



Supplement of

Aerosol oxidative potential and reactive species predicted with a chemical kinetics model (KM-OP)

Ashmi Mishra et al.

Correspondence to: Ashmi Mishra (a.mishra@mpic.de) and Thomas Berkemeier (t.berkemeier@mpic.de)

The copyright of individual parts of the supplement might differ from the article licence.

1 Supplementary Figures

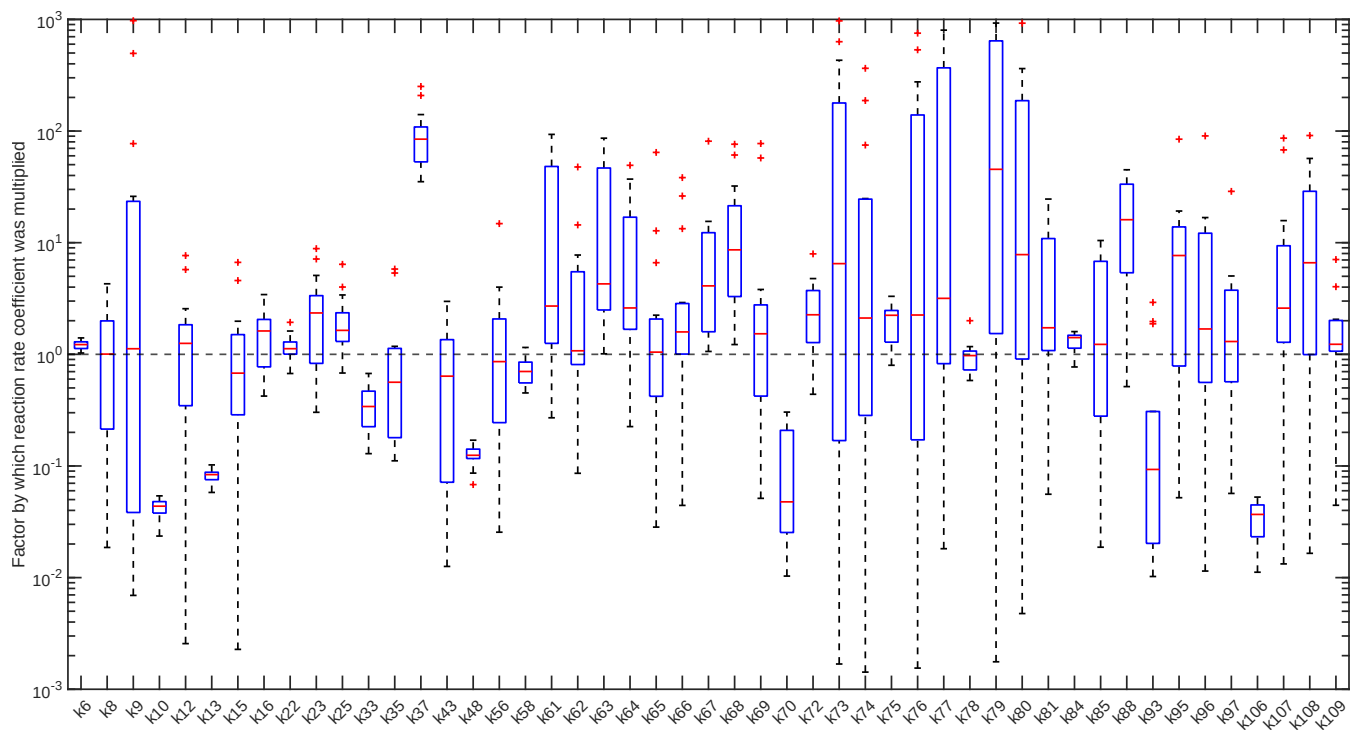


Figure S1. Ranges for kinetic parameters obtained with global optimization to experimental data. Multiple optimizations give rise to estimations of fit parameter uncertainty.

Figures S2–S10 show the main sources and sinks for different model species with respect to the chemical reactions that they undergo in the model.

Figures S2 and S3 show the main chemical reactions that contribute to H_2O_2 production as a function of quinones and copper, respectively.

Across all quinones, we find that the main source of H_2O_2 is the reaction of ascorbic acid (AA) with HO_2 , leading to the formation of the ascorbyl radical ($\text{AA}\bullet$) and H_2O_2 (R49, Tab. S1, Fig. S1). For NQN12, at high concentration, the contribution of H_2O_2 from R49 decreases, while the reaction of the ascorbyl radical with O_2^- (R81, Tab. S1) increases, resulting in an approximately equal contribution from both pathways (Fig. S2a).

For copper, we find that at low concentrations, the main source of H_2O_2 stems from the reaction of ascorbic acid (AA) with HO_2 , leading to the formation of the ascorbyl radical ($\text{AA}\bullet$) and H_2O_2 (R49, Tab. S1, Fig. S1). At higher Cu concentrations, the reaction $\text{Cu(I)} + \text{O}_2^-$ (R35, Tab. S1) also begins to contribute significantly to H_2O_2 production.

Figure S4 shows the main chemical reactions that contribute to OH production as a function of copper concentration. At low Cu concentrations, OH production occurs primarily through the reaction of AA with H_2O_2 (R48, Tab. S1), whereas at higher Cu concentrations, the pseudo-Fenton reaction of Cu(I) with H_2O_2 (R56, Tab. S1) becomes dominant.

Figure S5 shows the concentrations of ROS and transition metals (Cu (A), Fe (B)) over time in the presence of ascorbic acid.

Figure S6 shows the main chemical reactions that contribute to DHA production as a function of Cu concentration. The largest source of DHA is the disproportionation reaction of the ascorbyl radical ($\text{AA}\bullet$, R44, Tab. S1), which can be produced by the redox reaction between AA and transition metal ions such as Fe and Cu.

Figure S7A shows the main reactions of DTT in the presence of manganese. The largest sink for DTT at low Mn(II) concentrations is HO_2 (R58, Tab. S1), whereas at higher concentrations, Mn(II) and Mn(III) become the dominant sinks.

Figure S7B shows the concentration of DTT at the end of the simulation as a function of Mn(II) concentration.

Figure S7C shows the main reaction channels that HO_2 undergoes in the simulation as a function of Mn concentration. At higher Mn(II) concentrations, HO_2 reacts with Mn(II) to form MnO_2 .

Figure S7D shows the MnO_2 concentration as a function of time. The higher the initial Mn concentration, the more MnO_2 accumulates in the kinetic model.

Figure S8A shows the concentration of DTT at the end of the simulation as a function of Cu(II) concentration. Figure S8B shows the main reactions of DTT in the presence of Cu. The largest sink of DTT is the formation of the $[\text{Cu}^{2+}(\text{DTT}^{2-})_2]^{2-}$ complex.

Figure S9 shows the main reactions that DTT undergoes in the simulation. The dominant reactions involving DTT are $\text{DTT} + \text{HO}_2$ and $\text{DTT} + \text{quinones}$.

Figure S10 shows the concentration of DTT at the end of the simulation as a function of quinone concentration.

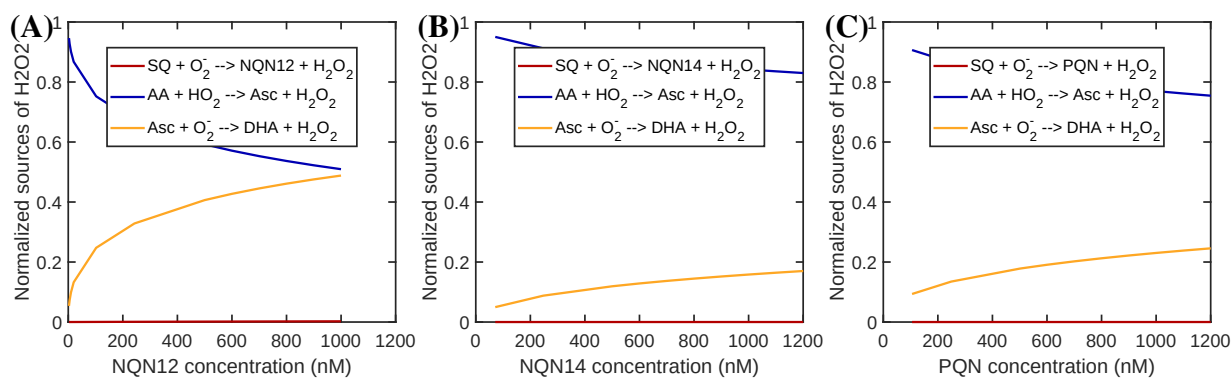


Figure S2. Normalized sources of H_2O_2 as a function of 1,2-NQN (A), 1,4-NQN (B) and PQN (C) concentrations.

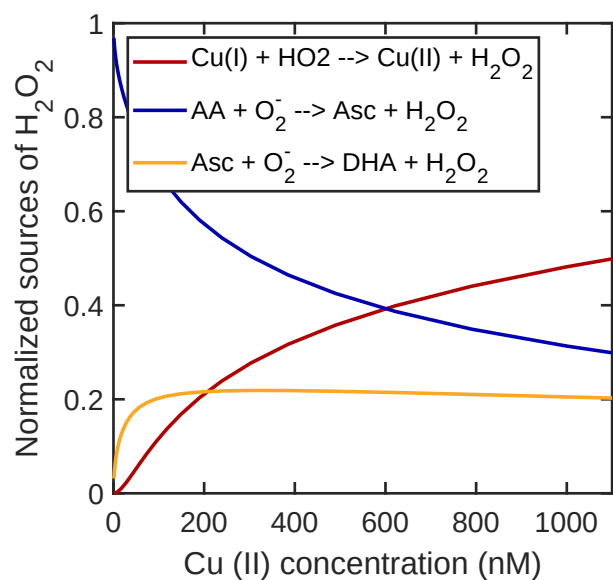


Figure S3. Normalized sources of H_2O_2 as a function of Cu concentration.

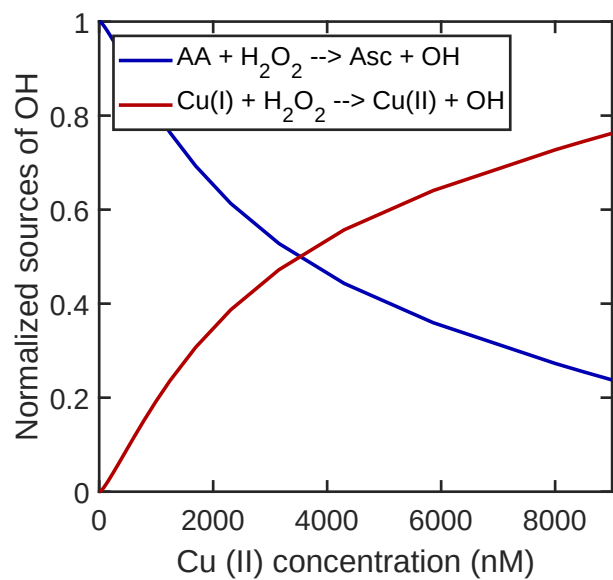


Figure S4. Normalized sources of $^{\bullet}\text{OH}$ as a function of Cu concentration.

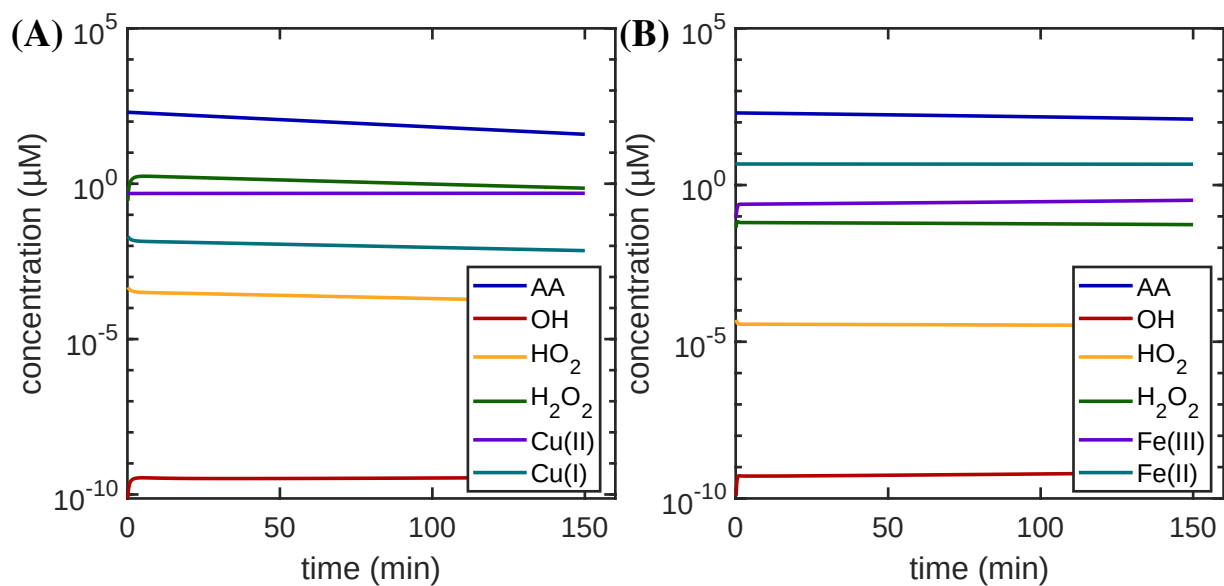


Figure S5. Concentration of ROS and TMs (Cu (A), Fe (B)) over time.

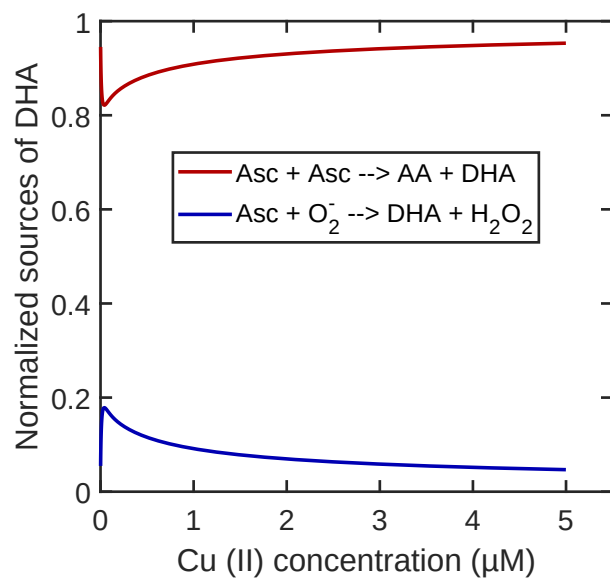


Figure S6. Normalized sources of DHA as a function of Cu concentration.

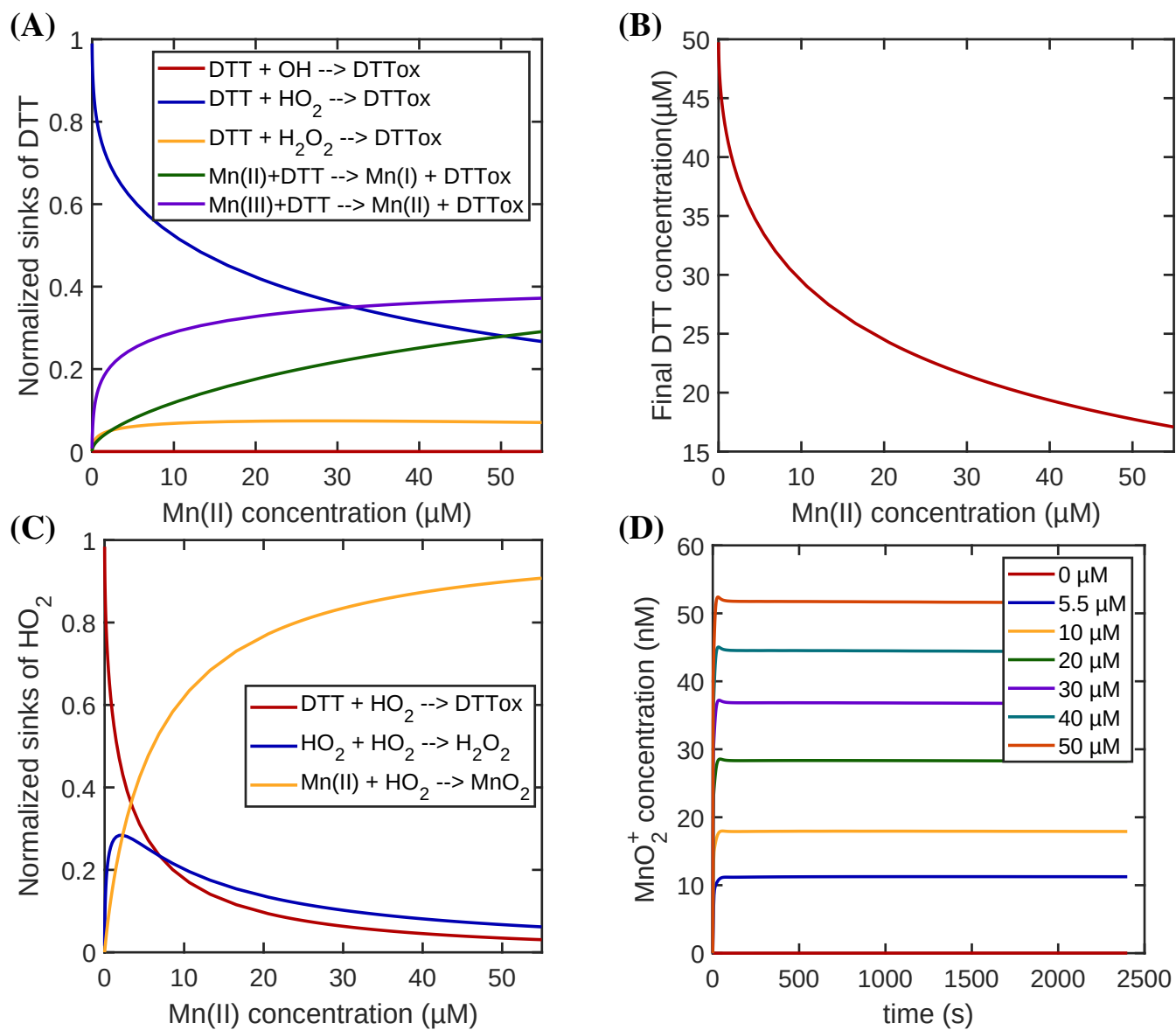


Figure S7. Normalized sinks of DTT (A), final DTT concentration (B), and normalized sinks of HO_2 (C) as a function of Mn concentration. Panel D shows the MnO_2^+ concentration over time.

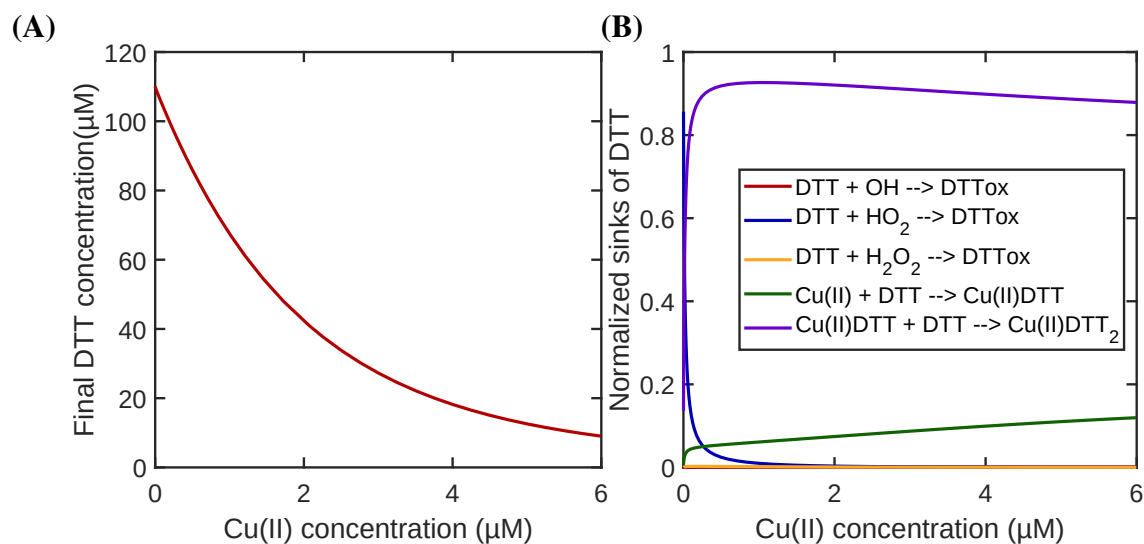


Figure S8. End concentration of DTT (A) and normalized sinks of DTT as a function of Cu concentration (B).

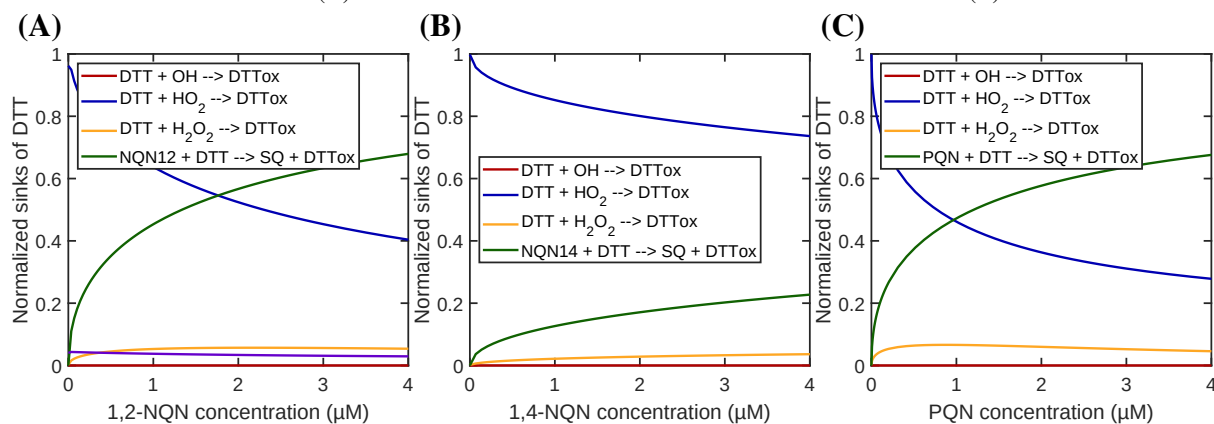


Figure S9. Normalized sinks of DTT as a function of 1,2-NQN (A), 1,4-NQN (B) and PQN (C) concentrations.

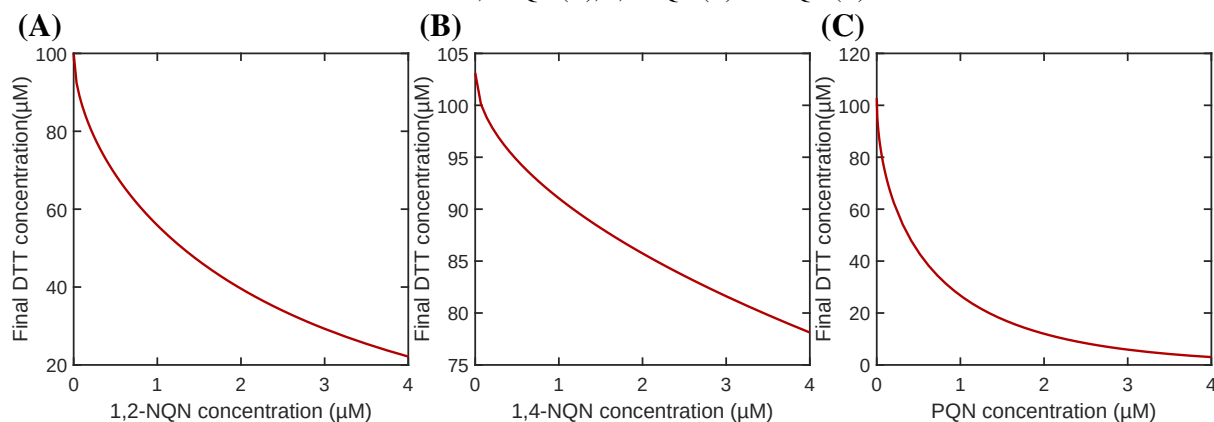


Figure S10. End concentration of DTT as a function of 1,2-NQN (A), 1,4-NQN (B) and PQN (C) concentrations.

