



Supplement of

Linking molecular composition of organic aerosols to reactive oxygen species formation using an MCR-VK framework

Fobang Liu et al.

Correspondence to: Kai Wang (kaiwang_ly@cau.edu.cn) and Haijie Tong (haijie.tong@hereon.de)

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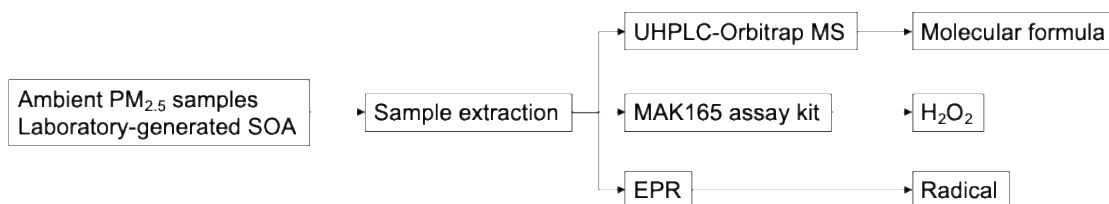


Figure S1. Schematic outline of the experimental approach: collection of ambient fine particulate matter (PM_{2.5}) samples and laboratory-generated secondary organic aerosols (SOA), sample extraction by water, and application of different experimental techniques to measure organic components, H₂O₂ yield, and radical yield.

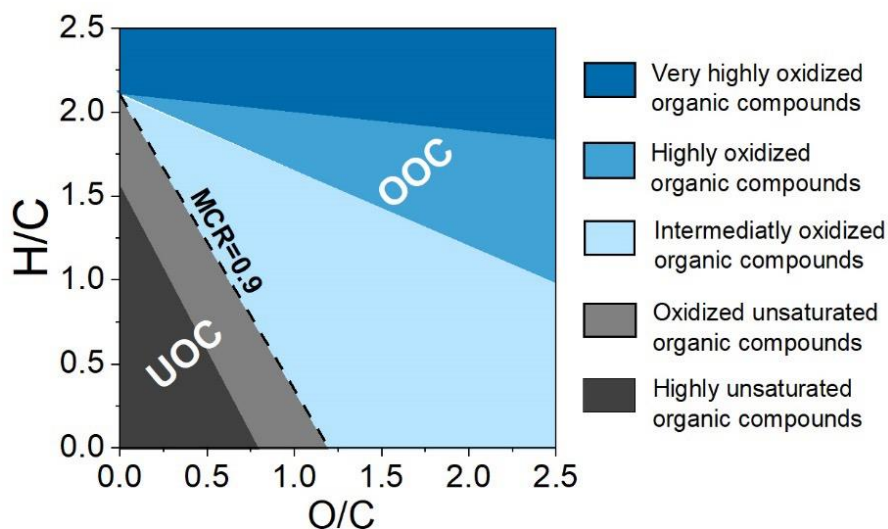


Figure S2. Maximum carbonyl ratio (MCR)-Van Krevelen (VK) diagram. Oxidized organic compounds (OOC) include very highly oxidized organic compounds (dark blue), highly oxidized organic compounds (blue), and intermediatly oxidized organic compounds (light blue); unsaturated organic compounds (UOC) include oxidized unsaturated organic compounds (gray) and highly unsaturated organic compounds (dark gray).

