



1 **Linking Molecular Composition of Organic Aerosols to Reactive Oxygen Species**
2 **Formation Using an MCR-VK Framework**

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26 Abstract

27 Reactive oxygen species (ROS) formation by atmospheric fine particulate matter (PM) is widely
28 implicated in adverse health effects, yet the molecular determinants of particle-level ROS
29 formation remain poorly constrained, largely due to the chemical complexity of organic aerosol
30 (OA). Here, we link ROS formation to molecular-level OA composition by applying a maximum
31 carbonyl ratio-Van Krevelen framework to ambient fine PM collected from four Chinese
32 megacities, a German semi-urban site, a boreal forest, and laboratory-generated secondary
33 organic aerosol (SOA) from multiple precursors. Using ultrahigh-resolution mass spectrometry
34 combined with hydrogen peroxide (H_2O_2) and radical measurements, we show the intrinsic ROS
35 (H_2O_2 +radicals) formation potential of fine PM is governed by OA composition rather than
36 particle mass. Volume-normalized ROS yields increase with fine PM mass concentration and
37 dominate overall exposure in polluted urban environments. In contrast, mass-normalized ROS
38 yields vary independently of particle loading and are strongly driven by the balance between
39 relative fractions of oxidized organic compounds (RF_{OOC}) and unsaturated organic compounds
40 (RF_{UOC}), i.e., $\text{RF}_{\text{OOC}}/\text{RF}_{\text{UOC}}$. Across urban sites, mass-normalized ROS and H_2O_2 yields exhibit strong
41 correlations with $\text{RF}_{\text{OOC}}/\text{RF}_{\text{UOC}}$, establishing this metric as a robust predictor of ROS formation.
42 Remote, biogenic-influenced aerosols exhibit higher $\text{RF}_{\text{OOC}}/\text{RF}_{\text{UOC}}$ and higher ROS yields per unit
43 mass, whereas urban aerosols exhibit the opposite behavior. Laboratory SOA further supports
44 these composition-reactivity relationships, with OOC-rich biogenic SOA exhibiting the highest
45 ROS yields. This study reveals molecular-level characteristics in governing aerosol ROS formation
46 and introduces a framework for assessing health-relevant aerosol oxidative activity of chemically
47 complex OA.

48

49 1 Introduction

50 Exposure to atmospheric fine particulate matter (PM) is linked to a wide range of adverse health
51 outcomes, including respiratory and cardiovascular diseases, and contributes to millions of
52 deaths annually (Burnett et al., 2018; Lelieveld et al., 2015; Zhang et al., 2025; Shiraiwa et al.,
53 2017). A key mechanism underlying these effects is the ability of PM to generate reactive oxygen



54 species (ROS) in biological fluids and cells, triggering oxidative stress, inflammation, and
55 cytotoxicity (Li et al., 2008; Gurgueira et al., 2002; Liu et al., 2022; Lakey et al., 2016). ROS,
56 including hydrogen peroxide (H_2O_2), hydroxyl radicals ($\cdot\text{OH}$), superoxide radicals ($\text{O}_2^{\cdot-}$), and
57 organic radicals, can be produced by a variety of chemically reactive constituents in fine PM,
58 including quinones, transition metals, environmentally persistent free radicals, and secondary
59 organic aerosols (SOA) (Tong et al., 2016; Lin and Yu, 2020; PöSchl and Shiraiwa, 2015;
60 Khachatryan et al., 2011; Yang et al., 2024).

61 Organic aerosol (OA) components are increasingly recognized as important contributors to
62 the ROS formation of atmospheric aerosols. Multiple field studies have quantified the ROS
63 formation of source-based OA components and demonstrated that OA is a major driver of the
64 ROS formation of ambient fine PM (Zhou et al., 2019; Daellenbach et al., 2020; Liu et al., 2023).
65 Field investigations have also found that some organic species, such as quinone-type compounds,
66 highly oxygenated molecules (HOMs), and organic peroxides, significantly contribute to ROS
67 formation (Verma et al., 2015; Tong et al., 2019; Tong et al., 2021). Complementary laboratory
68 studies have examined the ROS formation of SOA formed from different gaseous precursors
69 under well-controlled conditions (Campbell et al., 2025; Tong et al., 2018; Fang et al., 2024; Liu
70 et al., 2020). These studies show that the oxidative properties of SOA largely depend on precursor
71 identity, reaction conditions, and resulting chemical composition. For example, SOA derived from
72 naphthalene, β -pinene, and isoprene, and have been shown to produce substantial H_2O_2 upon
73 aqueous extraction, with organic hydroperoxides identified as the major ROS contributors (Tong
74 et al., 2018). While these field and laboratory studies highlight the importance of specific OA
75 sources and organic species, most of them have focused on bulk OA characteristics or small sets
76 of target compounds. Consequently, the contributions of individual organic molecules and their
77 structural classes to ROS formation in atmospheric aerosols remain poorly resolved.

78 This knowledge gap persists largely because atmospheric OA is chemically complex:
79 thousands of species are present, yet only 10–30% of OA mass is typically identified as specific
80 compounds by the existing analytical techniques (Noziere et al., 2015; Hoffmann et al., 2011).
81 Advances in ultrahigh-resolution mass spectrometry (UHRMS) have substantially expanded
82 molecular-level characterization of OA. Fourier transform ion cyclotron (FT-ICR) and Orbitrap MS



83 combined with soft ionization techniques including electrospray ionization (ESI) and atmospheric
84 pressure chemical ionization (APCI), enable the assignment of thousands of molecular formulas
85 (Zuth et al., 2018; Liu et al., 2025; Wang et al., 2024; Wang et al., 2018a). Molecular metrics such
86 as aromaticity equivalent and double bond equivalent (DBE) are then commonly applied to
87 interpret structural features such as aromaticity and unsaturation (Koch and Dittmar, 2006;
88 Yassine et al., 2014). However, these parameters do not fully capture functional group chemistry
89 that governs redox reactivity.

90 To overcome this limitation, we recently developed the maximum carbonyl ratio (MCR), a
91 new metric that estimates the maximum number of carbonyl groups a molecule could contain
92 based on its molecular formula (Zhang et al., 2021; Huang et al., 2025). By incorporating MCR
93 into the traditional Van Krevelen (VK) diagram (plots by H/C ratio against O/C ratio) (Ng et al.,
94 2011), we further established an MCR-VK framework that classifies individual compounds into
95 distinct chemical regions. Some of these regions correspond to functional groups or structural
96 features that may be associated with health-related effects. For example, higher MCR values
97 indicate greater carbonyl functionality and electrophilic character, while lower MCR values
98 reflect the dominance of highly oxidized, non-carbonyl species such as (hydro)peroxides, both of
99 which may induce oxidative stress in the respiratory system. As MCR can be easily obtained from
100 UHRMS-assigned formulas, the MCR-VK framework offers a promising new approach to identify
101 organic constituents potentially responsible for ROS formation.