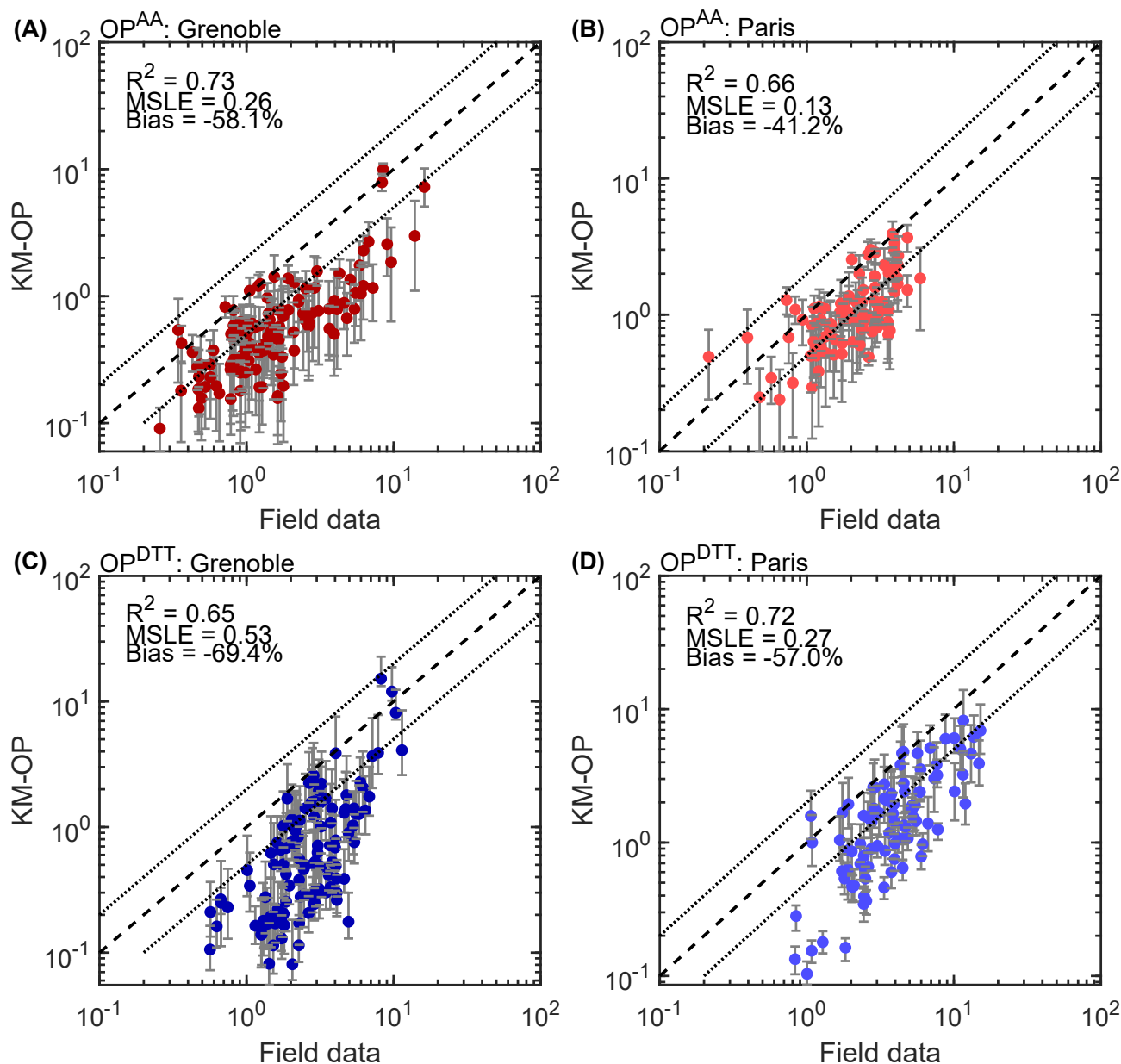


Figure S11. Correlation scatter plots of model-predicted and measured OP for particulate matter samples using source-apportioned SOA as input for samples from Grenoble (OP^{AA} : panel A, and OP^{DTT} : panel C) and Paris (OP^{AA} : panel B, and OP^{DTT} : panel D). Data shown in blue indicate OP^{DTT} (in units of $\text{nmol min}^{-1} \text{m}^{-3}$), while the red and pink data show OP^{AA} (in units of $\text{nmol min}^{-1} \text{m}^{-3}$) and OP^{DHA} (in units of nmol m^{-3}). The dashed lines indicate the 1:1 line. The dotted lines indicate the 2:1 and 1:2 lines. The error bars indicate the maximum and minimum values from the ensemble fits.

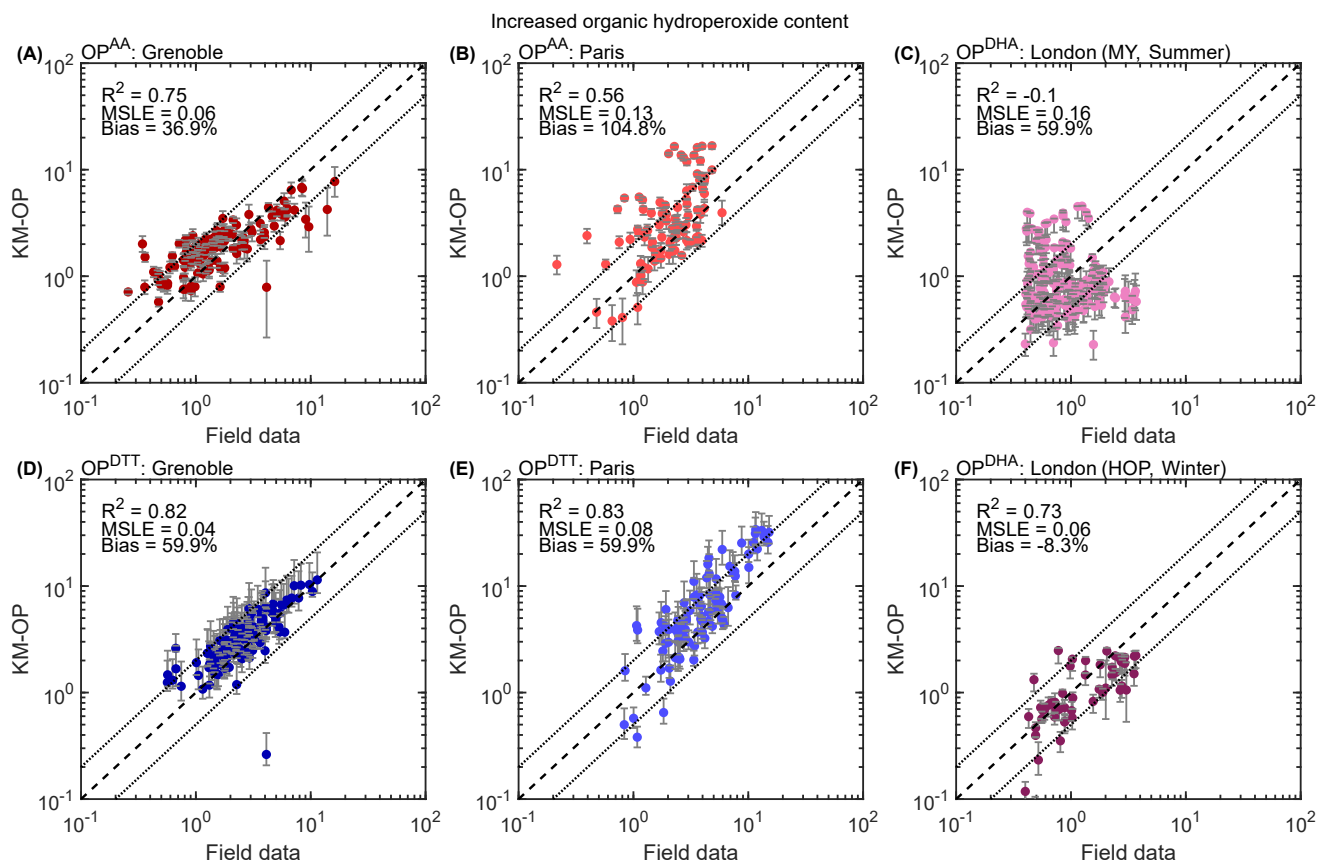


Figure S12. Sensitivity study on the correlation of model-predicted and measured OP using an increased organic hydroperoxide (ROOH) content of 80% of total OA.

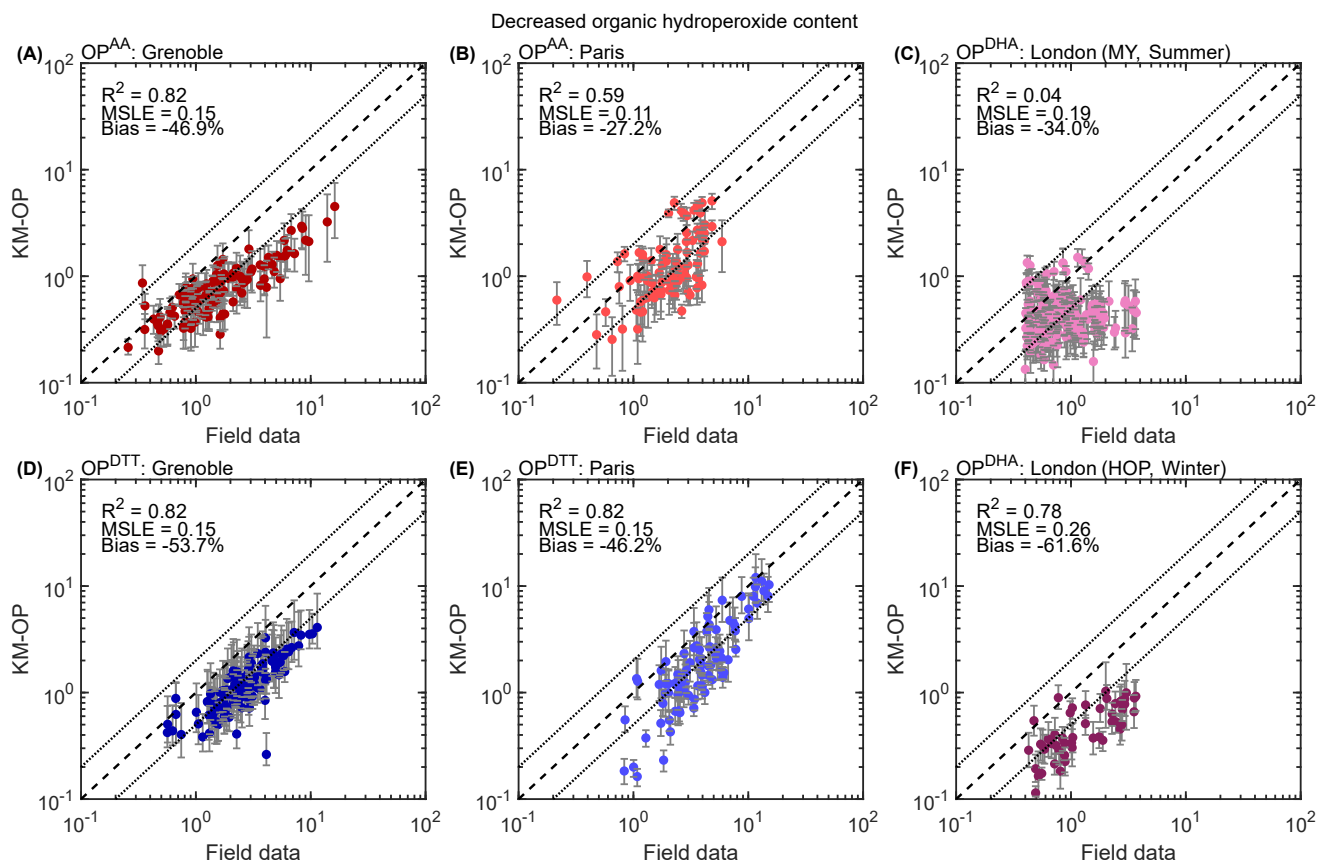


Figure S13. Sensitivity study on the correlation of model-predicted and measured OP using a decreased organic hydroperoxide (ROOH) content of 20% of total OA.

Decreased solubility content for organics and quinones

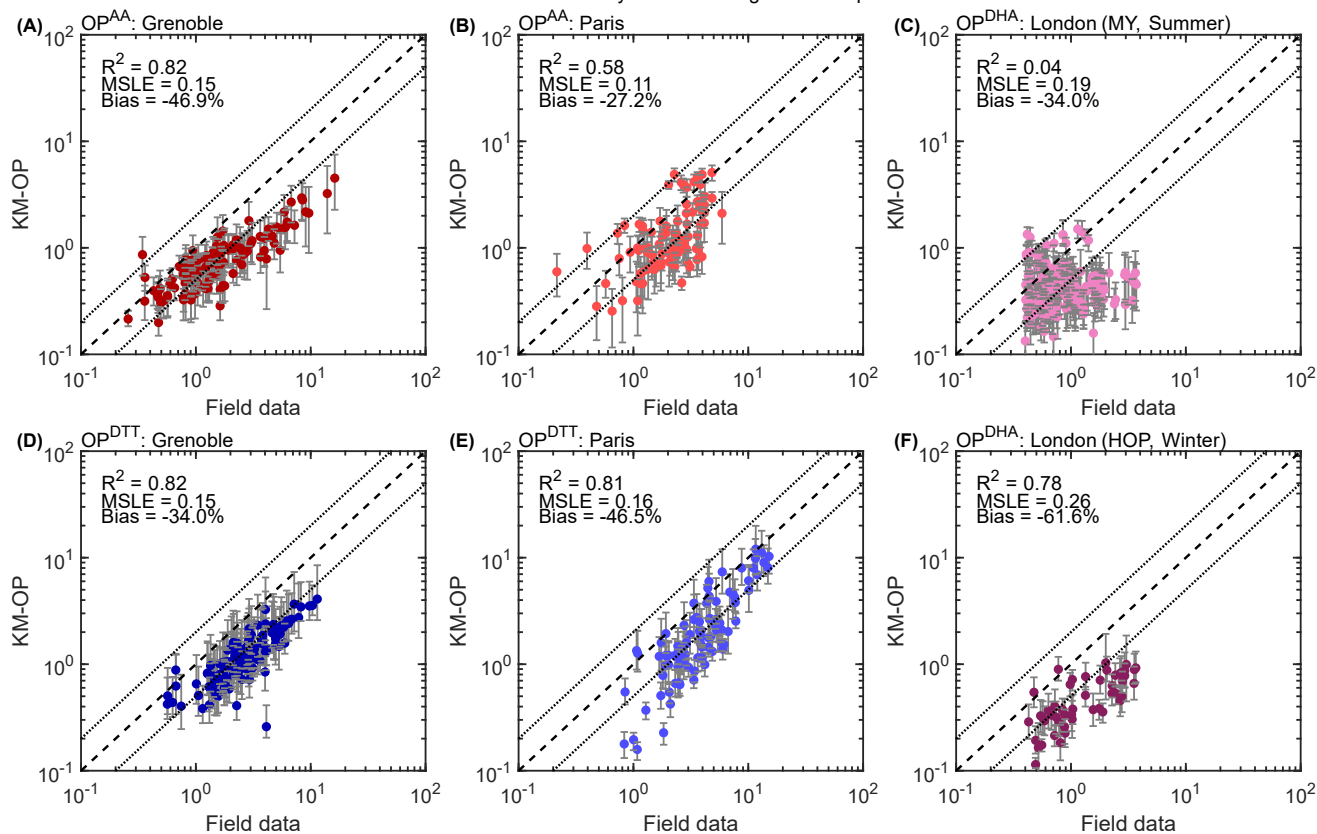


Figure S14. Correlation scatter plots of model-predicted and measured OP for particulate matter samples collected in three different sites across Europe by applying a solubility factor of 40% for organics and 10% for quinones.

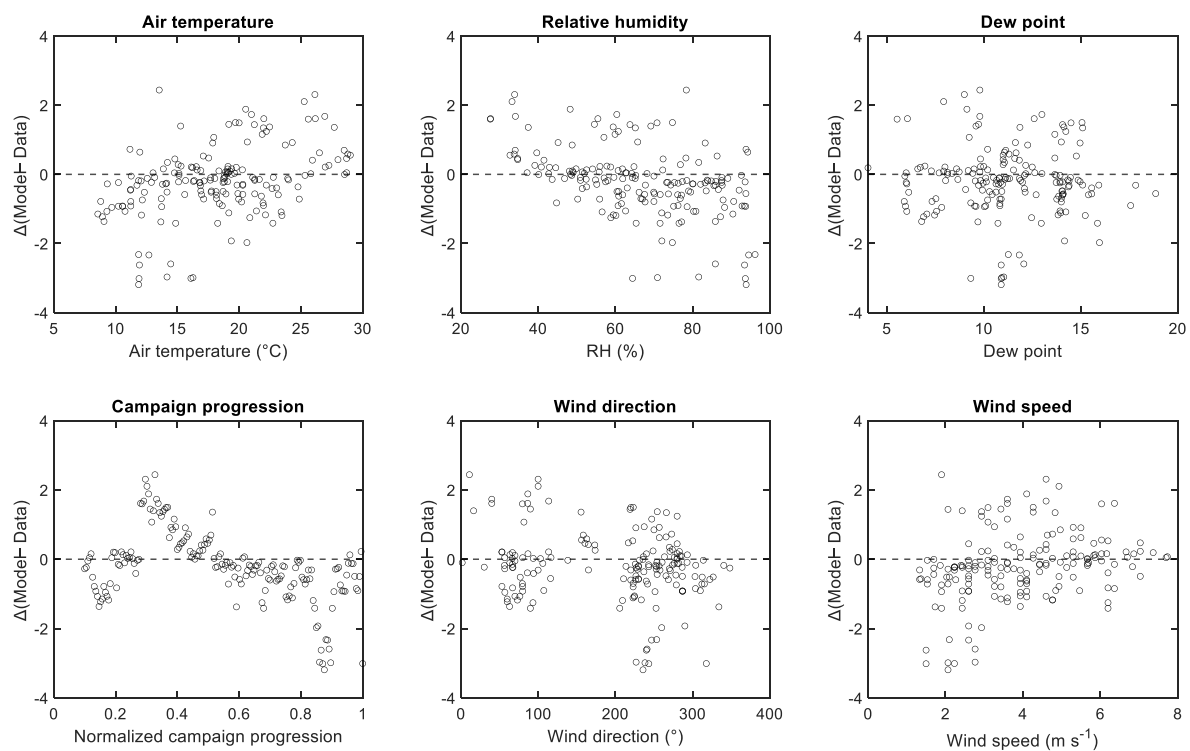


Figure S15. Difference between model-predicted and measured OP particulate matter samples collected in London during Summer at MY as a function of meteorological conditions.

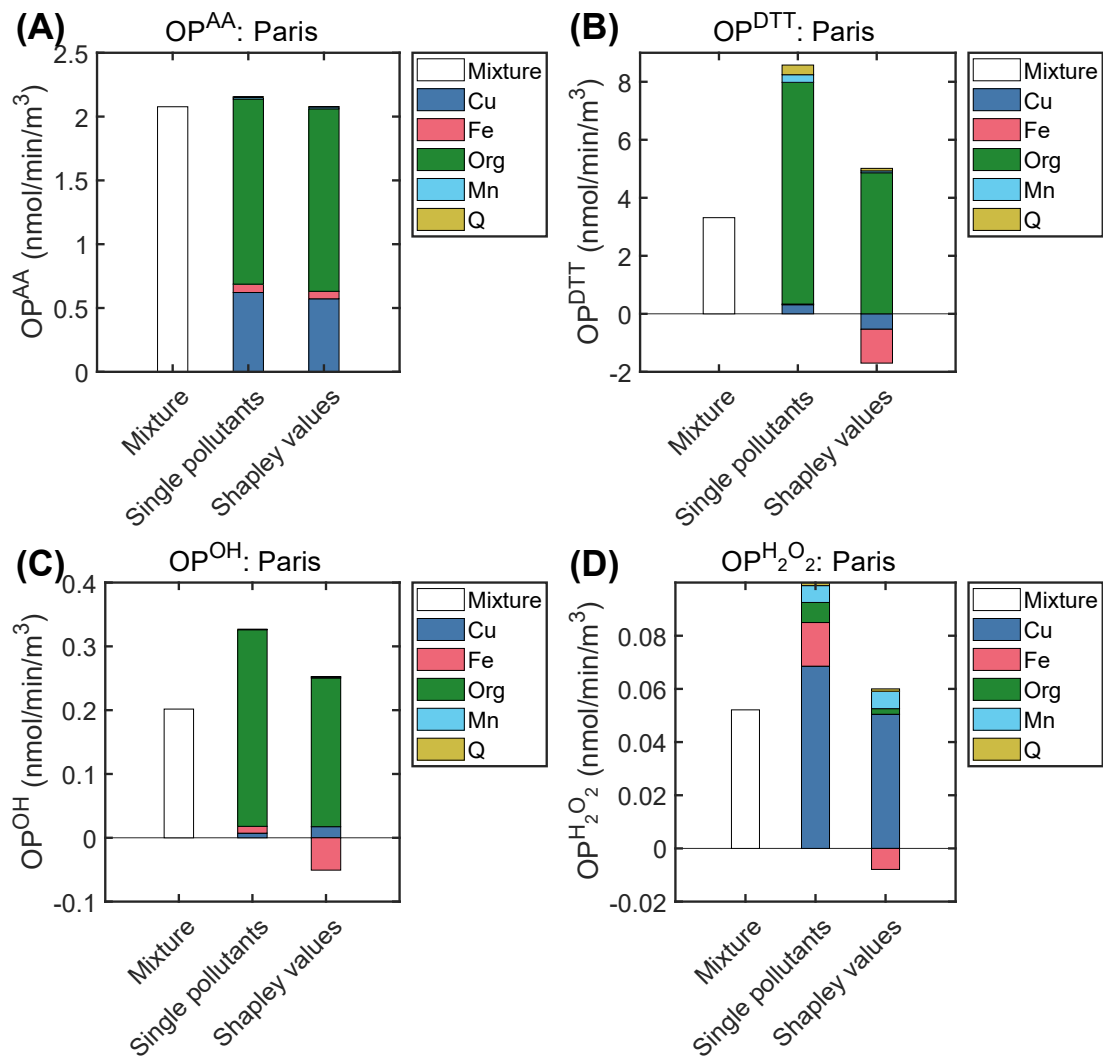


Figure S16. Contributions of different PM constituents to OP^{AA} (A), OP^{DTT} (B), OP^{OH} (C), and $OP^{H_2O_2}$ (D) in Paris. The "Mixture" bar shows the model result when all species are included in the model. The "Single pollutants" bar indicates a scenario where only one specific species was included. The "Shapley values" bar is calculated using the Shapley analysis.

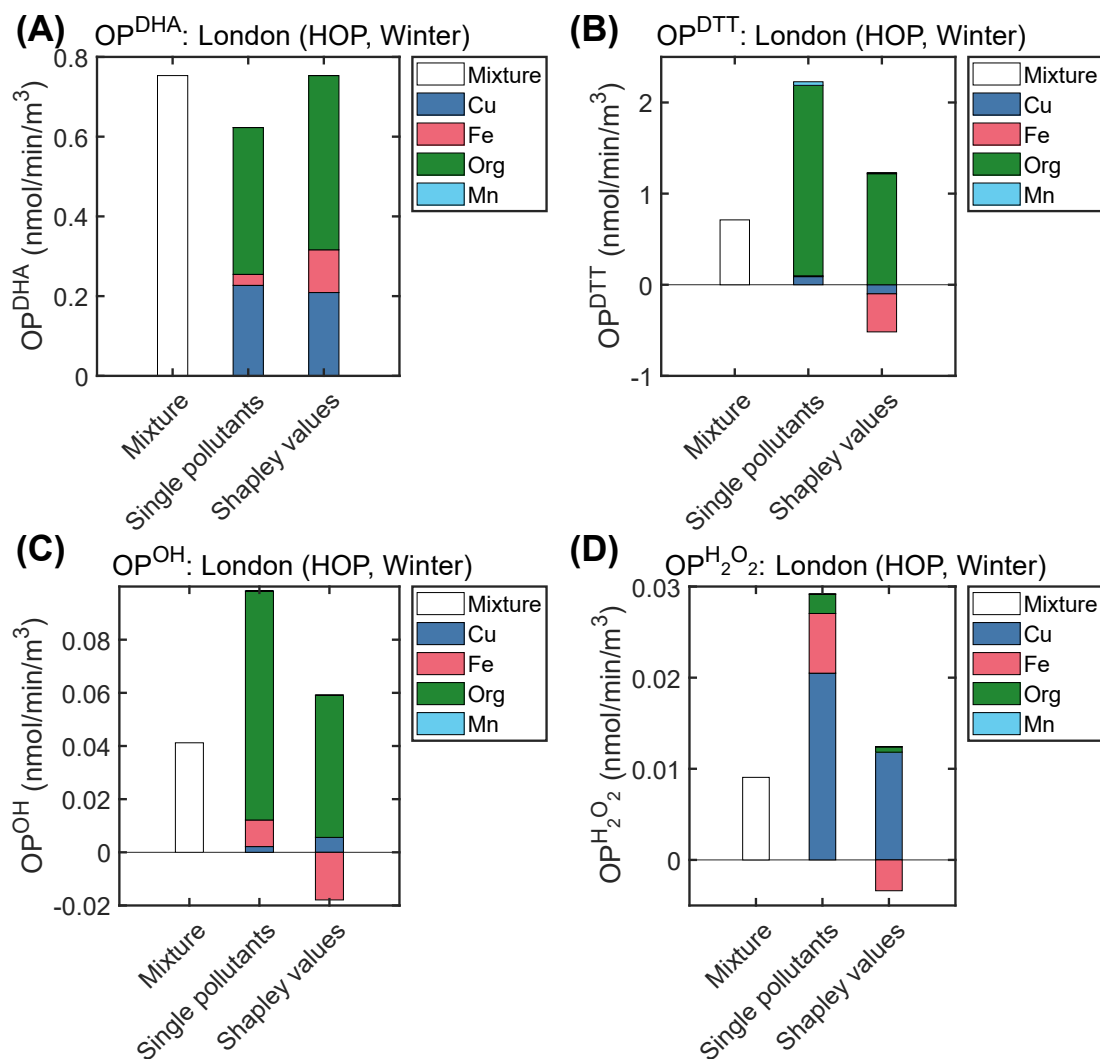


Figure S17. Contributions of different PM constituents to OP^{DHA} (A), OP^{DTT} (B), OP^{OH} (C), and $OP^{H_2O_2}$ (D) in London during Winter at HOP. The "Mixture" bar shows the model result when all species are included in the model. The "Single pollutants" bar indicates a scenario where only one specific species was included. The "Shapley values" bar is calculated using the Shapley analysis.

