Supplement

1 Chemical preparation

5 mM Ferrozine-acetate reagent was made by a mixture of 246.2 mg ferrozine dissolved in 50 mL DI water and 19.27 g ammonium acetate dissolved in 50 mL DI water.

2.8 mM Bathocuproine was prepared by dissolving 504.6 mg bathocuproine in 500 mL DI water.

1.6 M Hydroxylamine hydrochloride was prepared by dissolving 50 g hydroxylamine hydrochloride in 450 mL DI water.

1 M Sodium citrate was prepared by dissolving 147.05 g sodium citrate dihydrate in 500 mL DI water.

5 M Sodium hydroxide was prepared by dissolving 20 g sodium hydroxide in 100 mL DI water.

2 Conversion of mass in Da to size in nm

The Dalton (or unified atomic mass unit, Da) is a unit of mass, defined as 1/12 of the mass of an unbound neutral atom of carbon-12 in its nuclear and electronic ground state and at rest (Taylor, 2009). The mass of one mole of a substance, measured in grams, is numerically equal to the average mass of one of its constituent particles, measured in daltons. Therefore,

$$1g = 6.023 \times 10^{23} Da,$$

where $6.023\text{x}10^{23}$ is Avagadro's Number.

There are several assumptions when calculating the conversion of mass in Da to size in nm. We assume that all the water-soluble species in $PM_{2.5}$ have approximately the same density of 1.4g cm^{-3}. The volume occupied by a spherical particle of mass M in Dalton is:

$$V(nm^3) = \frac{M(mass)}{\rho(density)} = \frac{10^{21} nm^3/cm^3}{1.4g/cm^3 \times 6.023 \times 10^{23} Da/g} \times M(Da) = 1.186 \times 10^{-3} \left(\frac{nm^3}{Da}\right) \times M(Da),$$

where 10^{21} is a unit conversion factor, 1.4 is the assumed particle density, and M (Da) is the particle mass in Daltons. Then assuming all the particles have the same simplest shape of a sphere. the volume of this sphere can be expressed as

$$V = \frac{4}{3}\pi(\frac{D_p}{2})^3.$$

Therefore, the diameter of the particle can be estimated by:

$$D_p(nm) = 2 \times (3V/4\pi)^{1/3} = 0.131M^{1/3}.$$

In this case, when $M = 3\ kDa$, $D_p = 1.89\ nm$; when $M = 30\ kDa$, $D_p = 4.08\ nm$ (Erickson, 2009).

Note that not all particles have a uniform density of 1.4 g cm^{-3}, this approximation and simplification may cause uncertainty in the calculation of the particle size. In addition, the particle shape is not always an ideal sphere. This “spherical particle” assumption will lead to underestimation of particle diameter.

3 Effects of membrane rejection

Membranes fabricated that have set average pore size were used for ultrafiltration permeation in this study. Nevertheless, these membranes can cause problems during ultrafiltration permeation and may lead to underestimation of particle concentration (passing through the membranes). For example, some colloidal?? materials may be rejected by the membranes due to charge repulsion. Additionally, high-concentration samples may cause accumulation of materials on the membranes, leading to rejection of smaller sized molecules and ultimately underestimation of the concentration. According to the permeation coefficient model, the actual filtrate concentration (c_f) could be expressed as

$$c_f = c_{r,0}\frac{1-F^{P_c}}{1-F}$$

where $c_{r,0}$ is the concentration of materials able to pass through the membrane. F is the fraction of the total filtrate volume remaining before the membrane. P_c refers to the permeation coefficient. In this study, to make the measured concentration $c_{r,0}$ as close as possible to the actual filtrate concentration, excessive centrifugation time was applied and F was close to 0. Therefore, the effects of membrane rejection in our study is expected to be small.

4 Effect of dilution ratio on soluble fraction of metal

What is considered water-soluble metal may be affected by the degree of dilution of the sample in the extraction process. Following methods developed for characterizing water-soluble organic carbon (Psichoudaki and Pandis, 2013), the effect of dilution ratio on the soluble fraction of metal (f) can be expressed with the variable P (cm^3 m^{-3}), which is the ratio of the volume of extract water (V_w (mL)) per volume of ambient air that passed through the portion of the filter ($V_a(m^3)$) that was analyzed. P is ~ 0.5 in this study.

