

Supporting Information

Fine Particle Iron in Soils and Road Dust is Modulated by Coal-Fired Power Plant Sulfur

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Aerosol pH and Liquid Water Content (LWC) Calculations

Aerosol particle pH was calculated with the thermodynamic equilibrium model ISORROPIA-II v.2.3 (<http://isorro피아.epfl.ch>), where pH is defined as;

$$\text{pH} = -\log_{10}(a_{\text{H}^+}) = -\log_{10}\left(\frac{1000 H_{\text{air}}^+}{W_i + W_o} \gamma_{\text{H}^+}\right) \quad (1)$$

a_{H^+} denotes the activity of hydrogen ions (H^+) in the particle aqueous solution on a molality basis (mole/kg water), H_{air}^+ is the hydrogen ion concentration in air (mole/ m^3), W_i the particle liquid water concentration in air due to the aerosol inorganic species, W_o the liquid water concentration in air due to organic species (both g m^{-3}), so particle liquid water content is $\text{LWC} = W_i + W_o$, 1000 is the conversion between g and kg. Unless otherwise noted, the pH was determined with $W_o=0$. The hydrogen ion activity coefficient, γ_{H^+} is the H^+ molal activity coefficient, assumed to equal 1. Note that pH here = pH_F in Pye et al.¹ The thermodynamic analysis only considered days for which most of the data required for ISORROPIA (as well as WS-Fe and total Fe measurements) were available during the time period of interest ($N = 2482$ for JST, $N = 263$ for CTR, $N = 435$ for YRK, $N = 200$ for OAK). For days with missing chloride, magnesium, and sodium data, we assume typical mass loadings of 0.02, 0.00, and 0.03 $\mu\text{g m}^{-3}$, respectively.²

Estimation on the Effect of Organics on Aerosol LWC

Following the approach of Guo et al.², Eq. 2 was used to calculate the amount of aerosol LWC associated with hygroscopic organic species (W_o):

$$W_o = \frac{m_{\text{org}} \rho_w}{\sigma_{\text{org}}} \frac{\kappa_{\text{org}}}{\left(\frac{1}{\text{RH}} - 1\right)} \quad (2)$$

Where m_{org} is the organic mass concentration, calculated from the measured OC concentrations using a conversion factor of 2,³ ρ_w is water density, a typical organic density (σ_{org}) of 1.4 g cm^{-3} is used,³⁻⁵ and RH is the 24-hour average of the measured relative humidity. While the hygroscopicity

parameter of the organics (κ_{org}) was not measured at the SEARCH site; but from another study the κ_{org} for ambient aerosols in the SE US during the summer of 2013 ranged from 0.1 – 0.2.⁶ Using this range of κ_{org} , we calculated the range of W_o . Aerosol liquid water content associated with organics and inorganics (W_i) for a representative period is shown in Figure S3.

Source Apportionment of Fe, Water-Insoluble Fe, and Water-Soluble Fe (WS-Fe)

Utilizing data from the SEARCH JST site, source apportionment analysis of water-insoluble Fe (WI-Fe) was performed with Positive Matrix Factorization⁷ using EPA PMF 5.0 software. WI-Fe was calculated from the difference in measured Total Fe and WS-Fe (for this analysis time period, WI-Fe accounted for on average 62% of the Total Fe). We focus on sources of WI-Fe to contrast with sources of WS-Fe instead of comparing Total Fe to WS-Fe, as WS-Fe is a subset of total Fe. Since Fe can be emitted in insoluble (WI-Fe) and soluble forms (WS-Fe), and WI-Fe transformed over time to WS-Fe, we have performed a factor analysis source apportionment approach, which assumes no *a priori* emission characteristics on these forms of iron, to provide insights on both emissions and atmospheric processing. (One can also do source apportionment on total Fe and then compare to WS-Fe results to infer WI-Fe sources; the results are similar to source apportionment on WI-Fe directly). The analysis was based on the measured 24-hr average concentrations of 16 trace elemental species (As, Ba, Br, Mn, Cu, Pb, Sb, Se, Sn, Ti, Al, Si, S, K, Ca, and Fe or WI-Fe), as well as corresponding reported measurement uncertainties and limit of detection⁸ over the time period 1 January 2000 to 31 December 2007; $N = 2378$. This period was used since measurements of some of the trace elemental species of interest were discontinued starting in 2008 (discussed in Sites and Methods of the text). The PMF model was executed to provide solutions of 2 to 6 factors. Based on the minimal Q values and physical interpretation of the solutions, the 4-factor solution was selected since solutions with additional factors split one or more of the 4