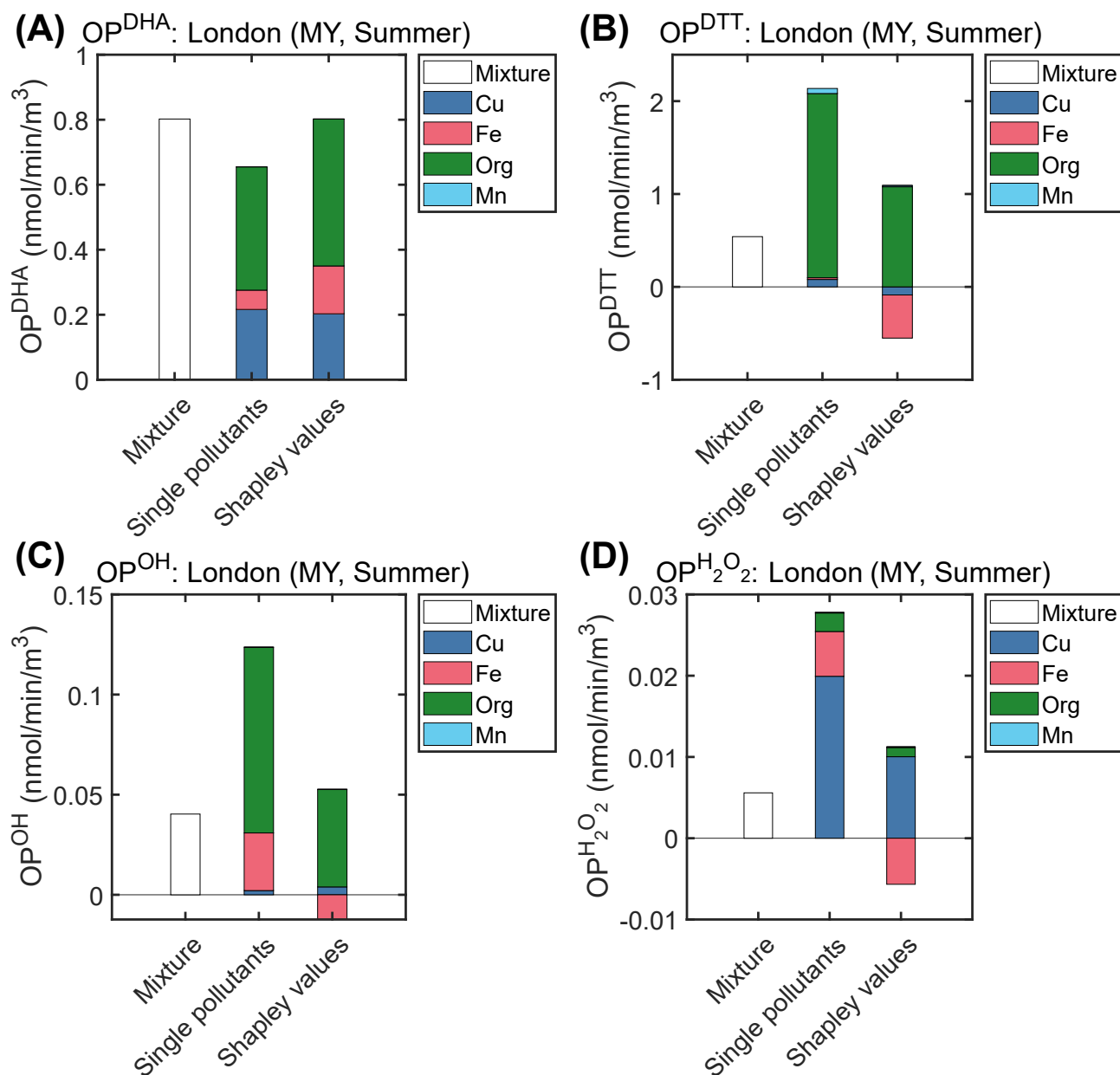


Figure S18. Contributions of different PM constituents to OP^{DHA} (A), OP^{DTT} (B), OP^{OH} (C), and $OP^{H_2O_2}$ (D) in London during Summer at MY. The "Mixture" bar shows the model result when all species are included in the model. The "Single pollutants" bar indicates a scenario where only one specific species was included. The "Shapley values" bar is calculated using the Shapley analysis.

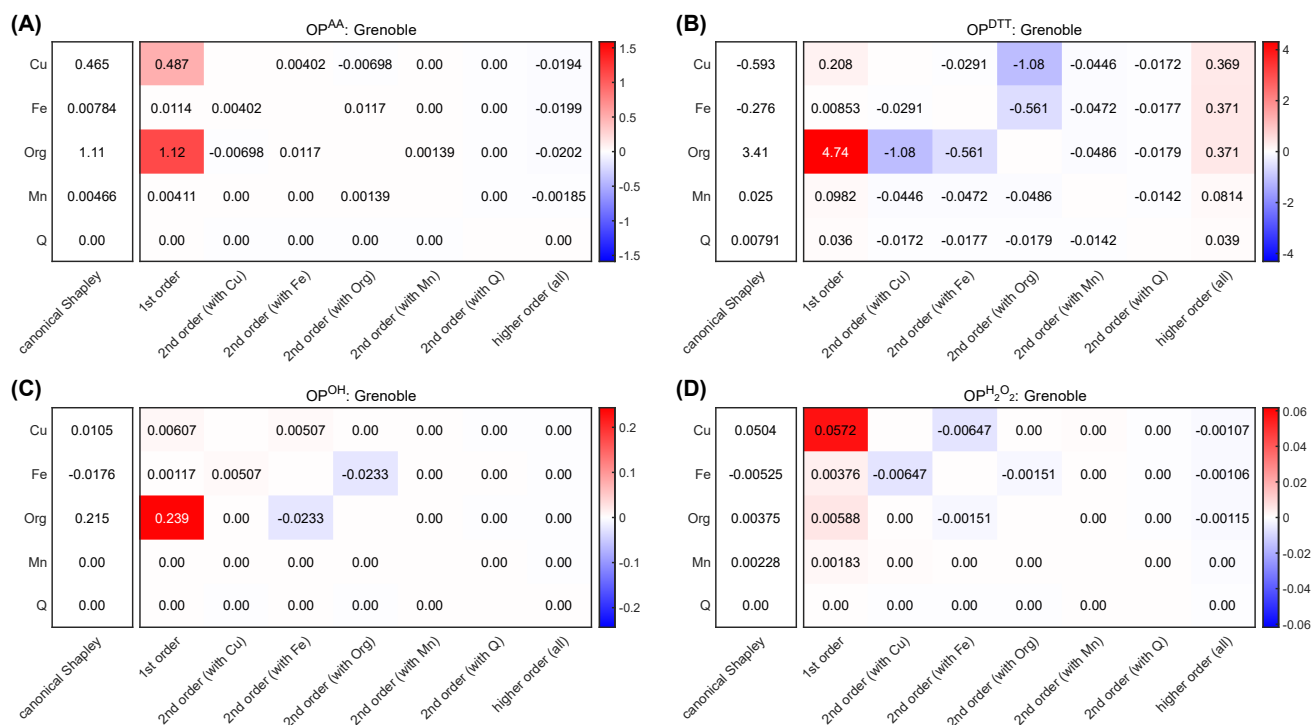


Figure S19. Deconvolution of the Shapley values into first and higher-order effects of PM constituents towards OP^{AA} (A), OP^{DTT} (B), OP^{OH} (C), and $OP^{H_2O_2}$ (D) in Grenoble.

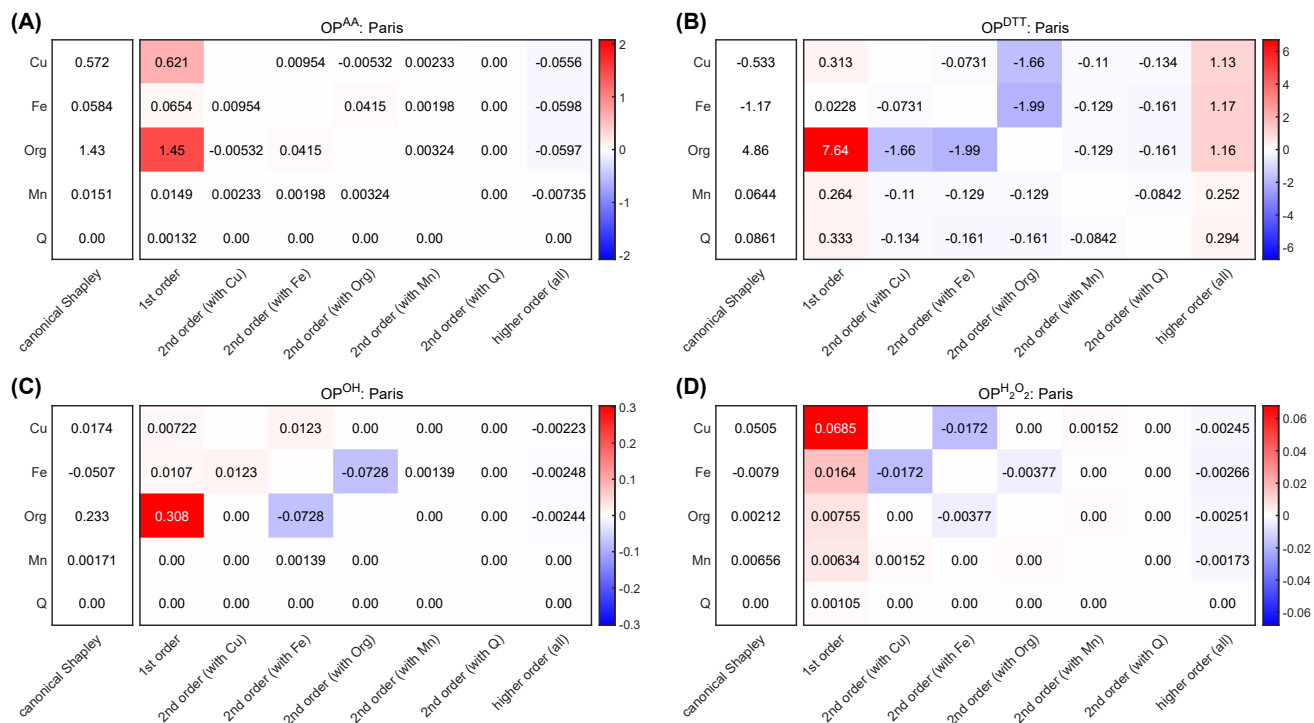


Figure S20. Deconvolution of the Shapley values into first and higher-order effects of PM constituents towards OP^{AA} (A), OP^{DTT} (B), OP^{OH} (C), and $OP^{H_2O_2}$ (D) in Paris.

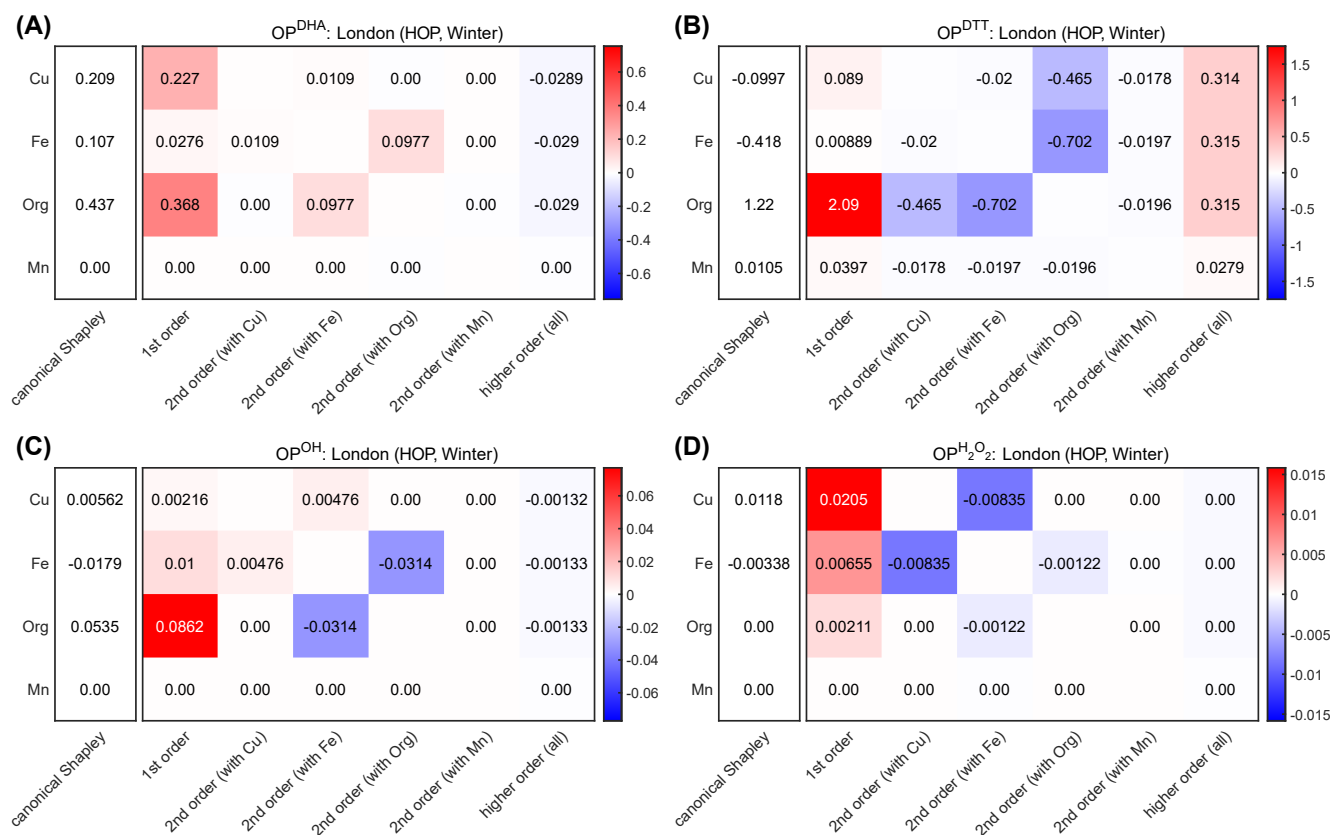


Figure S21. Deconvolution of the Shapley values into first and higher-order effects of PM constituents towards OP^{DHA} (A), OP^{DTT} (B), OP^{OH} (C), and $OP^{H_2O_2}$ (D) in London during Winter at HOP.

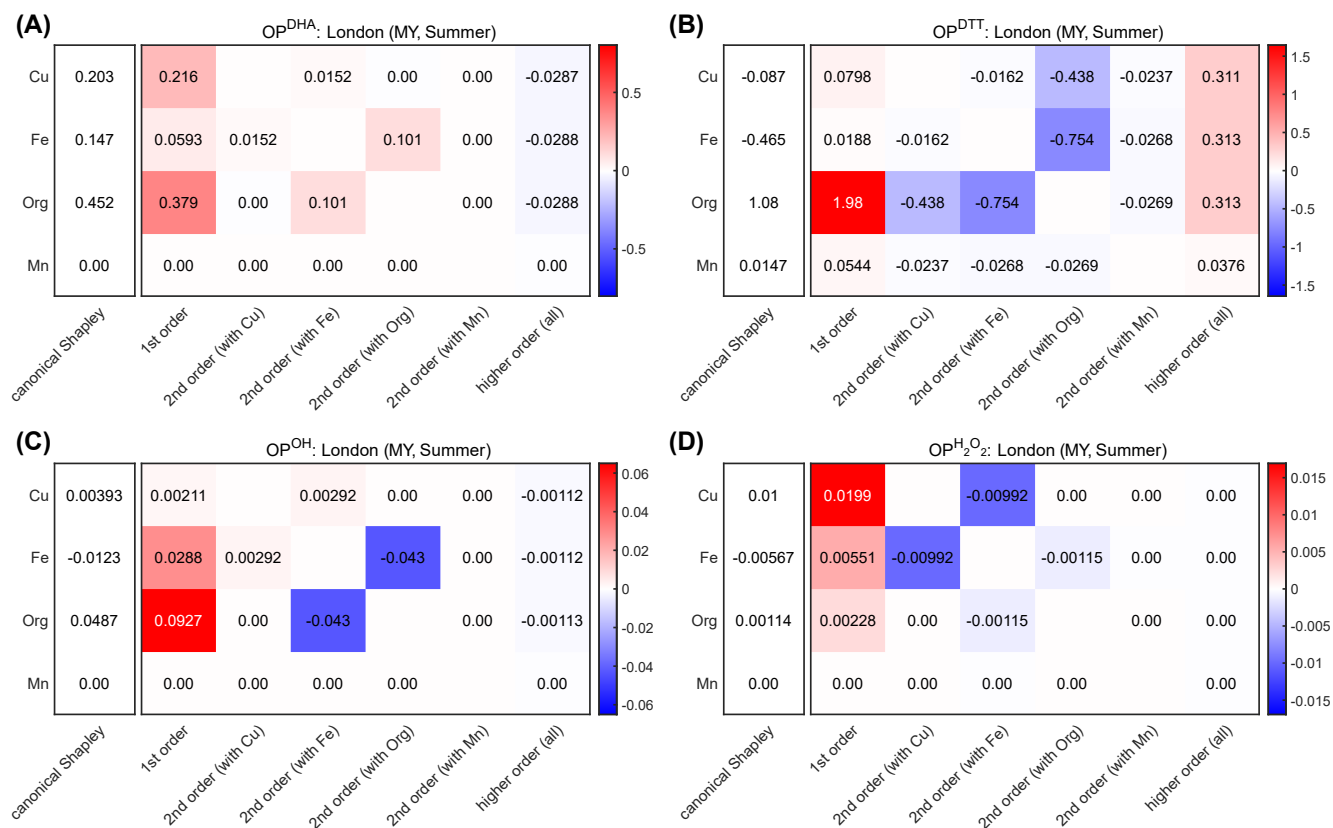


Figure S22. Deconvolution of the Shapley values into first and higher-order effects of PM constituents towards OP^{DHA} (A), OP^{DTT} (B), OP^{OH} (C), and $OP^{H_2O_2}$ (D) in London during Summer at MY.

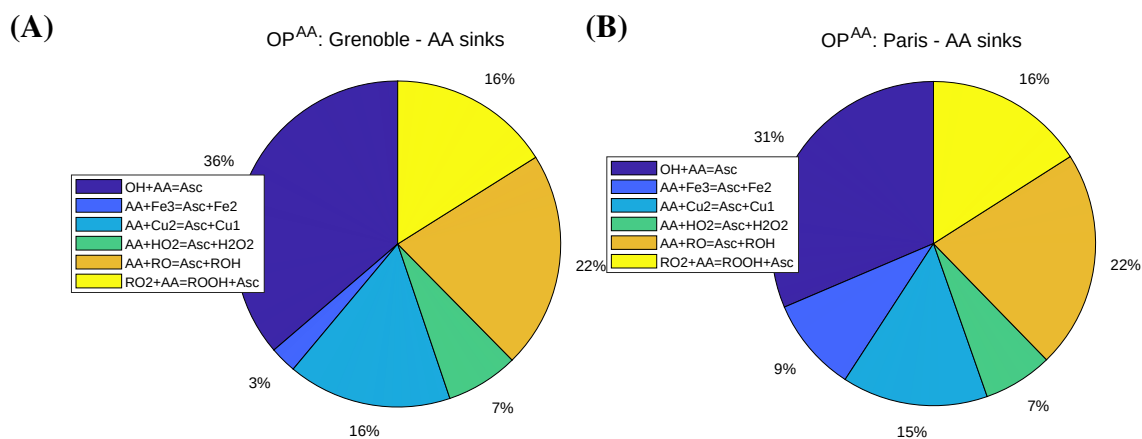
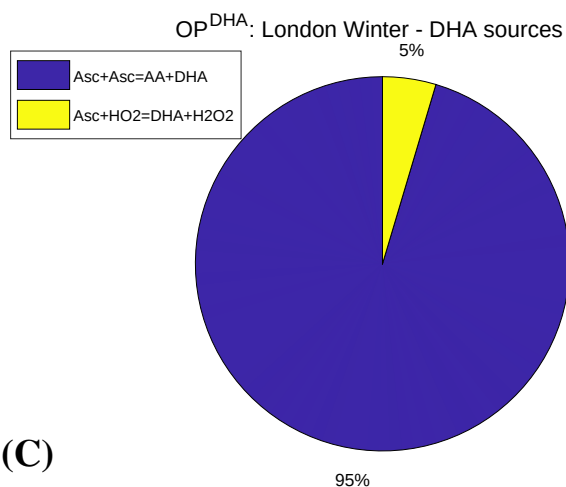
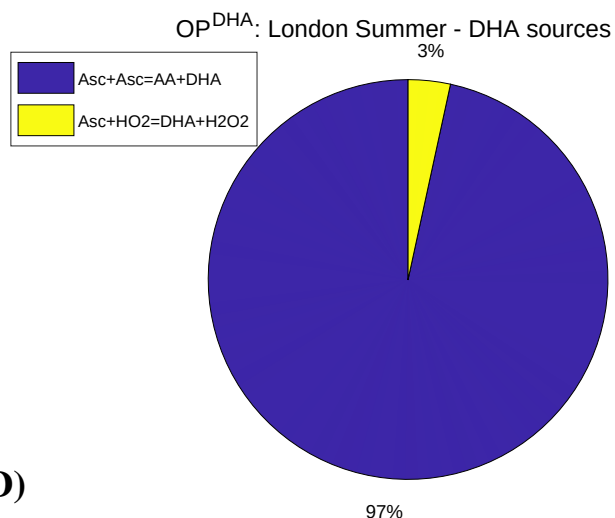


Figure S23. Main sinks of ascorbic acid for Grenoble (A) and Paris (B).

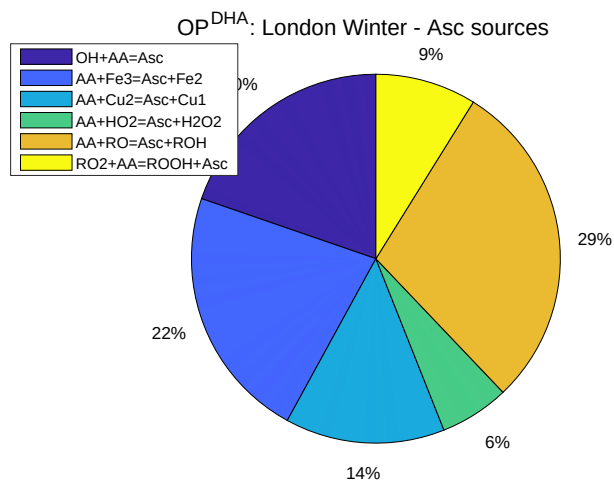
(A)



(B)



(C)



(D)

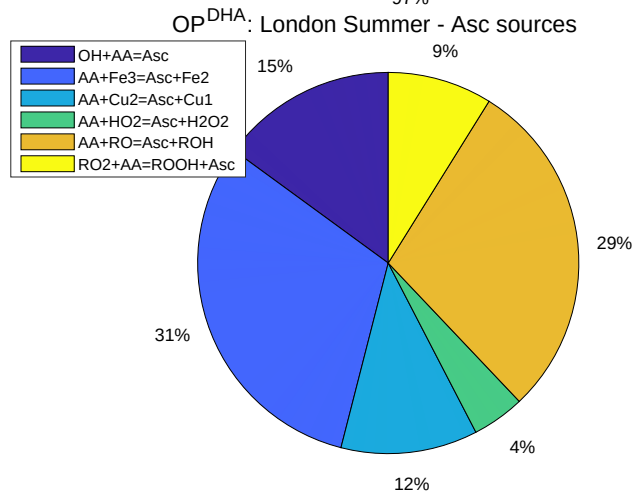
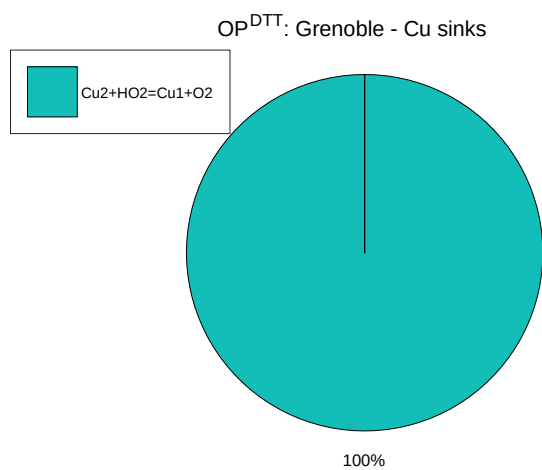


Figure S24. Main sources of dehydroascorbic acid for London Winter (A) and London Summer (B). Main sources of ascorbyl radical for London Winter (C) and London Summer (D).