Assume that the dissolution of a single compound is not affected by the presence of the other components. The mass of a Fe- or Cu-contained compound A that can be dissolved during the extraction (assuming the system reaches equilibrium) is equal to $V_w \cdot S_A$, where S_A (ng mL^{-1}) is the saturated solubility of metal A. The total mass of A is equal to $V_A \cdot C_A$, where C_A (ng m^{-3}) is the ambient concentration of metal A. Now the fraction of A in the aqueous phase is given by

$$f_A = \frac{V_w \cdot S_A}{V_A \cdot C_A} = \frac{P \cdot S_A}{C_A}.$$

This model predicts that the water-soluble fraction of A is proportional to the P parameter. As predicted by this model, Figure S8 shows the water-soluble fraction of a compound as a function of its solubility, for different ambient concentrations when P = 0.5 $cm^3\ m^{-3}$. According to Fig. S8, Fe- or Cu-contained compound with solubility higher than 10^{-3} g L^{-1} always contribute all of their mass to the water-soluble fraction of Fe or Cu, regardless of their ambient concentration, while species with solubility less than 10^{-6} g L^{-1} do not contribute significantly. Slight change in P can affect the soluble fraction of components with solubility within 10^{-6} to 10^{-3} g L^{-1}. The solubilities of most soluble Fe and Cu components are much higher than 10^{-3} g L^{-1} (e.g. $Fe(II)SO_4$), which could be fully dissolved even if P-value decreases to 0.01. Thus, the value of P = 0.5 $cm^3\ m^{-3}$ is acceptable in this study for extracting most soluble Fe and Cu species in the ambient aerosol. Note that there is no unified P-value for the extraction of WS metals and the level of WS metals in different aerosol samples varies greatly. WS metal measurements under high concentration might tend to give low values unless higher P values are used.

5 Tables & Figures

Table S1: Statistical summary of transition metal concentrations in $PM_{2.5}$ measured in Atlanta in 2017 (N = 355) based on ICP-MS measurement.

	Total Fe	Total Cu	Total Mn	WS Fe	WS Cu	WS Mn
Mean (ng m^{-3})	203.7	30.7	4.0	19.5	15.2	2.0
Median (ng m^{-3})	156.3	26.0	3.44	11.9	11.7	1.8
Maximum (ng m^{-3})	1643.4	204.5	19.3	123.7	141.5	6.4
Minimum (ng m^{-3})	< LOD	< LOD	< LOD	< LOD	< LOD	< LOD
RSD	0.90	0.68	0.72	1.11	0.83	0.57

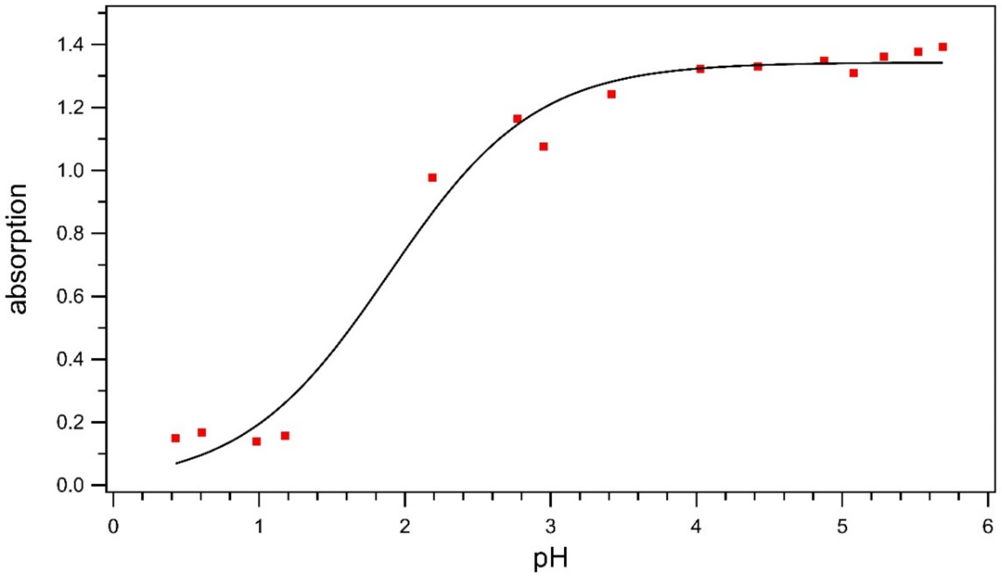

Figure S1: Effect of pH on the formation of Cu(I) complex of bathocuproine. The y-axis represents the light absorption at 484 nm.

