

Supporting Information
for
Relationship between Chemical Composition and Oxidative Potential of
Secondary Organic Aerosol from Polycyclic Aromatic Hydrocarbons

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Section S1. Additional chemical information.

Dithiothreitol (99%), 5,5'-dithio-bis(2-nitrobenzoic acid) (98%), phosphate buffer (0.1 M, pH 7.4 (25 °C)), hydrogen peroxide (30 wt. % in H₂O, ACS reagent), cumene peroxide (technical grade, 80%), tert-Butyl peroxide (98%), benzoyl peroxide (reagent grade, ≥98%), 1,4-naphthoquinone (≥96.5%, HPLC grade), 1,2-naphthoquinone (97%), 5-hydroxy-1,4-naphthoquinone (97%), Anthraquinone (≥99.0% HPLC grade), 1,3-dihydroxynaphthalene (≥99%), 2,3-dihydroxynaphthalene (≥98%), copper(II) sulfate (≥99.99%) were purchased from Sigma Aldrich.

Section S2. Supporting figures and tables

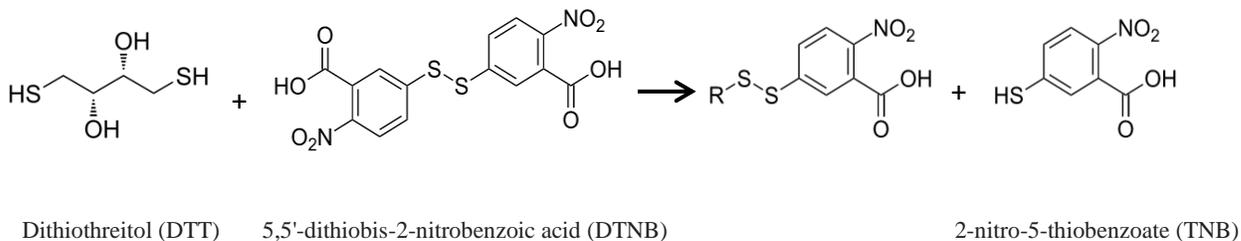


Figure S1. Scheme of the DTT assay (Cleland, 1964; Ellman, 1959).

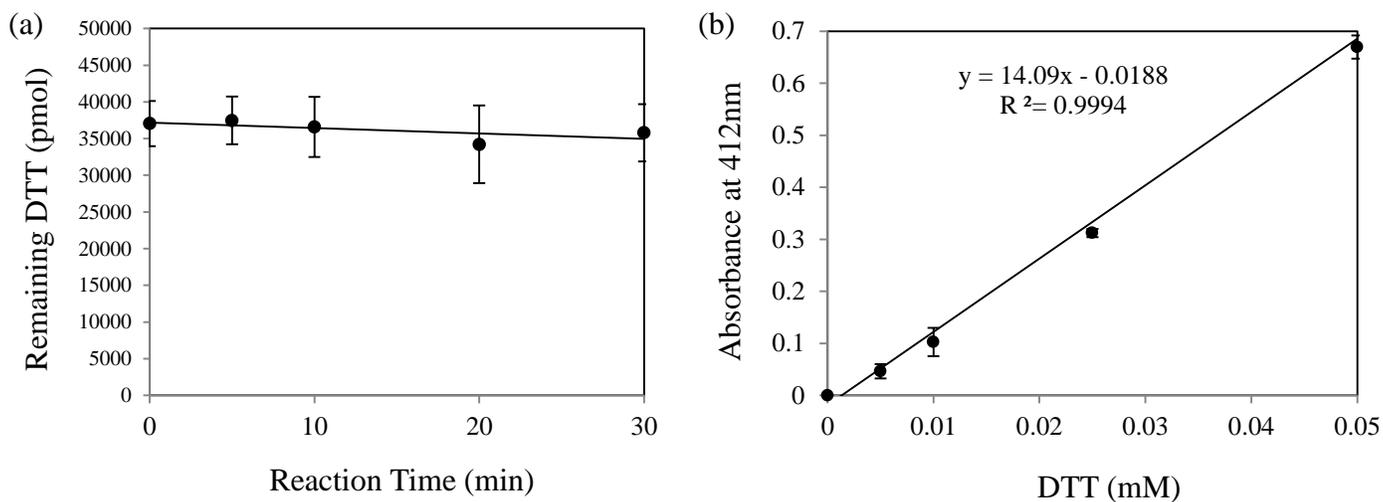


Figure S2. (a) Blank control for DTT assay. (b) Calibration curve used in DTT assay. Slope is determined from the averaged linear regression of the triplicates. Error bar of each data point represents the standard deviation of replicates (n=3).