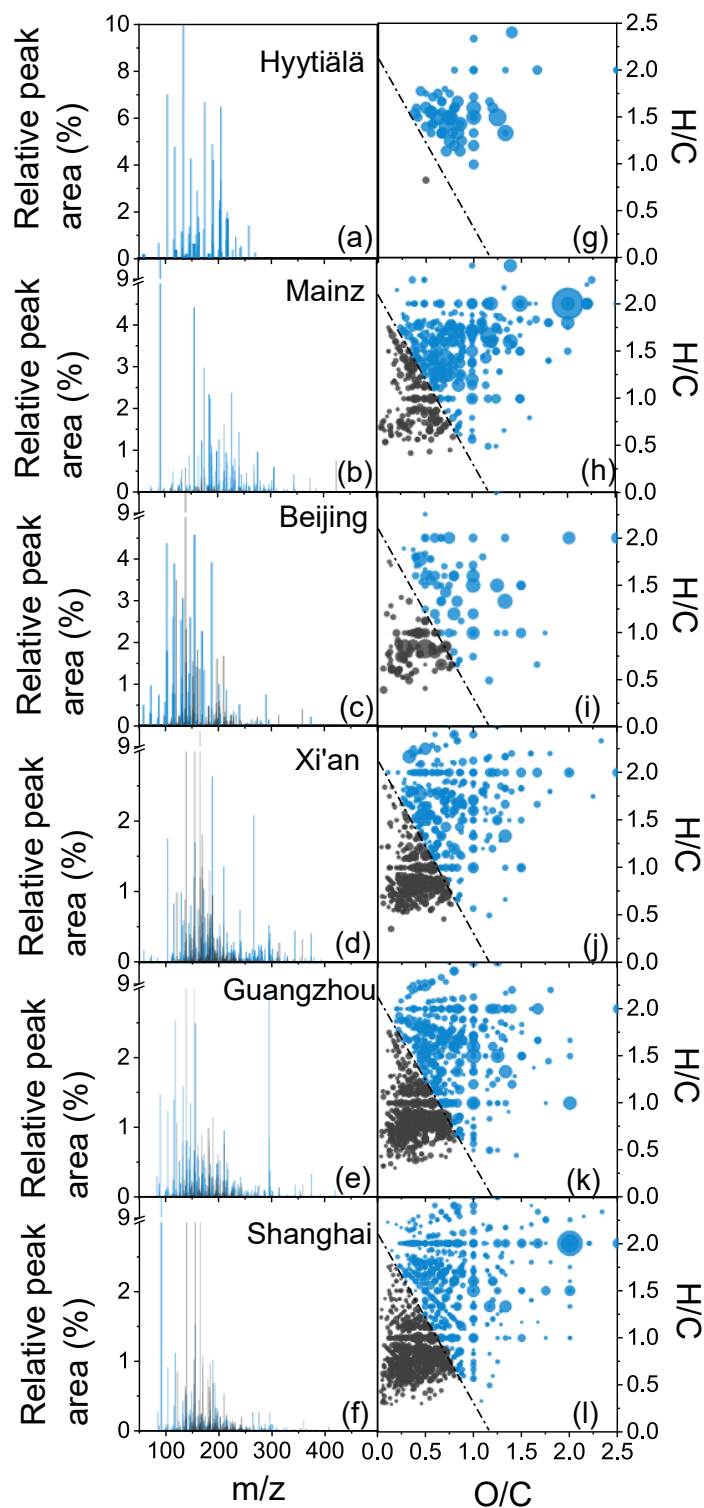


Figure S3. Mass spectra (a-f) and MCR-VK diagrams (g-l) of OOC (blue) and UOC (gray) in ambient fine PM samples collected from different locations. The size of symbols in MCR-VK diagrams is proportional to the fourth root of the abundance of each compound.

