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Aqueous-phase reactive species formed by fine particulate matter from remote forests and polluted urban air

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Abstract. In the aqueous phase, fine particulate matter can form reactive species (RS) that influence the aging, properties, and health effects of atmospheric aerosols. In this study, we explore the RS yields of aerosol samples from a remote forest (Hyytiälä, Finland) and polluted urban locations (Mainz, Germany; Beijing, China), and we relate the RS yields to different chemical constituents and reaction mechanisms. Ultra-high-resolution mass spectrometry was used to characterize organic aerosol composition, electron paramagnetic resonance (EPR) spectroscopy with a spin-trapping technique was applied to determine the concentrations of $^{\bullet}OH$, $O_2^{\bullet -}$, and carbon- or oxygen-centered organic radicals, and a fluorometric assay was used to quantify H_2O_2. The aqueous H_2O_2-forming potential per mass unit of ambient $PM_{2.5}$ (particle diameter $< 2.5\,\mu m$) was roughly the same for all investigated samples, whereas the mass-specific yields of radicals were lower for sampling sites with higher concentrations of $PM_{2.5}$. The abundances of water-soluble transition metals and aromatics in ambient $PM_{2.5}$ were positively correlated with the relative fraction of $^{\bullet}OH$ and negatively correlated with the relative fraction of carbon-centered radicals. In contrast, highly oxygenated organic molecules (HOM) were positively correlated with the relative fraction of carbon-centered radicals and negatively correlated with the relative fraction of $^{\bullet}OH$. Moreover, we found that the relative fractions of different types of radicals formed by ambient $PM_{2.5}$

were comparable to surrogate mixtures comprising transition metal ions, organic hydroperoxide, H_2O_2, and humic or fulvic acids. The interplay of transition metal ions (e.g., iron and copper ions), highly oxidized organic molecules (e.g., hydroperoxides), and complexing or scavenging agents (e.g., humic or fulvic acids) leads to nonlinear concentration dependencies in aqueous-phase RS production. A strong dependence on chemical composition was also observed for the aqueous-phase radical yields of laboratory-generated secondary organic aerosols (SOA) from precursor mixtures of naphthalene and β-pinene. Our findings show how the composition of $PM_{2.5}$ can influence the amount and nature of aqueous-phase RS, which may explain differences in the chemical reactivity and health effects of particulate matter in clean and polluted air.

1 Introduction

Atmospheric fine particulate matter with a particle diameter $< 2.5\,\mu m$ ($PM_{2.5}$) can form reactive species (RS) upon dissolution in the aqueous phase (Bates et al., 2015; Lakey et al., 2016; Park et al., 2018; Li et al., 2018; Tong et al., 2019). The umbrella term RS comprises reactive oxygen species (e.g., $^{\bullet}OH$, $O_2^{\bullet -}$, $^1O_2$, H_2O_2, and ROOH) as well as C- and O-centered organic radicals (Halliwell and Whiteman, 2004; Sies et al., 2017), which influence the chemical aging of atmospheric aerosols and their interaction with the biosphere (Pöschl and Shiraiwa, 2015; Reinmuth-Selzle et al., 2017; Shiraiwa et al., 2017). For example, Fenton-like reactions of hydroperoxides with transition metal ions contribute to the formation of aqueous-phase radicals including $^{\bullet}OH$ (Jacob, 2000; Enami et al., 2014; Anglada et al., 2015; Tong et al., 2016a), enhancing the conversion of organic precursors to secondary organic aerosols (SOA) (Donaldson and Valsaraj, 2010; Ervens et al., 2011; Gligorovski et al., 2015; Gilardoni et al., 2016). Moreover, $PM_{2.5}$ may generate excess concentrations of RS in human airways, causing antioxidant depletion, oxidative stress, and respiratory diseases (Nel, 2005; Cui et al., 2015; Lakey et al., 2016; Qu et al., 2017; Lelieveld and Pöschl, 2017; Rao et al., 2018).

