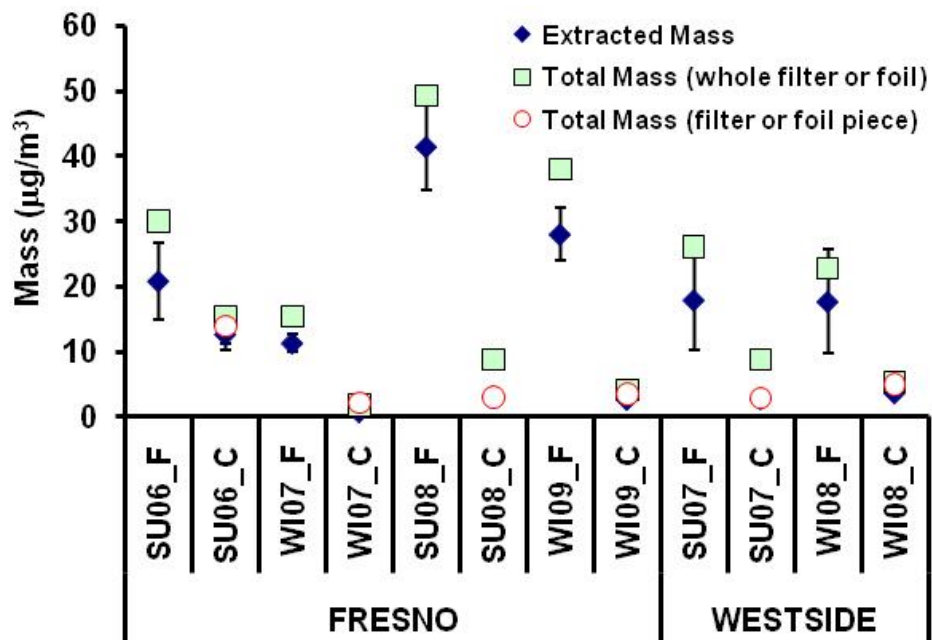## Supplementary Material

Figure S1. Mass concentration of SJV PM. The extracted mass was calculated by subtraction of the weight of filter or foil piece before PM extraction with the corresponding weight after PM extraction. Total mass (filter or foil piece) was calculated by subtraction of the weight of filter or foil piece before PM extraction with the corresponding weight after extraction and wiped clean using a cotton swab soaked in 70 % ethanol. Total mass (whole filter or foil) was provided by SAHERC. Values are means ± SD, n = 5 to 8. F, fine PM; C, coarse PM. In general, the total mass determined from our foil pieces agreed with the total mass determined from the whole foil except for two samples (Fresno summer 2008 and Westside summer 2007 coarse PM). The ratio of Total mass (filter or foil piece) over Total mass (whole filter or foil) was 0.76 ± 0.34 (Mean ± SD).