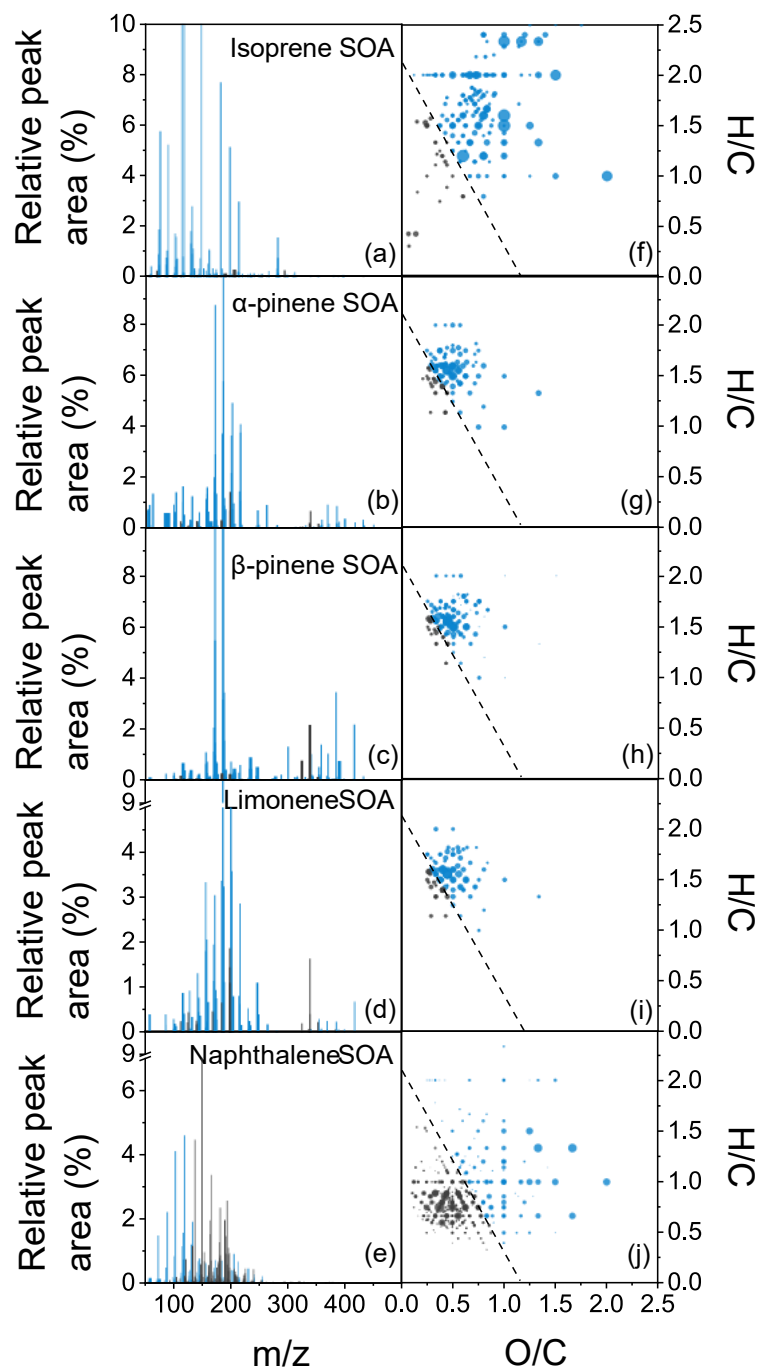


Figure S4. Mass spectra (a-e) and MCR-VK diagrams (f-j) of OOC and UOC in laboratory-generated SOA samples. The size of symbols in MCR-VK diagrams is proportional to the fourth root of the abundance of each compound.

