Supplementary Information

On dithiothreitol (DTT) as a measure of oxidative potential for ambient particles: Evidence for the importance of soluble transition metals.

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Submitted to *Atmospheric Chemistry and Physics*, April 20th 2012
Revised Version Submitted September 5st 2012

S1. Relative reactivity of soluble metals as a function of metal concentration.

Figure S1 shows the calculated rate of DTT loss of each metal divided by that of Fe(II). For simplicity we assume metals are at the same concentration (x-axis) and calculate the DTT response based on the concentration-response equations in Table 1 of the manuscript. We divide the DTT response from each metal by the DTT loss from Fe(II) to give an idea of the relative reactivity of each metal. Ni(II), V(V), Fe(II) and Fe(III) have a single relative reactivity across the entire concentration range, i.e., the relative reactivity does not change as a function of PM mass added to the reaction solution. This is because these metals have linear concentration-response curves (Table 1). Cu(II) and Mn(II), on the other hand, show decreasing reactivity relative to Fe(II) with increasing metal concentration, a consequence of their non-linear concentration-response curves (Table 1). Cu(II) is 300 times more reactive than Fe(II) at metal concentrations of 0.01 µM, decreasing to a factor of approximately 20 at metal concentrations of 1 µM. Mn(II) is 100 times more reactive than Fe(II) at 0.01 µM, decreasing to 10 times more at 1 µM metal. Thus the relative DTT loss from each metal species changes as a function of the concentration of metal in the DTT solution. Because actual PM samples will not have equal concentrations of all metal species, the behavior in Fig. S1 is only an example. However, these results indicate that the rate of DTT loss will not be linearly related to the mass of PM added to the reaction solution in cases where Cu and/or Mn dominate DTT oxidation, which appears to be common in ambient fine PM samples (as we show later in the manuscript).

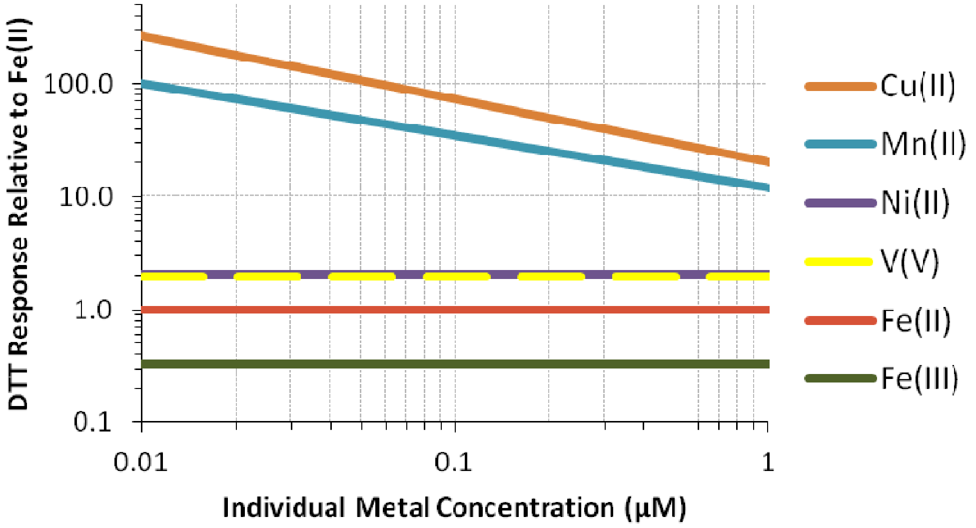

Figure S1. The reactivity of each soluble metal relative to Fe(II), expressed as the ratio of the rate of DTT loss by a given metal divided by the rate with Fe(II). Calculations are based on the measured concentration-response equations in the manuscript (Table 1).