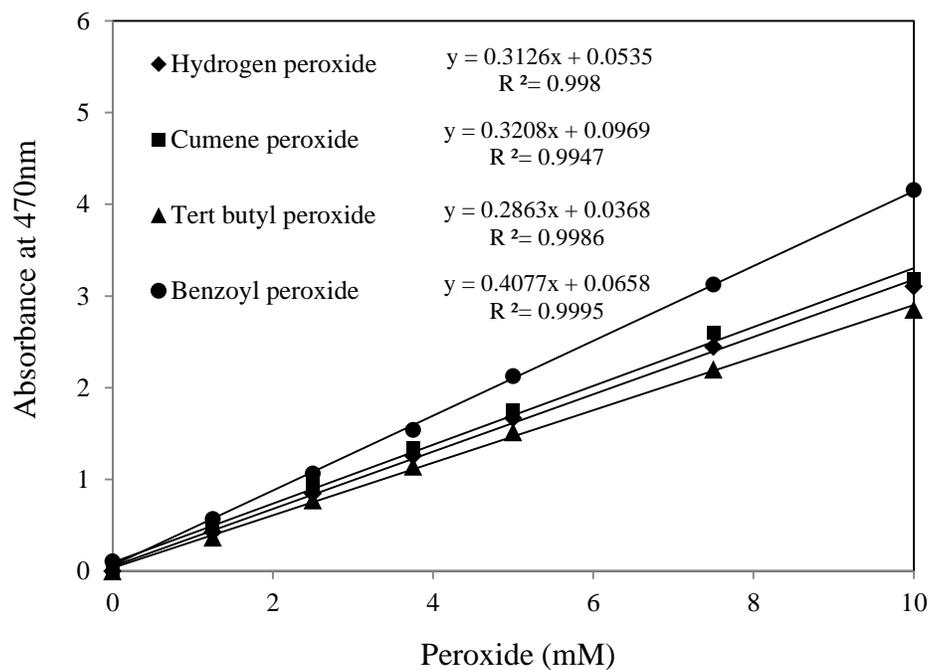


Figure S3. KI calibration curves for hydrogen peroxide (30% in H₂O), cumene hydroperoxide (80%), tert-Butyl peroxide (98% in H₂O), benzoyl peroxide (98%) at a series of concentration of 0 mM, 1.25 mM, 2.5 mM, 3.75 mM, 5 mM, 7.5 mM and 10 mM.