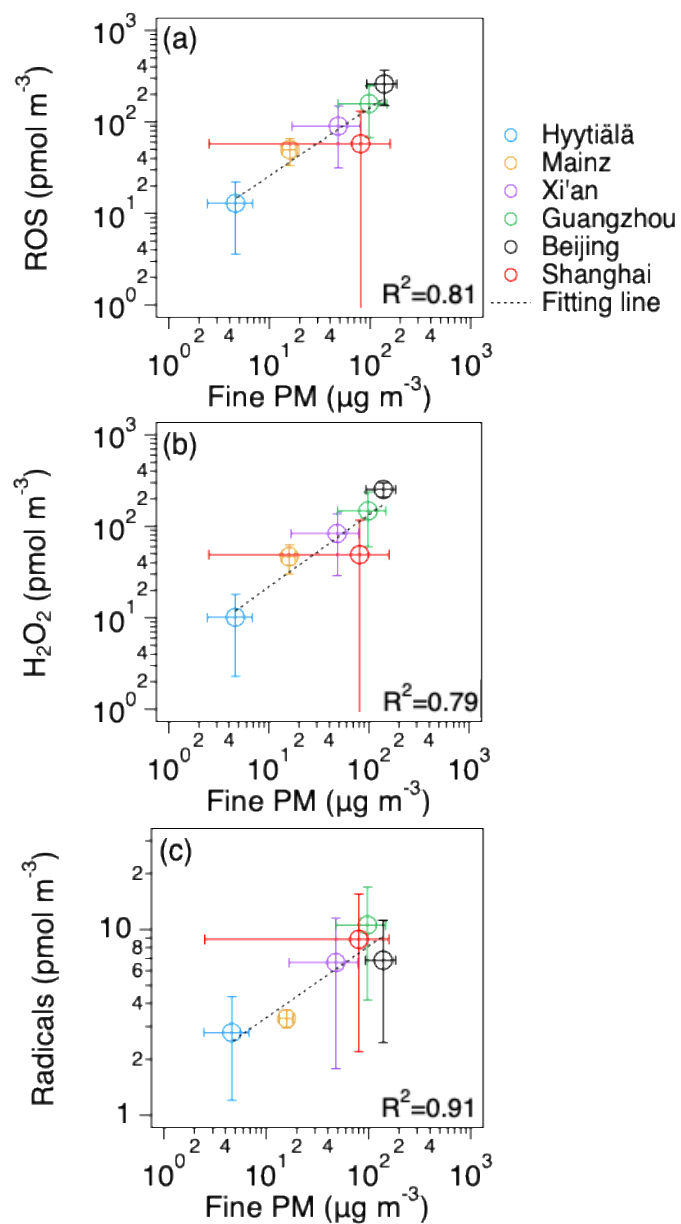


Figure S5. Correlation of volume-normalized ROS yield (a), H_2O_2 yield (b), and radical yield (c) with mass concentration of ambient fine PM samples. The dots and error bars represent the mean values and standard deviations, respectively.

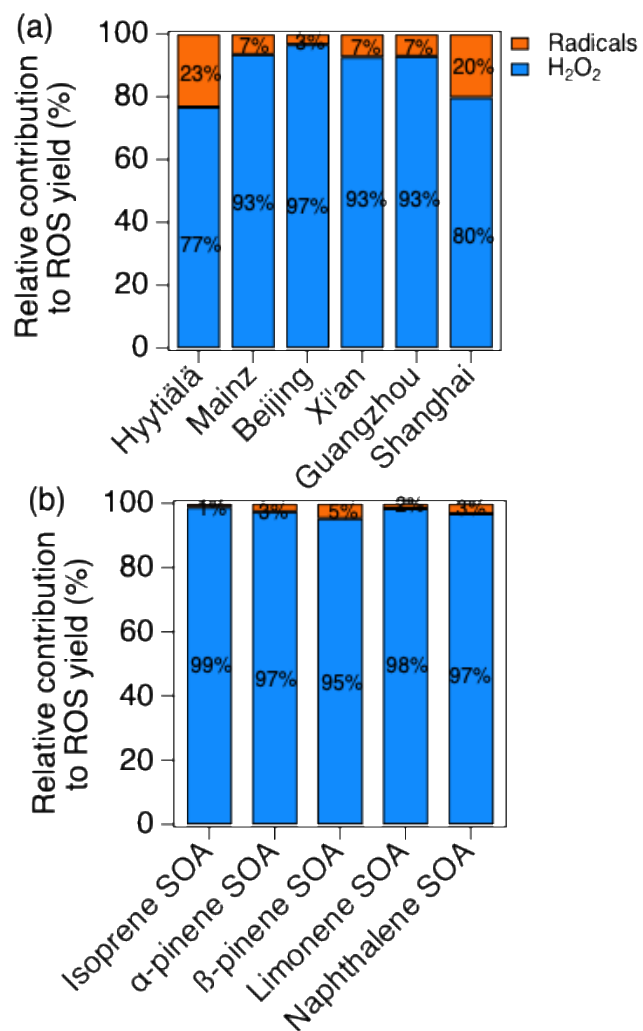


Figure S6. Relative contributions of H_2O_2 and radicals to total ROS yield in ambient fine PM (a) and laboratory-generated SOA (b).