(A)



(B)

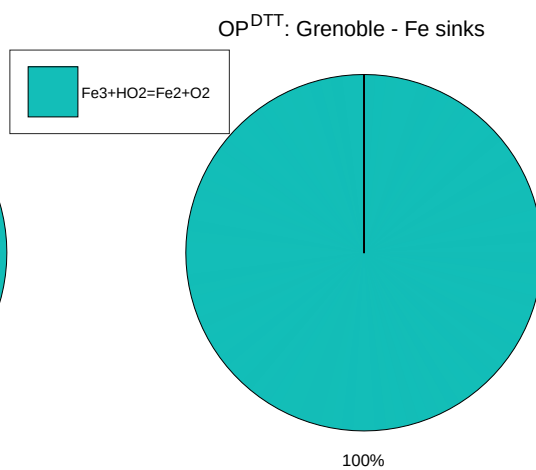


Figure S25. Main sinks of Cu(II) and Fe(III) in the DTT assay for Grenoble data.

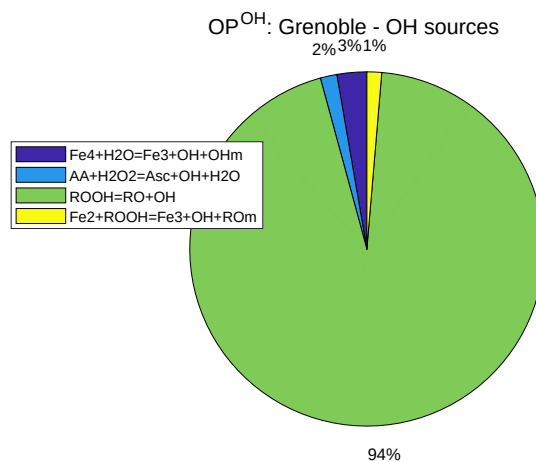


Figure S26. Main sources of [•]OH for Grenoble data.

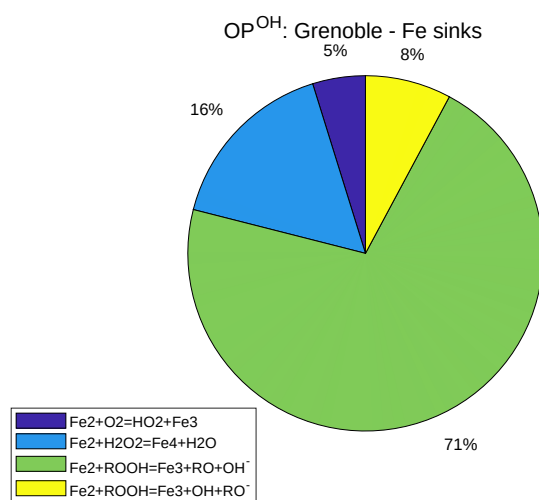
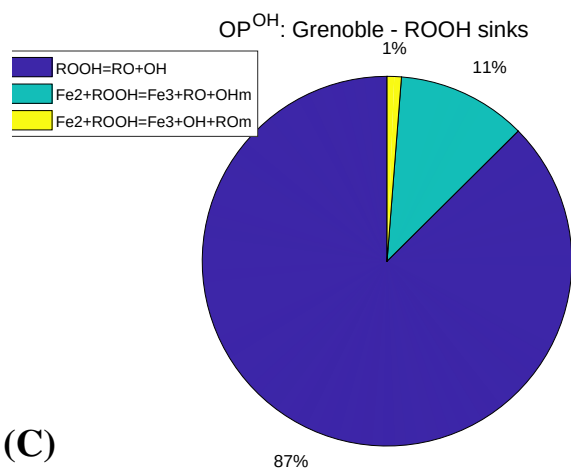
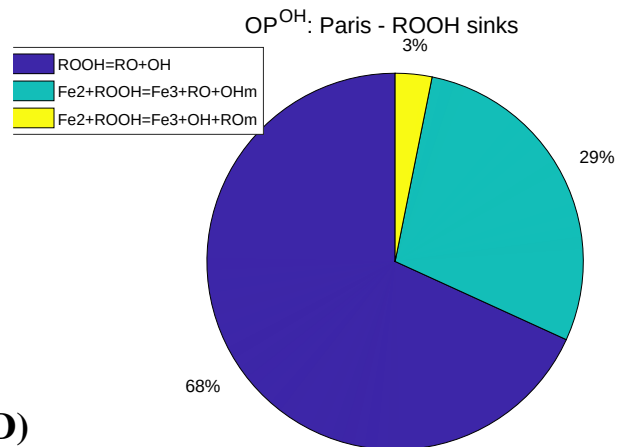


Figure S27. Main sinks of Fe(II) in the [•]OH assay for Grenoble data.

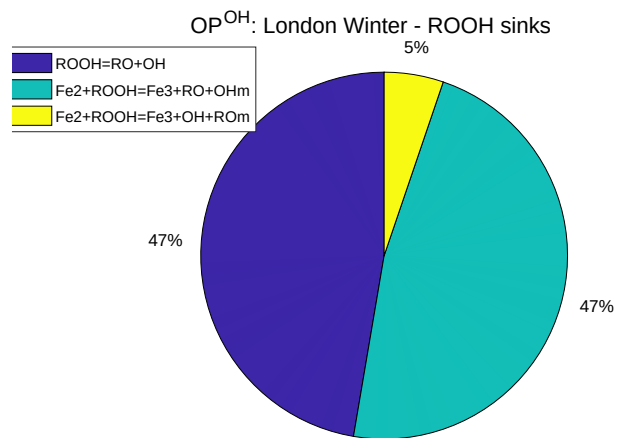
(A)



(B)



(C)



(D)

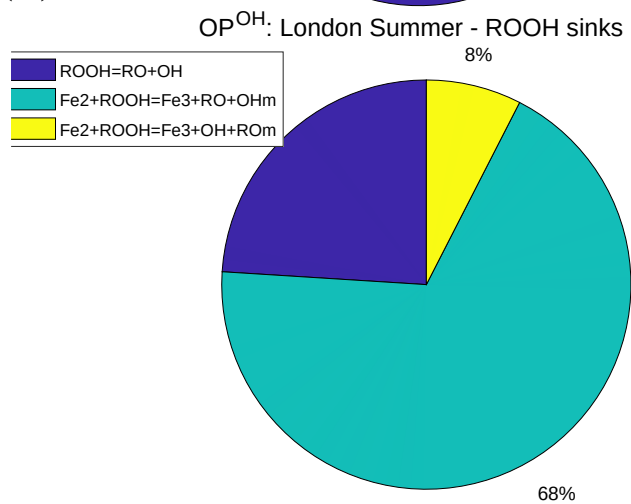


Figure S28. Main sinks of ROOH in the [•]OH assay for Grenoble (A), Paris (B), London in Winter (C) and London in Summer (D).

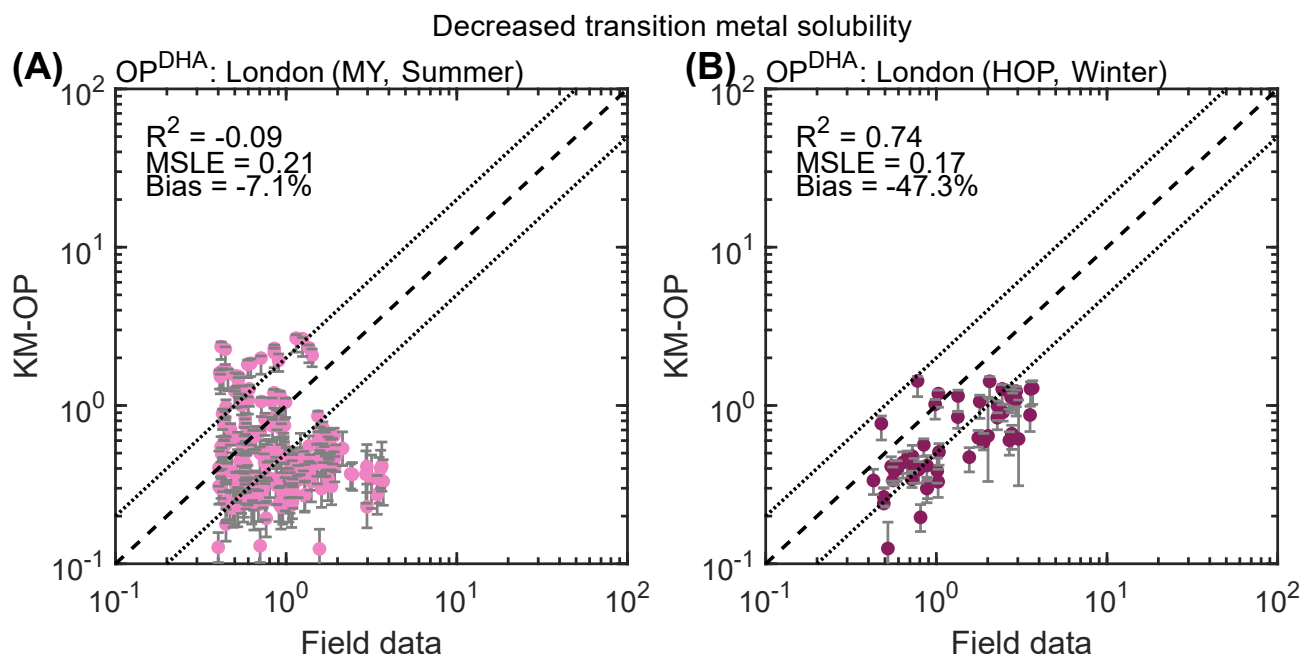


Figure S29. Sensitivity study of using lowered soluble fractions of transition metal ions for the simulation of OP^{DHA} for particulate matter samples collected in London during (A) Summer at MY and (B) Winter at HOP.

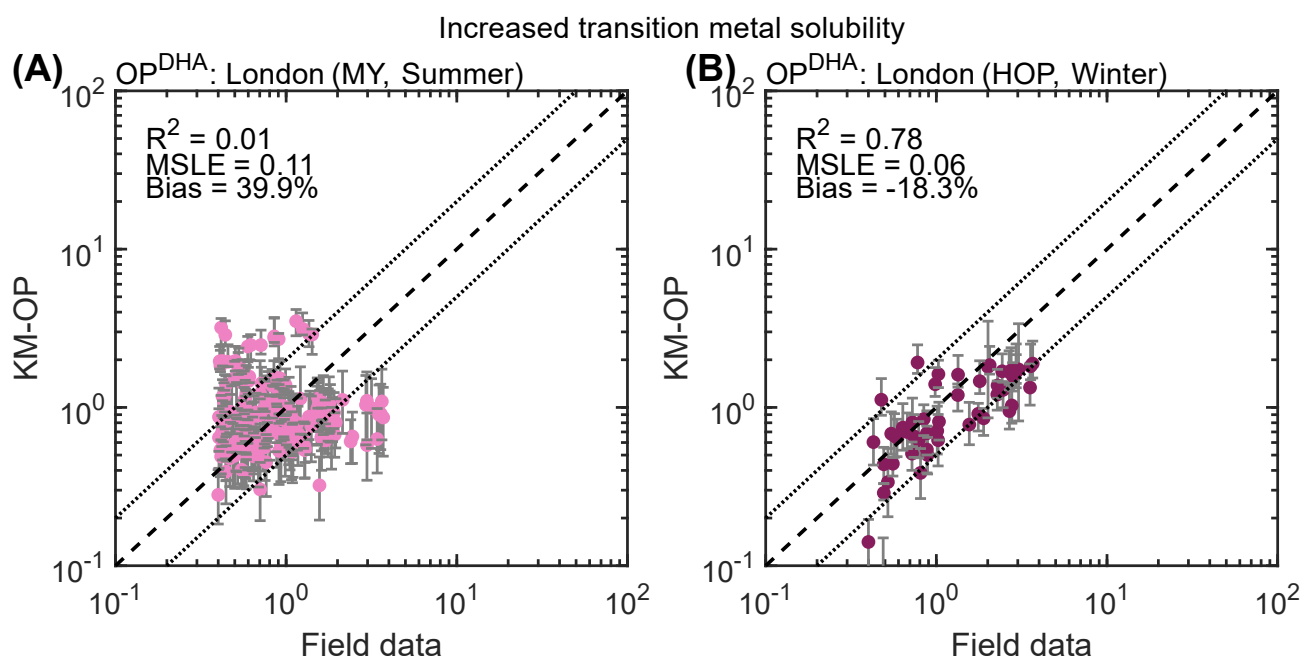


Figure S30. Sensitivity study of using increased soluble fractions of transition metal ions for the simulation of OP^{DHA} for particulate matter samples collected in London during (A) Summer at MY and (B) Winter at HOP.

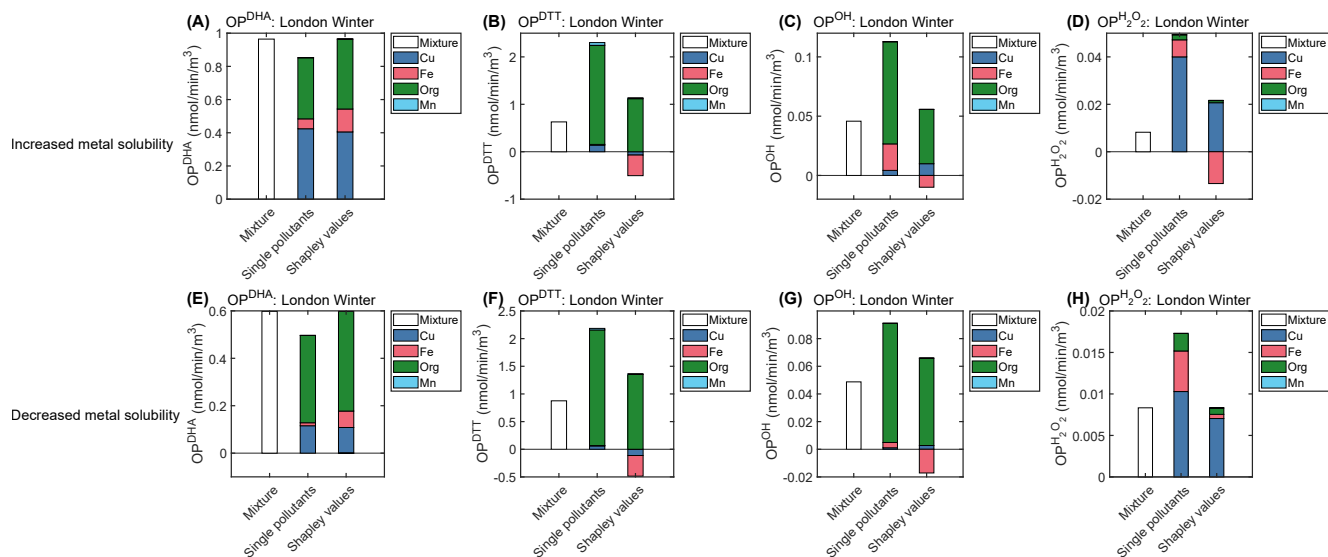


Figure S31. Sensitivity study on the contributions of different PM constituents to OP^{DHA} , OP^{DTT} , OP^{OH} , $OP^{H_2O_2}$ in London during Winter at HOP with (A-D) 2 times higher and (E-H) 2 times lower metal solubility.

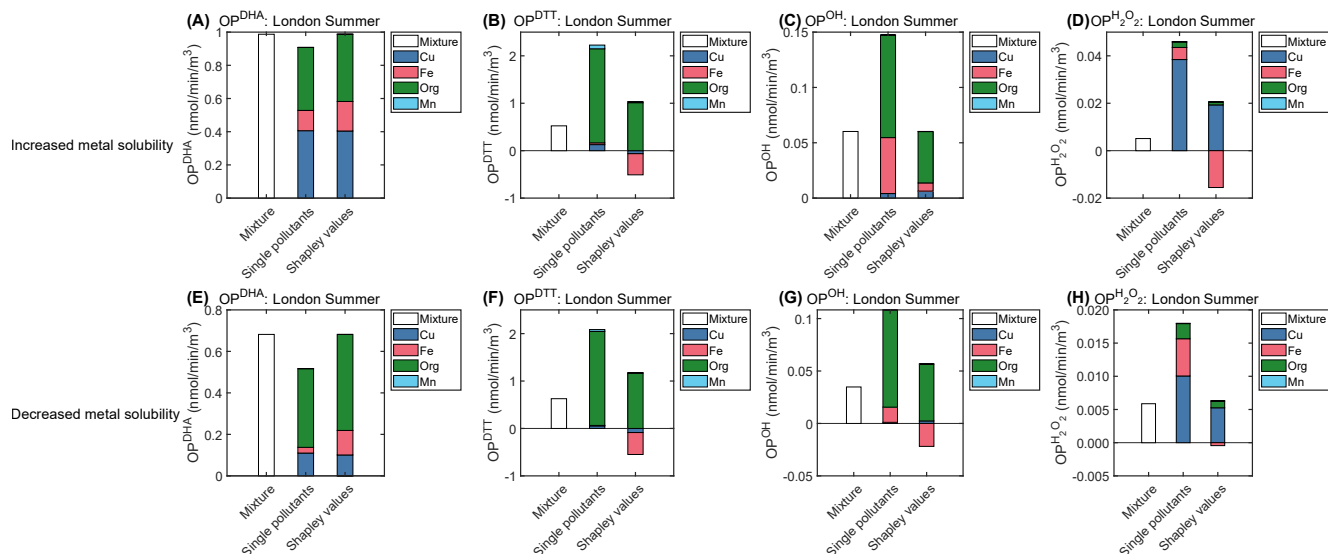


Figure S32. Sensitivity study on the contributions of different PM constituents to OP^{DHA} , OP^{DTT} , OP^{OH} , $OP^{H_2O_2}$ in London during Summer at MY with (A-D) 2 times higher and (E-H) 2 times lower metal solubility.

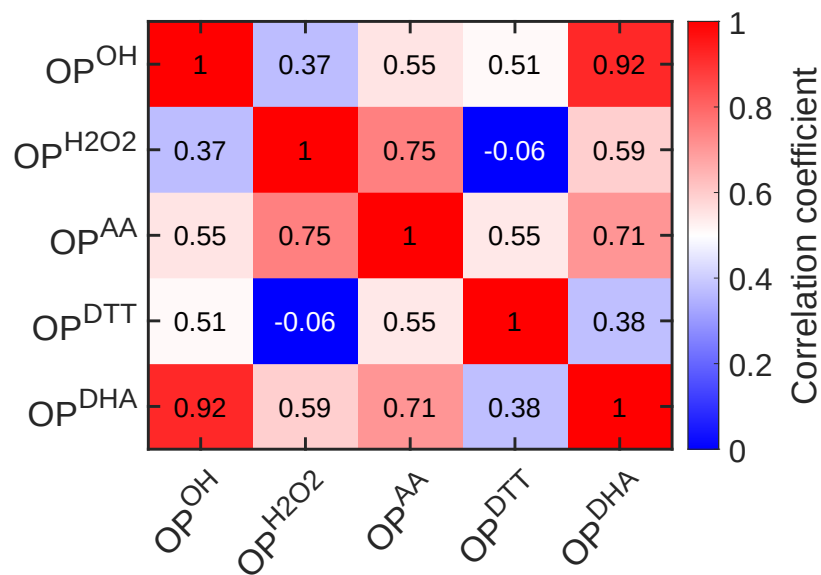


Figure S33. Correlation matrix between intrinsic OP assays in Grenoble.

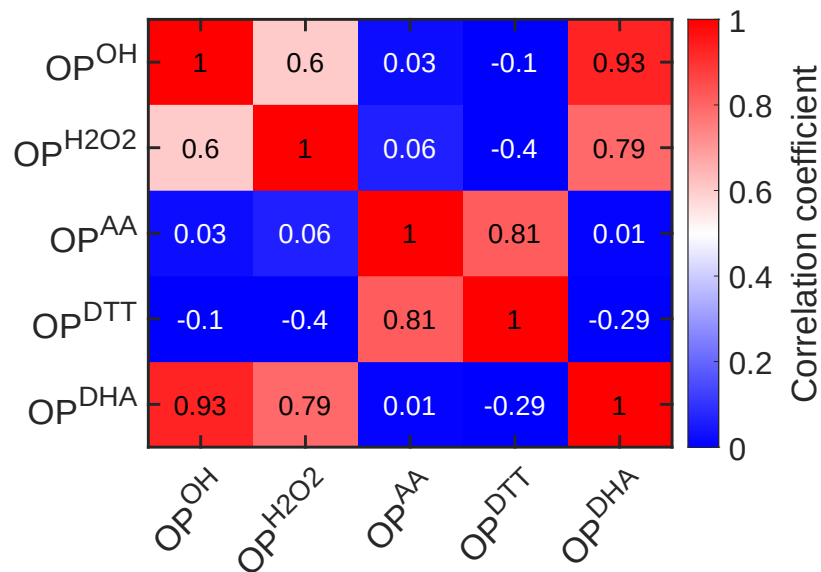


Figure S34. Correlation matrix between intrinsic OP assays in Paris.

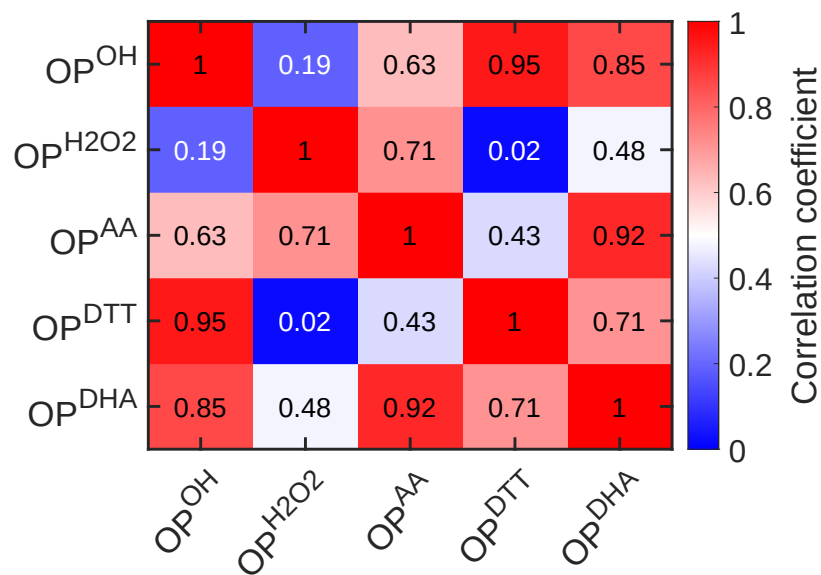


Figure S35. Correlation matrix between intrinsic OP assays in London during Winter at HOP.

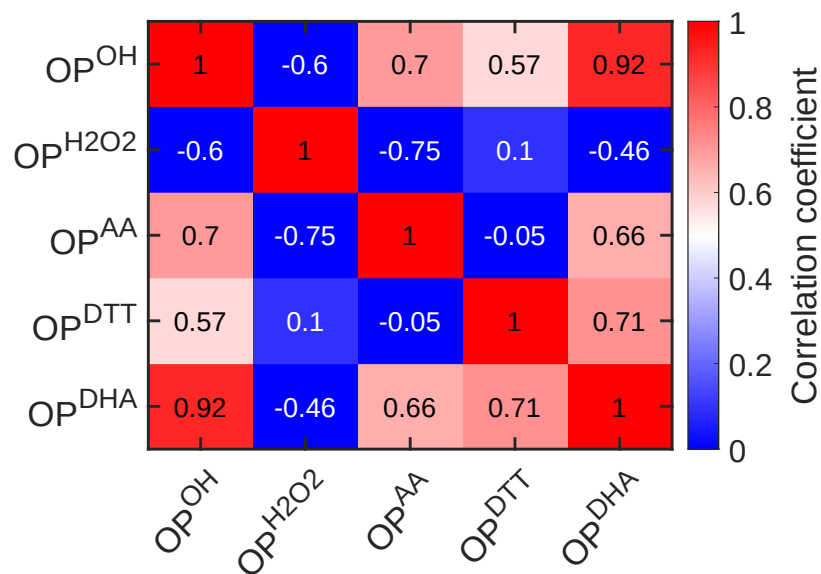


Figure S36. Correlation matrix between intrinsic OP assays in London during Summer at MY.

