

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

Jessica G. Charrier^{a,b} and Cort Anastasio^{a,b}

^aDepartment of Land, Air and Water Resources

^bAgricultural and Environmental Chemistry Graduate Group

University of California, Davis

1 Shields Ave.

Davis, CA USA 95616

Submitted to *Atmospheric Chemistry and Physics*, April 20th 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. This means the relative DTT loss from each metal species changes as a function of the concentration of metal added to 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; as we show later in the manuscript, it appears that Cu and Mn typically dominate DTT oxidation for fine PM samples.

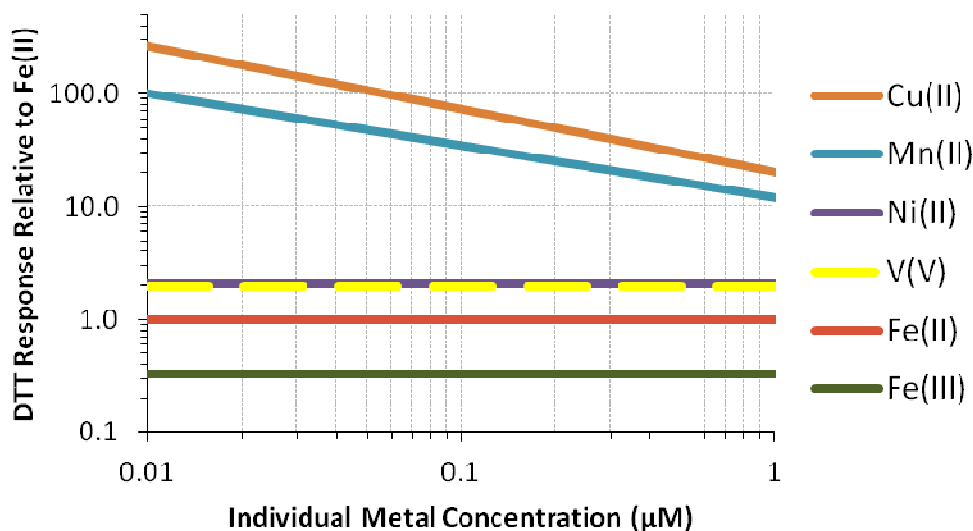
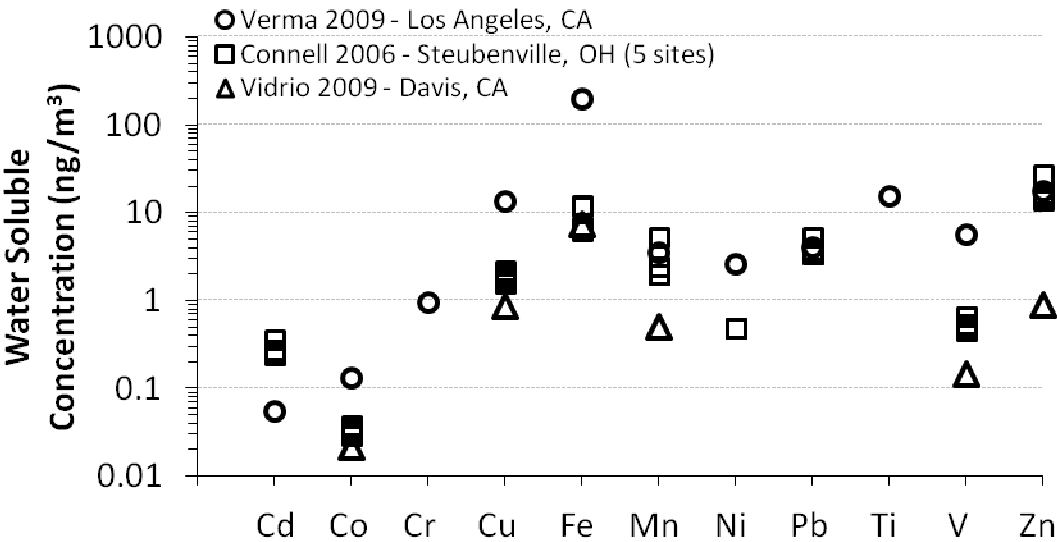


Figure S1. The reactivity of each soluble metal relative to Fe(II), expressed as the ratio of the rate of DTT loss by a given metal divided by the rate with Fe(II). Calculations are based on the measured concentration-response equations in the manuscript (Table 1).