102 In this study, we apply the MCR-VK framework to investigate the relationship between OA
103 molecular composition and ROS formation by ambient and laboratory-generated aerosols in
104 liquid water (the scheme is illustrated in Figure S1). PM samples were collected from urban
105 megacities (Beijing, Xi'an, Shanghai, Guangzhou), a European semi-urban site (Mainz), and a
106 boreal forest site (Hyytiälä), and laboratory-generated SOA was formed from isoprene,
107 monoterpenes, limonene, and naphthalene. Their molecular composition was analyzed using an
108 ultra-high-performance liquid chromatography system coupled with an ESI-Orbitrap mass
109 spectrometer (UHPLC/ESI-Orbitrap-MS). Based on their positions in the MCR-VK diagram,
110 individual molecular formulas were categorized into oxidized organic compounds (OOC) and
111 unsaturated organic compounds (UOC). ROS formation, including both H₂O₂ and radical yields,



112 was quantified. H₂O₂ yields in aerosol aqueous extracts were quantified using a fluorometric
113 probe, and radical yields were measured using electron paramagnetic resonance (EPR)
114 spectroscopy in combination with a spin-trapping method. By integrating molecular-level
115 chemical characterization with ROS measurements, the main objective is to evaluate whether
116 the balance between OOC and UOC can serve as a generalized predictor of ROS formation by
117 atmospheric aerosols. The findings provide a mechanistic basis for understanding OA-driven
118 oxidative stress, offering a molecularly resolved metric to assess ROS formation by fine PM across
119 diverse environments.

120 **2 Materials and Methods**

121 **2.1 Ambient Sample Collection**

122 The ambient PM samples were from six filed campaigns, including a boreal-forest station in
123 Hyytiälä, Finland; an urban site in Mainz, Germany; and four Chinese urban sites in Beijing, Xi'an,
124 Shanghai, and Guangzhou. The key sampling details are presented below, while the complete
125 sampling information is shown in Table S1.

126 At SMEAR II in Hyytiälä, 47-mm PALL Teflon filters were paired with a Dekati impactor
127 operated at 35 L min⁻¹ between 2 and 14 June 2017 (Hari et al., 2012). In Mainz, a model 110-R
128 micro-orifice uniform-deposition impactor (MOUDI; MSP Corporation) was deployed on the roof
129 of the Max Planck Institute for Chemistry from 22 to 30 August 2017. Operating at 30 L min⁻¹, the
130 particles were collected on 47-mm Teflon membranes supplied by Merck Chemicals GmbH (100-
131 nm pore size). In Beijing (Peking University), a TH-16 low-volume (flow rate at 16.7 L min⁻¹)
132 instrument (Tianhong Company, China) was applied for sample collection through 47-mm
133 Whatman® Teflon filters from 26 February 2019 to 10 March 2019. For Xi'an, during 5–9
134 November 2018, a model TE-20-800 low-pressure cascade impactor (Tisch, USA; ~50 L min⁻¹) was
135 used to collect PM samples through 90-mm Omnipore JVWP09025 Teflon filters (100-nm pore
136 size, Millipore) on the roof of Xi'an Jiaotong University. Shanghai and Guangzhou fine PM samples
137 were collected onto prebaked quartz-fiber filters (8×10 in.) using a high-volume air sampler (Tisch,
138 Cleveland, OH, USA) at a flow rate of 1050 L min⁻¹ from 5 to 27 January 2014.



139 2.2 Laboratory SOA generation and Collection

140 The SOA generation experiments were operated in a 7 L volume quartz flow tube and a 19 L
141 volume potential aerosol mass (PAM) chamber. In the flow tube, particles were formed through
142 gas-phase ozonolysis of α -pinene, β -pinene, or limonene with around 1000 ppbO₃. In the PAM
143 chamber, isoprene and naphthalene SOA were produced through gas-phase photooxidation
144 under an $\cdot$ OH concentration of $\sim 5.0 \times 10^{11} \text{ cm}^{-3}$. The concentrations of α -pinene, β -pinene, and
145 limonene were 1-2 ppm, while it was while 0.5-1 ppm for isoprene and naphthalene. The
146 generated SOA particle samples were captured onto 47 mm Omnipore Teflon membrane filters
147 (JVWP04700), which were extracted immediately. The complete information of the SOA
148 generation and sampling is presented in our previous papers (Tong et al., 2018; Tong et al., 2019).

149 2.3 Ultrahigh Resolution Mass Spectrometer Measurements and Data Processing

150 The process of sample preparation and instrumental analysis followed established protocols
151 (Zhang et al., 2021; Wang et al., 2018a). Briefly, portions of each filter containing approximately
152 600 μg of particle mass were extracted two times through ultrasonics for 30 min with 1.5 mL
153 methanol. The two methanolic extracts were pooled and passed through a 0.2- μm Teflon syringe
154 membrane to eliminate insoluble residues. After gentle nitrogen evaporation to dryness, the
155 residue was reconstituted in 1.0 mL of a 1:9 (v/v) acetonitrile-water solution before instrumental
156 analysis.

157 An UHRMS platform was used for molecular identification. Chromatographic separation was
158 performed on a Dionex UltiMate 3000 UHPLC coupled via a heated electrospray ionization (HESI)
159 source to a Q-Exactive mass spectrometer (Thermo Scientific, Germany). Analytes were resolved
160 with a Hypersil Gold C18 column (50 $\times$ 2.0 mm; 1.9- μm particles; Thermo Scientific, Germany). At
161 0.5 mL min⁻¹, the binary gradient combined solvent A (ultrapure water containing 2% acetonitrile
162 and 0.04% formic acid) with solvent B (acetonitrile containing 2% ultrapure water). The complete
163 gradient and UHPLC/HESI-Orbitrap settings were adopted from earlier work (Zhang et al., 2021;
164 Zhang, 2023). Data acquisition used negative-ion electrospray (ESI⁻), a resolving power of 70,000
165 at m/z 200, and an m/z window of 50–500. The ESI⁻ mode preferentially detects polar
166 oxygenated organic compounds and therefore may not capture all organic species in the filter



167 samples. However, all samples were analyzed using the same analytical protocol, enabling
168 consistent comparison of the molecular composition across different ambient environments.

169 Non-target feature screening was carried out in the open-source package MZmine (v2.37)
170 using the chromatographic and mass-spectral files. Table S2 lists the processing sequence and
171 parameter settings. Signals were considered when peak abundance exceeded 1×10^5 ; for each
172 eligible ion, the software enumerated molecular formulas within ± 2 ppm. Candidate
173 compositions followed the notation $C_cH_hO_oN_nS_s$. Allowed atom counts were $C = 1-39$, $H = 1-72$,
174 $O = 0-20$, $N = 0-7$, and $S = 0-4$. Additional chemical-plausibility filters limited H/C to 0.3–3, O/C
175 to 0–3, N/C to 0–1.3, and S/C to 0–0.8 (Zhang et al., 2021).