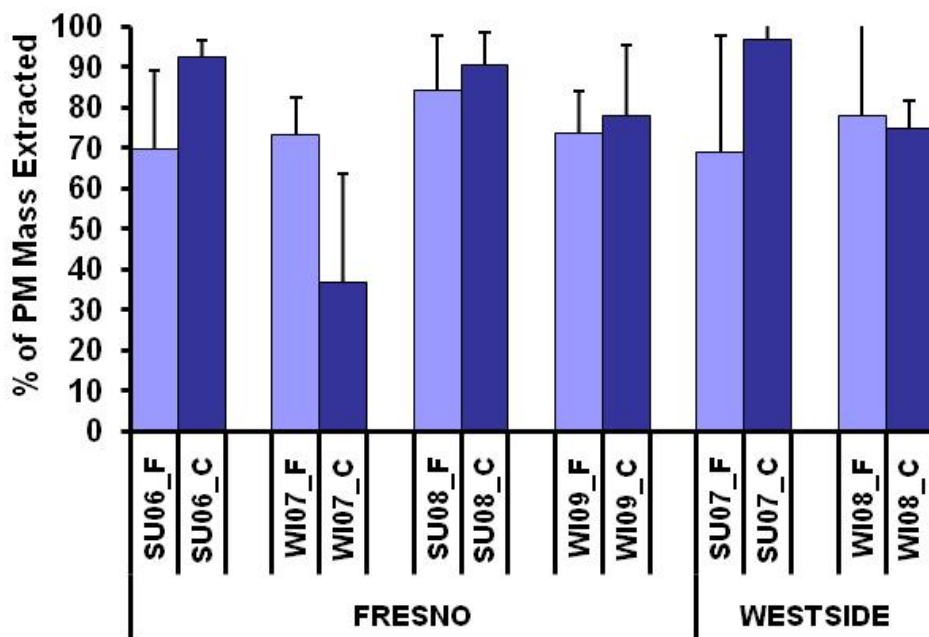
Figure S2. Mass extraction efficiency from SJV PM. Percent of PM mass extracted from each sample is shown. The percent of mass extracted from the fine PM was calculated using the total mass (whole filter) provided by SAHERC. 69 to 84 % of the total fine PM mass was extracted. The percent of mass extracted from the coarse PM was calculated using our data of total mass (foil piece). 75 to 97 % of the total coarse PM mass was extracted except for the Fresno winter 2007 sample where only 37 % of the total PM mass was extracted. Values are means ± SD, n = 5 to 8.
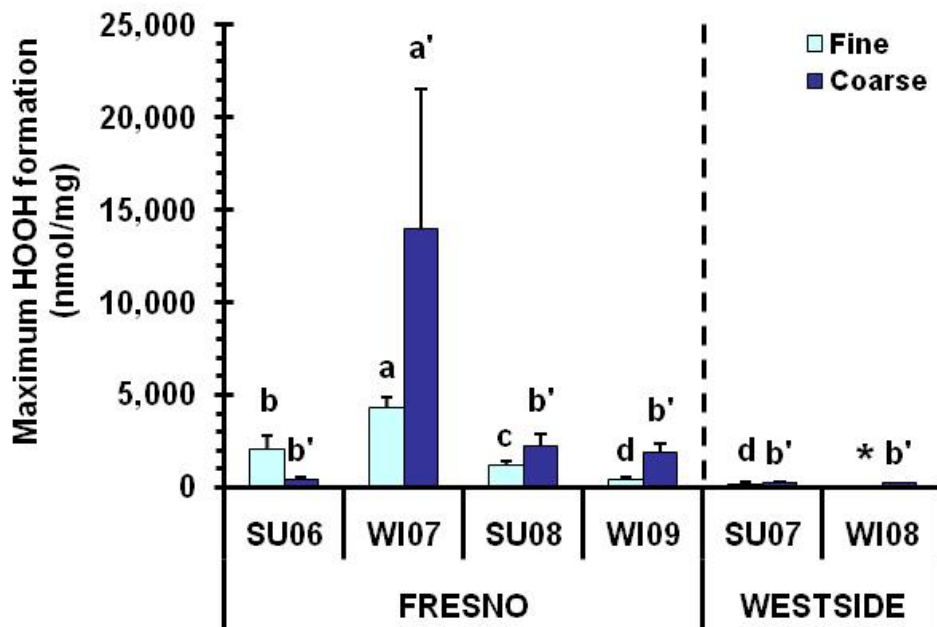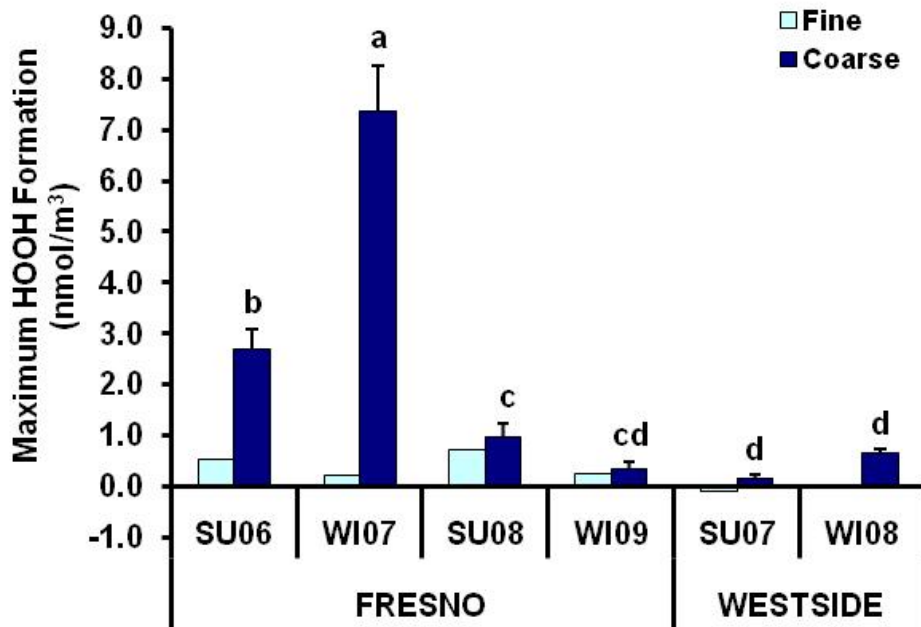
A
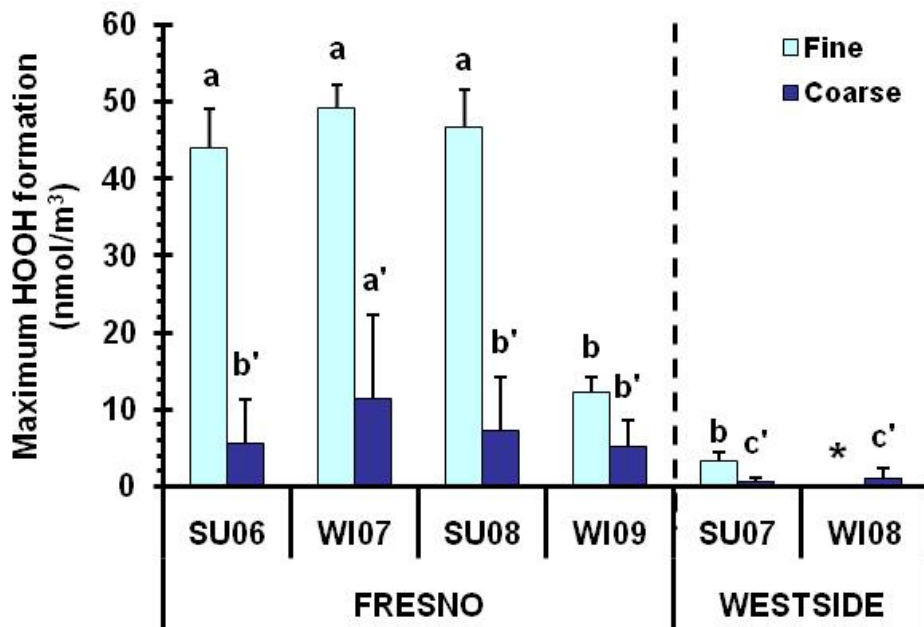
B