factors without providing additional physical insights. The four factors are labeled based on the loadings in a given factor that identified the main source; Biomass Burning, Mineral Dust, Brake Wear and Coal Combustion (or Electrical Generating Units, EGU, emissions). Figure S5 shows the trace metal composition of each factor for the 4-factor solution for WI-Fe. The relative contributions to WI-Fe and time series of each of these factors are shown in Figure S6. The first factor, biomass burning, is characterized by high contributions of potassium (K), a typical tracer for biomass burning, and bromine (Br), which has been identified in aerosols emitted from wood combustion.⁹ This factor also has higher contributions in the winter compared to summer ($\text{winter}_{\text{avg}}/\text{summer}_{\text{avg}} \approx 2.5$), consistent with previous observations of winter enhancement of biomass burning emissions to $\text{PM}_{2.5}$ in Atlanta¹⁰. It contributed on average 12% to the WI-Fe. The second factor, mineral dust, was characterized by high contributions of aluminum (Al), silicon (Si), and calcium (Ca), which are indicators of crustal material. It contributed 39% to WI-Fe. The third factor is identified as a brake wear source as it contains high contributions of metals found in vehicle brake pads or linings, such as barium (Ba),^{11, 12} titanium (Ti),¹³ and copper (Cu).^{11, 13, 14} This factor contributed to 49% of the WI-Fe, indicating that brake wear is a major source for WI-Fe in an urban environment. The last factor, dominated by selenium (Se), a tracer for fly ash particles emitted during EGUs burning coal, i.e., coal combustion,^{15, 16} and sulfur (S), is identified as a coal combustion source. Coal combustion contributed practically nothing to WI-Fe (Figure S5).

Kinetics of WS-Fe Formation by Acid Dissolution

The role of insoluble Fe, aerosol pH and LWC in the formation of WS-Fe can be illustrated by considering the acid-promoted dissolution rate in the aqueous phase of a specific Fe-containing mineral particle (mole of Fe per gram of mineral i per s), RFe_i (Eq. 3)^{17, 18}:

$$RFe_i = NFE_i \times K_i(T) \times \alpha[H^+]^{m_i} \times f_i \times A_i \quad (3)$$

where NFE_i is the number of moles of Fe per mole of Fe-containing mineral i , $K_i(T)$ is the temperature-dependent dissolution rate coefficient of mineral i ($\text{mol m}^{-2} \text{s}^{-1}$), $\alpha[H^+]$ is the proton activity in solution with an empirical reaction order m_i , ($\alpha[H^+]^{m_i}$ equals $[H^+]^{m_i}$ if the activity coefficient is assumed equal to 1, see pH discussion above), f_i considers the change in dissolution rate due to deviation from equilibrium (assumed to be 1 for simplicity¹⁹), and A_i is the specific surface area for mineral i ($\text{m}^2 \text{g}^{-1}$).

The first-order approximation of the aqueous phase formation rate of WS-Fe (g s^{-1} , Eq. 3) is therefore related to the dissolution rate of Fe from mineral i (RFe_i):

$$\frac{d}{dt} m_{\text{WS-Fe,aq}} = RFe_i \times M_i \times MM_{Fe} \quad (4)$$

$$= NFE_i \times K_i(T) \times \alpha[H^+]^{m_i} \times f_i \times A_i \times M_i \times MM_{Fe} \quad (5)$$

where $m_{\text{WS-Fe,aq}}$ and M_i are the mass concentrations of WS-Fe and Fe-containing mineral i in the aqueous phase (g L^{-1}), respectively, and MM_{Fe} is the molar mass of Fe ($55.845 \text{ g mol}^{-1}$). Given that the aqueous volume is the volume of the aerosol liquid water, Eq. 4 is multiplied by the aerosol LWC ($\text{g of liquid water per m}^3 \text{ of air}$) and the conversion of grams to liters of water ($1000 \text{ g} = 1 \text{ L}$), to express the production rate of WS-Fe in air ($\text{g m}^{-3} \text{s}^{-1}$):

$$\frac{d}{dt} m_{\text{WS-Fe, air}} = NFE_i \times K_i(T) \times \alpha[H^+]^{m_i} \times f_i \times A_i \times M_i \times MM_{Fe} \times \text{LWC} \times \frac{1}{1000} \quad (6)$$