S2. Calculated rate of DTT loss in a hypothetical PM sample based on median concentrations of quinones and soluble metals reported in the literature

To determine the typical concentration of each DTT-active species in our hypothetical PM sample we use literature values for $PM_{2.5}$ for urban locations in the United States; for a given species we use the median of the average concentrations from each of the cited studies. The study averages used to calculate the median for each species are summarized in Figs. S2 and S3. Quinone (and PHEN) concentrations are total particulate-phase quinones as summarized by Walgreave et al. (2010); the specific reference for the concentration of each species in our hypothetical $PM_{2.5}$ sample is listed inTable 2 in the manuscript. Quinone measurements are typically made by extracting PM samples in an organic solvent at elevated temperature (e.g., Cho et al., 2004); therefore, these concentrations are probably upper bounds for the quinone concentrations that can be extracted from particles in the aqueous DTT assay. In contrast, the metal concentrations listed here represent soluble metals from PM extracted in water; a small amount of organic solvent was added in some cases to wet the Teflon filters (Connell et al., 2006). For calculation purposes, we assume that 32.8 m^3 of air was sampled onto a filter and the whole filter PM mass was added to the 3.0 mL of DTT reaction solution. The DTT response was then calculated using the concentration-response equations in Table 1 of the manuscript.

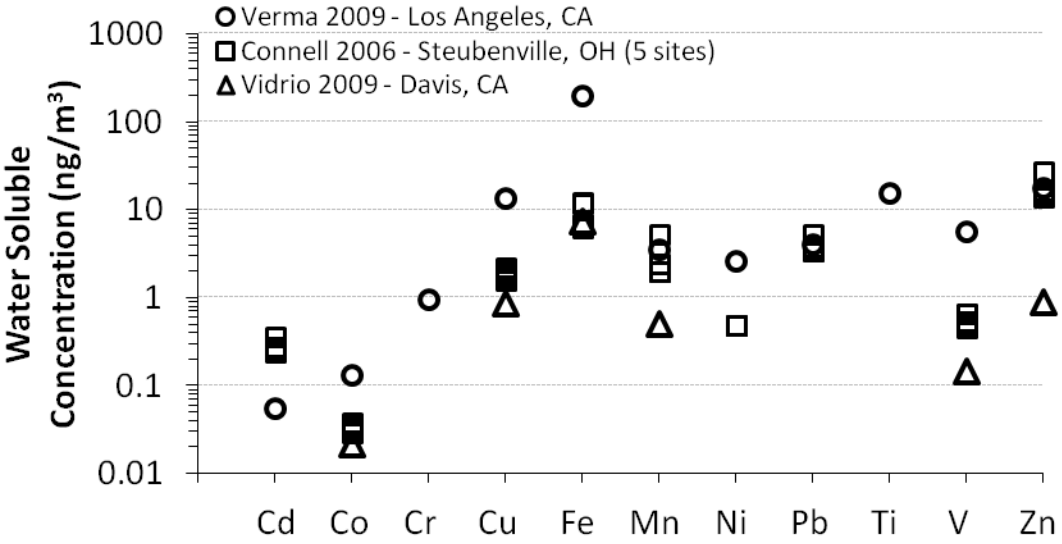

Figure S2. Water-soluble metal concentrations in US urban $PM_{2.5}$ from the literature (Connell et al., 2006; Verma et al., 2009; Vidrio et al., 2009). Each symbol represents the average value for a given site.