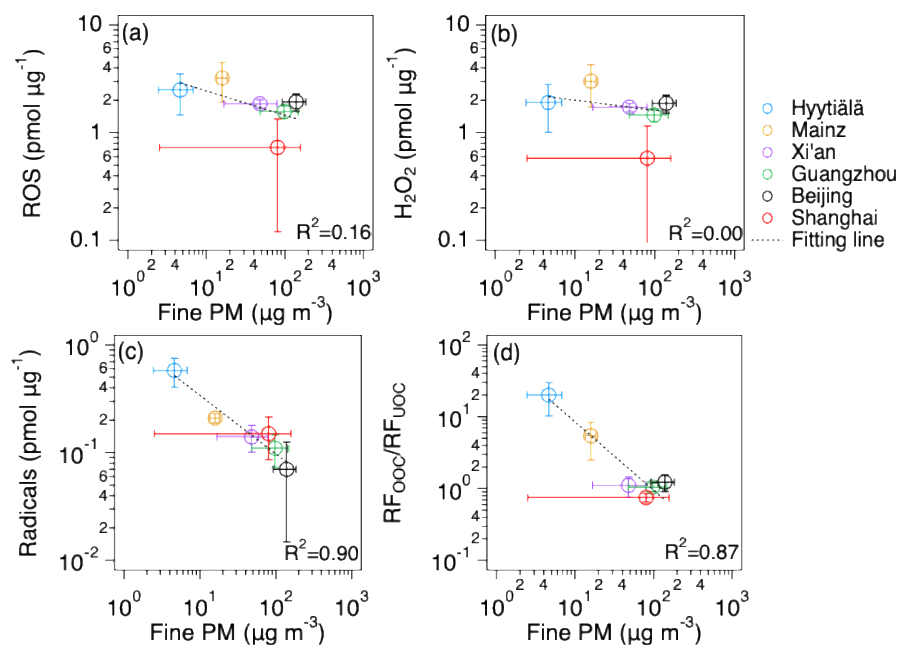


Figure S7. Correlation of mass-normalized ROS yield (a), H_2O_2 yield (b), radical yield (c), and the ratio of OOC to UOC fractions ($\text{RF}_{\text{OOC}}/\text{RF}_{\text{UOC}}$) with mass concentration of ambient fine PM samples. The dots and error bars represent the mean values and standard deviations, respectively.