Considering the dissolution of some average mineral composition (i , given the aerosol is likely consistently from a common source), of a fairly constant surface area and a specific temperature, the production rate of WS-Fe in air is dependent on $\alpha[H^+]$ (i.e., pH and m_i are constant, $\alpha[H^+] = (10^{-\text{pH}})^{m_i}$, or $\log([H^+]^{m_i}) = m_i \text{ pH}$, and the H^+ activity is 1), concentration of Fe-containing mineral i in solution, and aerosol LWC. If the mass concentration of Fe-containing mineral i and aerosol pH is constant (see Fig. S4c), and $m_{\text{WS-Fe}}$ is independent of LWC, then the formation rate of WS-

Fe will scale with aerosol LWC and integration of Eq (6) leads to a linear dependence between m_{WS-Fe} and LWC. We also performed all the analysis (correlations, scaling, etc) with the $\log(\text{LWC})$ and find no significant difference if the analysis is done with LWC or $\log(\text{LWC})$.

Table S1. Sampling sites and durations at each SEARCH site

Site	Description	Sampling Period	Number of Data
Jefferson Street (JST)	Urban	August 1998 to December 2013	2482
Centerville (CTR)	Rural background	August 1998 to December 1998 and April 2008 to December 2010	435
Yorkville (YRK)	Rural to suburban	August 1998 to December 1999 and April 2008 to December 2011	263
Oak Grove (OAK)	Rural background	August 1998 to December 1998 and January 2009 to December 2010	157

Table S2: Test of statistical difference in various species and parameters comparing before and after installation of SO₂ scrubbers (i.e., 1998-2008 compared to 2009-2013).

	<i>Significant Difference ($p < 0.05$)</i>	<i>No Significant Difference ($p > 0.05$)</i>	<i>Number of Data points 1998-2008*</i>	<i>Number of Data points 2009-2013*</i>
All Data	SO ₂ emission, Sulfate, WS Fe, LWC, pH, [H ⁺] _{air}	Total Fe	1981	501
Summer	SO ₂ emission, Sulfate, WS Fe, Fe Solubility, LWC	Total Fe, pH, [H ⁺] _{air}	492	139
Winter	SO ₂ emission, Sulfate, WS Fe, Fe Solubility, LWC, pH	Total Fe, [H ⁺] _{air}	499	91

All data is PM_{2.5}. WS Fe = water soluble Fe; LWC = particle liquid water content; Total Fe = elemental Fe (e.g., measured by XRF or ICPMS); Fe Solubility = WS Fe divided by total Fe; pH = model predicted bulk PM_{2.5} particle pH, [H⁺]_{air} = model-predicted proton concentration in air.

* Number of sulfate data points, number for other species is similar, but there is variability due to various performance of the instruments, for example, SO₂ emissions for All Data are 120 (1998-2008) and 60 (2009-2013) and 30 and 15 for Summer and Winter.

Table S3. Regression Analysis (Pearson's R) between WS-Fe and various parameters for summer and winter (1998 – 2013) at JST.