176 2.4 H_2O_2 assay

177 H_2O_2 was quantified in aqueous filter extracts. A quarter of each filter was extracted for 15 min
178 on a vortex shaker with 1.0 mL ultrapure water. Insoluble material was removed by centrifugation
179 for 3 min at 9000 rpm (Eppendorf Minispin), and the supernatant was analyzed with a
180 fluorometric kit from Sigma (Hydrogen Peroxide Assay Kit, MAK165). The assay protocol followed
181 our earlier work (Tong et al., 2021; Tong et al., 2018). In each well of a 96-well plate, 50 μ L
182 supernatant was combined with 50 μ L detection reagent containing Amplex Red substrate and
183 horseradish peroxidase. Following a 30 min incubation, a Synergy™ NEO microplate reader
184 (BioTek) recorded fluorescence at 540 nm excitation and 590 nm emission. Extract H_2O_2
185 concentrations were calculated from a calibration curve prepared with standard H_2O_2 solutions
186 and corrected using blank measurements.

187 2.5 EPR measurement of trapped radicals

188 Radical formation in the aqueous extracts of ambient PM and laboratory-generated SOA was
189 quantified using EPR with a spin-trapping method, following the procedures established in our
190 previous studies. For ambient PM samples, a section representing 25% of the filter was used,
191 while the complete SOA-loaded filter was processed for laboratory-generated SOA samples. Each
192 filter was immersed in 10 mM BMPO (Enzo Life Sciences GmbH; high-purity 5-tert-
193 butoxycarbonyl-5-methyl-1-pyrroline N-oxide), which acted as the radical trap, and agitated for
194 15 min on a Heidolph Reax 1 vortex shaker. During this process, short-lived radicals present in



195 PM extracts were assumed to rapidly react with BMPO to form stable radical adducts suitable for
196 EPR detection.

197 Adduct spectra were recorded for identification and quantification on an EMXplus-10/12
198 continuous-wave X-band instrument (Bruker Corporation). Consistent with earlier work,
199 acquisition settings were a 100-G magnetic-field span; 100-kHz modulation at 1.0-G amplitude;
200 2.1-mW microwave power (20 dB); 40-dB receiver gain; and 50 accumulated scans. Radical
201 concentrations were obtained through spectral fitting and spin counting in the Bruker Xenon
202 software package.

203 **3 Results and Discussion**

204 **3.1 MCR-VK-based molecular classification of OOC and UOC in ambient fine PM and laboratory-** 205 **generated SOA**

206 The UHRMS technique has become a powerful tool for characterizing the molecular composition
207 of OA, enabling the assignment of elemental formulas to thousands of individual compounds in
208 highly complex samples. To extract structural insights from UHRMS datasets, several metrics
209 derived from elemental composition, such as DBE, aromaticity index (AI), and aromaticity
210 equivalent (Xc), have been widely applied to capture unsaturation and aromaticity (Koch and
211 Dittmar, 2006; Yassine et al., 2014; Steimer et al., 2020). We recently introduced MCR to estimate
212 the maximum possible contribution of carbonyl-/epoxide-type functionalities based solely on
213 molecular formula information (Zhang et al., 2021). For a given molecular formula of $C_cH_hO_oN_nS_s$,
214 MCR is defined as the ratio of DBE to the number of oxygen atoms (O) when $O \geq DBE$, while MCR
215 is set to unity when $O < DBE$. The equation of MCR is shown below:

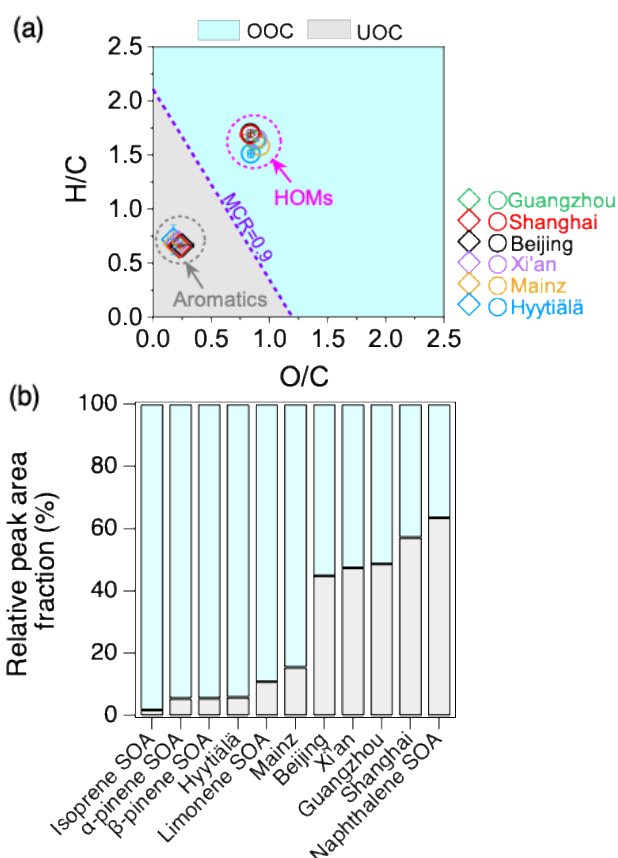
$$216 \quad MCR = \frac{DBE}{O}, \text{ for } O \geq DBE \quad (1)$$

$$217 \quad MCR = 1, \text{ for } O < DBE \quad (2)$$

218 By integrating MCR into the traditional VK diagram, we developed the MCR-VK framework,
219 which enables classification of OA compounds into chemically meaningful groups (Zhang et al.,
220 2021). As shown in Figure 1, the MCR-VK diagram is divided into two major areas by an MCR
221 threshold of 0.9. Compounds with $MCR < 0.9$ are classified as OOC, while those with $MCR \geq 0.9$
222 are classified as UOC. The OOC comprise a wide range of oxygen-rich species, including very



highly oxidized compounds such as organic peroxides and isoprene epoxydiols (IEPOX)-derived products, highly oxidized multifunctional molecules (e.g., 2-methyl-1,2,3-butanetricarboxylic acid (MBTCA) and other HOMs), and intermediately oxidized products such as pinic and pinonic acids derived from monoterpene oxidation (Figure S2) (Yasmeen et al., 2012; Müller et al., 2012; Nguyen et al., 2014; Zhang et al., 2021; Mutzel et al., 2015). In contrast, UOC are dominated by oxidized unsaturated compounds, including aromatic SOA products, combustion-related organics, and species formed through condensational aging processes (Figure S2) (Zhang et al., 2021; Srivastava et al., 2022; Al-Naiema et al., 2020; Chan et al., 2009).