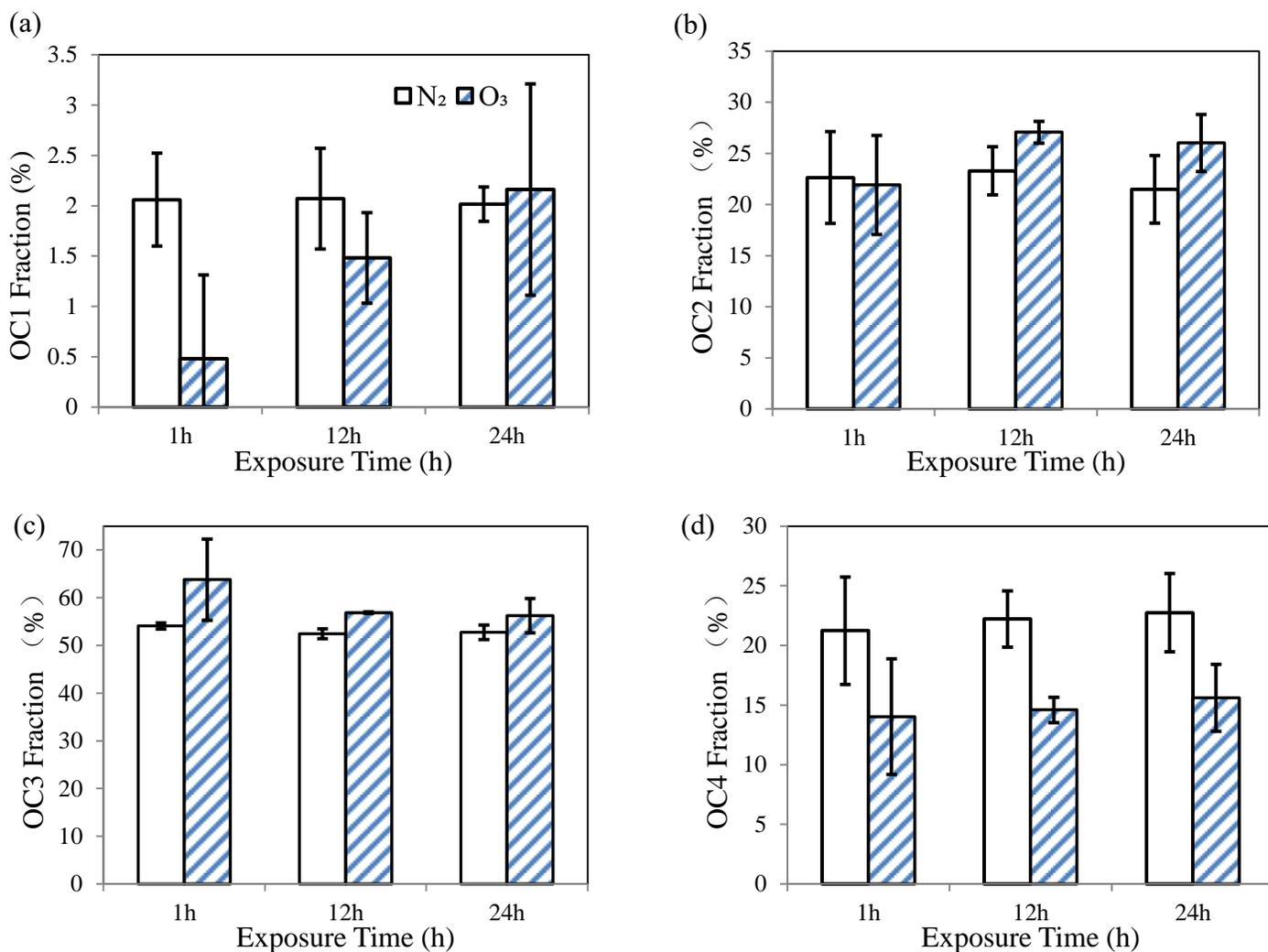


Figure S4. Changes in OC fractions (a)OC1, (b)OC2, (c)OC3, (d)OC4 (Chow et al., 1993) of NSOA filters exposed to N_2/O_3 for 1h, 12h and 24h. Error bar of each data point represents standard deviation of the replicates (n=3).