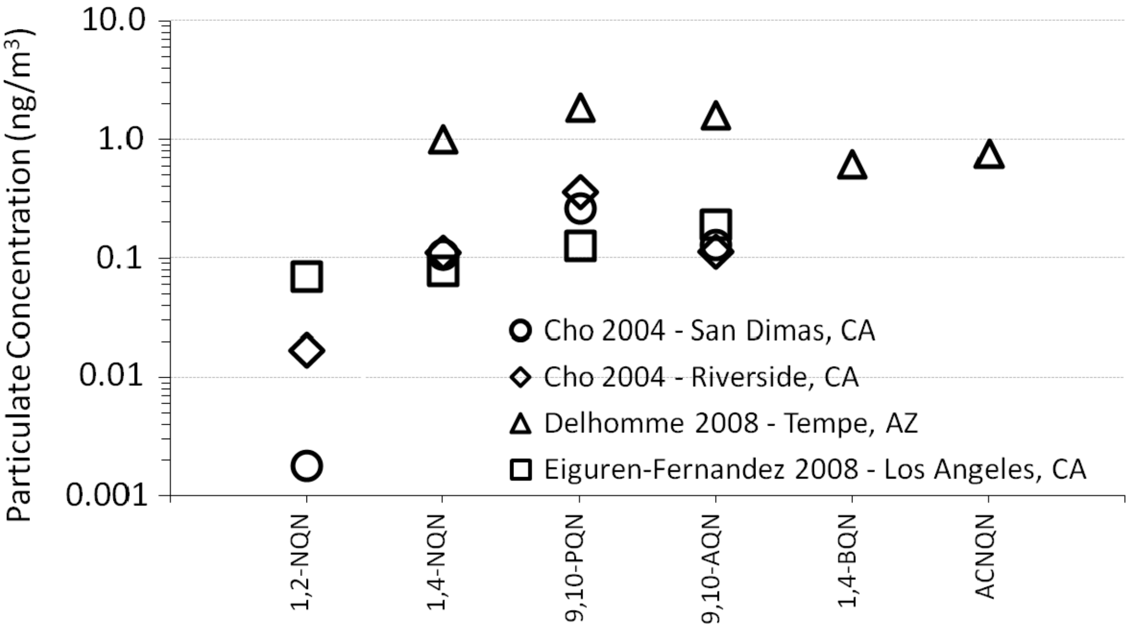

Figure S3. Total particulate quinone concentrations in US urban $PM_{2.5}$ from the literature (Cho et al., 2004; Delhomme et al., 2008; Eiguren-Fernandez et al., 2008). Each symbol represents the average value for a given site.

S3. Ambient $PM_{2.5}$ collected in Fresno and Westside, California.

We measured the DTT loss from six ambient $PM_{2.5}$ samples collected in the San Joaquin Valley of California (see Section 3.3 of the manuscript). We also calculated the expected DTT response from each metal in the $PM_{2.5}$ samples using our previous measurements of soluble metals (Shen et al., 2011) and our concentration-response for each metal (Table 1). We then calculated the percent contribution from each metal to the total measured DTT loss for each sample. The remaining DTT loss not attributed to one of our four measured metals is labeled “unknown”. This DTT loss is from other chemical species in the PM that we did not quantify, e.g., quinones. The average percent of total DTT loss from each soluble metal and the unknown fraction was calculated from the six samples and is shown below in Fig. S4.

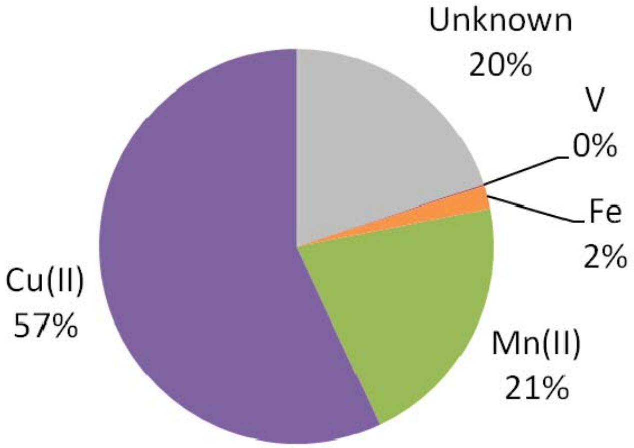

Figure S4. Calculated average contributions to DTT loss by four metals and unidentified species in six ambient $PM_{2.5}$ samples collected in Fresno and Westside, CA.

S4. Effect of EDTA

We measured the rate of DTT loss in blanks with various concentrations of EDTA (Fig. S5) in order to accurately blank-correct our quinone and metal results in the presence of this chelator. Similar to the results for PQN shown in Fig. 7b in the text, addition of EDTA also reduces the rate of loss of DTT in the blank, probably by chelating trace metals that were not removed by Chelex treatment of the phosphate buffer.