231

232 **Figure 1.** (a) MCR-VK diagram to classify organic compounds in atmospheric aerosols. The dashed
233 line represents the boundary (MCR=0.9) between the oxidized organic compounds (OOC,



234 MCR<0.9, cyan area) and unsaturated organic compounds (UOC, MCR>0.9, grey area). Dots and
235 diamonds indicate the positions of highly oxygenated molecules (HOMs) and aromatics identified
236 in ambient fine PM samples. (b) Relative peak area-weighted fractions of OOC and UOC in
237 ambient fine PM samples and laboratory-generated SOA.

238

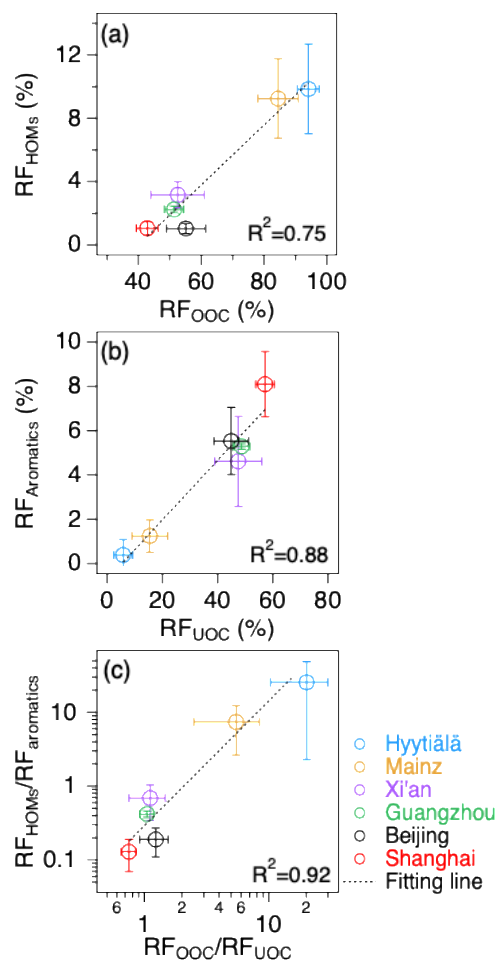
239 Figure 1b summarizes the relative peak-area-weighted fractions of OOC (RF_{OOC}) and UOC
240 (RF_{UOC}) in ambient fine PM and laboratory-generated SOA samples, averaged for each site or
241 experiment. Representative mass spectra and MCR-VK diagrams in ambient fine PM and
242 laboratory-generated SOA samples are shown in Figures S3 and S4, respectively. Distinct
243 differences in OA composition are observed across precursor types and environments (Figure 1b).
244 Isoprene SOA exhibits the highest RF_{OOC} (98%), consistent with its dominant formation of highly
245 oxygenated, low-MCR products such as 2-methyltetrols, in which most oxygen atoms are present
246 as hydroxyl groups (Wang et al., 2018b; Surratt et al., 2010; Zhang et al., 2023; Surratt et al.,
247 2006). Similarly, α -pinene and β -pinene SOA are overwhelmingly composed of OOC (95% and
248 94%, respectively), reflecting the prevalence of oxygen-rich ozonolysis products such as pinonic
249 acid, pinic acid, nopinone, and MBTCA (Müller et al., 2012; Zhang et al., 2015; Mutzel et al., 2021;
250 Fan et al., 2020). The fine PM samples collected in the boreal forest at Hyytiälä also exhibit a high
251 RF_{OOC} (94%), comparable to that observed in monoterpene-derived SOA, reflecting the dominant
252 contribution of biogenic precursors, particularly α - and β -pinene, to SOA formation at this
253 site (Kourtchev et al., 2013; Roldin et al., 2019; Kourtchev et al., 2014; Petäjä et al., 2022).

254 In contrast, naphthalene SOA is characterized by a substantially higher RF_{UOC} (64%),
255 indicating a strong contribution from aromatic, ring-retaining oxidation products. This
256 observation is consistent with previous studies showing that naphthalene photooxidation under
257 conditions of low nitrogen oxides (NO_x) predominantly yields aromatic quinones and ring-
258 opening products while largely retaining at least one benzene ring (Kautzman et al., 2010;
259 Lannuque and Sartelet, 2024). Urban fine PM samples display a wide range of RF_{UOC} (15–57%),
260 reflecting the diversity of emission sources and atmospheric processing pathways in urban
261 environments. Samples from Chinese megacities of Beijing, Xi'an, Guangzhou, and Shanghai
262 exhibit particularly high RF_{UOC} (45–57%), indicating a substantial contribution from aromatic and



263 combustion-related organics. This result agrees with our previous findings that mono- and
264 polyaromatic compounds constitute a major fraction of OA in Chinese megacities (Wang et al.,
265 2021). In contrast, fine PM samples from Mainz show substantially lower RF_{UOC} (15%), suggesting
266 a weaker contribution of aromatic emissions and a relatively greater biogenic influence
267 compared with Chinese megacities, which is consistent with our previous study showing fewer
268 compounds with high degree of unsaturation observed in Mainz OA compared to Beijing OA
269 (Wang et al., 2018a).

270 To assess whether the MCR-VK-based classification reflects intrinsic molecular functionality,
271 we further examined its relationships with independent structural indicators derived from the
272 UHRMS data. Aromatic compounds and HOMs were identified from the assigned molecular
273 formulas using established UHRMS-based criteria (Tong et al., 2019; Yassine et al., 2014). As
274 shown in Figure 1a, the aromatics of ambient fine PM samples from all sampling sites cluster
275 within the UOC region in the MR-VK diagram based on their average O/C and H/C values, whereas
276 HOMs consistently fall within the OOC region, reflecting their distinct degrees of unsaturation
277 and oxygenation. Importantly, the MCR-VK-based classification shows strong quantitative
278 agreements with these independent indicators. Across all samples, the RF_{OOC} correlates well with
279 the relative fraction of HOMs ($R^2 = 0.75$, Figure 2a), while the RF_{UOC} is strongly correlated with
280 the abundance of aromatics ($R^2 = 0.88$, Figure 2b). These strong correlations arise from clear
281 environmental contrasts, whereby biogenic-influenced sites show high fractions of HOMs and
282 low aromatic contributions, while urban megacities exhibit the reverse trend. Moreover, the
283 ratio of OOC to UOC fractions (RF_{OOC}/RF_{UOC}) correlates well with the ratio of HOMs to aromatic
284 fractions ($R^2 = 0.92$, Figure 2c), further demonstrating that the framework captures the balance
285 between unsaturated, aromatic moieties and oxygen-rich, multifunctional compounds.
286 Collectively, these results indicate that the MCR-VK-based classification reflects underlying
287 molecular functionality. Importantly, unlike HOM or aromatics identification, which requires
288 specific compositional criteria and captures only a subset of organic compounds, the OOC/UOC
289 classification encompasses the entire detected OA composition and therefore provides a more
290 comprehensive representation of molecular functionality relevant to ROS formation.