	<i>Summer</i>	<i>Winter</i>	<i>Whole Study</i>
<i>Total Fe</i>	0.65	0.64	0.63
<i>Sulfate</i>	0.60	0.42	0.65
<i>Aerosol LWC</i>	0.34	0.17	0.40
<i>Aerosol pH</i>	-0.21	-0.02	-0.30
<i>PM_{2.5}</i>	0.67	0.62	0.67
<i>RH</i>	-0.22	-0.00	-0.03
<i>Temp.</i>	0.29	0.13	0.44
<i>EC</i>	0.67	0.56	0.47
<i>OC</i>	0.56	0.58	0.39
<i>K</i>	0.25	0.30	0.29

Bold: $P \leq 0.05$

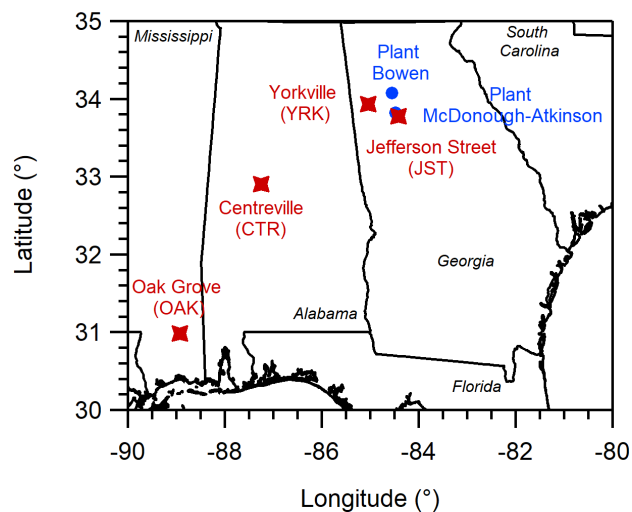


Figure S1. Locations of SEARCH measurement sites (red star) utilized in this study and two coal fired electrical generating units discussed in the paper (blue circle).

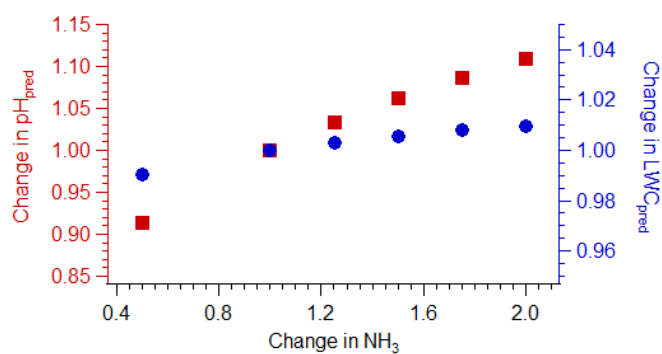


Figure S2. Relative changes to calculated aerosol pH (red square) and LWC (blue circle) due to relative changes in ISORROPIA-input values of ammonia (initial NH₃ concentration = 1.12 $\mu\text{g m}^{-3}$).

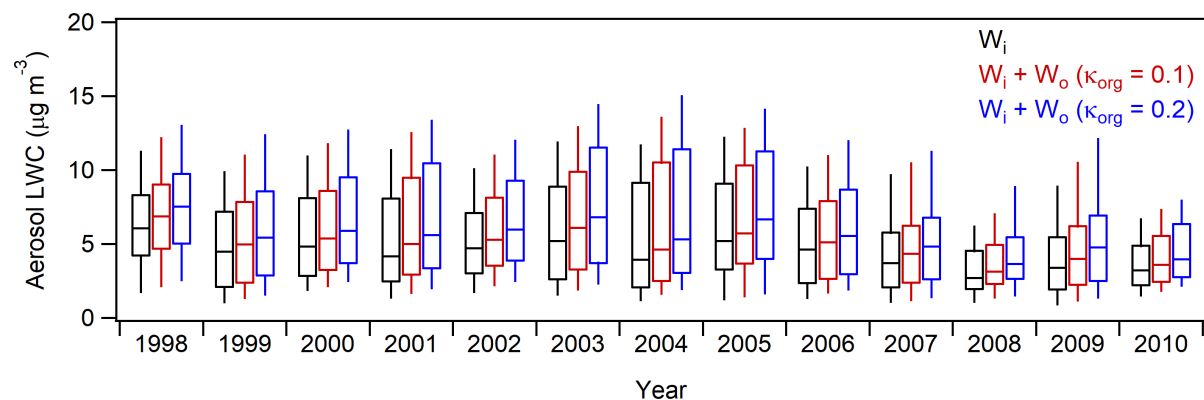


Figure S3. Box and whisker plot illustrating representative ISORROPIA-calculated aerosol liquid water content (LWC) associated with inorganics only (W_i , black), inorganics with organics ($W_i + W_o$, red) for $\kappa_{\text{org}} = 0.1$ and inorganics with organics ($W_i + W_o$, blue) for $\kappa_{\text{org}} = 0.2$. The lines in the boxes indicate the median values, the upper and lower box boundaries indicate the 75th and 25th percentiles, and the whiskers indicate the 90th and the 10th percentiles for each corresponding calculated aerosol LWC.