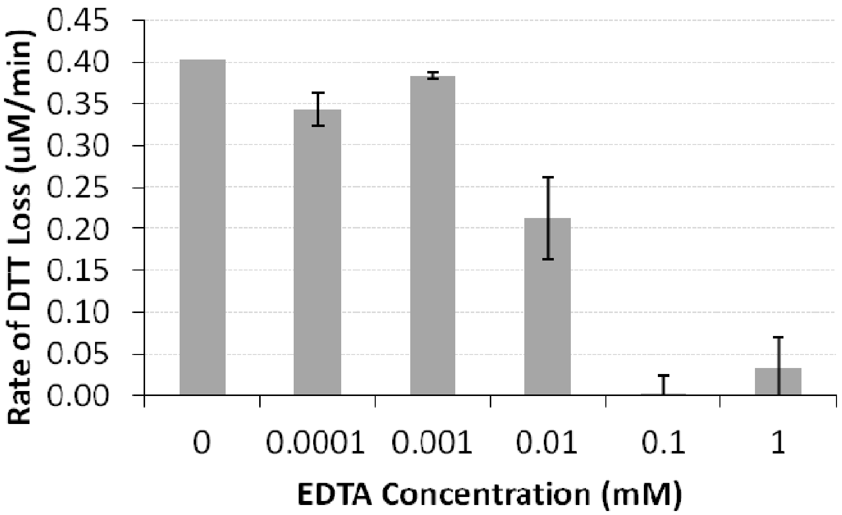

Figure S5. Rate of DTT loss in the blank with increasing concentrations of EDTA

S5. Direct degradation of DTT by HOOH

Kumagai et al. (2002) showed evidence that DTT could react directly with HOOH, which would complicate the interpretation of the DTT assay as a measure of the oxidative potential of PM. We observed formation of HOOH both in the DTT blank (2-13 µM) and in mixtures of DTT and 0.1 µM PQN (up to 30 µM) at 25 ˚C after 15 minutes. We tested the ability of HOOH to degrade DTT by adding 5 to 35 µM of HOOH to the DTT assay (without any other redox-active species added) (Fig. S6). HOOH stock concentrations were verified on the day of the experiment using the absorbance at 240 nm using a UV/VIS spectrophotometer. Based on this data, direct degradation of DTT by HOOH may account for up to 20% of total DTT loss in our DTT blanks and from 0.1 µM PQN. We have not measured HOOH production from mixtures of DTT and metals.

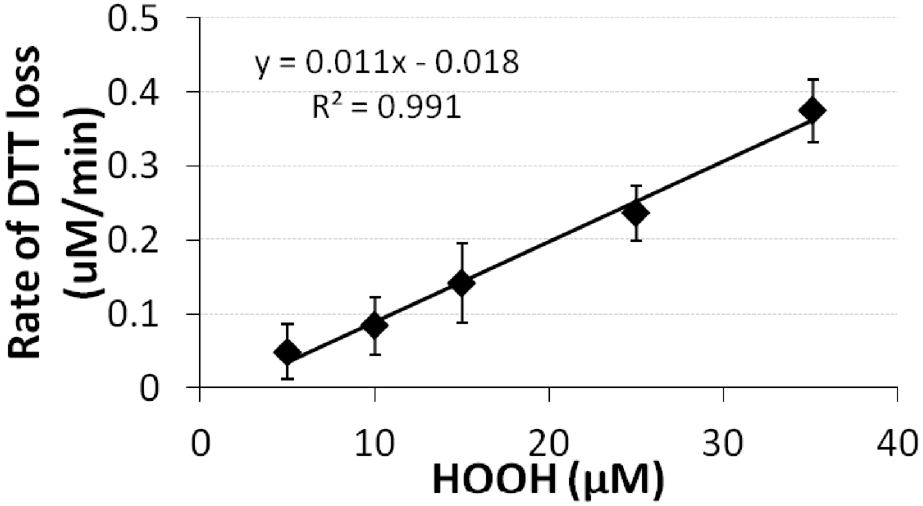

Figure S6. The blank-corrected rate of DTT loss as a function of added HOOH.