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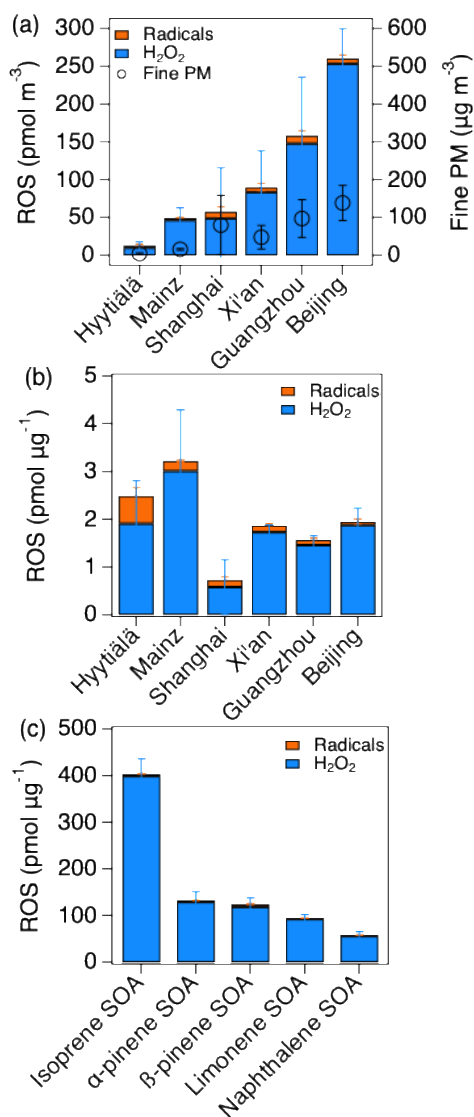
292 **Figure 2.** (a) Correlation between relative peak area-weighted fractions of OOC (RF_{OOC}) and HOMs
 293 (RF_{HOMs}); (b) Correlation between relative peak area-weighted fractions of UOC (RF_{UOC}) and
 294 aromatics ($RF_{Aromatics}$); (c) Correlation between the ratio of OOC to UOC fractions (RF_{OOC}/RF_{UOC})
 295 and the ratio of HOMs to aromatic fractions ($RF_{HOMs}/RF_{Aromatics}$). The dots and error bars represent
 296 the mean values and standard deviations, respectively.

297



298 3.2 ROS yields and formation potential of ambient fine PM and laboratory-generated SOA

299 Figure 3a compares the volume-normalized ROS yields (H_2O_2 +radicals) together with fine PM
300 mass concentrations across all ambient sites. Substantial site-to-site variability is observed,
301 reflecting differences in both aerosol loadings and atmospheric environments. Urban megacities
302 such as Beijing, Guangzhou, Shanghai, and Xi'an exhibit substantially higher volume-normalized
303 ROS yields ($57.8\text{--}260.5\text{ pmol m}^{-3}$) than the boreal forest site at Hyytiälä (13.0 pmol m^{-3}) and the
304 semi-urban site in Mainz (49.9 pmol m^{-3}). This spatial pattern exhibits a similar trend with the
305 corresponding fine PM mass concentrations (Figure 3a), indicating that environments with higher
306 particle loadings contain greater amounts of ROS-generating substances per unit air volume (Gali
307 et al., 2020; Lakey et al., 2016). Across all sites, H_2O_2 dominates the ROS budget, accounting for
308 approximately 78–97% of total ROS. For example, H_2O_2 yields reach 253.7 pmol m^{-3} in Beijing and
309 148.0 pmol m^{-3} in Guangzhou, whereas radical yields remain comparatively low ($\leq 10.6\text{ pmol m}^{-3}$).
310 A similar dominance of H_2O_2 is observed at Hyytiälä and Mainz, despite their much lower ROS
311 yields. We further examined the relationship between volume-normalized ROS and fine PM mass
312 concentration. Strong positive correlations are observed between fine PM mass and volume-
313 normalized total ROS, H_2O_2 , and radical yields (Figure S5). These correlations indicate that on an
314 air-volume basis, ambient ROS exposure is largely governed by particle loading.



315

316 **Figure 3.** (a) The volume-normalized ROS yields (bars, H_2O_2 +radicals) and fine PM mass
 317 concentrations (dots) in ambient fine PM; (b) The mass-normalized ROS yields (H_2O_2 +radicals) in
 318 ambient fine PM; (c) The mass-normalized ROS yields (H_2O_2 +radicals) in laboratory-generated
 319 SOA. The error bars represent the standard deviations

320



321 However, volume-normalized metrics alone do not capture intrinsic differences in the ROS
322 formation potential of particles themselves. Figure 3b shows the mass-normalized ROS yields
323 across all ambient sites, expressed as pmol of ROS per microgram of fine PM. In contrast to the
324 volume-normalized results, mass-normalized ROS yields show markedly different trends across
325 sites and no longer scale with fine PM mass concentrations. For total ROS, the mass-normalized
326 yields range from 0.73 pmol μg^{-1} in Shanghai to 3.32 pmol μg^{-1} in Mainz, with the boreal forest
327 site at Hyytiälä also exhibiting relatively high values (2.49 pmol μg^{-1}) despite its low fine PM mass
328 concentration. This divergence clearly indicates that intrinsic particle composition, rather than
329 particle mass, governs ROS formation on a per-mass basis. This observation further supports
330 previous studies showing that intrinsic particle oxidative activity is more strongly governed by
331 chemical composition than by PM mass concentration alone (Salana et al., 2024; Daellenbach et
332 al., 2020). Across all sites, mass-normalized H_2O_2 yields dominate total ROS and exhibit a similar
333 spatial pattern to total ROS, reflecting the widespread formation of relatively stable peroxide
334 species in ambient fine PM. In contrast, radical yields exhibit a distinctly different behavior.
335 Radical yields are the highest at the biogenic site Hyytiälä (0.58 pmol μg^{-1}) and remain elevated
336 in Mainz (0.21 pmol μg^{-1}) but are substantially lower in some megacities such as Beijing (0.07
337 pmol μg^{-1}) and Guangzhou (0.11 pmol μg^{-1}). These differences point to pronounced variability in
338 the chemical nature of fine PM across environments. The contrasting behaviors of H_2O_2 and
339 radicals are further illustrated by their relative contributions to total ROS (Figure S6). At Hyytiälä,
340 radicals account for nearly one-quarter of total ROS (23%), consistent with a greater contribution
341 of reactive, short-lived ROS species in biogenic aerosols. In most urban environments, radical
342 contributions are considerably smaller, typically around 7%, and drop to as low as 3% in Beijing.
343 Notably, Shanghai exhibits a relatively high radical fraction (20%) despite having the lowest total
344 ROS yield, highlighting that radical contributions are not simply controlled by total ROS
345 production but instead reflect distinct compositional features of the aerosol.