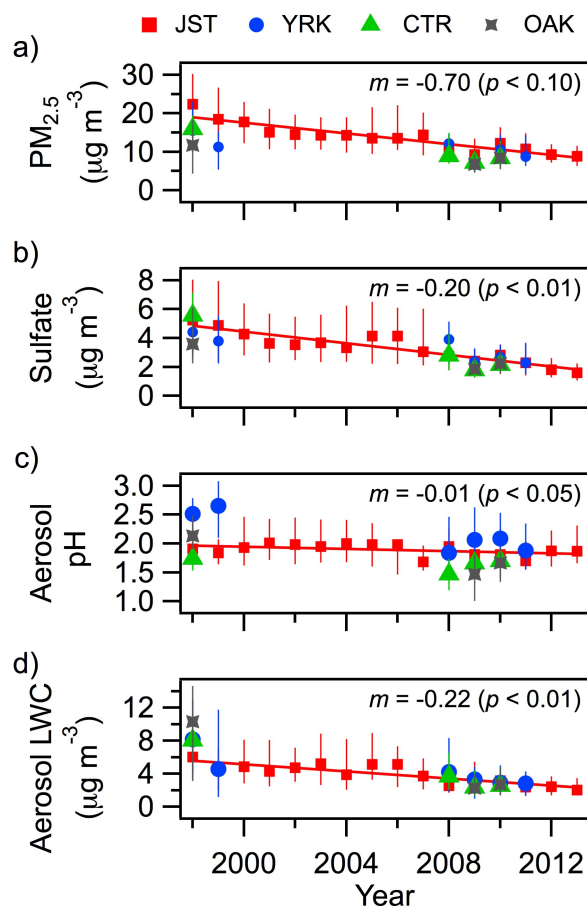


Figure S4. Time series of median concentrations or values of a) PM_{2.5} mass, b) sulfate, c) ISORROPIA-calculated aerosol pH and d) ISORROPIA-calculated aerosol liquid water content (LWC) for SEARCH sites: JST (red square), YRK (blue circle), CTR (green triangle), and OAK (black star). The top and bottom of the error bars for the JST observations represent the 75th and 25th percentiles. For each parameter, a linear fit including all 4 SEARCH site data is shown as the red line, with the slope (m) and the statistical significance of the fit listed on each panel. Note that the trends for total Fe, Fe solubility, and aerosol pH are not statistically significant for $P = 0.05$.

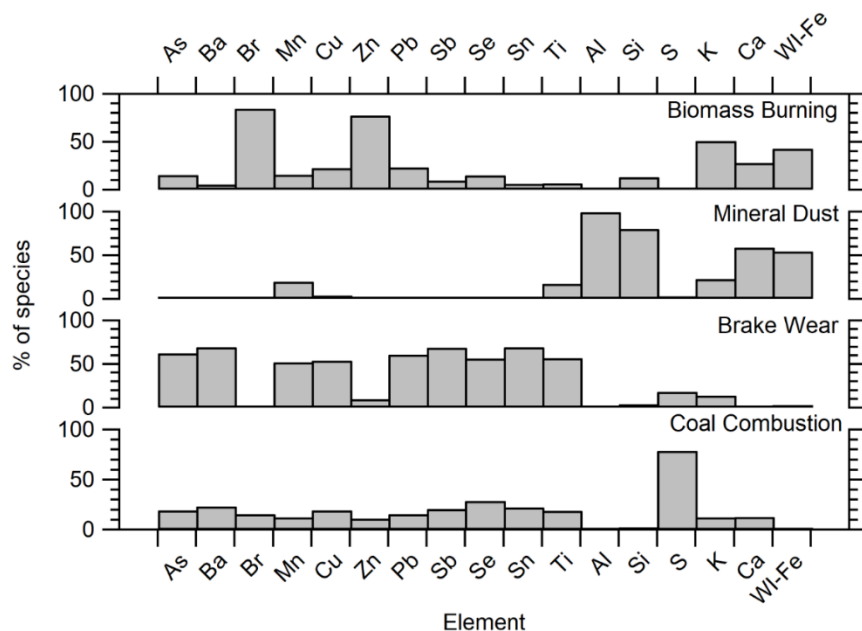


Figure S5. The composition of trace elemental species for the 4 PMF resolved factors.