Figure S3. Maximum HOOH generation in the presence of 50 µM ascorbate. Panel (A) shows air-volume-normalized maximum levels of HOOH formation, while (B) shows PM-mass-normalized maxima. Values are means ± SD, n = 3. Letters above bars indicate statistically different maxima: a > b > c > d for fine PM, while a' > b' > c' for coarse PM. The asterisk for the WEWI08 sample indicates that HOOH formation was not statistically different from zero.
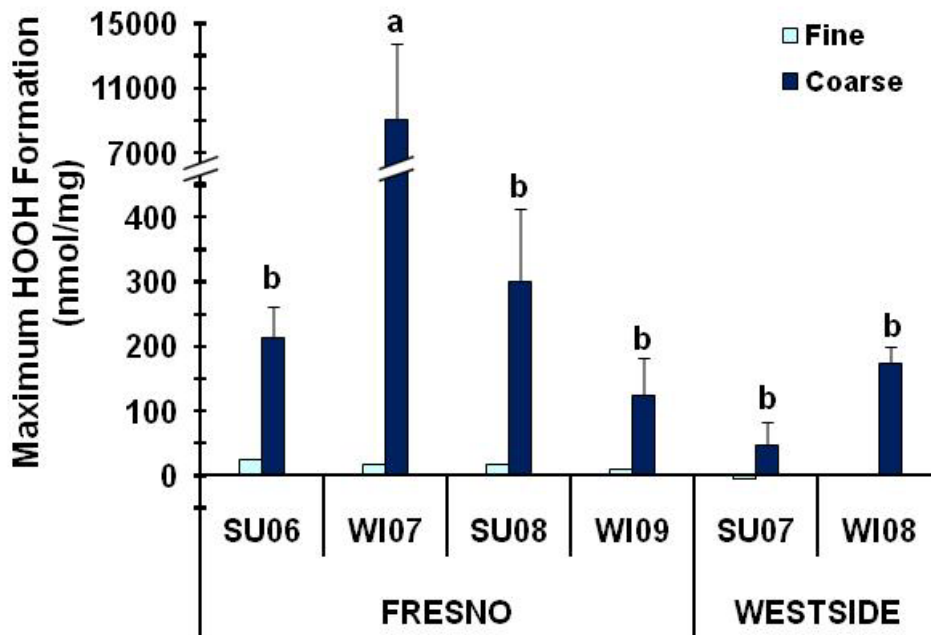
A