2 Supplementary Tables

Table S1. Chemical reactions included in the KM-OP model. The respective lower and upper boundaries indicate the initial constraints of the fit ensemble. Values that were fixed during the fitting procedure are indicated using square brackets. Species in parenthesis in the chemical reaction refer to those that partake in the chemical reaction but do not influence the reaction rate and order. The rate coefficients are for 298 K in units of $\text{cm}^3 \text{s}^{-1}$, unless otherwise noted. For their temperature dependence, all reaction rate coefficients were assumed to follow Arrhenius behavior with an activation energy of 50 kJ mol^{-1} . The rate coefficients R111-R135 are for 310 K. Fast proton transfer reactions in the model are not explicitly resolved, instead the protonated or deprotonated forms are lumped into one single model species. For the chemical reactions that only the protonated or deprotonated forms undergo, we infer their individual concentrations based on the pH.

Reaction number	Reaction	Range	Best fit	Reference
SR1	$\bullet\text{OH} + \text{AA} \rightarrow \text{AA}\bullet + \text{OH}^-$	$[1.20 \times 10^{-11}]$		Shen et al. (2021)
SR2	$\bullet\text{OH} + \text{UAH} \rightarrow \text{UA} + \text{OH}^-$	$[1.20 \times 10^{-11}]$		Lakey et al. (2016)
SR3	$\bullet\text{OH} + \text{GSH} \rightarrow \text{GS} + \text{OH}^-$	$[1.70 \times 10^{-11}]$		Lakey et al. (2016)
SR4	$\bullet\text{OH} + \text{GSSG} \rightarrow \text{product} + \text{OH}^-$	$[1.20 \times 10^{-11}]$		Assumed to be fast
SR5	$\bullet\text{OH} + \text{Cit} \rightarrow \text{product} + \text{OH}^-$	$[9.7 \times 10^{-14}]$		Liu et al. (2017)
SR6	$1,2\text{-NQN} + \text{AA} \rightarrow 1,2\text{-NQN}\bullet + \text{AA}\bullet$	$1.50 \times 10^{-22} - 1.50 \times 10^{-16}$	1.74×10^{-19}	This study
SR7	$1,2\text{-NQN}\bullet + \text{O}_2 \rightarrow 1,2\text{-NQN} + \text{O}_2^-$	$[1.35 \times 10^{-14}]$		This study
SR8	$1,2\text{-NQN}\bullet + \text{O}_2^- (+ 2\text{H}^+) \rightarrow 1,2\text{-NQN} + \text{H}_2\text{O}_2$	$3.3 \times 10^{-15} - 3.3 \times 10^{-11}$	4.91×10^{-12}	This study
SR9	$1,2\text{-NQN}\bullet + \text{Fe(III)} \rightarrow 1,2\text{-NQN} + \text{Fe(II)}$	$1.00 \times 10^{-19} - 1.00 \times 10^{-13}$	1.19×10^{-16}	This study
SR10	$1,4\text{-NQN} + \text{AA} \rightarrow 1,4\text{-NQN}\bullet + \text{AA}\bullet$	$1.50 \times 10^{-22} - 1.50 \times 10^{-16}$	5.37×10^{-21}	This study
SR11	$1,4\text{-NQN}\bullet + \text{O}_2 \rightarrow 1,4\text{-NQN} + \text{O}_2^-$	$[3.06 \times 10^{-14}]$		This study
SR12	$1,4\text{-NQN}\bullet + \text{O}_2^- (+ 2\text{H}^+) \rightarrow 1,4\text{-NQN} + \text{H}_2\text{O}_2$	$3.3 \times 10^{-15} - 3.3 \times 10^{-11}$	3.72×10^{-12}	This study
SR13	$\text{PQN} + \text{AA} \rightarrow \text{PQN}\bullet + \text{AA}\bullet$	$1.50 \times 10^{-22} - 1.50 \times 10^{-16}$	1.45×10^{-20}	This study
SR14	$\text{PQN}\bullet + \text{O}_2 \rightarrow \text{PQN} + \text{O}_2^-$	$[2.31 \times 10^{-14}]$		This study
SR15	$\text{PQN}\bullet + \text{O}_2^- (+ 2\text{H}^+) \rightarrow \text{PQN} + \text{H}_2\text{O}_2$	$3.30 \times 10^{-15} - 3.30 \times 10^{-11}$	1.25×10^{-12}	This study
SR16	$\text{Fe(III)} + \text{AA} \rightarrow \text{Fe(II)} + \text{AA}\bullet$	$6.97 \times 10^{-21} - 6.97 \times 10^{-19}$	2.39×10^{-19}	This study
SR17	$\text{Fe(II)} + \text{O}_2 \rightarrow \text{Fe(III)} + \text{O}_2^-$	$[4.48 \times 10^{-21}]$		Gonzalez et al. (2021)
SR18	$\text{Fe(II)} + \text{O}_2^- (+ 2\text{H}^+) \rightarrow \text{Fe(III)} + \text{H}_2\text{O}_2$	$[1.66 \times 10^{-14}]$		Ervens et al. (2003)
SR19	$\text{Fe(II)} + \bullet\text{OH} \rightarrow \text{Fe(III)} + \text{OH}^-$	$[5.81 \times 10^{-13}]$		Halliwell and Gutteridge (2015)
SR20	$\text{Fe(III)} + \text{HO}_2 \rightarrow \text{Fe(II)} + \text{O}_2 + \text{H}^+$	$[2.16 \times 10^{-16}]$		Ervens et al. (2003)
SR21	$\text{Fe(III)} + \text{O}_2^- \rightarrow \text{Fe(II)} + \text{O}_2$	$[2.49 \times 10^{-13}]$		Ervens et al. (2003)
SR22	$\text{Fe(II)} + \text{H}_2\text{O}_2 (+ 2\text{H}^+) \rightarrow \text{Fe(IV)} + 2\text{H}_2\text{O}$	$8.14 \times 10^{-19} - 8.14 \times 10^{-17}$	1.10×10^{-17}	This study
SR23	$\text{Fe(II)} + \text{H}_2\text{O}_2 \rightarrow \text{Fe(III)} + \bullet\text{OH} + \text{OH}^-$	$1.26 \times 10^{-20} - 1.26 \times 10^{-18}$	2.96×10^{-19}	This study
SR24	$\text{Fe(II)} + \text{Fe(IV)} \rightarrow \text{Fe(III)} + \text{Fe(III)}$	$[6.60 \times 10^{-18}]$		Lakey et al. (2016)
SR25	$\text{Fe(IV)} (+ \text{H}_2\text{O}) \rightarrow \text{Fe(III)} + \bullet\text{OH} + \text{H}^+$	$1.30 \times 10^{-4} - 1.30 \text{ s}^{-1}$	0.0102	This study
SR26	$\text{H}_2\text{O}_2 + \bullet\text{OH} \rightarrow \text{HO}_2 + \text{H}_2\text{O}$	$[5.50 \times 10^{-14}]$		Lakey et al. (2016)
SR27	$\bullet\text{OH} + \bullet\text{OH} \rightarrow \text{H}_2\text{O}_2$	$[8.60 \times 10^{-12}]$		Lakey et al. (2016)
SR28	$\bullet\text{OH} + \text{HO}_2 \rightarrow \text{O}_2 + \text{H}_2\text{O}$	$[1.66 \times 10^{-11}]$		Ervens et al. (2003)
SR29	$\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	$[1.40 \times 10^{-15}]$		Lakey et al. (2016)
SR30	$\text{H}_2\text{O}_2 + \text{HO}_2 \rightarrow \bullet\text{OH} + \text{O}_2 + \text{H}_2\text{O}$	$[5.00 \times 10^{-21}]$		Lakey et al. (2016)
SR31	$\text{HO}_2 + \text{O}_2^- (+ \text{H}_2\text{O}) \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 + \text{OH}^-$	$[1.70 \times 10^{-13}]$		Ervens et al. (2003)
SR32	$\bullet\text{OH} + \text{O}_2^- \rightarrow \text{O}_2 + \text{OH}^-$	$[1.83 \times 10^{-11}]$		Ervens et al. (2003)

Table S1. Continued.

Reaction number	Reaction	Range	Best fit	Reference
SR33	$\text{Cu(II)} + \text{AA} \rightarrow \text{Cu(I)} + \text{AA}^\bullet$	$1.46 \times 10^{-19} - 1.46 \times 10^{-17}$	4.98×10^{-19}	This study
SR34	$\text{Cu(I)} + \text{O}_2 \rightarrow \text{Cu(II)} + \text{O}_2^-$	$[7.64 \times 10^{-16}]$		Ervens et al. (2003)
SR35	$\text{Cu(I)} + \text{O}_2^- (+ 2\text{H}^+) \rightarrow \text{Cu(II)} + \text{H}_2\text{O}_2$	$1.56 \times 10^{-12} - 1.56 \times 10^{-10}$	1.74×10^{-12}	This study
SR36	$\text{Cu(I)} + \bullet\text{OH} \rightarrow \text{Cu(II)} + \text{OH}^-$	$[4.98 \times 10^{-12}]$		Ervens et al. (2003)
SR37	$\text{Cu(I)} + \text{H}_2\text{O}_2 \rightarrow \text{Cu(III)} + \text{OH}^- + \text{OH}^-$	$1.16 \times 10^{-19} - 1.16 \times 10^{-14}$	5.11×10^{-16}	This study
SR38	$\text{Cu(I)} + \text{Cu(III)} \rightarrow \text{Cu(II)} + \text{Cu(II)}$	$[5.80 \times 10^{-12}]$		Lakey et al. (2016)
SR39	$\text{Cu(II)} + \text{H}_2\text{O}_2 \rightarrow \text{Cu(I)} + \text{HO}_2 + \text{H}^+$	$[7.64 \times 10^{-19}]$		Pham et al. (2013)
SR40	$\text{Cu(II)} + \text{O}_2^- \rightarrow \text{Cu(I)} + \text{O}_2$	$[1.83 \times 10^{-11}]$		Ervens et al. (2003)
SR41	$\text{Cu(II)} + \text{HO}_2 \rightarrow \text{Cu(I)} + \text{O}_2 + \text{H}^+$	$[1.66 \times 10^{-13}]$		Ervens et al. (2003)
SR42	$\text{Cu(I)} + \text{HO}_2 (+\text{H}^+) \rightarrow \text{Cu(II)} + \text{H}_2\text{O}_2$	$[4.98 \times 10^{-12}]$		Ervens et al. (2003)
SR43	$\text{Cu(III)} (+\text{H}_2\text{O}) \rightarrow \text{Cu(II)} + \bullet\text{OH} + \text{H}^+$	$2.32 \times 10^{-3} - 2.32 \text{ s}^{-1}$	0.59	This study
SR44	$\text{AA}^\bullet + \text{AA}^\bullet \rightarrow \text{AA} + \text{DHA}$	$[5.00 \times 10^{-16}]$		Lakey et al. (2016)
SR45	$\text{AA} + \text{GS} \rightarrow \text{AA}^\bullet + \text{GSH}$	$[1.00 \times 10^{-12}]$		Lelieveld et al. (2021)
SR46	$\text{AA} + \text{UA} \rightarrow \text{AA}^\bullet + \text{UAH}$	$[1.70 \times 10^{-15}]$		Lelieveld et al. (2021)
SR47	$\text{UAH} + \text{GS} \rightarrow \text{UA} + \text{GSH}$	$[5.00 \times 10^{-14}]$		Lelieveld et al. (2021)
SR48	$\text{AA} + \text{H}_2\text{O}_2 \rightarrow \text{AA}^\bullet + \bullet\text{OH} + \text{OH}^-$	$2.19 \times 10^{-23} - 2.19 \times 10^{-19}$	2.54×10^{-22}	This study
SR49	$\text{AA} + \text{HO}_2 (+\text{H}^+) \rightarrow \text{AA}^\bullet + \text{H}_2\text{O}_2$	$[2.65 \times 10^{-17}]$		Lelieveld et al. (2021)
SR50	$\text{AA} + \text{O}_2^- (+ 2\text{H}^+) \rightarrow \text{AA}^\bullet + \text{H}_2\text{O}_2$	$[5.10 \times 10^{-17}]$		Lelieveld et al. (2021)
SR51	$\bullet\text{OH} + \text{Benzoate} \rightarrow \text{BenzOH}$	$[1.00 \times 10^{-11}]$		Lakey et al. (2016)
SR52	$\text{O}_2^- + \text{O}_2^- (+ 2\text{H}^+) \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	$[2.49 \times 10^{-14}]$		Kohen and Nyska (2002)
SR53	$\text{GS}^- + \text{H}_2\text{O}_2 \rightarrow \text{GSSG} + \text{H}_2\text{O} + \text{OH}^-$	$[1.44 \times 10^{-21}]$		Lelieveld et al. (2021)
SR54	$\text{GS}^- + \text{H}_2\text{O}_2 \rightarrow \text{GSOH} + \text{OH}^-$	$[1.60 \times 10^{-21}]$		Lelieveld et al. (2021)
SR55	$\text{O}_2^- + \text{GSH} \rightarrow \text{GS} + \text{H}_2\text{O}_2$	$[3.32 \times 10^{-19}]$		Lelieveld et al. (2021)
SR56	$\text{Cu(I)} + \text{H}_2\text{O}_2 \rightarrow \text{Cu(II)} + \bullet\text{OH} + \text{OH}^-$	$1.16 \times 10^{-19} - 1.16 \times 10^{-15}$	2.44×10^{-17}	This study
SR57	$\text{DTT} + \bullet\text{OH} (+\text{H}^+) \rightarrow \text{DTT}^\bullet + \text{H}_2\text{O}$	$[1.66 \times 10^{-11}]$		Netto and Stadtman (1996)
SR58	$\text{DTT} + \text{HO}_2 (+\text{H}^+) \rightarrow \text{DTT}^\bullet + 2\text{OH}^-$	$2.65 \times 10^{-17} - 2.65 \times 10^{-13}$	1.86×10^{-15}	This study
SR59	$\text{DTT} + \text{H}_2\text{O}_2 (+\text{H}^+) \rightarrow \text{DTT}^\bullet + \text{H}_2\text{O} + \text{OH}^-$	$[3.04 \times 10^{-21}]$		Netto and Stadtman (1996)
SR60	$\text{Fe(III)} + \text{DTT} \rightarrow \text{DTT}^\bullet + \text{Fe(II)}$	$[4.65 \times 10^{-21}]$		Netto and Stadtman (1996)
SR61	$\text{Cu(II)} + \text{DTT} \rightarrow [\text{Cu}^{2+}(\text{DTT}^{2-})]$	$2.00 \times 10^{-21} - 2.00 \times 10^{-17}$	8.43×10^{-20}	This study
SR62	$[\text{Cu}^{2+}(\text{DTT}^{2-})] + \text{DTT} \rightarrow [\text{Cu}^{2+}(\text{DTT}^{2-})_2]^{2-}$	$2.00 \times 10^{-19} - 2.00 \times 10^{-15}$	1.55×10^{-16}	This study

Table S1. Continued.

Reaction number	Reaction	Range	Best fit	Reference
SR63	$[\text{Cu}^{2+}(\text{DTT}^{2-})_2]^{2-} \rightarrow [\text{Cu}^+(\text{DTT}^{2-})(\text{DTT}^{\bullet-})]^{2-}$	$2.00 \times 10^{-3} - 2.00 \times 10^1 \text{ s}^{-1}$	0.49	This study
SR64	$[\text{Cu}^+(\text{DTT}^{2-})(\text{DTT}^{\bullet-})]^{2-} + \text{O}_2 \rightarrow [\text{Cu}^+(\text{DTT}^{2-})(\text{DTTOO}^{\bullet-})]^{2-}$	$2.00 \times 10^{-19} - 2.00 \times 10^{-15}$	1.33×10^{-17}	This study
SR65	$[\text{Cu}^+(\text{DTT}^{2-})(\text{DTTOO}^{\bullet-})]^{2-} + \text{DTT} \rightarrow [\text{Cu}^{2+}(\text{DTT}^{2-})] + 2 \text{RSSR}$	$2.00 \times 10^{-18} - 2.00 \times 10^{-14}$	3.11×10^{-16}	This study
SR66	$[\text{Cu}^{2+}(\text{DTT}^{2-})] \rightarrow [\text{Cu}^+(\text{DTT}^{\bullet-})]$	$2.00 \times 10^{-3} - 2.00 \times 10^1 \text{ s}^{-1}$	0.54	This study
SR67	$[\text{Cu}^+(\text{DTT}^{\bullet-})] + \text{O}_2 \rightarrow [\text{Cu}^+(\text{DTTOO}^{\bullet-})]$	$2.00 \times 10^{-23} - 2.00 \times 10^{-19}$	2.87×10^{-21}	This study
SR68	$[\text{Cu}^+(\text{DTTOO}^{\bullet-})] \rightarrow \text{Cu(I)} + \text{RSSR} + \text{HO}_2$	$2.00 \times 10^{-6} - 2.00 \times 10^{-2} \text{ s}^{-1}$	6.35×10^{-4}	This study
SR69	$\text{Fe(IV)} + \text{DTT} \rightarrow \text{Fe(III)} + \text{DTT}^{\bullet}$	$5.00 \times 10^{-19} - 5.00 \times 10^{-15}$	1.30×10^{-16}	This study
SR70	$\text{DTT}^{\bullet} + \text{DTT} \rightarrow \text{RSSR}^{\bullet-}$	$1.00 \times 10^{-14} - 1.00 \times 10^{-11}$	1.36×10^{-13}	This study
SR71	$\text{DTT}^{\bullet} + \text{O}_2 \rightarrow \text{RSS} + \text{HO}_2$	$[1.18 \times 10^{-12}]$		This study
SR72	$1,2\text{-NQN} + \text{DTT} \rightarrow 1,2\text{-NQN}^{\bullet} + \text{DTT}^{\bullet}$	$8.00 \times 10^{-23} - 8.00 \times 10^{-17}$	2.11×10^{-19}	This study
SR73	$\text{RSSR}^{\bullet-} + 1,2\text{-NQN} \rightarrow \text{RSSR} + 1,2\text{-NQN}^{\bullet}$	$1.00 \times 10^{-19} - 1.00 \times 10^{-13}$	1.70×10^{-17}	This study
SR74	$\text{DTT}^{\bullet} + 1,2\text{-NQN} \rightarrow \text{RS} - 1,2\text{-NQN}$	$1.00 \times 10^{-18} - 1.00 \times 10^{-12}$	2.11×10^{-15}	This study
SR75	$1,4\text{-NQN} + \text{DTT} \rightarrow 1,4\text{-NQN}^{\bullet} + \text{DTT}^{\bullet}$	$5.00 \times 10^{-24} - 5.00 \times 10^{-18}$	1.22×10^{-20}	This study
SR76	$\text{RSSR}^{\bullet-} + 1,4\text{-NQN} \rightarrow \text{RSSR} + 1,4\text{-NQN}^{\bullet}$	$1.00 \times 10^{-19} - 1.00 \times 10^{-13}$	7.53×10^{-14}	This study
SR77	$\text{DTT}^{\bullet} + 1,4\text{-NQN} \rightarrow \text{RS} - 1,4\text{-NQN}$	$1.00 \times 10^{-18} - 1.00 \times 10^{-12}$	5.19×10^{-13}	This study
SR78	$\text{PQN} + \text{DTT} \rightarrow \text{PQN}^{\bullet} + \text{DTT}^{\bullet}$	$6.00 \times 10^{-22} - 6.00 \times 10^{-16}$	3.61×10^{-19}	This study
SR79	$\text{RSSR}^{\bullet-} + \text{PQN} \rightarrow \text{RSSR} + \text{PQN}^{\bullet}$	$1.00 \times 10^{-19} - 1.00 \times 10^{-13}$	6.76×10^{-14}	This study
SR80	$\text{DTT}^{\bullet} + \text{PQN} \rightarrow \text{RS} - \text{PQN}$	$1.00 \times 10^{-18} - 1.00 \times 10^{-12}$	2.42×10^{-16}	This study
SR81	$\text{AA}^{\bullet} + \text{O}_2^{\cdot-} (+ 2\text{H}^+) \rightarrow \text{DHA} + \text{H}_2\text{O}_2$	$1.00 \times 10^{-16} - 1.00 \times 10^{-12}$	4.35×10^{-14}	This study
SR82	$\text{DHA} + \text{}^{\bullet}\text{OH} \rightarrow \text{product}$	$[1.66 \times 10^{-11}]$		Shen et al. (2021)
SR83	$\text{DHA} + \text{H}_2\text{O}_2 \rightarrow \text{product}$	$[6.97 \times 10^{-23}]$		Shen et al. (2021)
SR84	$\text{DHA} (+ \text{H}_2\text{O}) \rightarrow \text{DKG}$	$4.8 \times 10^{-6} - 4.8 \times 10^{-2} \text{ s}^{-1}$	8.89×10^{-4}	This study
SR85	$\text{Mn(II)} + \text{DTT} \rightarrow \text{Mn(I)} + \text{DTT}^{\bullet}$	$5.00 \times 10^{-23} - 5.00 \times 10^{-19}$	3.01×10^{-21}	This study
SR86	$\text{RSSR}^{\bullet-} + \text{O}_2 \rightarrow \text{RSSR} + \text{HO}_2$	$[1.00 \times 10^{-12}]$		Kumagai et al. (2002)
SR87	$\text{Mn(II)} + \text{}^{\bullet}\text{OH} \rightarrow \text{Mn(III)} + \text{OH}^-$	$[3.32 \times 10^{-14}]$		Jacobsen et al. (1998)
SR88	$\text{Mn(II)} + \text{HO}_2 \rightarrow \text{MnO}_2^+ + \text{H}^+$	$1.00 \times 10^{-17} - 1.00 \times 10^{-13}$	2.78×10^{-14}	Jacobsen et al. (1998)
SR89	$\text{MnO}_2^+ + \text{MnO}_2^+ (+ 2\text{H}^+) \rightarrow 2 \text{Mn(II)} + \text{H}_2\text{O}_2 + \text{O}_2$	$[9.96 \times 10^{-15}]$		Morgan (2005)
SR90	$\text{Mn(III)} + \text{H}_2\text{O}_2 \rightarrow \text{Mn(II)} + \text{HO}_2 + \text{H}^+$	$[1.21 \times 10^{-16}]$		Jacobsen et al. (1998)
SR91	$\text{Mn(III)} + \text{H}_2\text{O}_2 \rightarrow \text{MnO}_2^+ + 2 \text{H}^+$	$[4.65 \times 10^{-18}]$		Jacobsen et al. (1998)
SR92	$\text{MnO}_2^+ + \text{HO}_2 (+ \text{H}^+) \rightarrow \text{Mn(II)} + \text{H}_2\text{O}_2$	$[1.66 \times 10^{-14}]$		Halliwell and Gutteridge (2015)

Table S1. Continued.