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

36 To determine the typical concentration of each DTT-active species in our hypothetical PM
37 sample we use literature values for PM_{2.5} for urban locations in the United States; for a given species we
38 use the median of the average concentrations from each of the cited studies. The study averages used to
39 calculate the median for each species are summarized in Figs. S2 and S3. Quinone (and PHEN)
40 concentrations are total particulate-phase quinones as summarized by Walgreave et al. (2010); the specific
41 reference for the concentration of each species in our hypothetical PM_{2.5} sample is listed in Table 2 in the
42 manuscript. Quinone measurements are typically made by extracting PM samples in an organic solvent at
43 elevated temperature (e.g., Cho et al., 2004); therefore, these concentrations are probably upper bounds
44 for the quinone concentrations that can be extracted from particles in the aqueous DTT assay. In contrast,
45 the metal concentrations listed here represent soluble metals from PM extracted in water; a small amount
46 of organic solvent was added in some cases to wet the Teflon filters (Connell et al., 2006). For
47 calculation purposes, we assume that 32.8 m³ of air was sampled onto a filter and the whole filter PM
48 mass was added to the 3.0 mL of DTT reaction solution. The DTT response was then calculated using the
49 concentration-response equations in Table 1 of the manuscript.



50

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

53

54

55

56

57

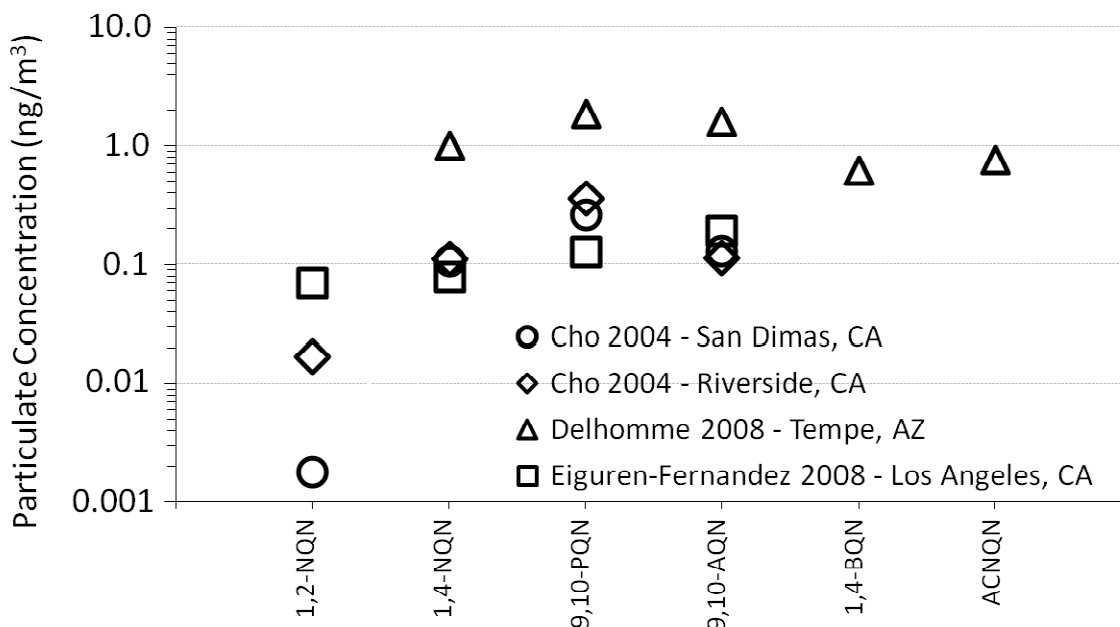


Figure S3. Total particulate quinone concentrations in US urban PM_{2.5} from the literature (Cho et al., 2004; Delhomme et al., 2008; Eiguren-Fernandez et al., 2008). Each symbol represents the average value for a given site.

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.

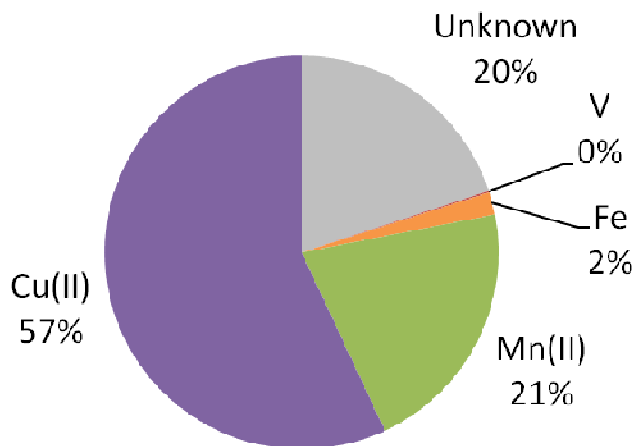


Figure S4. Calculated average contributions to DTT loss by four metals and unidentified species in six ambient PM_{2.5} samples collected in Fresno and Westside, CA.