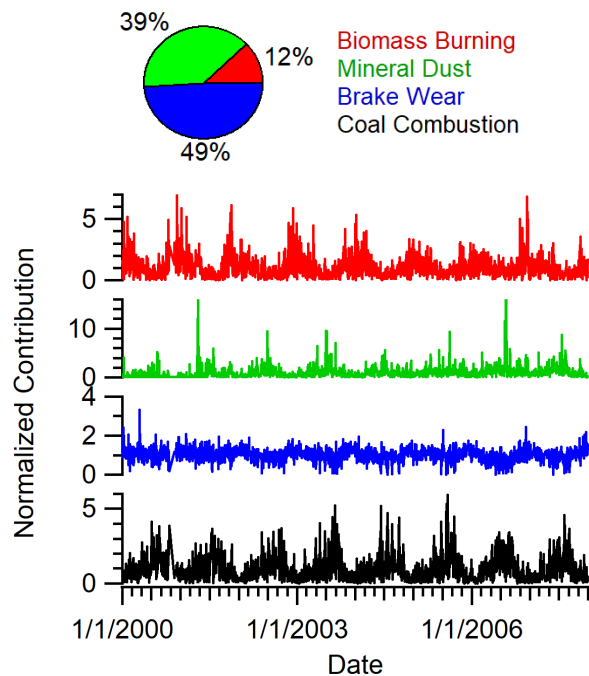


Figure S6. The contributions and the time series profile of the 4 PMF factors (biomass burning, red; mineral dust, green; brake wear, blue; coal combustion, black) to water-insoluble (WI) Fe concentration in $PM_{2.5}$ in a central Atlanta site (JST).

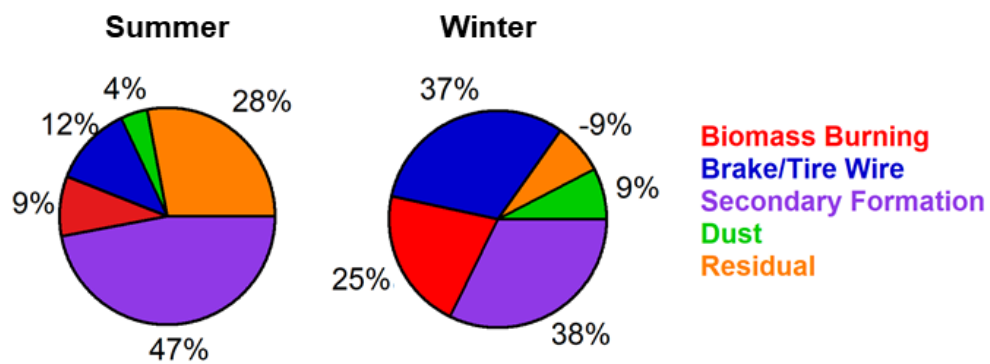


Figure S7. PMF factor contributions for WS-Fe in the summer and wintertime in Atlanta, data from Fang et al.²⁰