B

Figure S4. Maximum HOOH generation in the absence of ascorbate. Panel (A) shows air-volume-normalized maximum levels of HOOH formation, while (B) shows PM-mass-normalized maxima. Fine PM, n = 1. Coarse PM, values are means ± SD, n = 3. Letters above bars indicate statistically different maxima: a > b > c > d.
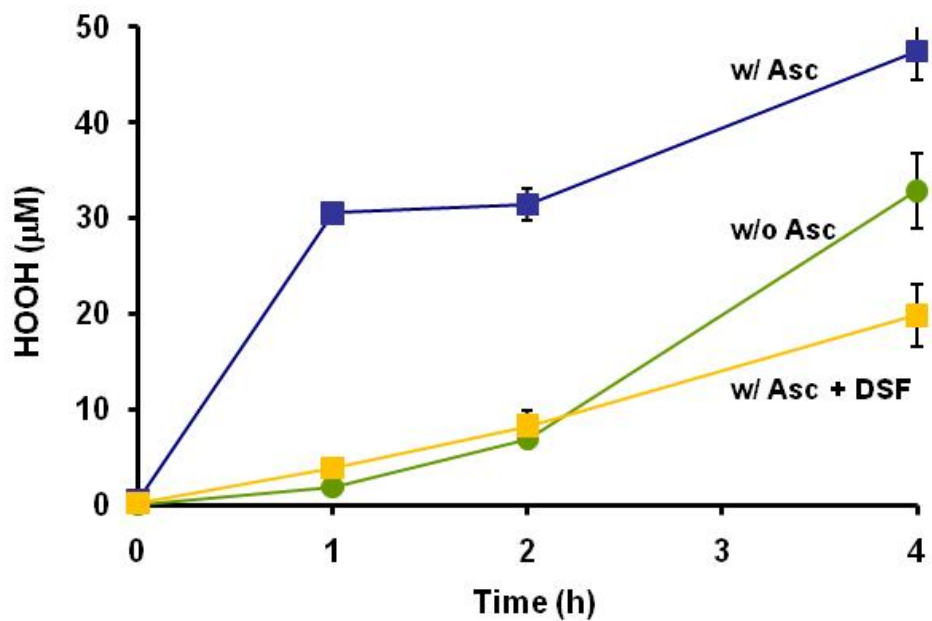
Figure S5. A time course study of HOOH generation from the Fresno winter 2007 coarse PM in SLF. Concentrations of HOOH at 0, 1, 2, and 4 h time points under different experimental conditions are shown.
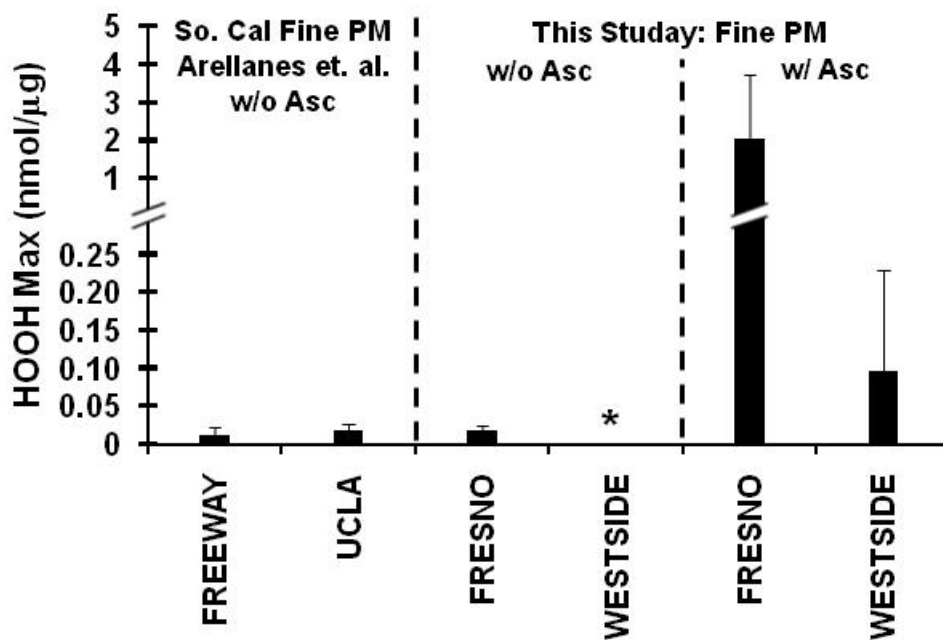
Figure S6. Comparison of HOOH generation in SJV particles with results for fine PM from southern California (Arellanes et al., 2006)**.