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, 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.

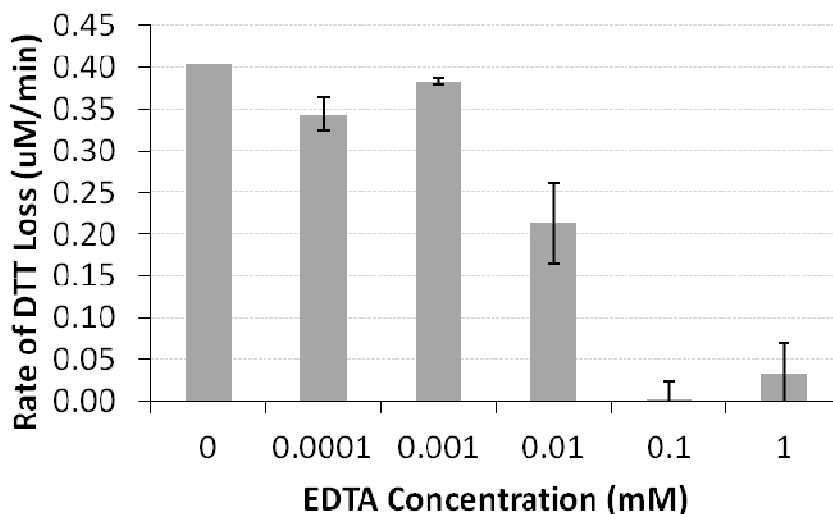


Figure S5. Rate of DTT loss in the blank with increasing concentrations of EDTA

References

- Cho, A. K., Di Stefano, E., You, Y., Rodriguez, C. E., Schmitz, D. A., Kumagai, Y., Miguel, A. H., Eiguren-Fernandez, A., Kobayashi, T., Avol, E., and Froines, J. R.: Determination of four quinones in diesel exhaust particles, SRM 1649a, an atmospheric PM_{2.5}, *Aerosol Sci. Technol.*, 38, 68-81, 2004.
- Connell, D. P., Winter, S. E., Conrad, V. B., Kim, M., and Crist, K. C.: The Steubenville Comprehensive Air Monitoring Program (SCAMP): Concentrations and solubilities of PM_{2.5} trace elements and their implications for source apportionment and health research, *J. Air Waste Manage. Assoc.*, 56, 1750-1766, 2006.
- Delhomme, O., Millet, M., and Herckes, P.: Determination of oxygenated polycyclic aromatic hydrocarbons in atmospheric aerosol samples by liquid chromatography-tandem mass spectrometry, *Talanta*, 74, 703-710, 2008.
- Eiguren-Fernandez, A., Miguel, A. H., Di Stefano, E., Schmitz, D. A., Cho, A. K., Thurairatnam, S., Avol, E. L., and Froines, J. R.: Atmospheric distribution of gas- and particle-phase quinones in Southern California, *Aerosol Sci. Technol.*, 42, 854-861, 2008.
- Shen, H., Barakat, A. I., and Anastasio, C.: Generation of hydrogen peroxide from San Joaquin Valley particles in a cell-free solution, *Atmos. Chem. Phys.*, 11, 753-765, 2011.
- Verma, V., Ning, Z., Cho, A. K., Schauer, J. J., Shafer, M. M., and Sioutas, C.: Redox activity of urban quasi-ultrafine particles from primary and secondary sources, *Atmos. Environ.*, 43, 6360-6368, 2009.
- Vidrio, E., Phuah, C. H., Dillner, A. M., and Anastasio, C.: Generation of hydroxyl radicals from ambient fine particles in a surrogate lung fluid solution, *Env. Sci. Technol.*, 43, 922-927, 2009.

113 Walgraeve, C., Demeestere, K., Dewulf, J., Zimmermann, R., and Van Langenhove, H.: Oxygenated
114 polycyclic aromatic hydrocarbons in atmospheric particulate matter: Molecular characterization
115 and occurrence, *Atmos. Environ.*, 44, 1831-1846, 2010.