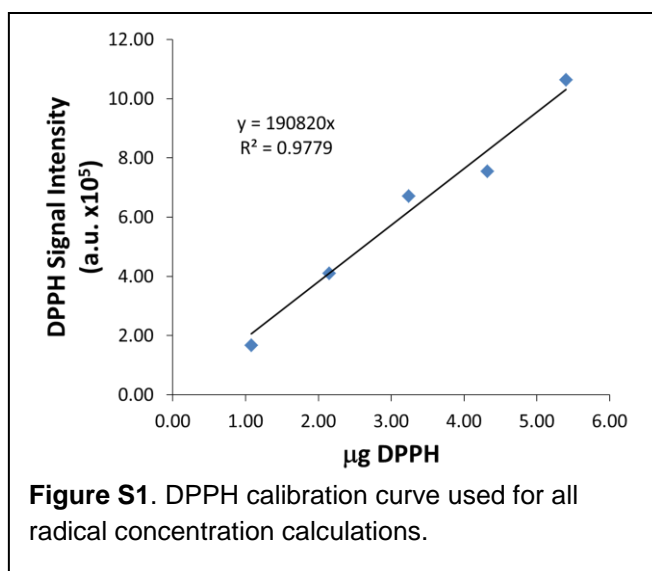


Hydroxyl Radical Generation from PM_{2.5}-Associated Environmentally Persistent Free Radicals (EPFRs)

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DPPH Calibration of EPR for Quantitative

Radical Concentration.

0.0054 g of DPPH was weighed out, placed in a 100 mL volumetric flask, and filled to the line with benzene. From this, 5 different aliquots were pipetted (20, 40, 60, 80, and 100 μ L), and placed in high purity quartz EPR tubes. The solution was dried by dry nitrogen, and the resulting powder placed under Ar as

well as sealed by critoseal. These powders were measured consecutively by EPR and plotted as the measured DPPH signal intensity ($(\Delta H_{p-p})^2$ multiplied by the relative intensity of the peak) vs. its respective weight in μ g, **Figure S1**. The weight of DPPH in μ g is directly proportional to the number of radicals as one molecule of DPPH contains one radical. The slope of this curve was utilized in calculating all radical concentrations by comparison to the samples' signal intensity.

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Chelex Treatment of PM_{2.5} samples. In an attempt to more closely match previous studies¹⁻⁴, Chelex was utilized for elimination of any trace metals present in the ultrahigh purity (UP) H₂O. The manufacturer batch method for preparation was adjusted to accommodate the smaller volume employed. This involved adding approximately 1.3 g of Chelex resin to 10 mL PBS solution and mixing rigorously for 1 hour. The PBS solutions with resin were left overnight before use and filtered from solution using a Fisherbrand P5 filter paper.

After multiple attempts, the Chelex treatment did not reduce the DMPO-OH signal as expected²⁻⁶. Instead, the DMPO-OH signals increased by an average of 140%. Similar phenomena was previously observed suggesting another pathway where Chelex participates in the reaction¹. To avoid any extra confounding factors, Chelex was not used in this study.

Effect of Chelating Agents. Using a 0.1 mM solution of DFO corresponded to a 72% reduction of the DMPO-OH signal from the PM_{2.5} suspension and this suggests an important role for Fe in the catalysis of H₂O₂ to •OH. Previous studies, regardless of assay type, had conflicting results from DFO. Some reports observed a substantial or nearly complete elimination of the ROS signal⁷⁻⁹. These studies used samples stored for long periods of time (from months to years) or were completely relying on the generation of •OH from H₂O₂. Therefore, these investigations were biased in favor of DFO to completely eliminate the signal by metal complexation.