** PM-mass-normalized HOOH maxima (nmol/μg) are shown. The Southern California fine PM samples were extracted for two h in an aqueous solution (0.10 mM EDTA, pH 3.5, no ascorbate) (Arellanes et al., 2006). The asterisk indicates that HOOH formation in these samples was not statistically different from zero.
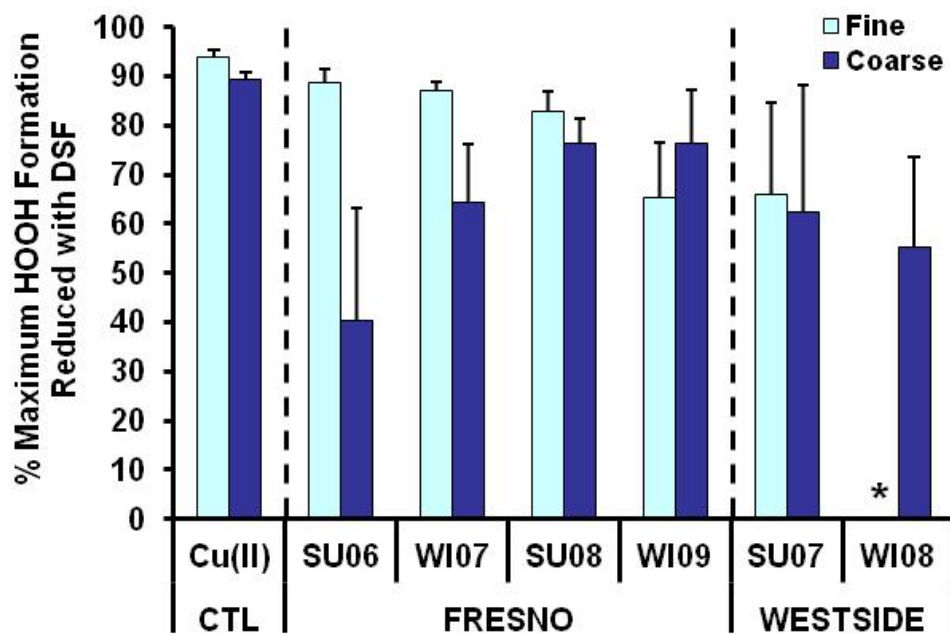
Figure S7. Inhibitory effect of DSF on the maximum HOOH generation in SLF with ascorbate for the Cu control and the SJV PM. Values are means ± SD. n = 3 for extractions without added DSF, and n = 2 for extractions with added DSF. The asterisk indicates that HOOH formation in this sample was not statistically different from zero.
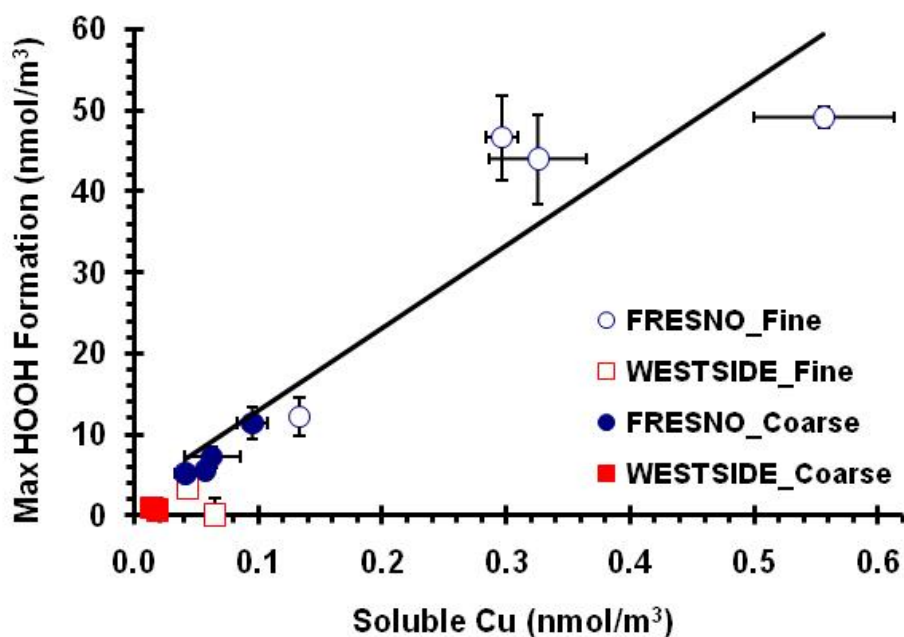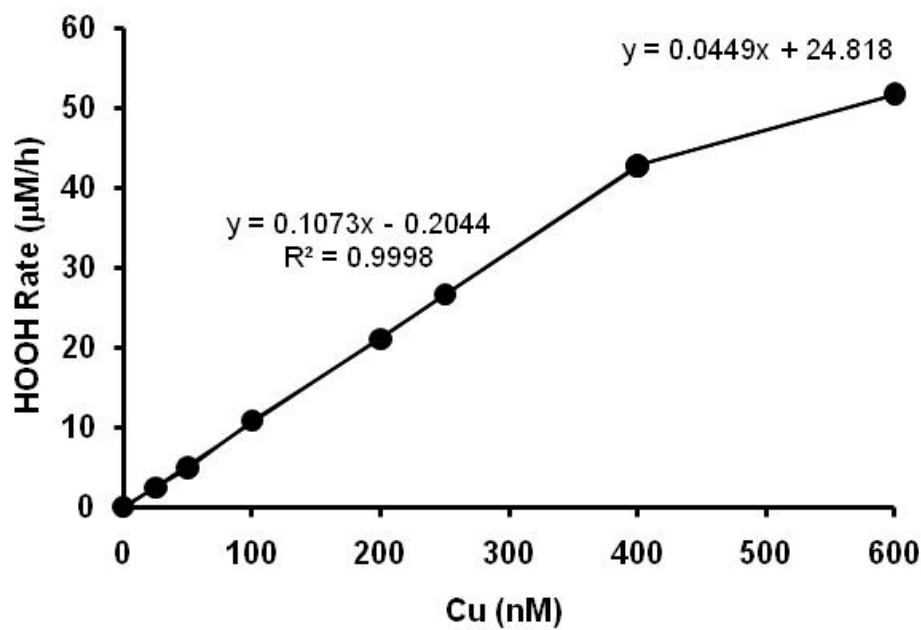
Figure S8. Correlation between the air-volume-normalized maximum level of HOOH generation in SLF with Asc and the SLF-soluble Cu concentration in corresponding PM extracts. Values are means ± SD. n = 3 except for the Cu concentrations of the Fresno summer 2006 coarse PM, the Fresno winter 2009 fine and coarse PM , and the Westside winter 2008 fine PM, where n = 2. The maximum levels of HOOH formation by Fresno fine and coarse PM were strongly correlated with the SLF-soluble Cu concentrations in corresponding PM extracts: $y = 101.97x + 2.68$, $R^2 = 0.86$). No correlation was observed between the SLF-soluble Cu concentrations and the maximum levels of HOOH formation from the Westside PM ($R^2 = 0.0004$).