Reaction number	Reaction	Range	Best fit	Reference
SR93	Mn(III) + DTT → Mn(II) + DTT [•]	$5.00 \times 10^{-17} - 5.00 \times 10^{-15}$	4.65×10^{-18}	This study
SR94	Mn(II) + O ₂ (+ H ⁺) → Mn(III) + HO ₂	$[3.98 \times 10^{-21}]$		Halliwell and Gutteridge (2015)
SR95	RS – PQN + DTT → RSSR + PQN [•]	$1.00 \times 10^{-21} - 1.00 \times 10^{-17}$	8.46×10^{-18}	This study
SR96	RS – 1,4–NQN + DTT → RSSR + 1,4–NQN [•]	$1.00 \times 10^{-21} - 1.00 \times 10^{-17}$	9.04×10^{-18}	This study
SR97	RS – 1,2–NQN + DTT → RSSR + 1,2–NQN [•]	$1.00 \times 10^{-21} - 1.00 \times 10^{-17}$	4.27×10^{-19}	This study
SR98	GSOO + GSOO → 0.56HO ₂ + product	$[6.79 \times 10^{-13}]$		Lelieveld et al. (2021)
SR99	GSOO + GSH → GSO + GSOH	$[3.32 \times 10^{-15}]$		Lelieveld et al. (2021)
SR100	GS + GS [–] → GSSG [–]	$[1.59 \times 10^{-14}]$		Lelieveld et al. (2021)
SR101	GSSG [–] → GS + GS [–]	$[1.60 \times 10^5 \text{ s}^{-1}]$		Lelieveld et al. (2021)
SR102	GSSG [–] + O ₂ → GSSG + O ₂ [–]	$[8.30 \times 10^{-12}]$		Lelieveld et al. (2021)
SR103	GS + GS → GSSG	$[8.30 \times 10^{-12}]$		Lelieveld et al. (2021)
SR104	GSOH + GSH → GSSG + H ₂ O	$[1.20 \times 10^{-18}]$		Lelieveld et al. (2021)
SR105	GSO + GSO → product	$[9.96 \times 10^{-14}]$		Lelieveld et al. (2021)
SR106	GSH + Cu(II) → [Cu ²⁺ (GSH)]	$1.00 \times 10^{-20} - 1.00 \times 10^{-16}$	4.34×10^{-20}	This study
SR107	[Cu ²⁺ (GSH)] + GSH → [Cu ²⁺ (GSH)(GSH)]	$1.00 \times 10^{-19} - 1.00 \times 10^{-15}$	5.09×10^{-17}	This study
SR108	2[Cu ²⁺ (GSH) ₂] + O ₂ → 2[Cu ²⁺ (GS)(GSH)] + H ₂ O ₂	$2.00 \times 10^{-36} - 2.00 \times 10^{-32} \text{ cm}^6 \text{ s}^{-1}$	2.03×10^{-34}	This study
SR109	2[Cu ²⁺ (GS)(GSH)] + O ₂ → 2[Cu ²⁺ (GS)(GS)] + H ₂ O ₂	$2.00 \times 10^{-41} - 2.00 \times 10^{-37} \text{ cm}^6 \text{ s}^{-1}$	2.21×10^{-39}	This study
SR110	[Cu ²⁺ (GS)(GS)] → Cu(II) + GSSG	$2.00 \times 10^{-4} \text{ s}^{-1}$		This study
SR111	ROOH → RO [•] + [•] OH	$[1.50 \times 10^{-3} \text{ s}^{-1}]$		Campbell et al. (2023)
SR112	[•] OH + ROOH → ROH + HO ₂	$[5.48 \times 10^{-16}]$		Campbell et al. (2023)
SR113	RO [•] → R + product	$[1.00 \times 10^5 \text{ s}^{-1}]$		Wei et al. (2022)
SR114	R + O ₂ → RO ₂	$[7.64 \times 10^{-12}]$		Chevallier et al. (2004)
SR115	AA + RO [•] → AA [•] + ROH	$[2.66 \times 10^{-12}]$		Buettner and Jurkiewicz (1996)
SR116	Fe(II) + ROOH → Fe(III) + RO [•] + OH [–]	$[6.64 \times 10^{-17}]$		Campbell et al. (2023)
SR117	Fe(II) + ROOH → Fe(III) + [•] OH + RO [–]	$[7.31 \times 10^{-18}]$		Campbell et al. (2023)
SR118	DTT + RO [•] → DTT [•] + ROH	$[2.66 \times 10^{-12}]$		Assumed to be the same as 115
SR119	Org + [•] OH → H ₂ O + R	$[1.66 \times 10^{-13}]$		Campbell et al. (2023)
SR120	Org + RO [•] → ROH + R	$[1.33 \times 10^{-16}]$		Walling (1967)
SR121	ROOH + RO [•] → ROH + RO ₂	$[5.48 \times 10^{-16}]$		Assumed to be the same as 112
SR122	R + R → product	$[2.00 \times 10^{-14}]$		Wei et al. (2022)
SR123	RO [•] + RO [•] → ROOR	$[2.32 \times 10^{-12}]$		Walling (1967)
SR124	RO ₂ + RO ₂ → RO [•] + RO [•] + O ₂	$[2.16 \times 10^{-13}]$		Mouchel-Vallon et al. (2017)
SR125	RO ₂ + RO ₂ → carbonyl + carbonyl + H ₂ O ₂	$[4.98 \times 10^{-14}]$		Mouchel-Vallon et al. (2017)
SR126	Fe(II) + ROOR → Fe(III) + RO [•] + RO [–]	$[5.00 \times 10^{-23}]$		Wei et al. (2022)
SR127	RO ₂ + O ₂ [–] (+ H ⁺) → ROOH + O ₂	$[7.97 \times 10^{-14}]$		Mouchel-Vallon et al. (2017)
SR128	RO [•] + O ₂ → carbonyl + O ₂ [–]	$[9.96 \times 10^{-15}]$		Wei et al. (2022)
SR129	RO ₂ + AA → ROOH + AA [•]	$[2.49 \times 10^{-15}]$		Buettner and Jurkiewicz (1996)
SR130	RO ₂ + DTT → ROOH + DTT [•]	$[1.74 \times 10^{-16}]$		Neta et al. (1990)
SR131	RO ₂ → O ₂ [–] + carbonyl	$[10 \text{ s}^{-1}]$		Chevallier et al. (2004)
SR132	spin-trap + RO [•] → spin-trap-RO	$[2.11 \times 10^{-18}]$		Sueishi et al. (2014)
SR133	spin-trap + [•] OH → spin-trap-OH	$[1.66 \times 10^{-12}]$		Halliwell and Gutteridge (2015)
SR134	spin-trap + O ₂ [–] → spin-trap-O ₂ [–]	$[1.99 \times 10^{-21}]$		Halliwell and Gutteridge (2015)
SR135	spin-trap + R → spin-trap-R	$[3.98 \times 10^{-15}]$		Kemp (1999)

Table S2. Environmental input parameters for the different laboratory experiments

Experiment number	Temperature (K)	Citric acid (μ M)	AA (μ M)	UAH (μ M)	GSH (μ M)	DTT (μ M)	Benzoate (mM)	Reference
1 – 10 (Fig. 3A, B)	298	300	200	100	100	0	0	Charrier et al. (2014)
11 – 12 (Fig. 3C)	298	300	200	100	100	0	10	Charrier and Anastasio (2015)
13 – 15 (Fig. 4A)	310	0	200	0	0	0	0	Expósito et al. (2024)
16 – 17 (Fig. 4B)	310	0	200	0	0	0	0	Shen et al. (2021)
18 – 21, 26 – 29 (Fig. 5A, D)	310	0	0	0	0	100	0	Charrier and Anastasio (2012)
22 – 23 (Fig. 5A, B)	310	0	0	0	0	50	0	Expósito et al. (2024)
24 – 25, 30 – 32 (Fig. 5C, E)	310	0	0	0	0	100	0	Xiong et al. (2017)

Table S3. Field data measurement for Grenoble site. Based on solubility measurements, the total Cu, Fe, and Mn concentrations were multiplied by 0.61, 0.017 and 0.54, respectively as input for the kinetic model. The metals are initialized as Cu(II), Fe(II), and Mn(II). SOA was determined using source apportionment outputs.

Date	1,4-NQN	1,2-NQN	9,10-PQN	Cu	Mn	Fe	Org	SOA	OP ^{DTT}	OP ^{AA}	PM10
	ng/m ³	ng/m ³	ng/m ³	ng/m ³	ng/m ³	ng/m ³	μg/m ³	μg/m ³	nmol/min/m ³	nmol/min/m ³	μg/m ³
1/2/2013	1.15E-03	6.52E-04	4.65E-04	4.76	1.55	104.99	6.33	0.17	1.26	1.63	10.94
1/5/2013	7.90E-03	7.55E-03	9.62E-03	16.69	21.19	492.40	14.87	0.67	3.68	4.81	27.19
1/8/2013	8.20E-03	6.64E-04	9.62E-03	24.60	23.62	669.13	18.77	0.94	5.55	5.51	38.17
1/11/2013	6.25E-03	1.73E-02	4.70E-04	12.57	7.93	246.16	11.12	1.10	3.05	3.66	18.33
1/14/2013	3.11E-03	6.59E-04	3.72E-04	4.64	3.11	163.72	6.38	0.28	1.34	1.28	16.51
1/17/2013	1.43E-02	1.27E-02	8.57E-03	19.04	16.30	665.03	14.60	0.76	4.61	2.26	43.81
1/20/2013	6.79E-03	9.03E-03	1.45E-02	5.00	4.08	146.46	9.84	1.06	2.13	2.11	20.88
1/23/2013	7.22E-03	6.58E-04	9.33E-02	27.69	20.62	612.05	20.50	1.09	6.42	7.23	36.35
1/26/2013	3.20E-02	6.65E-04	1.33E-01	30.80	9.80	427.00	20.93	3.37	7.85	6.24	44.07
1/29/2013	6.48E-03	5.53E-02	1.81E-03	33.10	12.14	631.00	16.66	0.55	5.41	5.99	30.50
2/1/2013	8.72E-03	1.36E-02	3.36E-02	29.72	26.84	763.87	20.57	1.30	5.81	6.23	31.70
2/4/2013	3.36E-03	6.67E-04	2.07E-03	13.69	5.13	257.12	13.05	0.43	3.83	3.95	23.98
2/7/2013	3.11E-03	6.62E-04	4.72E-04	5.62	2.43	107.39	3.83	0.13	1.52	0.90	9.72
2/10/2013	9.98E-03	6.65E-04	1.81E-01	5.69	3.37	164.51	12.27	2.31	2.90	2.51	20.96
2/13/2013	7.64E-03	1.03E-02	5.27E-03	4.47	3.39	113.52	12.49	1.06	3.46	1.59	31.57
2/16/2013	8.24E-03	6.64E-04	5.46E-02	16.87	13.74	415.06	18.89	1.21	4.72	4.61	32.93
2/19/2013	1.49E-02	6.68E-04	1.44E-01	24.46	16.26	557.67	20.70	1.73	6.18	5.07	38.90
2/22/2013	7.71E-03	6.63E-04	1.44E-02	8.82	7.91	256.76	10.47	0.84	3.81	1.67	36.47
2/25/2013	1.26E-02	6.67E-04	8.56E-03	9.32	6.96	225.89	18.19	2.06	4.04	2.11	49.69
2/28/2013	2.76E-02	6.60E-04	2.01E-01	50.33	24.70	745.89	30.14	1.83	11.40	6.76	72.24
3/3/2013	1.04E-02	1.43E-02	3.82E-02	16.84	9.32	461.91	23.19	1.70	7.18	4.29	60.19
3/6/2013	6.08E-03	6.44E-04	2.25E-03	23.01	12.23	588.70	14.93	0.36	3.04	3.63	34.00
3/9/2013	5.95E-03	6.52E-04	1.47E-02	12.59	10.88	301.49	11.58	0.91	2.11	2.58	27.00
3/12/2013	3.39E-03	6.52E-04	1.62E-04	7.87	3.48	182.10	5.03	0.44	1.77	1.16	9.85
3/15/2013	4.46E-03	7.14E-03	4.70E-04	7.20	5.01	222.44	5.91	0.26	2.45	0.81	18.85
3/18/2013	6.33E-03	1.12E-02	1.52E-03	26.41	5.32	230.79	7.12	0.61	2.85	2.81	16.71
3/21/2013	3.81E-03	6.52E-04	1.89E-03	23.39	10.97	367.35	7.84	0.31	2.96	2.65	14.61
3/24/2013	1.22E-02	1.04E-02	3.05E-02	7.69	5.04	199.45	12.42	0.24	4.04	0.93	42.18
3/27/2013	7.49E-03	6.52E-04	1.51E-02	17.14	8.80	500.76	13.03	0.68	4.95	1.76	32.76
3/30/2013	3.28E-03	1.16E-02	6.22E-03	5.34	6.07	150.39	6.10	0.27	1.80	1.22	10.52
4/3/2013	3.63E-03	7.61E-03	2.01E-03	13.21	7.32	340.34	11.35	0.76	3.74	1.44	33.59
4/5/2013	4.60E-03	6.52E-04	1.34E-02	12.31	9.11	343.78	11.62	0.87	4.78	1.63	46.21
4/8/2013	6.98E-03	6.52E-04	1.22E-02	14.81	7.24	418.06	12.54	0.86	4.77	1.92	39.24
4/11/2013	2.20E-03	6.52E-04	4.58E-04	6.71	11.71	249.43	6.91	0.40	1.63	0.91	12.25
4/14/2013	4.54E-03	6.52E-04	1.32E-04	9.18	3.81	244.23	8.91	0.71	1.85	1.01	15.12
4/17/2013	2.34E-03	9.13E-03	4.54E-04	16.89	12.49	603.94	13.08	0.19	3.71	1.51	27.77

Table S4. Continued

Date	1,4-NQN	1,2-NQN	9,10-PQN	Cu	Mn	Fe	Org	SOA	OP ^{DTT}	OP ^{AA}	PM10
	ng/m ³	ng/m ³	ng/m ³	ng/m ³	ng/m ³	ng/m ³	μg/m ³	μg/m ³	nmol/min/m ³	nmol/min/m ³	μg/m ³
4/20/2013	3.38E-03	6.52E-04	4.66E-04	2.45	1.15	62.39	2.98	0.99	0.75	0.47	6.00
4/23/2013	5.01E-03	6.47E-03	4.58E-04	11.54	7.45	347.74	9.27	0.25	3.12	0.98	20.88
4/26/2013	2.54E-03	6.73E-03	1.87E-04	154.91	11.96	728.23	8.70	0.26	5.38	13.94	30.36
4/29/2013	6.68E-03	1.65E-02	4.63E-04	12.37	4.77	223.06	9.11	0.49	3.23	1.66	20.32
5/2/2013	1.92E-03	5.97E-03	1.29E-04	9.61	14.05	775.15	7.82	0.12	2.64	1.21	28.93
5/5/2013	1.24E-03	6.52E-04	4.61E-04	6.86	5.40	273.06	8.58	0.56	2.45	0.82	19.11
5/8/2013	1.67E-03	6.52E-04	4.49E-04	7.27	6.01	255.41	9.65	1.90	2.19	1.02	16.80
5/11/2013	1.83E-03	6.52E-04	4.74E-04	4.19	2.10	99.02	4.22	0.28	1.30	0.49	10.44
5/14/2013	6.33E-04	8.97E-03	4.50E-04	17.05	6.19	330.11	12.08	0.19	4.11	2.09	20.88
5/17/2013	1.02E-03	6.52E-04	4.57E-04	6.29	3.76	168.95	4.09	0.56	0.57	0.57	9.00
5/20/2013	8.95E-04	6.52E-04	4.54E-04	5.01	2.04	120.39	6.52	0.19	1.27	0.65	10.57
5/23/2013	2.18E-03	1.07E-02	4.58E-04	5.39	3.52	160.40	8.26	0.21	1.72	0.62	13.39
5/26/2013	2.33E-03	1.50E-03	4.61E-04	3.51	2.98	223.40	5.15	0.46	1.32	0.78	9.64
5/29/2013	1.31E-03	1.13E-02	1.46E-04	5.48	4.63	141.52	4.08	0.70	0.63	0.52	6.00
6/1/2013	1.32E-03	3.89E-02	4.60E-04	89.38	12.16	164.61	6.55	0.00	2.04	9.63	29.83
6/4/2013	9.96E-04	6.52E-04	4.52E-04	9.57	8.04	323.48	7.61	0.15	2.28	1.04	15.71
6/7/2013	1.16E-03	3.15E-02	1.16E-04	11.54	6.28	327.95	9.62	0.82	2.28	1.40	18.42
6/10/2013	1.44E-04	6.52E-04	4.53E-04	7.09	5.08	220.69	6.05	1.56	2.93	0.59	11.33
6/13/2013	5.68E-04	2.32E-02	4.53E-04	11.23	10.56	481.76	10.92	0.56	4.04	0.82	22.33
6/16/2013	1.31E-03	6.52E-04	4.49E-04	7.71	4.56	271.03	10.39	1.95	2.30	0.82	18.90
6/19/2013	1.34E-03	6.52E-04	4.47E-04	14.99	14.60	680.49	11.63	0.02	4.94	0.94	33.68
6/22/2013	4.06E-03	6.52E-04	4.48E-04	4.98	2.53	136.30	4.71	0.39	1.38	0.47	9.31
6/25/2013	7.66E-06	6.52E-04	4.56E-04	5.90	4.55	199.65	5.23	0.38	1.86	0.47	13.64
6/28/2013	4.56E-04	8.02E-03	4.56E-04	10.05	7.35	305.09	6.77	1.42	4.00	0.78	15.72
7/1/2013	2.99E-04	6.52E-04	3.02E-05	9.57	4.88	223.17	8.33	2.42	2.13	1.08	14.74
7/4/2013	7.63E-06	6.52E-04	4.54E-04	4.71	4.37	147.47	5.29	1.47	1.01	0.46	9.61
7/7/2013	2.32E-04	6.52E-04	4.46E-04	7.09	4.59	201.07	10.81	3.71	1.89	0.72	17.14
7/10/2013	7.73E-04	8.74E-02	4.50E-04	10.05	9.20	257.76	9.06	2.15	2.24	1.23	14.71
7/13/2013	3.74E-04	3.44E-02	4.53E-04	15.93	6.66	306.96	12.20	4.64	2.80	1.92	21.22
7/16/2013	2.42E-03	6.52E-04	4.46E-04	11.02	9.38	415.58	11.25	4.02	2.66	1.20	22.75
7/19/2013	5.15E-04	8.60E-03	4.55E-04	9.76	6.17	217.82	8.92	1.66	1.86	0.98	13.56
7/22/2013	7.57E-06	6.52E-04	4.51E-04	9.40	5.10	255.92	11.55	2.93	2.51	0.81	17.88
7/25/2013	3.40E-04	6.52E-04	4.46E-04	12.74	8.73	360.71	11.41	4.26	3.23	1.24	21.61
7/28/2013	7.47E-06	1.56E-02	4.45E-04	6.14	10.64	501.03	7.78	1.10	1.62	0.36	21.49
7/31/2013	2.61E-04	6.52E-04	4.45E-04	11.94	7.20	258.73	7.09	1.97	2.12	1.14	12.95
8/3/2013	9.41E-04	7.33E-03	4.46E-04	9.45	5.69	312.37	9.20	1.67	2.24	0.84	16.76
8/6/2013	5.14E-04	6.52E-04	4.44E-04	12.30	8.51	458.05	9.83	3.33	3.10	1.05	23.34
8/9/2013	2.40E-04	6.52E-04	4.54E-04	5.54	2.32	130.61	5.61	2.08	1.46	0.43	10.10
8/12/2013	3.96E-04	5.96E-03	4.46E-04	8.94	3.74	220.11	6.42	1.96	1.71	0.90	11.90
8/15/2013	2.39E-03	2.68E-02	2.86E-05	7.75	4.45	215.97	8.56	2.71	2.03	0.91	15.38
8/18/2013	9.23E-04	5.15E-02	4.46E-04	21.28	3.47	193.62	9.80	3.97	3.16	2.53	16.41

Table S5. Continued

Date	1,4-NQN	1,2-NQN	9,10-PQN	Cu	Mn	Fe	Org	SOA	OP ^{DTT}	OP ^{AA}	PM10
	ng/m ³	ng/m ³	ng/m ³	ng/m ³	ng/m ³	ng/m ³	μg/m ³	μg/m ³	nmol/min/m ³	nmol/min/m ³	μg/m ³
8/21/2013	9.66E-04	6.52E-04	4.54E-04	18.63	6.10	278.15	7.09	3.44	2.88	2.27	14.53
8/24/2013	2.72E-04	6.39E-04	4.56E-04	8.85	4.14	218.05	7.32	2.72	1.78	0.95	14.01
8/27/2013	6.51E-04	6.43E-04	3.85E-04	9.90	4.22	208.92	4.86	1.68	1.78	1.04	10.31
8/30/2013	1.04E-03	6.31E-04	3.92E-04	12.89	10.28	337.62	8.50	3.44	2.76	1.39	18.55
9/2/2013	3.54E-04	6.35E-04	4.53E-04	9.57	6.36	276.60	5.44	0.93	2.52	1.30	15.19
9/5/2013	5.44E-03	6.26E-04	1.51E-03	87.90	12.05	594.62	10.59	3.81	5.94	9.04	23.77
9/8/2013	7.65E-06	6.37E-04	4.55E-04	21.98	11.30	425.65	9.57	0.47	0.67	0.34	9.00
9/11/2013	7.45E-04	6.44E-04	4.60E-04	6.90	4.23	185.81	3.73	0.84	1.05	0.57	11.00
9/14/2013	1.71E-03	6.37E-04	9.29E-04	10.27	4.66	245.15	5.30	1.14	1.95	1.31	9.29
9/17/2013	2.36E-03	6.59E-04	4.62E-04	7.80	3.50	185.15	3.12	0.32	1.31	0.91	9.33
9/20/2013	7.37E-04	4.18E-03	4.52E-04	8.52	4.90	240.33	3.50	0.18	2.27	0.98	8.06
9/23/2013	2.23E-03	6.34E-04	4.53E-04	33.39	13.89	697.07	10.13	2.49	2.80	1.54	25.00
9/26/2013	7.22E-03	1.56E-02	5.58E-03	18.07	13.38	547.86	9.69	0.69	5.29	5.42	37.00
9/29/2013	1.87E-03	6.37E-04	4.55E-04	9.98	4.40	263.65	6.73	0.47	2.33	1.53	13.24
10/2/2013	1.94E-03	6.36E-04	4.54E-04	18.73	18.51	499.49	8.32	0.19	2.88	1.47	16.03
10/5/2013	1.10E-03	6.40E-04	4.57E-04	5.92	2.41	129.81	3.84	0.30	0.56	0.36	6.00
10/8/2013	1.99E-03	6.39E-04	2.59E-04	6.50	2.07	143.41	3.29	0.43	1.53	0.78	21.00
10/11/2013	1.25E-03	6.47E-04	4.62E-04	29.92	8.12	361.41	7.46	0.16	3.12	2.43	15.45
10/14/2013	2.75E-03	1.57E-02	1.30E-03	20.96	7.36	416.78	9.91	0.25	2.83	2.64	15.57
10/17/2013	1.70E-03	6.94E-04	4.96E-04	14.11	10.14	326.22	5.87	0.28	1.79	1.08	11.00
10/20/2013	2.45E-03	6.46E-04	1.37E-03	8.49	3.92	241.78	7.12	0.13	1.73	0.78	11.87
10/23/2013	1.92E-03	3.91E-02	5.09E-03	8.68	9.62	333.02	4.08	0.28	1.57	0.49	11.66
10/26/2013	3.38E-03	6.48E-04	5.18E-03	24.09	25.96	618.78	9.20	0.14	3.47	1.78	22.00
10/29/2013	1.59E-03	6.43E-04	2.21E-03	9.70	7.20	221.41	3.09	0.38	1.15	0.81	8.00
11/1/2013	4.94E-03	6.47E-04	2.43E-02	26.92	12.40	567.66	11.61	0.25	4.12	3.09	22.01
11/4/2013	2.19E-03	6.52E-04	3.10E-02	7.53	3.74	190.63	5.72	0.40	1.40	1.72	8.70
11/7/2013	4.97E-03	4.15E-02	1.04E-02	37.48	10.43	662.97	9.35	0.26	3.62	3.96	17.38
11/13/2013	3.33E-02	6.52E-04	5.73E-05	44.28	19.02	752.37	16.33	0.00	4.61	2.89	34.83
11/16/2013	1.59E-02	6.52E-04	3.39E-02	15.39	14.29	395.20	10.77	1.06	3.21	1.41	26.94
11/19/2013	3.27E-03	6.52E-04	2.37E-03	8.42	4.98	191.44	7.47	0.00	2.05	0.91	14.12
11/22/2013	9.24E-03	6.52E-04	5.62E-03	3.88	1.60	91.13	4.08	0.55	1.46	1.63	7.74
11/28/2013	2.99E-02	6.52E-04	4.79E-04	25.87	29.94	615.46	16.47	0.00	2.90	1.72	39.74
12/1/2013	1.12E-02	6.52E-04	1.93E-03	8.82	5.78	240.97	10.95	0.23	2.28	1.74	25.13
12/4/2013	1.36E-02	1.88E-03	7.88E-02	46.20	23.94	939.80	23.52	1.38	6.83	5.88	41.01
12/7/2013	1.27E-02	6.52E-04	1.83E-01	19.14	11.15	439.25	13.47	4.24	2.86	3.01	25.74
12/10/2013	4.07E-02	4.27E-03	1.26E-01	169.70	40.43	1259.02	27.35	8.83	10.34	16.19	48.12
12/13/2013	3.36E-02	1.53E-02	3.79E-01	58.03	41.92	1375.40	31.27	16.64	8.21	8.48	53.94
12/16/2013	3.82E-02	4.52E-02	1.75E-01	63.07	25.99	1502.18	31.51	11.58	9.74	8.34	57.40
12/19/2013	1.64E-02	6.52E-04	2.11E-02	9.75	16.85	254.15	6.77	1.22	1.76	1.37	12.61
12/22/2013	1.58E-02	6.52E-04	5.58E-02	6.36	7.41	134.25	6.03	0.02	1.42	1.78	11.56
12/25/2013	4.58E-03	6.52E-04	4.59E-04	1.51	1.77	30.54	3.94	0.59	0.67	0.26	7.40
12/31/2013	1.91E-02	6.52E-04	1.71E-01	30.28	7.11	584.12	13.77	3.27	4.11	4.13	22.32

Table S6. Field data measurement for Paris site. Based on solubility measurements, the total Cu, Fe, and Mn concentrations were multiplied by 0.77, 0.061 and 0.95, respectively as input for the kinetic model. The metals are initialized as Cu(II), Fe(II), and Mn(II). SOA was determined using source apportionment outputs.