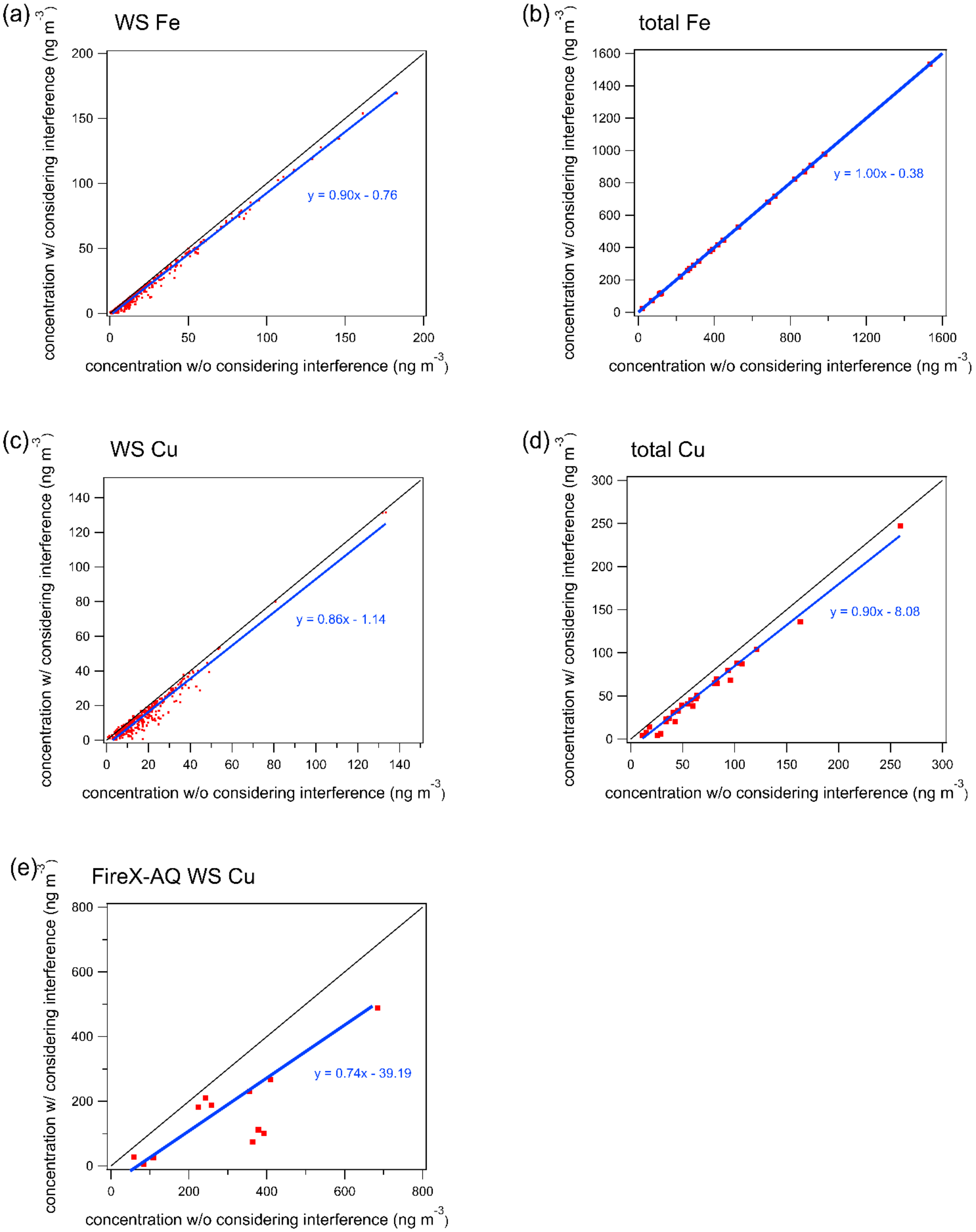

Figure S2: Influence of light absorption of other species in the sample on the determination of (a) WS Fe, (b) total Fe, (c) WS Cu, (d) total Cu for data collected in Atlanta. Plot (e) shows an extreme example (FireX-AQ) involving the sampling of wildfire smoke, which has high concentrations of BC and BrC and low levels of Fe and Cu. York regressions