A

$y = 0.0449x + 24.818$

$y = 0.1073x - 0.2044$
$R^2 = 0.9998$

HOOH Rate (µM/h)

Cu (nM)

B

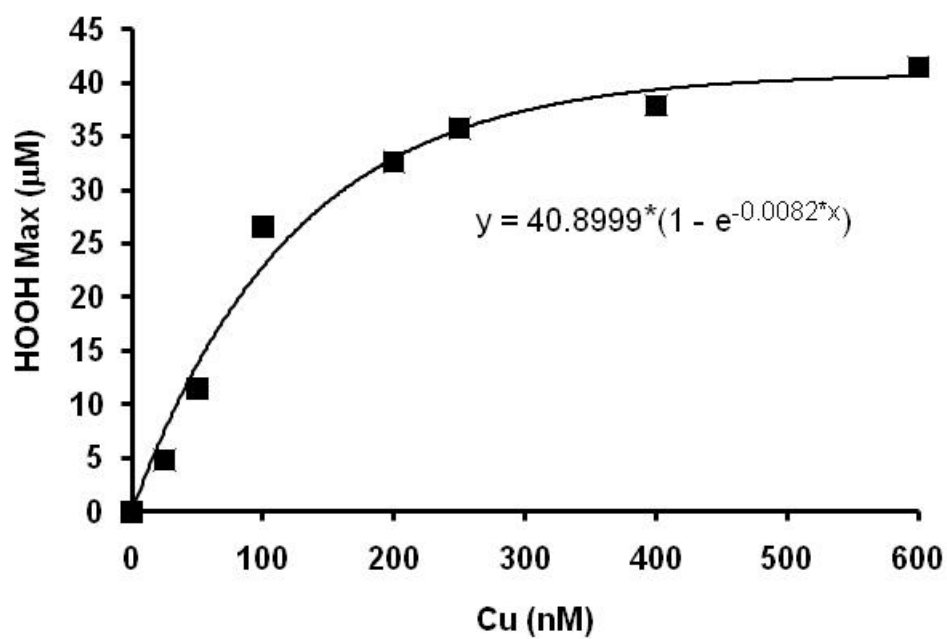$y = 40.8999*(1 - e^{-0.0082*x})$

HOOH Max (µM)

Cu (nM)

Figure S9. HOOH formation as a function of soluble Cu concentration in SLF with ascorbate. A. Initial rate of HOOH formation as a function of Cu. B. Maximum HOOH formation as a function of Cu.
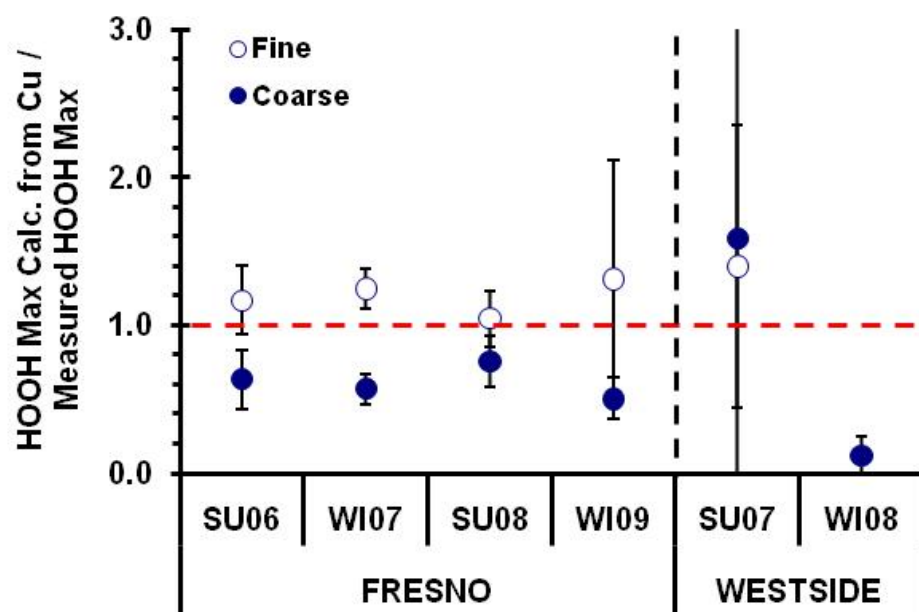
Figure S10. Contribution of SLF-soluble Cu to the maximum HOOH generation in SLF with Asc. Each point represents the ratio of the maximum level of HOOH formation expected from the measured concentration of Cu in the SLF extract of the PM to the maximum level of HOOH formation measured for the sample. Values are means ± SD. n = 3 except for the calculated HOOH max for the Fresno summer 2006 coarse PM and the Fresno winter 2009 fine and coarse PM, where n = 2. The Westside winter 2008 fine PM data point is not shown because HOOH generation in this sample was not significantly different from zero.