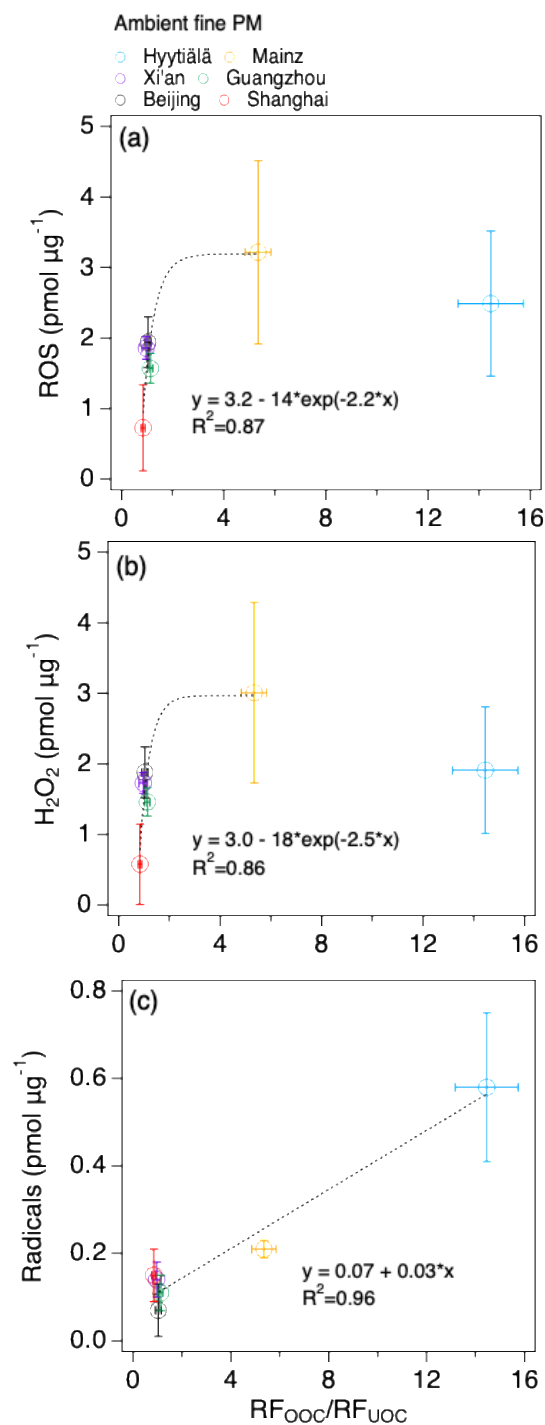


Figure S8. Correlations of mass-specific ROS yields (a), H_2O_2 yields (b), and radical yields (c) with CHO-only $\text{RF}_{\text{OOC}}/\text{RF}_{\text{UOC}}$ ratio in ambient fine PM samples. The $\text{RF}_{\text{OOC}}/\text{RF}_{\text{UOC}}$ ratio was recalculated using only CHO molecular formulas. The dots and error bars represent the mean values and standard deviations, respectively.

Table S1. Detailed information on the ambient particle sampling.

Site	Location	Air flow rate L ⁻¹ min ⁻¹	Volume of air/m ³	Particle size	Sampler	Sampling time		
Hyytiälä	61.85°N, 24.29°E	35	293	PM _{2.5}	Dekati PM ₁₀ impactor (Dekati Ltd., Tampere, Finland)	02-05/06/2017		
			252	PM _{2.5}		07-09/06/2017		
			100	PM _{2.5}		09-12/06/2017		
			99	PM _{2.5}		12-14/06/2017		
Mainz	49.99°N, 8.23°E	30	80	PM _{1.8}	MOUDI (122R, MSP corporation, USA)	22-24/08/2017		
			80	PM _{1.8}		26-28/08/2017		
			80	PM _{1.8}		28-30/08/2017		
			80	PM _{1.8}		25-27/09/2017		
Beijing	116.27°E, 40.15°N	16.7	22	PM _{2.5}	PM _{2.5} sampler (TH-16, Tianhong company, China)	26-27/02/2019		
			22	PM _{2.5}		27-28/02/2019		
			22	PM _{2.5}		28-29/02/2019		
			22	PM _{2.5}		01-02/03/2019		
			22	PM _{2.5}		02-03/03/2019		
			21	PM _{2.5}		03-04/03/2019		
			22	PM _{2.5}		04-05/03/2019		
			22	PM _{2.5}		08-09/03/2019		
			22	PM _{2.5}		09-10/03/2019		
			22	PM _{2.5}		10-11/03/2019		
Shanghai	121.43°E, 34.50°N	1050	1585	PM _{2.5}	PM _{2.5} sampler (Tisch, Cleveland, OH, USA)	19-20/01/2014		
			1620	PM _{2.5}		20-21/01/2014		
			1628	PM _{2.5}		24-25/01/2014		
			1614	PM _{2.5}		26-27/01/2014		
			1612	PM _{2.5}		27-28/01/2014		
Guangzhou	113.27°E, 23.13°N		1690	PM _{2.5}		05-06/01/2014		
			1599	PM _{2.5}		06-07/01/2014		
			1596	PM _{2.5}		11-12/01/2014		
			1601	PM _{2.5}		08-09/01/2014		
			1616	PM _{2.5}		12-13/01/2014		
			1646	PM _{2.5}		13-14/01/2014		
			Xi'an	108.95°E, 34.27°N		50	72	PM _{2.5}
72	PM _{2.5}						06-07/11/2018	
72	PM _{2.5}						07-08/11/2018	
72	PM _{2.5}						08-09/11/2018	
	60	PM _{2.5}		09-10/11/2018				