are shown and the predicted intercept is interpreted as the average systematic offset caused by the interference of other light-absorbing species.

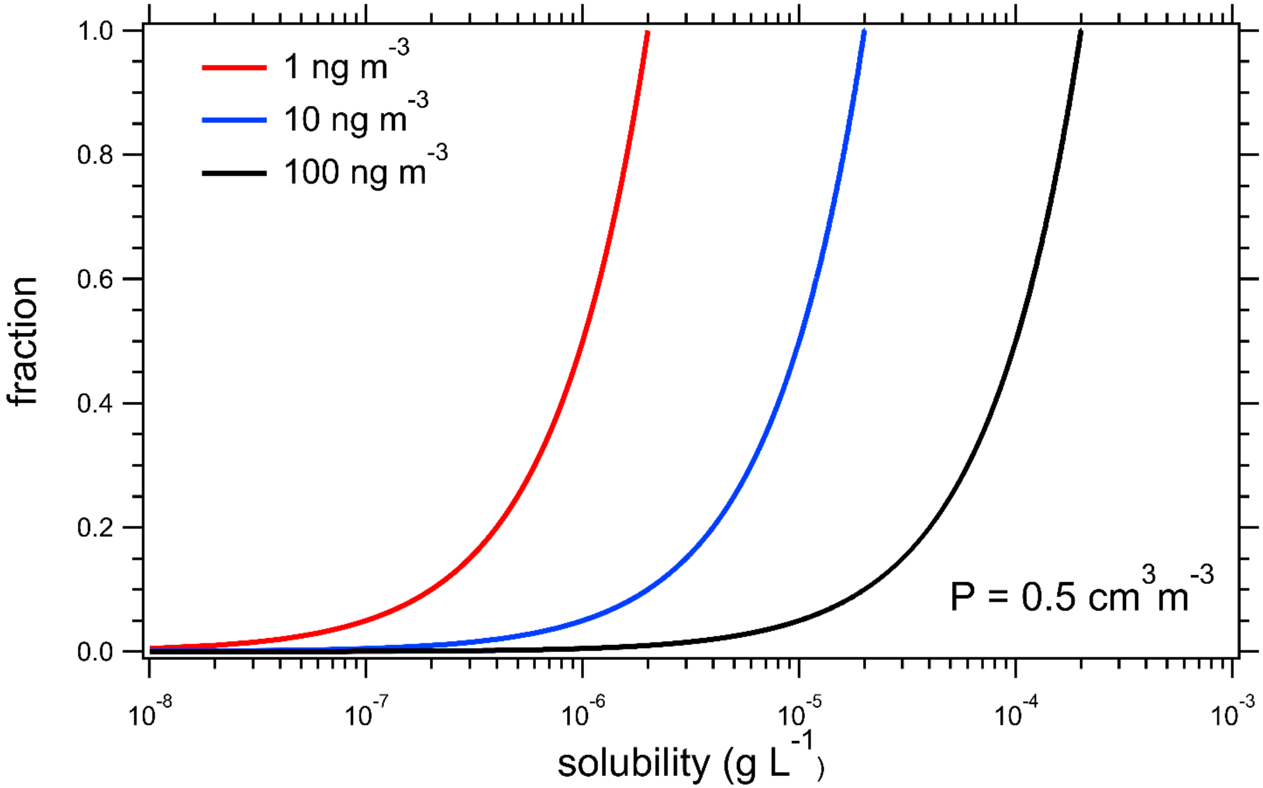

Figure S3. Water-soluble fraction of a compound as a function of its solubility and ambient concentration for P = 0.5 cm^3 m^{-3}.

References

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