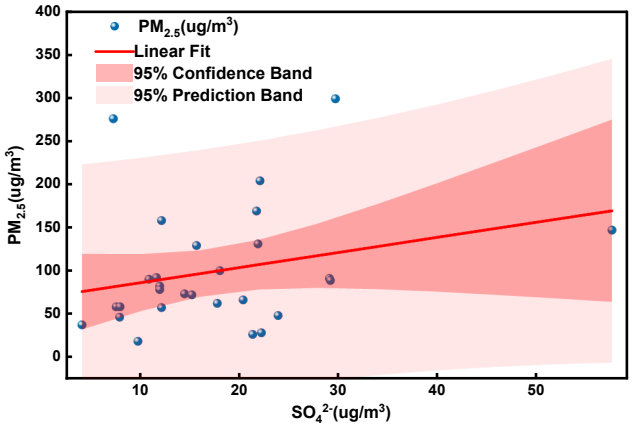

Figure S3. Scatter plot of SO_4^{2-} in $PM_{2.5}$ in Nanjing.

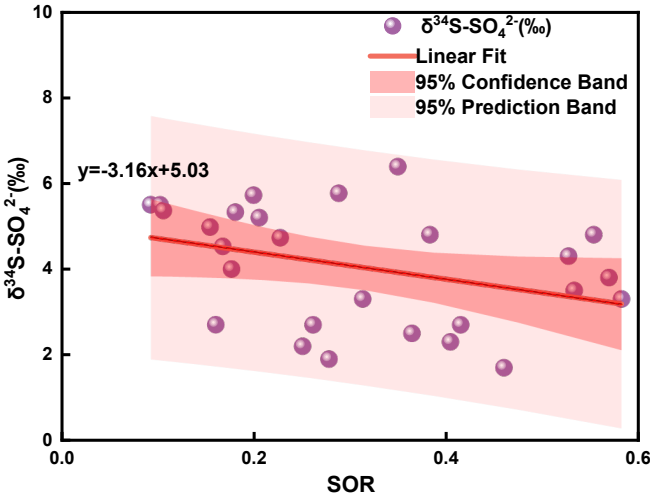

Figure S4. Scatter plot of $\delta^{34}S\text{-}SO_4^{2-}$ values against SOR in Nanjing during the sampling period.

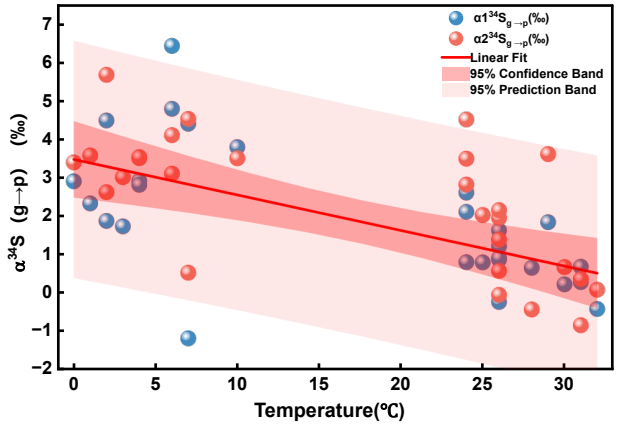

Figure S5. Scatter plot of $\alpha^{34}S_{g\rightarrow p}$ against the ambient temperature in Nanjing during the sampling period.

Table S1. The δ^{34}S-SO_2 values of various Chinese emission sources used in this study.

Source	δ^{34}S(‰)	Reference
Coal combustion	4.6±2.7	Zheng et al.[6] Zhang et al.[17] Wei et al.[18]
Traffice emission	6.6±2.1	Wei et al.[18] Feng et al.[19]
Biomass burning	7.2±1.5	Fan et al.[1] Wei et al.[18] Guo et al.[20]
Oil combustion	6.5±2.4	Zheng et al.[6] Wei et al.[18] Guo et al.[20]

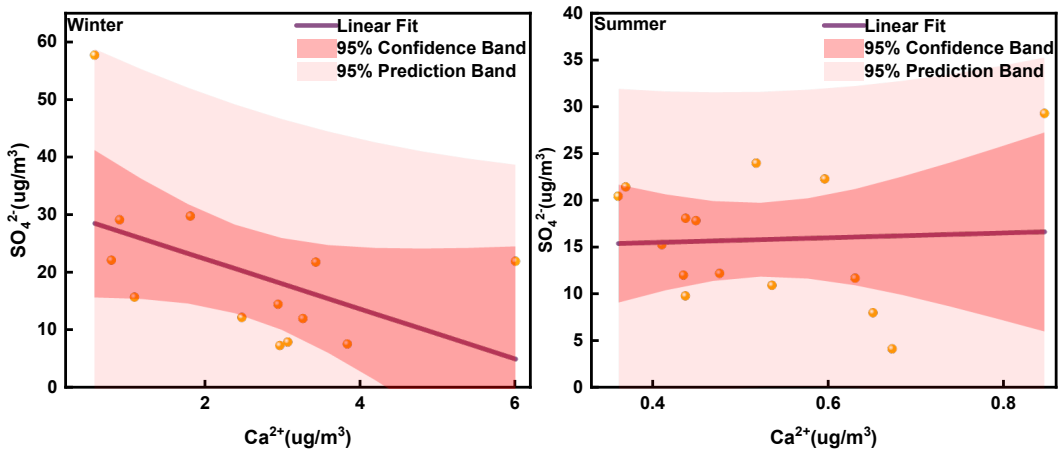

Figure S6. Scatter plot of SO_4^{2-} versus Ca^{2+} in $PM_{2.5}$ during the sampling periods in Nanjing during the sampling period.

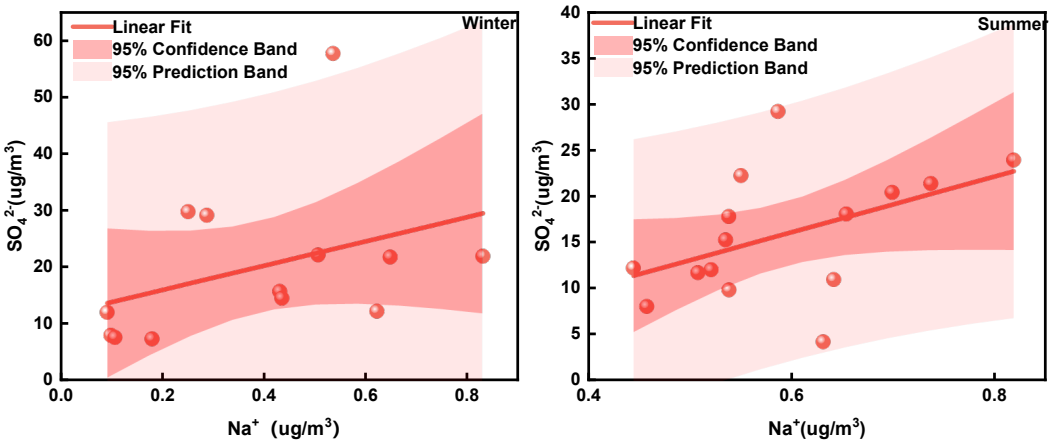

Figure S7. Scatter plot of SO_4^{2-} versus Na^+ in $PM_{2.5}$ during the sampling periods in Nanjing during the sampling period.

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