The formation pathways and yields of RS from ambient PM and laboratory-generated SOA have been investigated in a wide range of studies (Valavanidis et al., 2005; Ohyama et al., 2007; Chen et al., 2010; Wang et al., 2011a, b; Verma et al., 2014; Badali et al., 2015; Bates et al., 2015; Verma et al., 2015; Arangio et al., 2016; Tong et al., 2016a; Kuang et al., 2017; Tong et al., 2017; Zhou et al., 2018; Tong et al., 2019; Chowdhury et al., 2019; Fang et al., 2019; Liu et al., 2020). The mass, surface area, and chemical composition of PM were discussed as key factors influencing the reactivity of atmospheric aerosols (Møller et al., 2010; Fang et al., 2015; Jin et al., 2019; Lammel et al., 2020). Among the substance groups associated with RS formation by PM in water are black carbon (Baumgartner et al., 2014), transition metals (Yu et al., 2018), oxidized aromatic compounds including quinones and environmentally persistent free radicals (EPFR) (Xia et al., 2004; Gehling et al., 2014; Charrier et al., 2014; Xiong et al., 2017), humic-like substances (HULIS) (Lin and Yu, 2011; Page et al., 2012; Fang et al., 2019), and peroxide-containing highly oxygenated organic molecules (HOM) (Chen et al., 2010; Wang et al., 2011b; Tong et al., 2016a, 2018, 2019; Fang et al., 2020; Qiu et al., 2020). Moreover, the HULIS and other multifunctional compounds containing carboxyl, carboxylate, phenolic, and quinoid groups may influence the redox activity of PM via chelating transition metals (Laglera and van den Berg, 2009; Kostić et al., 2011; Catrouillet et al., 2014; Gonzalez et al., 2017; Y. Wang et al., 2018; Win et al., 2018; Wei et al., 2019).

To assess the oxidative potential of ambient PM, the following cellular or acellular assays have been used: dichloro-dihydro-fluorescein diacetate (DCFH-DA), dithiothreitol (DTT), ascorbic acid (AA), macrophage, electron paramagnetic resonance (EPR), and surrogate lung fluids (SLF) (Landreman et al., 2008; Charrier and Anastasio, 2012; Kalyanaraman et al., 2012; Charrier et al., 2014; Charrier and Anastasio, 2015; Fang et al., 2016; Tong et al., 2018; Bates et al., 2019; Fang et al., 2019; Molina et al., 2020; Crobeddu et al., 2020). However, the interplay of different PM constituents often results in nonadditive characteristics of the RS yields or oxidative potential of PM (Charrier et al., 2014; Lakey et al., 2016; S. Wang et al., 2018). Thus, unraveling the adverse health effects of ambient PM requires systematic investigations of the RS formation and chemical reactivity of PM from different sources and environments (Shiraiwa et al., 2017).

The concentration of $PM_{2.5}$ and the composition of airborne organic matter vary considerably between clean forest and polluted urban environments. For example, the $PM_{2.5}$ concentrations at the Hyytiälä forest site are typically below $10\,\mu g\,m^{-3}$, with organic matter accounting for $\sim 70\,\%$ (Laakso et al., 2003; Maenhaut et al., 2011), whereas the $PM_{2.5}$ concentrations in Beijing during winter can reach and exceed daily average values of $150\,\mu g\,m^{-3}$, with organic matter accounting for $\sim 40\,\%$ (Huang et al., 2014). Moreover, anthropogenic emissions can enhance the formation of biogenic SOA and HOM as well as the levels of particulate transition metals and humic-like substances and the PM oxidative potential (Goldstein et al., 2009; Hoyle et al., 2011; Liu et al., 2014; Xu et al., 2015; Ma et al., 2018; Pye et al., 2019; Shrivastava et al., 2019).