346 Correlation analysis further supports the interpretation that particle chemistry, rather than
347 particle loading, governs intrinsic ROS formation potential. While volume-normalized ROS, H_2O_2 ,
348 and radical yields all show strong positive correlations with fine PM mass concentration, no
349 significant correlations are observed between fine PM mass concentration and mass-normalized



total ROS or H₂O₂ yields (Figures S7a and S7b). In contrast, radical yields display a significant negative correlation with fine PM mass concentration ($R^2=0.90$, Figure S7c). This inverse relationship indicates that although polluted environments generate higher total radical concentrations per unit air volume, individual particles in these environments are intrinsically less efficient at producing radicals. Conversely, particles in clean or biogenic environments, despite contributing less to the total atmospheric radical burden, exhibit a substantially higher radical yield on a per-mass basis. Interestingly, a similar negative relationship is observed between fine PM mass concentration and the RF_{OOC}/RF_{UOC} derived from the MCR-VK classification ($R^2=0.87$, Figure S7d). Urban megacities with high fine PM mass concentrations tend to exhibit lower RF_{OOC}/RF_{UOC} values, consistent with a greater contribution from unsaturated, aromatic-rich organic aerosols. In contrast, biogenic-influenced sites characterized by lower fine PM mass show higher RF_{OOC}/RF_{UOC} values, reflecting a dominance of highly oxygenated, multifunctional organic species (Huang et al., 2024; Roldin et al., 2019). The parallel trends observed for radical yields and RF_{OOC}/RF_{UOC} suggest that environments favoring oxygen-rich OA composition also enhance the intrinsic capacity of particles to generate reactive radical species.

Laboratory-generated SOA provides additional context for interpreting these ambient patterns. Mass-normalized ROS yields of SOA derived from different precursors (Figure 3c) span a wide range, with isoprene SOA exhibiting exceptionally high ROS yields (403 pmol μg^{-1}), followed by α -pinene and β -pinene SOA (125–133 pmol μg^{-1}), and substantially lower yields for limonene SOA (94 pmol μg^{-1}) and naphthalene SOA (58 pmol μg^{-1}). Although ROS yields of laboratory-generated SOA exceed those of ambient fine PM, the relative ordering among precursors provides a mechanistic framework for understanding ambient observations. Specifically, aerosols enriched in highly oxygenated, biogenic SOA components are expected to exhibit higher intrinsic ROS activity, whereas aerosols dominated by aromatic, less oxygenated organics are comparatively less efficient at generating ROS on a mass basis (Tong et al., 2018). This interpretation is consistent with the elevated mass-normalized ROS yields observed at Hyytiälä and the lower yields in megacities such as Shanghai and Beijing, despite the much higher aerosol mass loading in the latter. It should be noted that previous studies have reported higher oxidative potential for anthropogenic aerosols, such as naphthalene SOA, than for biogenic SOA



379 based on the dithiothreitol (DTT) assay (Tuet et al., 2017; Bates et al., 2019). This discrepancy
380 likely arises because the DTT assay quantifies electron-transfer capacity and is sensitive to redox-
381 active species such as quinones, whereas the present study measures hydrogen peroxide and
382 radical formation in aqueous extracts, reflecting product-based ROS formation pathways.

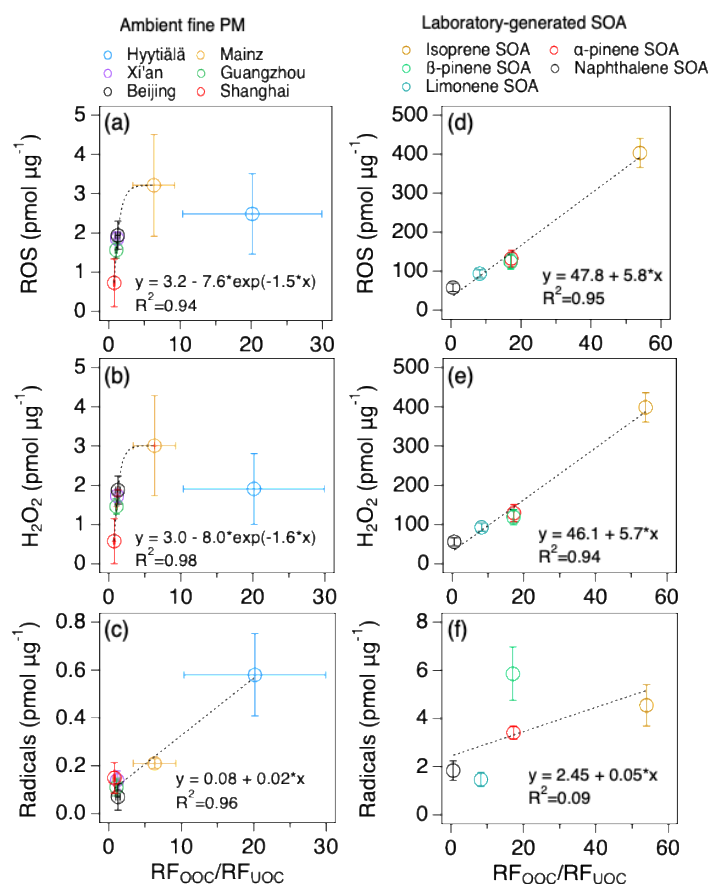
383 Overall, these results indicate that fine PM mass largely controls the total atmospheric ROS
384 burden, whereas particle-level ROS formation potential is governed by OA composition. This
385 contrast highlights the need for a molecularly resolved metric to link intrinsic ROS activity with
386 OA chemistry.

387

388 3.3 Associations of RFOOC/RFUOC with ROS yields in ambient fine PM and laboratory- 389 generated SOA

390 To elucidate how molecular-level OA composition governs particle-level ROS formation, we
391 examined the relationships between particle mass-normalized ROS yields (total ROS, H₂O₂, and
392 radicals) and the RF_{00C}/RF_{U0C} derived from the MCR-VK framework for both ambient fine PM and
393 laboratory-generated SOA (Figures 4).