Table S2. Parameters and settings used for the non-target data analysis workflow in Mzmine 2.37

1) Import data		
Raw data methods	Raw data import	
2) Peak detection		
Raw data methods	Peak detection	Mass detection
Parameters	Raw data files	All raw data files
	Scans_set filters	All
	Mass detector	Wavelet transform
		Noise level = 1000
	Mass list name	masses
3) FTMS shoulder peaks filter		
Raw data methods	Peak detection	FTMS shoulder peak filter
Parameters	Raw data files	All raw data files
	Mass list	masses
	Mass resolution	70000
	Peak model function	Gaussian
	Suffix	filtered
	Remove original peak list	Off
4) ADAP chromatogram builder		
Raw data methods	Peak detection	ADAP chromatogram builder
Parameters	Raw data files	All raw data files
	Scans_set filters	
		MS level: 1
		Polarity: Any
		Spectrum type: Any
	Mass list	masses
	Min group size in # of scans	6
	Group intensity threshold	1000
	Min highest intensity	10000
	m/z tolerance	4.0E-4 m/z or 2.0 ppm
	Suffix	chromatograms
5) Smoothing		
Peak list methods	Smoothing	
Parameters	Peak lists	Those created by previous batch step
	Filename suffix	smoothed
	Filter width	5
	Remove original peak list	Off
6) Chromatogram deconvolution		
Peak list methods	Chromatogram deconvolution	
	Peak lists	Those created by previous batch step
	Suffix	deconvoluted

	Algorithm	Wavelets (ADAP)
		S/N threshold = 10
		S/N estimator = Intensity window SN
		Min feature height = 10000
		coefficient/area threshold = 110
		Peak duration range = 0.03 – 1.00
		RT wavelet range = 0.01 – 0.2
	m/z center calculation	MEDIAN
	m/z range for MS2 scan pairing	Off
	RT range for MS2 scan pairing	Off
	Remove original peak list	Off
7) Remove isotope chromatograms		
Peak list methods	isotopes	Isotopic peaks grouper
	Peak lists	Those created by previous batch step
	Name suffix	deisotoped
	m/z tolerance	4.0E-4 m/z or 2.0 ppm
	RT tolerance	0.1 absolute (min)
	Monotonic shaoe	Off
	Maximum charge	1
	Representative isotope	Most intense
	Remove original peak list	Off
8) Finds and removes adduct signals from peak list		
Peak list methods	Identification	Adduct search
	Peak lists	Those created by previous batch step
	RT tolerance	0.1 absolute (min)
	Adducts	[M +CH2O2] 46.0055 m/z
		[M+ACN] 41.0266 m/z
	m/z tolerance	4.0E-4 m/z or 2.0 ppm
	Max relative adduct peak height	50%
9) Finds and removes ion complexes from peak list		
Peak list methods	Identification	Complex search
	Peak lists	Those created by previous batch step
	Ionization method	[M-H]-
	RT tolerance	0.1 absolute (min)
	m/z tolerance	4.0E-4 m/z or 2.0 ppm
	Max complex peak height	50%
10) Sort peak lists (Join aligner, finds signals from same molecules in different samples, joins peak lists of different samples into one table)		
Peak list methods	Alignment	Join aligner
	Peak lists	Those created by previous batch step
	Peak list name	Aligned peak list
	m/z tolerance	4.0E-4 m/z or 2.0 ppm