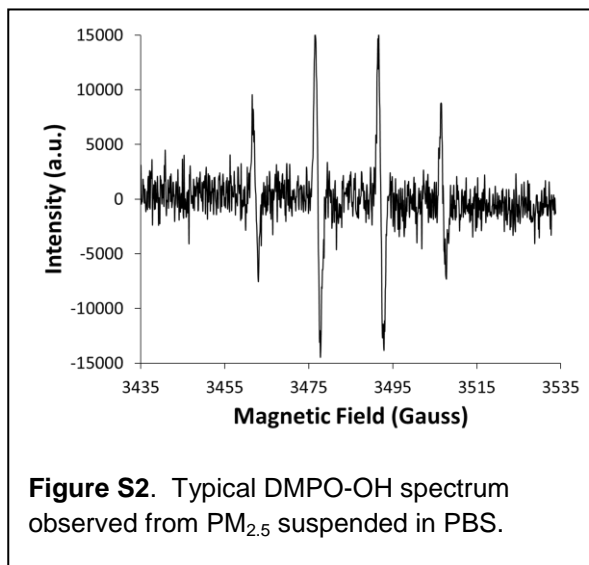


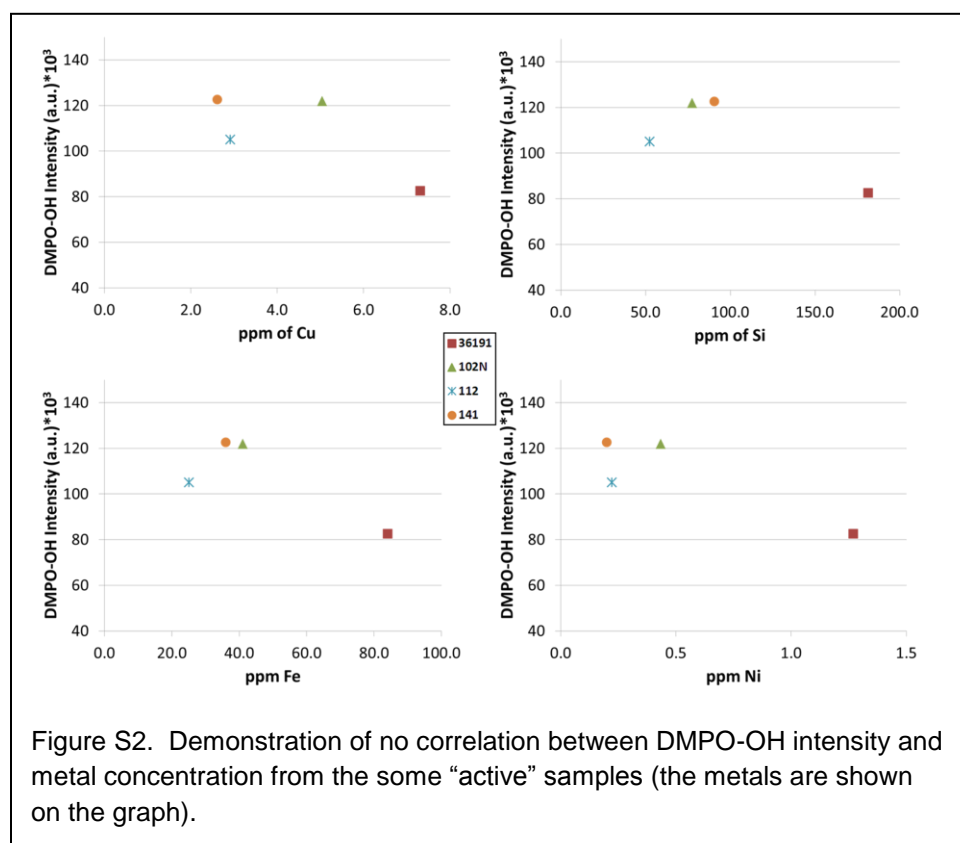
Figure S2. Typical DMPO-OH spectrum observed from PM_{2.5} suspended in PBS.

Other reports only reduced the signal suggesting other pathways¹⁰⁻¹⁵. Recognizing DFO is very selective towards iron leaves the possibility of the other redox metals in the PM_{2.5} to catalyze an exogenous Fenton reaction. Although the amount of the other redox active metals is minor when compared to iron, they are still present on the surface to catalyze the exogenous Fenton reaction.

Accompanying the complexation of metals, DFO was observed to scavenge the tetrachlorosemiquinone anion radical¹⁶. Such elimination would suggest a role in scavenging for other semiquinone type radicals. Either from metal complexation or eliminating the semiquinone radicals, the addition of DFO reduced the adduct intensity in these experiments.

DETAPAC exhibited unpredictable behavior in PM_{2.5} solutions. Particularly, using DETAPAC in this work reduced the •OH signal intensity by 53% while, in contrast, a previous study exhibited a higher •OH signal¹⁷.

Based on these observations, the above reagents were not included in the spin trapping experiments for PM_{2.5}. Instead, a comparative method^{33, 34}, where the same sample was utilized under different conditions (air vs. N₂ purging, fresh vs. aged), was chosen to monitor the •OH generating capacity of ambient PM_{2.5} particles collected from Louisiana industrial corridor.



Metal Dependence.

Previous studies report a metal association for ROS generation in PM, such as As¹⁸, Ba¹⁹, Cd¹⁸, Co^{5, 6, 20}, Cr^{6, 19, 20}, Cu^{9, 15, 19-25}, Fe^{5-7, 20-23, 26, 27}, Mn^{6, 20, 28}, Ni^{5, 18}, V^{18, 28}, Zn^{21, 28, 29}, and Zr¹⁹.

Most of the studies

listed above included the presence of reducing agents or H₂O₂ thereby favoring the metal mediated generation of •OH. In addition to total metals, correlations suggested associations with soluble Fe^{7, 8, 29, 30}. Soluble transition metals from PM are suggested important due to their bioavailability^{3, 6, 14, 28}. The soluble Fe oxidation state in PM_{2.5} also displayed no significant changes over 40 days³². However, particle bound transition metals (or the particle itself) also demonstrated increased ROS generation when compared to the soluble metals present^{24, 31}.

Straightforward dependencies between metal content and DMPO-OH concentration were not observed in this study; although, only the total metals from a nitric acid digestion were studied. There was no investigation into the soluble metals. Using only the “active” samples, there was no correlation between the DMPO-OH intensity and individual, **Figure S3**, or total metals (not presented but similar behavior as **Figure S3**). When applying the “passive” samples as well, there were still no correlations from the metals data (data not shown).

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