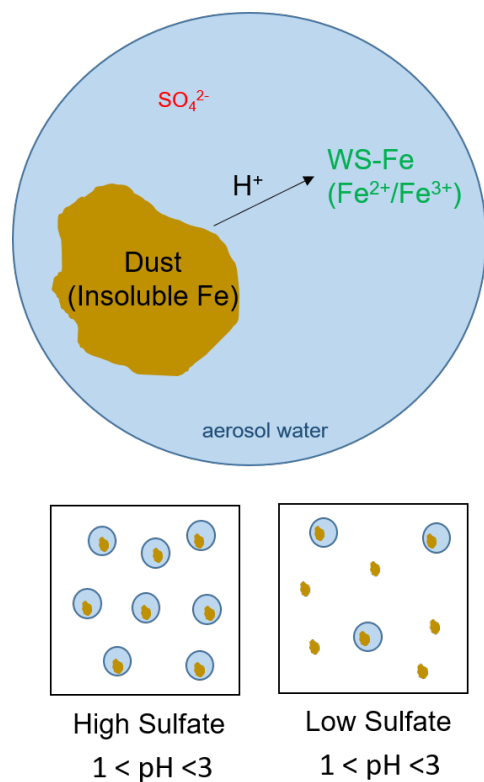


Figure S8. Illustration of the production of WS-Fe from the acid-promoted dissolution of insoluble Fe in dust within an aqueous aerosol. At stable aerosol pH and concentrations of dust, the net production of WS-Fe scales with sulfate concentration, as sulfate controls the aerosol liquid water content, which serves as the medium for the acid-dissolution reaction.

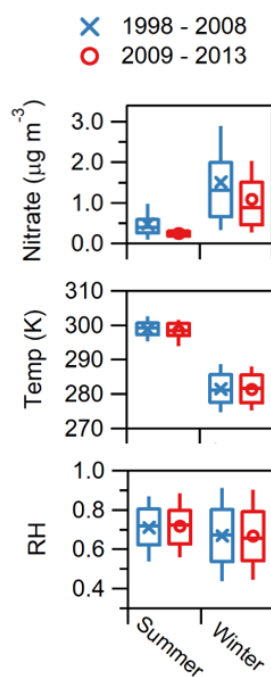


Figure S9. Box and whisker plots of nitrate, temperature and relative humidity (RH) at JST for summer and wintertime before (blue) and after (red) the installation of SO₂ scrubber at the Plant Bowen electric generating units in the SE USA. The lines in the boxes indicate the median values, the upper and lower box boundaries indicate the 75th and 25th percentiles, and the whiskers indicate the 90th and the 10th percentiles for each corresponding time period. The markers indicate the average value for each corresponding period (cross: 1998 – 2008 and circle: 2009 – 2013).

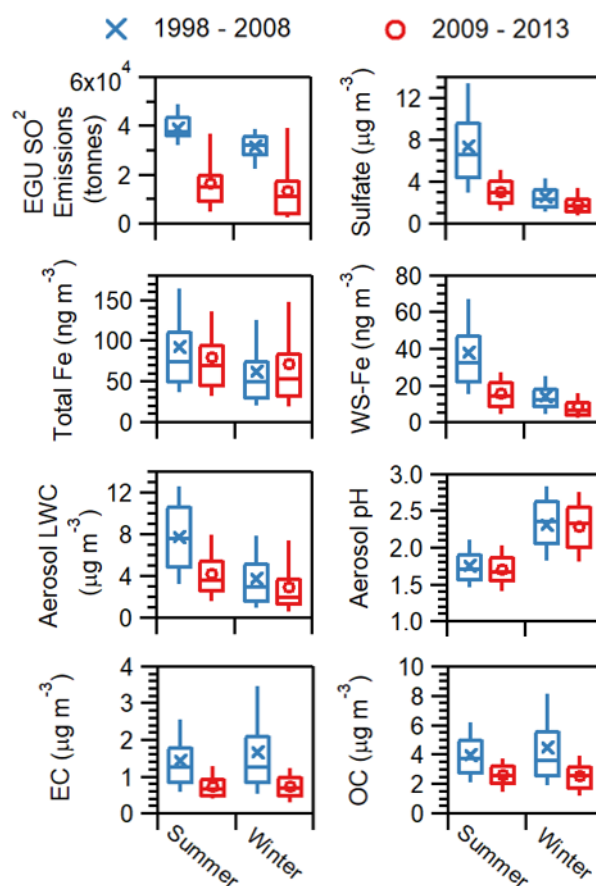


Figure S10. Sulfate, total Fe, WS-Fe, ISORROPIA-calculated aerosol pH and liquid water content (LWC), as well as elemental carbon (EC) and organic carbon (OC) concentrations at JST for summer and wintertime before (blue) and after (red) the installation of SO₂ scrubbers at the major electricity generating units in the SE USA. The lines in the boxes indicate the median values, the upper and lower box boundaries indicate the 75th and 25th percentiles, and the whiskers indicate the 90th and the 10th percentiles for each corresponding time period. The markers indicate the average value for each corresponding period (cross: 1998 – 2008 and circle: 2009 – 2013).