	Weight for m/z	5
	Retention time tolerance	0.2 absolute (min)
	Weight for RT	4
	Require same charge state	Off
	Require same ID	Off
	Compare isotope patter	On
		Isotope m/z tolerance = 0.001 m/z or 5.0 ppm
		Minimum absolute intensity = 1000
		Minimum score = 85%
11) Formula prediction		
Peak list methods	Identification	Formula prediction
	Charge	1
	ionization type	[M-H]-
	Peak lists	Those created by previous batch step
	m/z tolerance	4.0E-4 m/z or 2.0 ppm
	max best formulas per peak	1
	Elements	
		C = 1–39
		H = 1–72
		O = 0–20
		N = 0–7
		S = 0–4
	Element count heuristics	On
		H/C ratio: yes
		NOPS/C ratio: yes
		Multiple element counts: yes
	RDBE restritions	On
		RDBE range=0-30
		RDBE must be an integer: yes
	Isotope pattern filter	On
		Isotope m/z tolerance: 0.001 m/z or 5.0 ppm
		Minimum absolute intensity: 500
		Minimum score = 75%
	MS/MS filter	Off
1) Export data		
Peak list methods	Export	Export to CSV file

Table S3. Regression statistics for the relationships shown in Figures 2 and 4.

Figure	Regression model	<i>p</i> value	Regression coefficient (95% CI)
2a	Linear	0.015	Slope = 2.63 (0.82–4.43)
2b	Linear	0.004	Slope = 1.36 (0.74–1.99)
2c	Linear	0.002	Slope = 1.69 (1.07–2.32)
4a	Exponential	0.001	$y_0 = 3.22$ (1.58–4.85); $A = -7.60$ (-14.90 to -0.29); $R_0 = -1.47$ (-3.05 to 0.12)
4b	Exponential	4.63×10^{-4}	$y_0 = 3.03$ (2.04–4.02); $A = -8.01$ (-12.82 to -3.20); $R_0 = -1.56$ (-2.58 to -0.54)
4c	Linear	4.12×10^{-4}	Slope = 0.02 (0.02–0.03)
4d	Linear	0.004	Slope = 5.82 (3.61–8.03)
4e	Linear	0.004	Slope = 5.73 (3.39–8.07)
4f	Linear	0.323	Slope = 0.05 (-0.09–0.19)

Table S4. Individual H₂O₂, radical, and total ROS (H₂O₂+radical) measurements (pmol µg⁻¹) for samples collected at each site.

Site	Sample size	Sampling time	H ₂ O ₂	Radical	Total ROS
Hyytiälä	4	02-05/06/2017	0.79	0.37	1.16
		07-09/06/2017	2.61	0.53	3.15
		09-12/06/2017	2.66	0.78	3.45
		12-14/06/2017	1.57	0.63	2.19
Mainz	4	22-24/08/2017	1.72	0.20	1.92
		26-28/08/2017	4.00	0.24	4.23
		28-30/08/2017	2.10	0.19	2.30
		25-27/09/2017	4.22	0.22	4.43
Beijing	10	26-27/02/2019	1.75	0.18	1.93
		27-28/02/2019	1.91	0.13	2.04
		28-29/02/2019	1.80	0.11	1.91
		01-02/03/2019	1.66	0.07	1.73
		02-03/03/2019	2.50	0.06	2.56
		03-04/03/2019	1.73	0.01	1.74
		04-05/03/2019	1.65	0.01	1.65
		08-09/03/2019	1.33	0.02	1.35
		09-10/03/2019	2.41	0.03	2.45
Shanghai	5	10-11/03/2019	2.04	0.03	2.07
		19-20/01/2014	1.03	0.11	1.14
		20-21/01/2014	0.30	0.08	0.38
		24-25/01/2014	1.36	0.25	1.60
		26-27/01/2014	0.10	0.17	0.27
Guangzhou	6	27-28/01/2014	0.12	0.13	0.25
		05-06/01/2014	1.69	0.07	1.76
		06-07/01/2014	1.65	0.16	1.81
		11-12/01/2014	1.15	0.09	1.23
		08-09/01/2014	1.40	0.15	1.55
		12-13/01/2014	1.48	0.10	1.59
Xi'an	5	13-14/01/2014	1.41	0.09	1.50
		05-06/11/2018	1.51	0.12	1.63
		06-07/11/2018	1.73	0.14	1.87
		07-08/11/2018	1.94	0.11	2.05
		08-09/11/2018	1.72	0.20	1.92
		09-10/11/2018	1.73	0.11	1.84