Date	1,4-NQN	1,2-NQN	9,10-PQN	Cu	Mn	Fe	Org	SOA	OP ^{DTT}	OP ^{AA}	PM10
	ng/m ³	ng/m ³	ng/m ³	ng/m ³	ng/m ³	ng/m ³	μg/m ³	μg/m ³	nmol/min/m ³	nmol/min/m ³	μg/m ³
06/03/2015 15:00:00	0.22	0.19	0.37	10.54	0.62	217.40	7.22	2.37	2.02	1.57	30.62
06/03/2015 19:00:00	0.21	0.00	0.45	9.46	14.00	318.92	9.98	9.81	2.83	3.95	32.49
06/03/2015 23:00:00	0.14	0.41	0.52	2.12	6.93	104.99	8.16	3.43	1.74	2.63	32.15
07/03/2015 03:00:00	0.26	0.25	0.92	4.39	9.74	187.13	9.82	7.15	2.89	3.11	34.23
07/03/2015 07:00:00	0.16	0.00	0.46	8.10	2.95	143.99	10.39	4.57	3.91	2.29	35.98
07/03/2015 11:00:00	0.17	0.08	0.35	4.47	6.03	119.92	8.43	1.89	1.90	0.57	23.72
07/03/2015 15:00:00	0.24	0.21	0.37	6.38	8.99	210.31	12.39	6.30	2.72	1.46	26.61
07/03/2015 19:00:00	0.23	0.31	0.47	8.65	6.52	164.30	23.35	7.13	3.36	3.61	30.26
07/03/2015 23:00:00	0.15	0.38	0.55	12.49	13.23	279.13	17.59	6.43	3.91	2.99	33.22
08/03/2015 03:00:00	0.20	0.53	0.59	5.23	16.03	227.84	14.55	5.78	1.92	2.45	32.93
08/03/2015 07:00:00	0.23	0.53	0.41	9.29	12.08	201.23	11.44	3.33	1.09	0.75	27.55
08/03/2015 11:00:00	0.26	0.14	0.34	12.48	7.99	244.09	7.51	0.94	0.85	1.34	18.37
08/03/2015 15:00:00	0.21	0.16	0.33	9.05	8.54	258.30	8.70	0.91	1.28	1.20	12.30
08/03/2015 19:00:00	0.11	0.26	0.37	10.92	8.90	313.76	13.38	2.04	2.46	1.11	29.09
08/03/2015 23:00:00	0.04	0.00	0.34	5.05	3.95	168.93	2.25	0.51	0.83	0.65	14.84
09/03/2015 03:00:00	0.04	0.01	0.34	7.16	5.60	219.54	2.17	0.77	1.08	0.80	12.58
09/03/2015 07:00:00	0.03	0.00	0.34	8.61	6.12	289.01	4.67	2.16	2.10	1.06	21.81
09/03/2015 11:00:00	0.12	0.00	0.34	9.16	6.88	334.03	6.24	1.23	2.45	0.22	27.21
09/03/2015 15:00:00	0.10	0.19	0.37	11.80	9.51	345.43	8.33	1.96	1.80	2.05	25.76
09/03/2015 19:00:00	0.04	0.04	0.39	7.46	7.97	271.65	8.45	2.74	2.75	2.29	30.86
09/03/2015 23:00:00	0.07	0.15	0.58	6.13	6.69	268.96	9.38	4.55	1.07	3.00	34.35
10/03/2015 03:00:00	0.04	0.00	0.59	8.26	6.29	266.37	12.67	4.28	3.11	3.54	37.30
10/03/2015 07:00:00	0.05	0.00	0.42	17.06	9.20	462.00	11.35	4.88	3.86	2.87	38.79
10/03/2015 11:00:00	0.02	0.00	0.34	10.42	8.01	347.54	7.28	0.69	2.44	1.73	33.25
10/03/2015 15:00:00	0.02	0.00	0.35	22.02	16.38	600.34	8.29	1.49	3.35	2.21	24.16
10/03/2015 19:00:00	0.03	0.00	0.37	48.52	24.64	1087.24	13.66	2.39	6.13	5.91	35.05
10/03/2015 23:00:00	0.04	0.04	0.74	11.73	18.77	545.84	8.27	3.63	4.18	2.08	35.16
11/03/2015 03:00:00	0.04	0.00	0.89	15.60	20.41	609.16	7.96	5.24	2.60	2.15	37.24
11/03/2015 07:00:00	0.03	0.00	0.42	24.26	21.04	842.97	11.95	3.28	5.29	2.42	53.79
11/03/2015 11:00:00	0.09	0.00	0.35	9.00	15.85	466.22	6.41	2.79	2.43	1.77	53.89
11/03/2015 15:00:00	0.04	0.00	0.33	22.89	24.79	750.05	11.18	2.99	4.71	1.94	48.75
11/03/2015 19:00:00	0.07	0.00	0.39	22.66	20.95	723.48	12.31	5.75	5.84	4.14	51.67
11/03/2015 23:00:00	0.07	0.14	0.45	10.83	21.60	449.98	9.41	3.65	3.96	2.71	41.52
12/03/2015 03:00:00	0.08	0.00	0.57	15.33	20.50	611.86	9.78	3.92	3.02	2.91	30.12
12/03/2015 07:00:00	0.08	0.00	0.43	19.50	24.11	675.57	11.22	2.44	3.95	2.46	33.22
12/03/2015 11:00:00	0.07	0.00	0.34	9.36	17.14	403.50	7.63	1.39	2.54	1.53	24.45
12/03/2015 15:00:00	0.14	0.00	0.35	10.30	17.45	412.96	6.12	1.93	2.05	1.24	24.48

Table S7. Continued

Date	1,4-NQN	1,2-NQN	9,10-PQN	Cu	Mn	Fe	Org	SOA	OP ^{DTT}	OP ^{AA}	PM10
	ng/m ³	ng/m ³	ng/m ³	ng/m ³	ng/m ³	ng/m ³	μg/m ³	μg/m ³	nmol/min/m ³	nmol/min/m ³	μg/m ³
12/03/2015 19:00:00	0.11	0.00	0.37	10.42	18.69	432.01	7.90	2.33	2.50	1.74	24.90
12/03/2015 23:00:00	0.29	0.08	0.50	6.71	8.30	288.74	6.33	3.13	1.73	1.16	21.41
13/03/2015 03:00:00	0.13	0.00	0.51	8.10	9.94	349.97	6.98	2.93	2.31	1.15	25.83
13/03/2015 07:00:00	0.11	0.00	0.42	22.17	16.99	737.17	11.43	3.46	4.87	2.38	36.75
13/03/2015 11:00:00	0.16	0.00	0.36	13.80	12.67	533.46	8.78	2.91	3.98	1.25	37.27
13/03/2015 15:00:00	0.14	0.00	0.36	13.66	11.49	516.52	7.86	3.14	3.40	1.45	31.57
13/03/2015 19:00:00	0.17	0.00	0.53	27.37	15.98	840.54	14.14	9.39	5.88	3.83	37.61
13/03/2015 23:00:00	0.15	0.00	1.20	17.47	13.33	567.06	15.98	13.82	5.65	2.93	46.38
14/03/2015 03:00:00	0.07	0.00	1.01	10.88	12.70	422.62	10.12	4.80	2.87	1.32	41.04
14/03/2015 07:00:00	0.15	0.04	0.66	12.05	12.03	450.65	8.71	3.56	3.63	0.94	36.39
14/03/2015 11:00:00	0.14	0.00	0.35	9.99	21.28	957.88	8.85	2.40	1.90	1.09	46.01
14/03/2015 15:00:00	0.08	0.00	0.36	12.40	21.28	963.64	11.18	2.99	5.54	1.22	58.71
14/03/2015 19:00:00	0.13	0.00	0.50	9.80	13.20	462.13	14.54	5.28	3.75	0.73	47.78
14/03/2015 23:00:00	0.07	0.00	0.42	9.18	11.13	345.23	13.21	2.14	5.25	1.20	65.75
15/03/2015 03:00:00	0.07	0.00	0.50	7.48	9.05	303.95	11.93	3.21	3.36	1.89	65.22
15/03/2015 07:00:00	0.15	0.00	0.42	9.24	9.60	351.21	11.46	4.00	4.63	1.78	54.73
15/03/2015 11:00:00	0.18	0.00	0.36	10.63	7.54	334.65	9.75	3.65	5.43	1.68	48.18
15/03/2015 15:00:00	0.16	0.38	0.34	11.08	8.64	381.66	10.15	3.07	2.31	2.36	33.15
15/03/2015 19:00:00	0.06	0.00	0.34	15.03	7.41	338.13	11.66	2.83	2.44	3.54	27.97
15/03/2015 23:00:00	0.08	0.00	0.45	8.96	7.82	268.27	10.67	3.62	1.68	3.58	29.07
16/03/2015 03:00:00	0.05	0.00	0.41	13.98	11.22	442.16	11.44	2.28	2.62	3.67	29.38
16/03/2015 07:00:00	0.17	0.00	0.39	31.25	21.26	992.28	16.57	5.36	5.22	2.89	46.86
16/03/2015 11:00:00	0.11	0.00	0.34	19.29	13.80	606.56	13.90	2.38	4.60	1.70	54.93
16/03/2015 15:00:00	0.47	0.00	0.34	24.43	19.34	1077.52	16.64	4.12	5.18	4.15	54.91
16/03/2015 19:00:00	0.41	0.62	0.39	17.30	14.11	602.94	18.48	7.60	4.34	4.00	59.57
16/03/2015 23:00:00	0.07	0.02	0.47	11.58	12.68	489.62	19.39	6.85	4.44	3.77	70.05
17/03/2015 03:00:00	0.04	0.00	0.46	12.89	14.74	488.04	20.64	6.27	4.55	3.60	75.55
17/03/2015 07:00:00	0.10	0.00	0.46	30.80	24.47	1156.53	22.99	9.18	10.07	3.83	87.09
17/03/2015 11:00:00	0.07	0.00	0.33	20.87	15.65	730.31	12.33	1.59	4.49	1.94	37.95
17/03/2015 15:00:00	0.16	0.00	0.34	40.50	24.39	1323.60	17.41	2.59	7.79	2.91	52.34
17/03/2015 19:00:00	0.28	0.64	0.40	36.47	18.03	1067.22	21.37	6.93	7.71	4.19	61.57
17/03/2015 23:00:00	0.11	0.11	0.57	19.02	15.45	681.70	20.44	7.21	7.63	4.15	63.50
18/03/2015 03:00:00	0.15	0.32	0.48	19.37	19.79	744.07	20.46	8.94	6.91	3.94	70.33
18/03/2015 07:00:00	0.04	0.00	0.37	28.62	28.24	1254.23	25.10	6.47	13.69	4.83	113.18
18/03/2015 11:00:00	0.04	0.00	0.34	21.52	24.02	1007.76	21.39	4.93	11.08	2.60	108.70
18/03/2015 15:00:00	0.23	0.00	0.35	19.01	23.72	947.83	19.51	5.54	8.76	2.72	113.10
18/03/2015 19:00:00	0.04	0.00	0.35	13.07	15.09	549.47	16.14	2.60	5.93	4.83	104.96
18/03/2015 23:00:00	0.14	0.00	0.37	7.87	8.14	302.61	9.44	2.62	3.55	2.30	59.77

Table S8. Continued

Date	1,4-NQN	1,2-NQN	9,10-PQN	Cu	Mn	Fe	Org	SOA	OP ^{DTT}	OP ^{AA}	PM10
	ng/m ³	ng/m ³	ng/m ³	ng/m ³	ng/m ³	ng/m ³	μg/m ³	μg/m ³	nmol/min/m ³	nmol/min/m ³	μg/m ³
19/03/2015 03:00:00	0.11	0.00	0.35	6.36	8.51	278.36	8.02	1.75	2.76	2.18	56.41
19/03/2015 07:00:00	0.12	0.00	0.34	14.02	15.36	733.30	10.56	0.88	3.76	1.43	56.58
19/03/2015 11:00:00	0.04	0.00	0.34	9.31	18.49	844.69	9.92	2.03	5.99	2.78	45.95
19/03/2015 15:00:00	0.06	0.00	0.34	13.28	11.11	493.02	9.27	1.02	2.03	0.39	37.10
19/03/2015 19:00:00	0.12	0.00	0.35	11.53	9.59	404.57	11.09	2.34	4.49	2.39	42.57
19/03/2015 23:00:00	0.10	0.00	0.38	8.26	10.49	394.09	12.10	2.78	4.56	1.12	76.78
20/03/2015 03:00:00	0.05	0.07	0.34	14.37	13.00	504.11	12.55	2.05	10.12	3.28	89.66
20/03/2015 07:00:00	0.03	0.00	0.35	23.03	22.22	1057.58	17.72	1.55	11.98	2.92	111.29
20/03/2015 11:00:00	0.12	0.00	0.35	22.75	22.40	1032.53	23.25	2.45	11.53	2.27	121.51
20/03/2015 15:00:00	0.06	0.00	0.34	23.38	22.55	1037.96	19.89	3.36	14.83	3.37	115.67
20/03/2015 19:00:00	0.05	0.00	0.37	21.74	19.39	892.14	23.80	5.89	15.18	3.96	120.07
20/03/2015 23:00:00	0.05	0.00	0.34	16.64	15.92	668.41	23.16	3.13	13.09	3.60	121.08
21/03/2015 03:00:00	0.03	0.00	0.38	10.14	12.15	419.70	19.04	4.59	11.62	2.02	130.00
21/03/2015 07:00:00	0.05	0.00	0.34	8.12	8.12	303.86	11.82	2.75	7.35	0.84	77.09
21/03/2015 11:00:00	0.11	0.00	0.36	7.04	13.45	330.20	7.77	1.95	6.68	1.33	54.68
21/03/2015 15:00:00	0.04	0.00	0.33	5.04	11.18	259.42	3.49	0.39	1.00	0.48	13.79
21/03/2015 19:00:00	0.04	0.00	0.35	6.27	7.63	203.14	3.80	0.82	1.83	1.09	13.49

Table S9. Field data measurement for London (MY) in the Summer. As soluble fractions of the metals were not measured, we use median values of the soluble metal fraction as determined from field measurement studies ((Connell et al., 2006; Manousakas et al., 2014; Heal et al., 2005; Giorio et al., 2025)). The metals are initialized as Cu(II), Fe(II), and Mn(II). Org was determined using PM composition data.

date	Cu	Mn	Fe	Org	OP ^{DHA}	PM2.5
	$\mu\text{g}/\text{m}^3$	$\mu\text{g}/\text{m}^3$	$\mu\text{g}/\text{m}^3$	$\mu\text{g}/\text{m}^3$	nmol/m^3	$\mu\text{g}/\text{m}^3$
23.05.2023 05:00	0.00146	2.00E-05	0.05924	2.05339	5.84	6.36368
23.05.2023 06:00	0.00209	5.00E-05	0.08393	1.76607	5.48	6.63467
23.05.2023 07:00	0.0082	5.60E-04	0.22657	1.7379	5.84	6.88302
23.05.2023 08:00	0.01431	0.00108	0.36921	1.78526	7.04	6.40472
23.05.2023 20:00	0.00545	3.00E-04	0.21892	6.23438	8.84	10.4316
23.05.2023 21:00	0.00572	2.40E-04	0.21208	6.0377	15.36	8.56321
23.05.2023 22:00	0.00599	1.90E-04	0.20523	4.28657	15.72	7.56863
23.05.2023 23:00	0.00612	1.80E-04	0.23616	3.95701	16.72	8.11297
24.05.2023 00:00	0.00625	1.70E-04	0.26709	3.81611	18.08	7.45566
24.05.2023 01:00	0.00604	4.70E-04	0.26585	2.6935	19.52	6.46462
24.05.2023 02:00	0.00584	7.70E-04	0.2646	3.15452	18.68	8.14387
24.05.2023 03:00	0.00577	7.10E-04	0.23611	4.09349	19.08	8.64929
24.05.2023 04:00	0.0057	6.50E-04	0.20762	4.85919	16.4	9.7842
24.05.2023 05:00	0.00437	5.40E-04	0.18987	4.2674	16.96	10.86085
24.05.2023 06:00	0.00304	4.40E-04	0.17212	3.08327	16.12	10.8184
24.05.2023 07:00	0.00281	6.30E-04	0.17188	2.97031	17	10.25472
24.05.2023 08:00	0.00258	8.30E-04	0.17164	3.29615	12.64	9.93137
24.05.2023 09:00	0.00258	5.30E-04	0.13917	2.79669	4.4	9.43608
24.05.2023 13:00	0.00218	2.30E-04	0.09569	5.14333	5.2	9.73349
26.05.2023 18:00	0.00687	8.40E-04	0.25632	3.86228	5.68	11.6816
31.05.2023 14:00	0.00195	2.00E-05	0.07723	3.11249	12.88	7.6842
31.05.2023 15:00	0.00154	1.00E-05	0.06422	3.05584	5.76	7.94646
03.06.2023 15:00	0.00158	1.00E-05	0.08398	4.29253	7.76	7.02972
03.06.2023 16:00	0.00175	1.00E-05	0.08596	4.62102	4.28	6.95731
04.06.2023 18:00	0.00332	1.00E-04	0.18375	4.68414	6.4	6.8783
04.06.2023 19:00	0.00438	5.70E-04	0.21497	4.89139	9.36	7.61958
04.06.2023 20:00	0.00545	0.00105	0.24618	4.25398	6.64	7.40189
05.06.2023 09:00	0.00604	2.00E-04	0.15008	1.55145	4.04	5.2533
07.06.2023 17:00	0.00615	0.00123	0.2257	4.91407	8.32	10.75236
07.06.2023 18:00	0.00632	9.60E-04	0.23672	5.50042	7.52	11.76651

Table S10. Continued

date	Cu	Mn	Fe	Org	OP ^{DHA}	PM2.5
	$\mu\text{g}/\text{m}^3$	$\mu\text{g}/\text{m}^3$	$\mu\text{g}/\text{m}^3$	$\mu\text{g}/\text{m}^3$	nmol/m^3	$\mu\text{g}/\text{m}^3$
07.06.2023 19:00	0.00584	0.00107	0.25252	5.29289	9.08	11.90802
07.06.2023 20:00	0.00535	0.00118	0.26833	4.86379	9.76	11.64151
07.06.2023 21:00	0.00343	5.90E-04	0.16813	3.39017	10.04	9.31179
08.06.2023 09:00	0.00249	9.00E-05	0.098	2.21778	4.16	8.32689
08.06.2023 11:00	0.00217	1.00E-05	0.08025	3.64314	5.36	8.83962
10.06.2023 17:00	0.00649	0.00171	0.24954	15.23334	6.2	18.83255
10.06.2023 18:00	0.00587	0.0013	0.24805	15.00493	5.96	17.96934
11.06.2023 16:00	0.00892	0.00232	0.33402	15.18721	7.12	20.19104
11.06.2023 17:00	0.00952	0.00629	0.34315	17.84065	4.4	20.61085
11.06.2023 18:00	0.01012	0.01027	0.35228	21.89867	11.44	24.5566
11.06.2023 21:00	0.01267	0.00319	0.46508	19.56444	12.48	28.63679
11.06.2023 22:00	0.0069	0.00227	0.34345	18.61022	13.6	31.67925
11.06.2023 23:00	0.00489	0.00113	0.23958	18.10934	14.2	30.37264
12.06.2023 01:00	0.00528	8.00E-04	0.21436	16.84179	9.04	27.14387
12.06.2023 02:00	0.00767	0.0016	0.29299	19.86018	4.16	28.89387
12.06.2023 08:00	0.01808	0.00328	0.49112	15.44187	8.52	27.44575
12.06.2023 09:00	0.01951	0.0027	0.45669	14.41594	8.52	21.70755
17.06.2023 16:00	0.00698	0.00329	0.26615	11.79703	5.04	16.21462
17.06.2023 17:00	0.00819	0.00348	0.32612	10.84835	5.28	16.1816
17.06.2023 18:00	0.0094	0.00367	0.3861	11.11287	4.56	15.59906
17.06.2023 19:00	0.00843	0.00351	0.36726	11.466	4.28	17.26651
17.06.2023 20:00	0.00746	0.00336	0.34843	11.89539	4.24	21.1533
17.06.2023 21:00	0.00613	0.00249	0.30307	12.10355	4.08	21.16745
20.06.2023 16:00	0.00554	6.10E-04	0.22294	6.25424	4.24	5.78137
20.06.2023 18:00	0.00735	6.10E-04	0.31783	8.65386	5.16	5.81392
20.06.2023 19:00	0.00726	4.60E-04	0.31521	8.80862	6.08	6.01014
20.06.2023 20:00	0.00716	3.20E-04	0.31259	10.37676	5.24	6.42925
20.06.2023 21:00	0.00671	3.60E-04	0.28148	8.76427	5	6.42311
23.06.2023 01:00	0.00534	5.60E-04	0.27103	4.88142	5.76	5.11085
23.06.2023 02:00	0.00461	6.00E-04	0.23803	4.72821	4.72	5.02358
24.06.2023 01:00	0.00482	1.60E-04	0.22619	5.16224	4.36	7.38255
27.06.2023 14:00	0.00659	7.90E-04	0.22216	5.03987	4.32	6.9717
27.06.2023 16:00	0.00816	7.50E-04	0.26471	5.18595	4.36	7.91934
27.06.2023 18:00	0.00723	6.50E-04	0.29629	8.83731	5.52	10.74057
02.07.2023 01:00	0.00448	9.20E-04	0.11277	8.66384	5.48	19.6934
02.07.2023 02:00	0.00393	5.30E-04	0.12182	8.40271	4.44	18.47406
02.07.2023 13:00	0.00448	5.00E-04	0.22417	3.70091	4.44	7.46887
02.07.2023 14:00	0.00395	5.10E-04	0.20924	3.34075	5.52	8.36604
02.07.2023 15:00	0.00341	5.20E-04	0.19431	3.24729	4.2	7.90943
02.07.2023 17:00	0.00239	2.50E-04	0.1989	3.5743	5.96	7.88656
02.07.2023 18:00	0.00378	3.80E-04	0.2097	4.75476	7.04	8.05519
02.07.2023 19:00	0.00518	5.00E-04	0.22049	4.12646	6.48	7.4941

Table S11. Continued

date	Cu	Mn	Fe	Org	OP ^{DHA}	PM2.5
	$\mu\text{g}/\text{m}^3$	$\mu\text{g}/\text{m}^3$	$\mu\text{g}/\text{m}^3$	$\mu\text{g}/\text{m}^3$	nmol/m^3	$\mu\text{g}/\text{m}^3$
02.07.2023 21:00	0.00606	5.00E-04	0.27883	3.21587	4.16	8.42618
04.07.2023 11:00	0.00629	3.30E-04	0.20777	5.72633	5.76	8.375
04.07.2023 12:00	0.00613	0.00167	0.21938	7.69142	9.92	10.06604
04.07.2023 13:00	0.00598	0.00301	0.23099	7.67072	8.28	11.28514
04.07.2023 14:00	0.00668	0.00169	0.23535	8.90546	8.48	12.15802
04.07.2023 15:00	0.00738	3.60E-04	0.23971	8.38157	9.2	11.04953
04.07.2023 16:00	0.00647	2.90E-04	0.21152	7.82144	7.16	9.97406
04.07.2023 17:00	0.00556	2.20E-04	0.18333	8.37361	6	10.88208
04.07.2023 18:00	0.00685	0.00131	0.31827	11.02169	4.12	9.40047
05.07.2023 01:00	0.00187	4.00E-05	0.0822	3.16805	4.48	5.5158
05.07.2023 02:00	0.00219	2.00E-05	0.08787	2.6562	6.6	5.73774
13.07.2023 15:00	0.0048	2.60E-04	0.17916	1.72116	6.36	6.33396
13.07.2023 16:00	0.00655	6.20E-04	0.24277	1.80411	4.24	6.48278
13.07.2023 17:00	0.0083	9.90E-04	0.30637	1.80486	4.04	5.82524
15.07.2023 18:00	0.0038	6.00E-05	0.13358	1.30839	4.68	11.1533
15.07.2023 19:00	0.00351	9.00E-05	0.13199	1.61196	6.44	13.12972
16.07.2023 17:00	0.0058	6.00E-05	0.17716	1.49688	5.96	5.75896
16.07.2023 18:00	0.00509	2.40E-04	0.17431	1.64284	5.08	7.08679
16.07.2023 19:00	0.00438	4.30E-04	0.17145	1.51388	10.96	7.25991
16.07.2023 21:00	0.00471	2.20E-04	0.17922	1.69114	5.12	7.36392
16.07.2023 22:00	0.00441	1.40E-04	0.17959	1.11696	5.64	5.91014
16.07.2023 23:00	0.00412	7.00E-05	0.17996	1.08488	5	6.55708
17.07.2023 02:00	0.00247	7.00E-05	0.1029	0.62433	7.04	5.59481
17.07.2023 03:00	0.00276	1.30E-04	0.12748	0.49247	15.68	5.6908
17.07.2023 06:00	0.00707	6.20E-04	0.2633	0.65547	6.48	6.97453
17.07.2023 07:00	0.00835	0.00123	0.31621	0.7043	10.36	6.05755
17.07.2023 08:00	0.00575	8.20E-04	0.25223	0.8174	10.76	5.15165
18.07.2023 17:00	0.00963	0.00105	0.33391	1.17878	5.12	5.61887
18.07.2023 18:00	0.00889	0.00109	0.30192	1.54693	4.8	6.01557
25.07.2023 05:00	0.00828	0.00234	0.47093	0.58967	9.56	5.09552
25.07.2023 06:00	0.00885	0.00286	0.52276	1.04132	8.72	6.89906
25.07.2023 07:00	0.00942	0.00339	0.57459	1.04418	7.44	6.74552
25.07.2023 08:00	0.00618	0.00249	0.4584	0.75678	6.28	5.26958
05.08.2023 02:00	0.00643	4.70E-04	0.23692	1.37928	8.8	7.91274
05.08.2023 03:00	0.00597	3.10E-04	0.19787	1.36016	7.32	8.06462
05.08.2023 04:00	0.00561	4.80E-04	0.17711	1.14999	5.68	8.74057
05.08.2023 05:00	0.00526	6.50E-04	0.15635	0.96636	5.2	9.29858
05.08.2023 06:00	0.0055	4.70E-04	0.15695	1.04361	4.44	10.73821
14.08.2023 10:00	0.00524	3.40E-04	0.15825	1.13802	7.52	6.70448
14.08.2023 18:00	0.00878	0.00128	0.24241	1.32291	17.64	5.03585
14.08.2023 20:00	0.00458	1.20E-04	0.20256	2.45287	19.24	5.72807
15.08.2023 18:00	0.00852	4.20E-04	0.24634	2.32305	15.16	6.48538