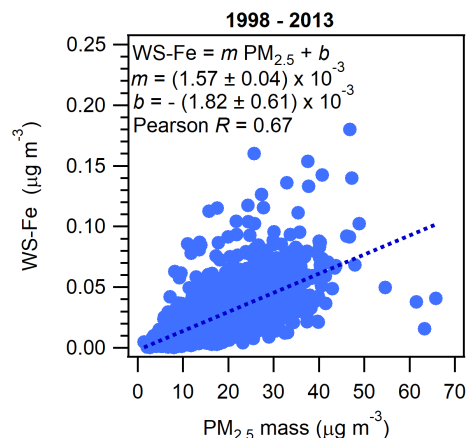


Figure S11. WS-Fe and total $PM_{2.5}$ mass measured at JST in Atlanta from 1998 to 2013. Results of an orthogonal distance regression fit are shown.

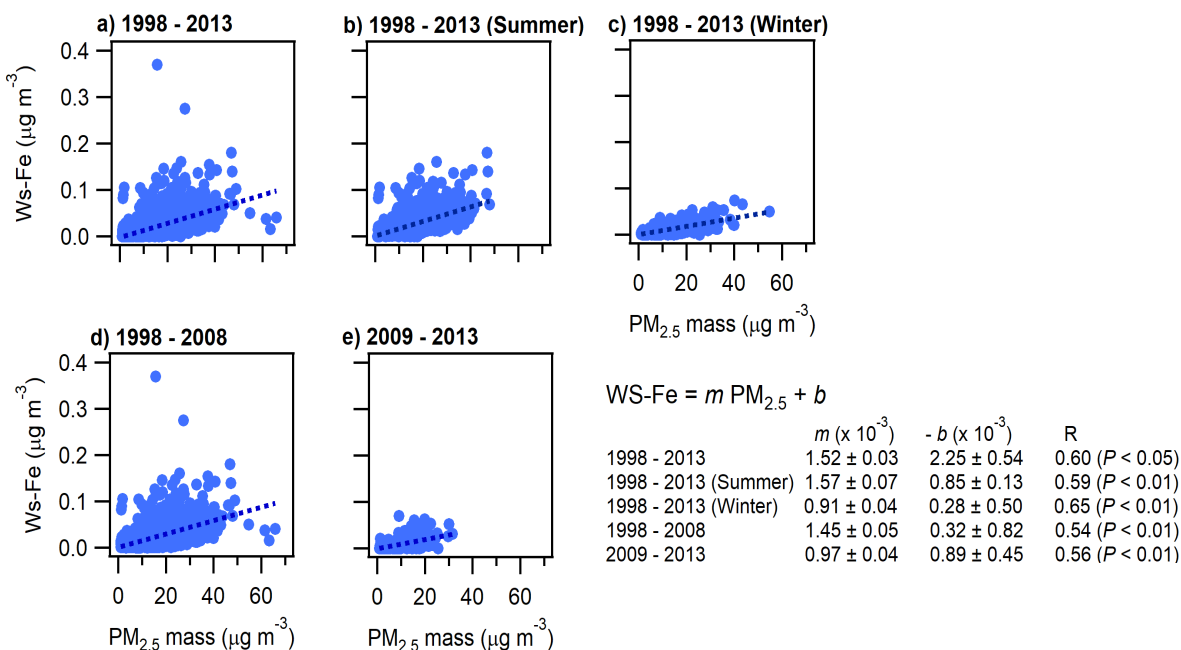


Figure S12. WS-Fe and $PM_{2.5}$ concentrations at the 4 SEARCH sites (JST, CTR, YRK, and OAK) for a) 1998-2013, b) summer months and c) winter months from 1998 – 2013, as well as the time period d) before and e) after 2008. The results of orthogonal distance regression fits are shown.

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