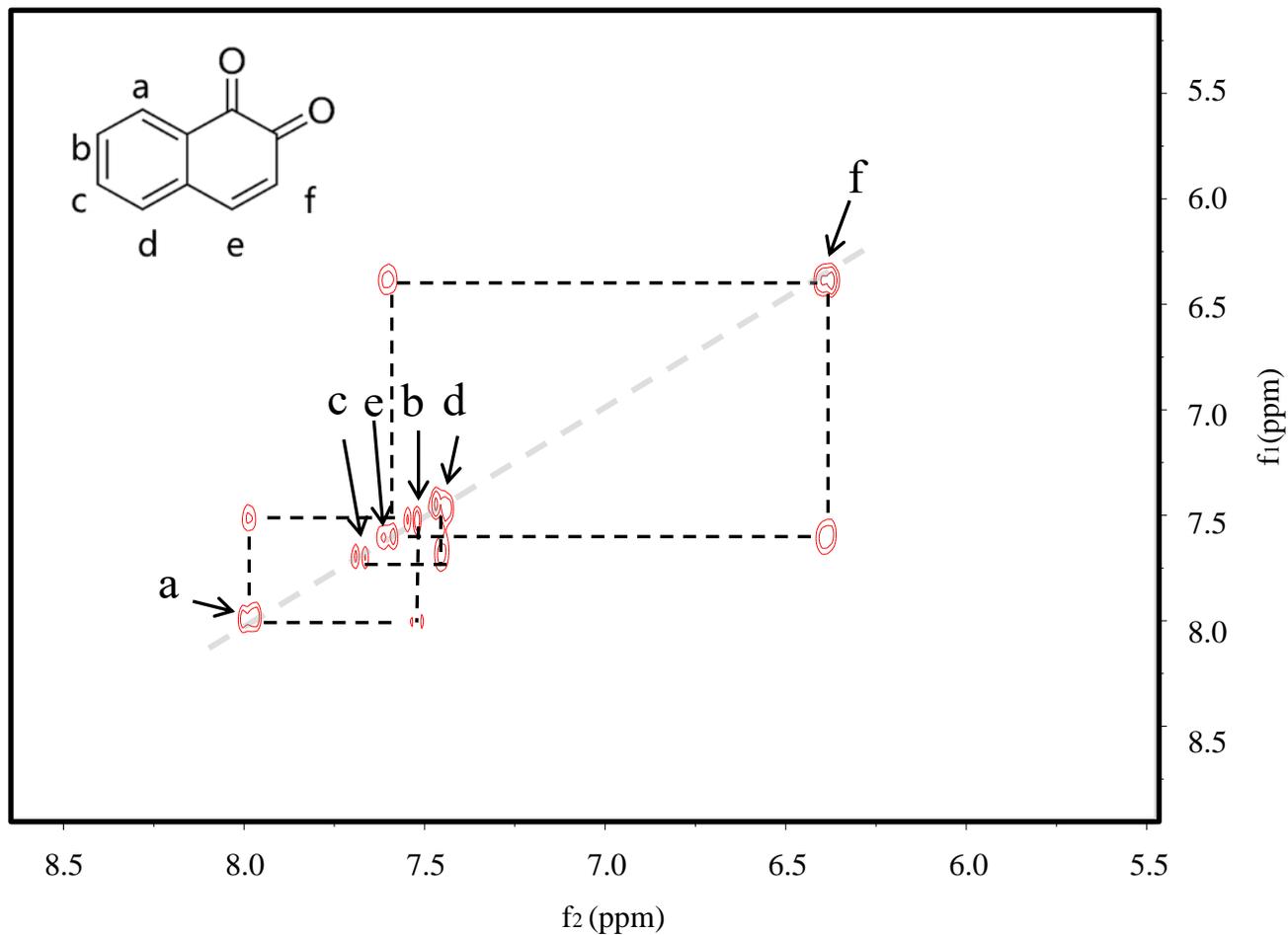


Figure S5. COSY spectra for 1,2-NQN, which were used for proton peak assignment. Proton peaks a, b, c, d, e, f could be assigned based on the coupling between ab, ef and cd. COSY NMR experiments were done in non-phase-sensitive mode, using gradients for coherence selection. 96 transients and 2048 data points were collected for each of the 196 increments in the F1. Both dimensions were processed using an unshifted sine-squared function, zero filling factor of 2 and a magnitude mode was used for projection.