S6. DTT loss from binary mixtures of DTT-active species.

To examine whether DTT reactivity is additive, we measured the rate of DTT loss in solutions containing two DTT-active species and compared the results to the sum of the responses from the two species measured separately. As shown in Fig. S7, the rate of DTT loss in the binary mixtures is very similar to the sum of the rates from individual species. Mixtures of 1,2-NQN with PQN, as well as Fe(II) with PQN, do not show a statistically different rate of DTT loss compared to the sum of the individual species. Mixtures of Cu(II) with PQN and Cu(II) with Fe(II) are statistically larger ($p = 0.05$) than the sum of individual species, but only by 14% and 18%, respectively.

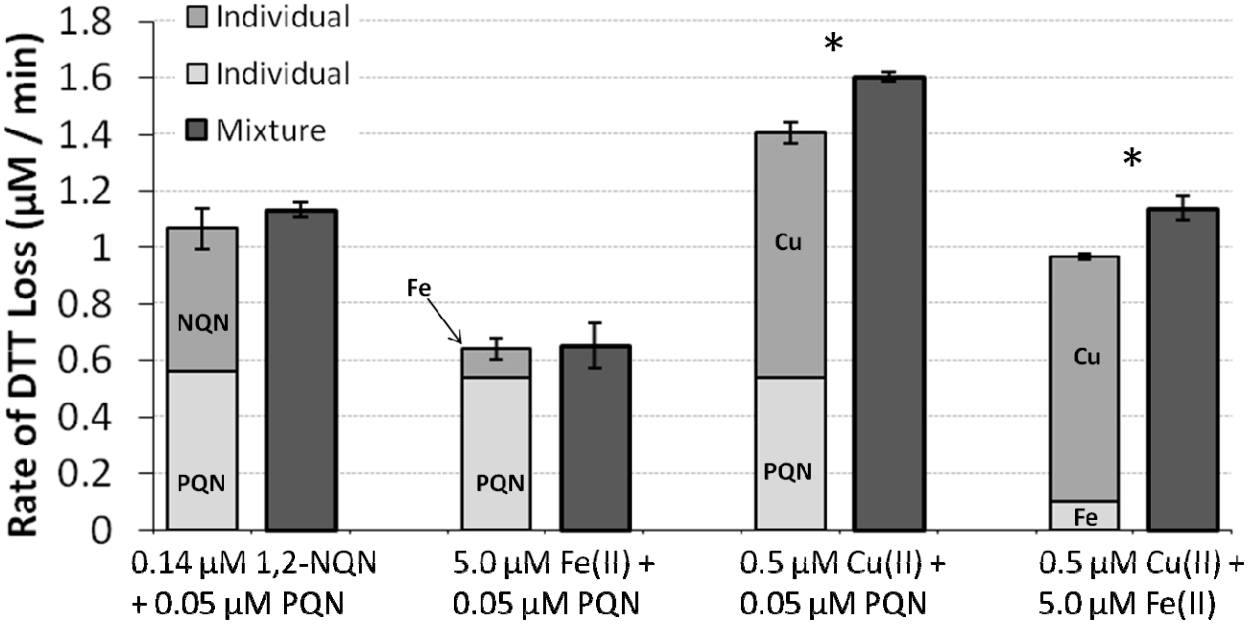

Figure S7. Blank-corrected rates of DTT loss from individual chemical species versus in binary mixtures. Stacked lighter bars are the sum of rates from individual species with the propagated standard deviation. Dark bars are the rate of DTT loss measured in the binary mixture with the standard deviation (n=2). An asterisk indicates a pair of bars is statistically different at the 95% confidence level.

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