Table S12. Continued

date	Cu	Mn	Fe	Org	OP ^{DHA}	PM2.5
	$\mu\text{g}/\text{m}^3$	$\mu\text{g}/\text{m}^3$	$\mu\text{g}/\text{m}^3$	$\mu\text{g}/\text{m}^3$	nmol/m^3	$\mu\text{g}/\text{m}^3$
15.08.2023 20:00	0.00576	4.60E-04	0.21859	3.30527	9.68	7.60684
15.08.2023 22:00	0.00672	0.00196	0.43329	1.87244	10.96	5.86981
16.08.2023 20:00	0.00504	0.00379	0.25237	1.26522	9.88	6.83137
16.08.2023 22:00	0.00349	0.00109	0.21292	1.64547	5.8	9.50448
17.08.2023 13:00	0.00475	2.80E-04	0.16476	0.98544	4.88	5.91958
17.08.2023 14:00	0.00401	3.00E-05	0.14049	1.226	6.88	5.44033
17.08.2023 18:00	0.00663	7.60E-04	0.2608	1.08627	10.52	5.16038
17.08.2023 19:00	0.00562	6.20E-04	0.22449	0.81358	9.32	5.22453
17.08.2023 20:00	0.0046	4.70E-04	0.18818	1.1005	9.08	6.56321
17.08.2023 21:00	0.00385	2.60E-04	0.17093	0.84524	7.64	7.72193
17.08.2023 22:00	0.0031	4.00E-05	0.15367	0.8459	4.44	7.65142
18.08.2023 01:00	0.00211	1.00E-05	0.09726	0.66439	4	8.16486
18.08.2023 16:00	0.00734	0.00184	0.26693	2.34348	16.72	24.82547
18.08.2023 17:00	0.00838	0.00328	0.31657	2.5194	18.16	30.8066
18.08.2023 18:00	0.00942	0.00473	0.36621	2.95657	17.88	34.48585
18.08.2023 19:00	0.00784	0.00339	0.33482	3.51145	15.44	34.37028
18.08.2023 20:00	0.00626	0.00205	0.30343	3.09941	17.64	33.33962
18.08.2023 21:00	0.0062	0.00183	0.28084	3.23171	13.6	32.45519
18.08.2023 22:00	0.00613	0.00161	0.25825	3.03763	8.8	30.07311
19.08.2023 01:00	0.00383	3.80E-04	0.19397	1.66026	4.12	8.13939
19.08.2023 11:00	0.0053	1.70E-04	0.18714	1.08603	4.48	6.61179
19.08.2023 20:00	0.00687	4.50E-04	0.2634	2.17863	5.8	7.83892
19.08.2023 21:00	0.00714	5.10E-04	0.27348	2.24588	10.84	8.14481
19.08.2023 22:00	0.00741	5.60E-04	0.28356	1.48206	10.84	6.67099
20.08.2023 18:00	0.00595	4.20E-04	0.23588	1.6371	11.72	5.22382
20.08.2023 19:00	0.00635	4.70E-04	0.25133	2.49115	11.64	7.22783
20.08.2023 20:00	0.00676	5.20E-04	0.26678	3.11171	9.72	7.62453
20.08.2023 21:00	0.00706	4.60E-04	0.27062	1.91077	10.92	5.82995
20.08.2023 22:00	0.00735	4.10E-04	0.27446	1.48903	8	6.41533
21.08.2023 16:00	0.00609	3.00E-05	0.19136	1.37617	16.12	6.03632
21.08.2023 17:00	0.00603	2.00E-05	0.2144	1.42735	18.44	6.19788
21.08.2023 19:00	0.00501	9.00E-05	0.20903	2.02887	24.44	6.72264
21.08.2023 20:00	0.00406	1.90E-04	0.18061	2.23245	23.88	6.78514
22.08.2023 22:00	0.00884	0.00217	0.43442	1.11544	35.04	5.07193
23.08.2023 03:00	0.00614	6.80E-04	0.12816	0.9027	29.76	7.49222
23.08.2023 04:00	0.0063	0.00123	0.1594	1.1996	34.16	6.1842
23.08.2023 05:00	0.00859	0.00264	0.38608	1.09321	37.04	6.86368
23.08.2023 06:00	0.01087	0.00405	0.61275	1.27363	29.72	7.09528
23.08.2023 07:00	0.01033	0.00377	0.59167	0.96414	29.36	6.81392
23.08.2023 08:00	0.00979	0.00349	0.57058	0.85327	31.64	6.18844
23.08.2023 18:00	0.01218	0.0015	0.40372	1.30181	36.36	5.30212
23.08.2023 19:00	0.01099	0.0015	0.39398	2.46628	21.4	8.90401

Table S13. Continued

date	Cu	Mn	Fe	Org	OP ^{DHA}	PM2.5
	$\mu\text{g}/\text{m}^3$	$\mu\text{g}/\text{m}^3$	$\mu\text{g}/\text{m}^3$	$\mu\text{g}/\text{m}^3$	nmol/m^3	$\mu\text{g}/\text{m}^3$
23.08.2023 20:00	0.0098	0.00151	0.38424	2.71819	16.52	8.50967
23.08.2023 21:00	0.00936	0.00143	0.37245	2.24242	9.36	8.40142
23.08.2023 22:00	0.00892	0.00135	0.36067	2.77582	9.68	8.24788
24.08.2023 01:00	0.00543	2.70E-04	0.21716	1.53002	6.56	5.4783
24.08.2023 02:00	0.00457	5.30E-04	0.1399	1.25349	10.88	5.61156
24.08.2023 03:00	0.00455	5.40E-04	0.13396	1.48768	12.88	7.10047
24.08.2023 04:00	0.00453	5.60E-04	0.12803	1.47078	12.84	6.31321
24.08.2023 05:00	0.00748	0.00152	0.26221	1.35469	14.04	6.28042
24.08.2023 06:00	0.01042	0.00249	0.39638	1.19363	10.4	8.17877
24.08.2023 07:00	0.01118	0.00351	0.44082	1.75288	7.84	9.31344
24.08.2023 09:00	0.01112	0.0046	0.4362	2.04771	5.68	11.69575
24.08.2023 10:00	0.01029	0.00468	0.38714	1.93393	7.68	9.61557
24.08.2023 11:00	0.0096	0.00407	0.39624	1.84664	7.48	8.41321
24.08.2023 13:00	0.00846	0.00201	0.33299	1.85109	10.68	6.98042
24.08.2023 14:00	0.00801	5.60E-04	0.26064	1.72426	13.8	6.19976
24.08.2023 15:00	0.01036	9.50E-04	0.29205	1.78198	15.24	6.63325
24.08.2023 16:00	0.0127	0.00134	0.32346	1.99735	12.12	9.43113
24.08.2023 19:00	0.01181	0.00226	0.46426	2.90776	5.84	9.57854
25.08.2023 19:00	0.00895	0.00106	0.35015	1.63872	35.8	5.42877

Table S14. Soluble fractions of the transition metals as determined from field measurement studies (Connell et al., 2006; Manousakas et al., 2014; Heal et al., 2005; Giorio et al., 2025).

Soluble fraction	Metal	Reference
0.32	Fe	Giorio et al. (2025)
0.11	Fe	Giorio et al. (2025)
0.21	Fe	Giorio et al. (2025)
0.19	Fe	Giorio et al. (2025)
0.42	Fe	Giorio et al. (2025)
0.28	Fe	Giorio et al. (2025)
0.37	Fe	Giorio et al. (2025)
0.29	Fe	Giorio et al. (2025)
0.15	Fe	Giorio et al. (2025)
0.082	Fe	Giorio et al. (2025)
0.142	Fe	Manousakas et al. (2014)
0.11	Fe	Connell et al. (2006)
0.163	Fe	Heal et al. (2005)
0.2975	Cu	Manousakas et al. (2014)
0.44	Cu	Manousakas et al. (2014)
0.51	Cu	Heal et al. (2005)
0.94	Cu	Connell et al. (2006)
0.1596	Mn	Manousakas et al. (2014)
0.45	Mn	Heal et al. (2005)
Median Fe	0.19	This study
Median Cu	0.48	This study
Median Mn	0.30	This study

3 Supplementary Text

35 3.1 H₂O₂ production experiments

In order to reproduce the experimental data of Charrier et al. (2014), in addition to the transition metals and quinones, the model includes 300 μ M of citric acid, 200 μ M ascorbic acid, 100 μ M uric acid and 100 μ M GSH. The final output is calculated by dividing the H₂O₂ concentration at 3600 seconds by 3600, resulting in a production rate of H₂O₂.

3.2 $\cdot$ OH production experiments

- 40 In order to reproduce the experimental data of Charrier and Anastasio (2015), in addition to the transition metals and quinones, the model includes 300 μ M of citric acid, 200 μ M ascorbic acid, 100 μ M uric acid, 100 μ M GSH and 10 mM of Benzoate. The rate of $\cdot$ OH production is calculated by taking the linear slope between 0 and 4 hrs.

3.3 Ascorbic acid experiments

- 45 In order to reproduce the experimental data of Expósito et al. (2024), in addition to the transition metals and quinones, the model includes an initial concentration of 200 μ M ascorbic acid. The simulations are conducted at 310 K.

3.4 DHA production experiments

- In order to reproduce the experimental data of Shen et al. (2021), the model include 200 μ M of ascorbic acid, and varying concentrations of transition metals. These are allowed to react for 20 mins. The simulations are conducted at 310 K. The oxidation of ascorbic acid is determined by quantifying the oxidation product dehydroascorbic acid (DHA) at the end of the 20 mins.
- 50

3.5 DTT experiments with transition metals and quinones

- In order to reproduce the experimental data of Charrier and Anastasio (2012) and Xiong et al. (2017), the model includes an initial DTT concentration of 100 μ M and varying concentrations of transition metals and quinones. The simulations are conducted at 310 K. To reproduce the data of Expósito et al. (2024), the initial DTT concentration is set to 50 μ M, as used in their study. The rate of DTT loss is calculated by taking the linear slope between 0 and 15 mins.
- 55

3.6 DTT experiments with SOA

In order to reproduce the experimental data of Tuet et al. (2017), we follow the experimental protocol from Fang et al. (2015). An initial DTT concentration of 0.1 mM is included in the model. The simulations are conducted at 310 K. The rate of DTT loss was determined by taking the linear slope at 0, 4, 13, 23, 30, and 41 mins.

60 3.7 EPR experiments with SOA

In order to reproduce the experimental data of Tong et al. (2018), we include an initial spin trap concentration of 10 mM, and an SOA concentration between 0 and 4 mM. As the SOA was freshly produced, we assume a low degree of aging, and do the simulations with 10% and 3% peroxide content Wang et al. (2018).

3.8 Relative bias calculation

65 The relative bias of the model is calculated as follows:

$$\frac{1}{N} \sum_{i=1}^N \left(\frac{\text{model}_i - \text{data}_i}{\text{data}_i} \times 100 \right)$$

References

- Buettner, G. R. and Jurkiewicz, B. A.: Catalytic Metals, Ascorbate and Free Radicals: Combinations to Avoid, *Radiation Research*, 145, 532–541, <https://doi.org/10.2307/3579271>, 1996.
- 70 Campbell, S. J., Uttinger, B., Barth, A., Paulson, S. E., and Kalberer, M.: Iron and Copper Alter the Oxidative Potential of Secondary Organic Aerosol: Insights from Online Measurements and Model Development, *Environ. Sci. Technol.*, 57, 13 546–13 558, <https://doi.org/10.1021/acs.est.3c01975>, 2023.
- Charrier, J. G. and Anastasio, C.: On dithiothreitol (DTT) as a measure of oxidative potential for ambient particles: evidence for the importance of soluble transition metals, *Atmos. Chem. Phys.*, 12, 9321–9333, <https://doi.org/10.5194/acp-12-9321-2012>, 2012.
- 75 Charrier, J. G. and Anastasio, C.: Rates of Hydroxyl Radical Production from Transition Metals and Quinones in a Surrogate Lung Fluid, *Environ. Sci. Technol.*, 49, 9317–9325, <https://doi.org/10.1021/acs.est.5b01606>, 2015.
- Charrier, J. G., McFall, A. S., Richards-Henderson, N. K., and Anastasio, C.: Hydrogen Peroxide Formation in a Surrogate Lung Fluid by Transition Metals and Quinones Present in Particulate Matter, *Environ. Sci. Technol.*, 48, 7010–7017, <https://doi.org/10.1021/es501011w>, 2014.
- 80 Chevallier, E., Jolibois, R., Meunier, N., Carlier, P., and Monod, A.: “Fenton-like” reactions of methylhydroperoxide and ethylhydroperoxide with Fe²⁺ in liquid aerosols under tropospheric conditions, *Atmospheric Environment*, 38, 921–933, <https://doi.org/10.1016/j.atmosenv.2003.10.027>, 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*
- 85 *Waste Manag. Assoc.*, 56, 1750–1766, <https://doi.org/10.1080/10473289.2006.10464580>, 2006.
- Ervens, B., George, C., Williams, J. E., Buxton, G. V., Salmon, G. A., Bydder, M., Wilkinson, F., Dentener, F., Mirabel, P., Wolke, R., and Herrmann, H.: CAPRAM 2.4 (MODAC mechanism): An extended and condensed tropospheric aqueous phase mechanism and its application, *Journal of Geophysical Research: Atmospheres*, 108, <https://doi.org/10.1029/2002JD002202>, 2003.
- Expósito, A., Mailló, J., Uriarte, I., Santibáñez, M., and Fernández-Olmo, I.: Kinetics of ascorbate and dithiothreitol oxidation by soluble
- 90 copper, iron, and manganese, and 1,4-naphthoquinone: Influence of the species concentration and the type of fluid, *Chemosphere*, 361, 142 435, <https://doi.org/10.1016/j.chemosphere.2024.142435>, 2024.
- Fang, T., Verma, V., Guo, H., King, L. E., Edgerton, E. S., and Weber, R. J.: A semi-automated system for quantifying the oxidative potential of ambient particles in aqueous extracts using the dithiothreitol (DTT) assay: results from the Southeastern Center for Air Pollution and Epidemiology (SCAPE), *Atmos. Meas. Tech.*, 8, 471–482, <https://doi.org/10.5194/amt-8-471-2015>, 2015.
- 95 Giorio, C., Borca, C. N., Zhrebker, A., D’Aronco, S., Saidikova, M., Sheikh, H. A., Harrison, R. J., Badocco, D., Soldà, L., Pastore, P., Ammann, M., and Huthwelker, T.: Iron Speciation in Urban Atmospheric Aerosols: Comparison between Thermodynamic Modeling and Direct Measurements, *ACS Earth Space Chem.*, 9, 649–661, <https://doi.org/10.1021/acsearthspacechem.4c00359>, 2025.
- Gonzalez, D. H., Diaz, D. A., Baumann, J. P., Ghio, A. J., and Paulson, S. E.: Effects of albumin, transferrin and humic-like substances on iron-mediated OH radical formation in human lung fluids, *Free Radical Biology and Medicine*, 165, 79–87, <https://doi.org/10.1016/j.freeradbiomed.2021.01.021>, 2021.
- 100 Halliwell, B. and Gutteridge, J. M. C.: *Free Radicals in Biology and Medicine*, OUP Oxford, Oxford, 2015.
- Heal, M. R., Hibbs, L. R., Agius, R. M., and Beverland, I. J.: Total and water-soluble trace metal content of urban background PM₁₀, PM_{2.5} and black smoke in Edinburgh, UK, *Atmos. Environ.*, 39, 1417–1430, <https://doi.org/10.1016/j.atmosenv.2004.11.026>, 2005.

- Jacobsen, F., Holcman, J., and Sehested, K.: Oxidation of manganese(II) by ozone and reduction of manganese(III) by hydrogen peroxide in acidic solution, *International Journal of Chemical Kinetics*, 30, 207–214, [https://doi.org/10.1002/\(SICI\)1097-4601\(1998\)30:3<207::AID-KIN6>3.0.CO;2-W](https://doi.org/10.1002/(SICI)1097-4601(1998)30:3<207::AID-KIN6>3.0.CO;2-W), 1998.
- Kemp, T. J.: Kinetic Aspects of Spin Trapping, *Progress in Reaction Kinetics*, 24, 287–358, <https://doi.org/10.3184/007967499103165102>, 1999.
- Kohen, R. and Nyska, A.: Invited Review: Oxidation of Biological Systems: Oxidative Stress Phenomena, Antioxidants, Redox Reactions, and Methods for Their Quantification, *Toxicol Pathol*, 30, 620–650, <https://doi.org/10.1080/01926230290166724>, 2002.
- Kumagai, Y., Koide, S., Taguchi, K., Endo, A., Nakai, Y., Yoshikawa, T., and Shimojo, N.: Oxidation of Proximal Protein Sulfhydryls by Phenanthraquinone, a Component of Diesel Exhaust Particles, *Chem. Res. Toxicol.*, 15, 483–489, <https://doi.org/10.1021/tx0100993>, 2002.
- Lakey, P. S. J., Berkemeier, T., Tong, H., Arangio, A. M., Lucas, K., Pöschl, U., and Shiraiwa, M.: Chemical exposure-response relationship between air pollutants and reactive oxygen species in the human respiratory tract, *Sci. Rep.*, 6, 32 916, <https://doi.org/10.1038/srep32916>, 2016.
- Lelieveld, S., Wilson, J., Dovrou, E., Mishra, A., Lakey, P. S. J., Shiraiwa, M., Pöschl, U., and Berkemeier, T.: Hydroxyl Radical Production by Air Pollutants in Epithelial Lining Fluid Governed by Interconversion and Scavenging of Reactive Oxygen Species, *Environ. Sci. Technol.*, 55, 14 069–14 079, <https://doi.org/10.1021/acs.est.1c03875>, 2021.
- Liu, M. J., Wiegel, A. A., Wilson, K. R., and Houle, F. A.: Aerosol Fragmentation Driven by Coupling of Acid–Base and Free-Radical Chemistry in the Heterogeneous Oxidation of Aqueous Citric Acid by OH Radicals, *J. Phys. Chem. A*, 121, 5856–5870, <https://doi.org/10.1021/acs.jpca.7b04892>, 2017.
- Manousakas, M., Papaefthymiou, H., Eleftheriadis, K., and Katsanou, K.: Determination of water-soluble and insoluble elements in PM_{2.5} by ICP-MS, *Sci. Total Environ.*, 493, 694–700, <https://doi.org/10.1016/j.scitotenv.2014.06.043>, 2014.
- Morgan, J. J.: Kinetics of reaction between O₂ and Mn(II) species in aqueous solutions, *Geochimica et Cosmochimica Acta*, 69, 35–48, <https://doi.org/10.1016/j.gca.2004.06.013>, 2005.
- Mouchel-Vallon, C., Deguillaume, L., Monod, A., Perroux, H., Rose, C., Ghigo, G., Long, Y., Leriche, M., Aumont, B., Patryl, L., Armand, P., and Chaumerliac, N.: CLEPS 1.0: A new protocol for cloud aqueous phase oxidation of VOC mechanisms, *Geosci. Model Dev.*, 10, 1339–1362, <https://doi.org/10.5194/gmd-10-1339-2017>, 2017.
- Neta, P., Huie, R. E., and Ross, A. B.: Rate Constants for Reactions of Peroxyl Radicals in Fluid Solutions, *Journal of Physical and Chemical Reference Data*, 19, 413–513, <https://doi.org/10.1063/1.555854>, 1990.
- Netto, L. E. and Stadtman, E. R.: The Iron-Catalyzed Oxidation of Dithiothreitol Is a Biphasic Process: Hydrogen Peroxide Is Involved in the Initiation of a Free Radical Chain of Reactions, *Archives of Biochemistry and Biophysics*, 333, 233–242, <https://doi.org/10.1006/abbi.1996.0386>, 1996.
- Pham, A. N., Xing, G., Miller, C. J., and Waite, T. D.: Fenton-like copper redox chemistry revisited: Hydrogen peroxide and superoxide mediation of copper-catalyzed oxidant production, *Journal of Catalysis*, 301, 54–64, <https://doi.org/10.1016/j.jcat.2013.01.025>, 2013.
- Shen, J., Griffiths, P. T., Campbell, S. J., Uttinger, B., Kalberer, M., and Paulson, S. E.: Ascorbate oxidation by iron, copper and reactive oxygen species: review, model development, and derivation of key rate constants, *Scientific Reports*, 11, 7417, <https://doi.org/10.1038/s41598-021-86477-8>, 2021.

- 140 Sueishi, Y., Hori, M., Ishikawa, M., Matsu-ura, K., Kamogawa, E., Honda, Y., Kita, M., and Ohara, K.: Scavenging rate constants of hydrophilic antioxidants against multiple reactive oxygen species, *Journal of Clinical Biochemistry and Nutrition*, 54, 67–74, <https://doi.org/10.3164/jcbn.13-53>, 2014.
- Tong, H., Lakey, P. S. J., Arangio, A. M., Socorro, J., Shen, F., Lucas, K., Brune, W. H., Pöschl, U., and Shiraiwa, M.: Reactive Oxygen Species Formed by Secondary Organic Aerosols in Water and Surrogate Lung Fluid, *Environ. Sci. Technol.*, 52, 11 642–11 651, <https://doi.org/10.1021/acs.est.8b03695>, 2018.
- 145 Tuet, W. Y., Chen, Y., Xu, L., Fok, S., Gao, D., Weber, R. J., and Ng, N. L.: Chemical oxidative potential of secondary organic aerosol (SOA) generated from the photooxidation of biogenic and anthropogenic volatile organic compounds, *Atmos. Chem. Phys.*, 17, 839–853, <https://doi.org/10.5194/acp-17-839-2017>, 2017.
- Walling, C.: Some aspects of the chemistry of alkoxy radicals, 15, 69–80, <https://doi.org/10.1351/pac196715010069>, 1967.
- 150 Wang, S., Ye, J., Soong, R., Wu, B., Yu, L., Simpson, A. J., and Chan, A. W. H.: Relationship between chemical composition and oxidative potential of secondary organic aerosol from polycyclic aromatic hydrocarbons, *Atmos. Chem. Phys.*, 18, 3987–4003, <https://doi.org/10.5194/acp-18-3987-2018>, 2018.
- Wei, J., Fang, T., Lakey, P. S. J., and Shiraiwa, M.: Iron-Facilitated Organic Radical Formation from Secondary Organic Aerosols in Surrogate Lung Fluid, *Environ. Sci. Technol.*, 56, 7234–7243, <https://doi.org/10.1021/acs.est.1c04334>, 2022.
- 155 Xiong, Q., Yu, H., Wang, R., Wei, J., and Verma, V.: Rethinking Dithiothreitol-Based Particulate Matter Oxidative Potential: Measuring Dithiothreitol Consumption versus Reactive Oxygen Species Generation, *Environ. Sci. Technol.*, 51, 6507–6514, <https://doi.org/10.1021/acs.est.7b01272>, 2017.