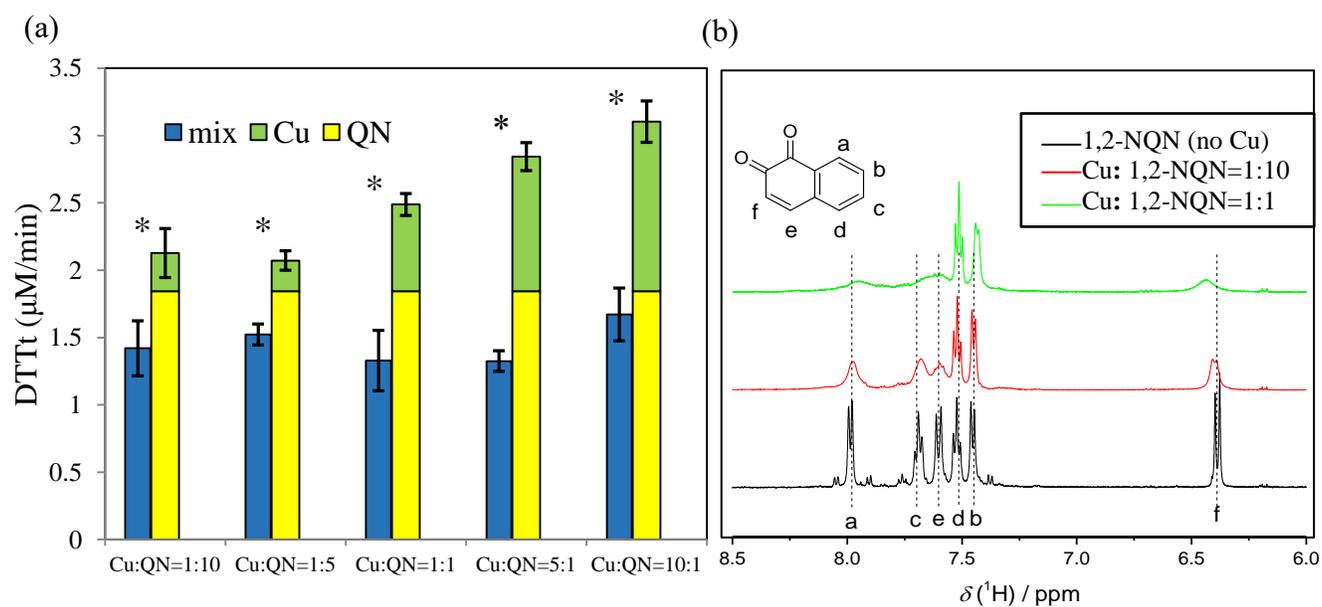


Figure S6. (a) Result of DTT assay on a series of mixture with the same amount of quinone but an increasing amount of Cu(II). Molar ratio of Cu (II):1,2-NQN ranges from 1:10, 1:5, 1:1, 5:1 to 10:1. The asterisk indicates significant difference between a pair of bars at the 95% confidence level. An increasing trend of OP depletion was observed with increasing ratios of Cu(II) to 1,2-NQN, which corresponded well with (b) an increasing extent of peak broadening observed in 1D ^1H NMR spectra (Rehmann and Barton, 1990;Kowalewski and Maler, 2006).

Table S1. ^1H NMR T1, T2 relaxation value for individual proton on 1,2-NQN (peak assignment shown in Fig. 9).

^1H peak	T ₁ (s)			T ₂ (s)		
	1,2-NQN	Cu:1,2-NQN 1:10	Cu:1,2-NQN 1:1	1,2-NQN	Cu:1,2-NQN 1:10	Cu:1,2-NQN 1:1
a	1.76	0.73	0.4	0.14	0.029	0.018
b	1.51	0.68	0.37	0.13	0.036	0.015
c	1.4	0.57	0.37	0.12	0.026	0.019
d	1.52	0.74	0.59	0.13	0.045	0.035
e	1.49	0.76	0.61	0.15	0.059	0.039
f	1.82	0.61	0.37	0.12	0.027	0.013

References:

- Chow, J. C., Watson, J. G., Pritchett, L. C., Pierson, W. R., Frazier, C. A., and Purcell, R. G.:
The DRI thermal/optical reflectance carbon analysis system: description, evaluation and
applications in US air quality studies, *Atmos. Environ., Part A. General Topics*, 27, 1185-1201,
1993.
- Cleland, W. W.: Dithiothreitol, a new protective reagent for SH groups, *Biochem.*, 3, 480-482,
1964.
- Ellman, G. L.: Tissue sulfhydryl groups, *Arch. Biochem. Biophys.*, 82, 70-77, 1959.
- Kowalewski, J., and Maler, L.: Nuclear spin relaxation in liquids: theory, experiments, and
applications, CRC press, 2006.
- Rehmann, J. P., and Barton, J. K.: Proton NMR studies of tris (phenanthroline) metal complexes
bound to oligonucleotides: characterization of binding modes, *Biochem.*, 29, 1701-1709, 1990.