394 For ambient urban fine PM samples (Mainz, Beijing, Xi'an, Guangzhou, and Shanghai), a
395 strong positive exponential relationship ($R^2=0.94$, Figure 4a) is observed between total ROS yields
396 and RF_{00C}/RF_{U0C}. Specifically, ROS yields increase rapidly with increasing RF_{00C}/RF_{U0C} at low to
397 moderate values, followed by a gradual saturation at higher RF_{00C}/RF_{U0C}. This behavior indicates
398 that ROS formation is initially limited by the availability of oxygenated organic functionalities but
399 becomes progressively constrained by competing chemical pathways and interactions as
400 oxidation increases. This saturation behavior likely reflects the chemically complex nature of
401 urban fine PM, in which diverse OA constituents, including unsaturated species, aromatics, and
402 redox-active components, interact to regulate ROS generation efficiency. Because these yields
403 are normalized to particle mass, the observed relationship directly reflects differences in
404 chemical composition rather than particle loading. The consistency of this relationship across
405 multiple cities with diverse emission profiles suggests that RF_{00C}/RF_{U0C} captures a fundamental
406 compositional control on ROS generation that is robust across urban environments.



407

408 **Figure 4.** Correlations of mass-specific ROS yields (a, d), H₂O₂ yields (b, e), and radical yields (c, f)
 409 with RF_{OOC}/RF_{UOC} in ambient fine PM samples (a–c) and laboratory-generated SOA samples (d–f).
 410 The dots and error bars represent the mean values and standard deviations, respectively.

411

412 Given the dominance of H₂O₂ in the total ROS of ambient urban fine PM (80–97%; Figure S6),
 413 its dependence on OA composition closely follows that of total ROS. Accordingly, H₂O₂ yields
 414 exhibit a similarly strong positive relationship with RF_{OOC}/RF_{UOC} ($R^2 = 0.98$, Figure 4b), reinforcing
 415 that oxygenated organic enrichment strongly promotes aqueous ROS formation. Consistent with
 416 this result, both total ROS and H₂O₂ yields show clear positive linear correlations with RF_{OOC}
 417 (Figure S7b), suggesting that the abundance of OOC is a major factor controlling ROS formation
 418 efficiency. Increases in OOC content therefore lead to higher mass-normalized ROS and H₂O₂



419 production. This behavior is consistent with previous studies showing that hydroperoxides,
420 organic peroxides, and peroxy acids, functional groups commonly associated with OOC, can
421 decompose or hydrolyze in aqueous environments to produce H_2O_2 (Wang et al., 2011; Tong et
422 al., 2018; Hasson et al., 2001; Venkatachari and Hopke, 2008; Li et al., 2025). Liu et al. (2023)
423 reported that the more oxidized oxygenated organic aerosols were associated with cellular ROS
424 production, with highly unsaturated species containing carbon–oxygen double bonds and
425 aromatic rings in OOA identified as important contributors. While oxidized organic species are
426 found to play an important role in both studies, the present study links higher RF_{OOC}/RF_{UOC} to
427 enhanced ROS formation. This difference likely reflects the different oxidative endpoints
428 investigated. The previous study evaluated intracellular ROS responses, whereas the present
429 study quantifies the intrinsic formation of hydrogen peroxide and radicals in aqueous extracts.

430 An important deviation from the urban trend is observed for the boreal forest site at Hyytiälä.
431 Although Hyytiälä fine PM exhibits a higher RF_{OOC}/RF_{UOC} ratio than urban samples, its H_2O_2 and
432 total ROS yields fall below the exponential relationship established for urban aerosols (Figures 4a
433 and 4b). This behavior indicates that the empirical relationship derived for urban fine PM cannot
434 be directly extrapolated to biogenic-dominated environments. The discrepancy likely reflects
435 fundamental differences in aerosol composition and ROS-forming pathways. Urban fine PM
436 typically contains higher abundances of quinones (classified as UOC), which can substantially
437 enhance H_2O_2 formation (Chung et al., 2006). In contrast, remote forest aerosols contain much
438 lower abundances of metals and aromatic quinones, suggesting that ROS generation at Hyytiälä
439 is dominated by biogenic SOA components.

440 Radical yields show a markedly different response to OA composition compared with H_2O_2 .
441 For ambient fine PM, radical yields exhibit a positive linear relationship with RF_{OOC}/RF_{UOC} when
442 the biogenic site is included (Figure 4c). This trend is largely driven by the elevated radical yields
443 observed at Hyytiälä, where exceptionally high RF_{OOC}/RF_{UOC} coincides with a high abundance of
444 HOMs (Figure 2). This behavior is consistent with our previous findings showing that HOMs, which
445 are preferentially classified as OOC, can play an important role in aqueous radical formation
446 (Tong et al., 2019). The enhanced radical yield at Hyytiälä likely reflects its HOM-rich OA
447 composition. Among the urban sites, however, radical yields exhibit relatively limited variation



despite differences in RF_{OOC}/RF_{UOC} , which could be due to additional influence by other aerosol constituents beyond the bulk balance between OOC and UOC. Therefore, RF_{OOC}/RF_{UOC} may be more useful in predicting radical formation when comparing aerosols spanning contrasting source regimes (e.g., biogenic versus urban).

Laboratory-generated SOA further supports the compositional control inferred from the ambient observations. Across SOA formed from isoprene, α -pinene, β -pinene, limonene, and naphthalene, total ROS yields increase with the increase of RF_{OOC}/RF_{UOC} and follow a strong positive linear relationship (Figure 4d, $R^2=0.95$). A similar dependence is observed for H_2O_2 yields (Figure 4e, $R^2=0.94$), consistent with the dominant contribution of H_2O_2 to total ROS in these systems. Unlike ambient urban PM, no saturation behavior is observed over the investigated compositional range, indicating that ROS formation in laboratory SOA remains composition-limited, with increasing oxygenation directly translating into higher intrinsic reactivity. The absence of non-linear behavior further suggests minimal interference from competing redox-active components for SOA formed under control conditions.

In contrast, no clear relationship is found between radical yields and either RF_{OOC}/RF_{UOC} for laboratory-generated SOA (Figure 4f). This further suggests that radical formation depends more strongly on the abundance of specific radical-producing molecular species than on the overall balance between OOC and UOC. For example, semiquinone-type functionalities in naphthalene SOA can generate radicals through redox cycling pathways (Tong et al., 2019), leading to deviations from the overall composition–reactivity trends.

4 Conclusions and Implications

In this work, by applying the MCR-VK framework to a diverse range of ambient and laboratory aerosols, we show that the intrinsic ROS formation potential of fine PM is governed not by particle mass, but by the balance between two functionally distinct classes of organic compounds: OOC and UOC. The relative abundance of OOC compared with UOC is a key determinant of the intrinsic ROS formation potential of fine PM. Particles enriched in OOC exhibit significantly higher mass-normalized ROS yields, particularly for H_2O_2 , indicating that the molecular composition of OA, rather than particle mass, governs aqueous ROS production.



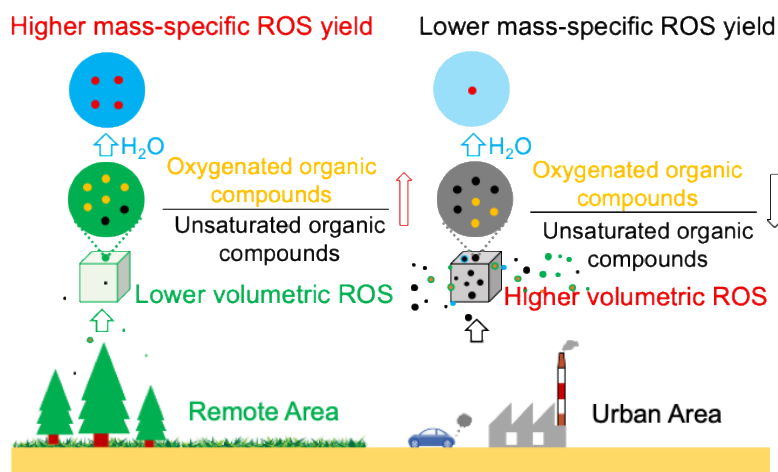
476 As illustrated in Figure 5, this compositional control leads to a clear contrast between urban
477 and remote environments. In polluted urban areas, high PM mass concentrations result in
478 elevated volume-normalized ROS, driving greater overall exposure to ROS. However, the aerosols
479 themselves are less efficient at generating ROS per unit mass due to a relatively smaller
480 contribution from OOC and a larger contribution from UOC. By contrast, in remote (e.g., forest)
481 areas, lower particle loadings produce lower volumetric ROS, yet individual particles are
482 intrinsically more reactive. This enhanced per-mass ROS formation is driven by the dominance of
483 OOC (e.g., HOMs), leading to higher RF_{OOC}/RF_{UOC} ratios. These results highlight that both particle
484 mass and particle composition independently shape ROS formation, and both must be jointly
485 considered when evaluating ROS-related health risks of ambient fine PM (Zheng et al., 2025;
486 Salana et al., 2024).

487 The strong, consistent correlations between RF_{OOC}/RF_{UOC} and mass-normalized ROS yields
488 observed across urban megacities establish this ratio as a simple yet robust predictor for ROS
489 formation potential of OA. Unlike previous studies that focused on specific ROS-active compound
490 classes such as HOMs, organic peroxides, or quinones (Tong et al., 2019; Verma et al., 2015), the
491 MCR-VK framework provides a generalized molecular-level descriptor that can be derived directly
492 from UHRMS data without requiring targeted compound identification. This feature makes the
493 framework broadly applicable to chemically diverse atmospheric aerosols and offers a scalable
494 approach for predicting aerosol oxidative activity.. Within this framework, lower RF_{OOC}/RF_{UOC}
495 corresponds to reduced mass-normalized ROS yields, while higher RF_{OOC}/RF_{UOC} likely indicates
496 intrinsically more ROS-active aerosols. As a result, regional differences in precursor sources and
497 atmospheric processing exert direct control over aerosol oxidative activity, providing a
498 mechanistic explanation for the pronounced spatial variability in ROS formation. Laboratory-
499 generated SOA further validates these conclusions. SOA formed from biogenic precursors such
500 as isoprene and α -/ β -pinene, characterized by high RF_{OOC}/RF_{UOC} , exhibits the highest ROS
501 formation efficiency, whereas SOA formed from naphthalene produces lower ROS yield per mass.
502 Collectively, these ambient and laboratory results demonstrate that molecular composition,
503 particularly the balance between OOC and UOC, provides a mechanistic basis for both the
504 magnitude and spatial variability of ROS formation in atmospheric aerosols.



505 While this study focuses on the role of organic aerosol molecular composition, transition
506 metals are also recognized contributors to ROS formation in ambient PM through metal-
507 catalyzed redox cycling and Fenton-like reactions, particularly in urban environments (Charrier et
508 al., 2014; Xiong et al., 2017; Tong et al., 2016). Interactions between redox-active metals and OA
509 components, such as quinone- or peroxide-containing species, may further influence ROS
510 formation pathways. In addition, ROS formation was quantified in aqueous extracts of particulate
511 matter in this study, providing a chemically controlled system to evaluate ROS formation
512 potential of aerosols and enabling consistent comparison across samples. However, simulated
513 lung fluids may better represent physiological conditions due to antioxidants and metal-binding
514 ligands, and future studies incorporating simulated lung fluids may refine the translation of ROS
515 formation to more biologically relevant exposure metrics. Nevertheless, the strong and
516 consistent correlations observed between ROS yields and RF_{OOC}/RF_{UOC} across diverse
517 environments indicate that OA composition plays a critical role in particle-level ROS formation.
518 Integrating molecularly resolved OA composition with metal speciation in future studies will be
519 important for fully resolving their coupled and potentially synergistic effects (Charrier and
520 Anastasio, 2015; Lin and Yu, 2026).

521 Overall, the MCR-VK framework offers a predictive, molecular-level approach to link OA
522 composition with ROS formation potential. Future efforts should prioritize long-term,
523 molecularly resolved measurements of OA across diverse environments, coupled with ROS assays,
524 as well as concurrent, comprehensive, and complementary aerosol and aerosol precursor
525 characterization during the sample collection, to capture the combined influence of particle
526 loading, chemical composition, and atmospheric processing. Such integrated approaches will
527 improve identification of the OA components most responsible for oxidative stress, advance
528 understanding of the health risks associated with ambient fine PM, and support the development
529 of more targeted and composition-aware air quality management strategies.



530

531 **Figure 5.** Schematic illustration of the relationships of volumetric ROS, the balance between
 532 oxidized and unsaturated organic compounds, and mass-normalized ROS yield of fine PM from
 533 remote and urban areas.

534

535 Data Availability

536 The data sets generated in the current study are available at Zenodo data repository

537 (<https://zenodo.org/records/19334829>).

538 Supporting Information

539 Table showing the detailed information for the ambient particle sampling; figures showing the
 540 schematic outline of the experimental approach, maximum carbonyl ratio (MCR)-Van Krevelen
 541 (VK) diagram, detailed mass spectra and MCR-VK diagram for both ambient and laboratory-
 542 generated SOA samples, correlations of volume-normalized/mass-normalized ROS yield, H₂O₂
 543 yield and radical yield with fine PM mass concentration, contributions of H₂O₂ and radicals to
 544 total ROS yield.

545

546 Author contributions

547



548 This study was conceived by TH, KW and HT. YZ and KW conducted the sample analysis. SY, HK,
549 TP, MK and PF assisted with the sample and data collections. FL and YZ wrote the original
550 manuscript. All authors contributed to the final interpretation and writing of the manuscript.

551 **Competing interests**

552 At least one of the (co-)authors is a member of the editorial board of Atmospheric Chemistry and
553 Physics.

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