In this study, we compared the RS yields of $PM_{2.5}$ in clean and polluted environments. We used three approaches to explore the RS formation by $PM_{2.5}$ from the remote forest of Hyytiälä (Finland), the intermediately polluted city of Mainz (Germany), and the heavily polluted megacity of Beijing (China) (Fig. 1). To quantify the abundances of redox-active PM constituents related to RS formation, we collected ambient $PM_{2.5}$ and measured the chemical composition of organic matter, the abundances of water-soluble transition metals, and the yield of radicals and H_2O_2 in the liquid phase (Fig. 1a). To assess the influence of anthropogenic–biogenic organic matter interactions on the RS formation by ambient $PM_{2.5}$, we analyzed the radical yield of SOA generated by the oxidation of mixed anthropogenic and biogenic precursors in a laboratory chamber (Fig. 1b). To gain insights into the radical formation mechanism of ambient $PM_{2.5}$ in water, we differentiated the influences of transition metal ions, organic hydroperoxide (ROOH), and water-soluble humic acid (HA) and fulvic acid (FA) on radical formation by Fenton-like reactions (Fig. 1c).

2 Materials and methods

2.1 Chemicals

The following chemicals were used as received without further purification: β-pinene (99 %, Sigma–Aldrich), naphthalene (99.6 %, Alfa Aesar GmbH & Co. KG), cumene hydroperoxide (80 %, Sigma–Aldrich), H_2O_2 (30 %, Sigma–Aldrich), $FeSO_4 \cdot 7H_2O$ (F7002, Sigma–Aldrich), $CuSO_4 \cdot 5H_2O$ (209198, Sigma–Aldrich), $NiCl_2$ (98 %, Sigma–Aldrich), $MnCl_2$ ($\geq$ 99 %, Sigma–Aldrich), VCl_2 (85 %, Sigma–Aldrich), NaCl (443824T, VWR International GmbH), KH_2PO_4 ($\geq$ 99 %, Alfa Aesar GmbH & Co. KG), Na_2HPO_4 ($\geq$ 99.999 %, Fluka), humic acid (53680, Sigma–Aldrich), fulvic acid (AG-CN2-0135-M005, Adipogen), 5-*tert*-butoxycarbonyl-5-methyl-1-pyrroline-*N*-oxide (BMPO, high-purity, Enzo Life Sciences, Inc.), H_2O_2 assay kit (MAK165, Sigma–Aldrich), ultrapure water (14211-1L-F, Sigma–Aldrich), 47 mm diameter Teflon filters (JVWP04700, Omnipore membrane filter), and micropipettes (50 µL, Brand GmbH & Co. KG). The neutral saline (pH = 7.4) used consists of 10 mM phosphate buffer (2.2 mM KH_2PO_4 and 7.8 mM Na_2HPO_4) and 114 mM NaCl, which was used to simulate physiologically relevant conditions.

2.2 Collection and extraction of ambient fine PM

Ambient fine particles were collected onto Teflon filters at all sites. The Hyytiälä $PM_{2.5}$ was collected using a three-stage cascade impactor (Dekati® PM10) at the Station for Measuring Forest Ecosystem–Atmosphere Relations (SMEAR II, Finland) during 31 May–19 July 2017 (Hari and Kulmala, 2005). The Mainz fine PM was collected using a micro-orifice uniform deposit impactor (MOUDI, 122-R, MSP Corporation) (Arangio et al., 2016) on the roof of the Max Planck Institute for Chemistry during 22 August–17 November 2017 and 23–31 August 2018. The Beijing winter $PM_{2.5}$ was collected using a four-channel $PM_{2.5}$ air sampler (TH-16, Wuhan Tianhong Instruments Co., Ltd.) in the campus of the Peking University, an urban site in Beijing, during 20 December–13 January 2016 and 6 November–17 January 2018 (Lin et al., 2015). The sampling times for a single filter sample in Hyytiälä, Mainz, and Beijing were 48–72, 25–54, and 5–24 h, respectively, depending on the local PM concentrations. More information about the sampling is shown in Table S1 in the Supplement. After sampling, all filter samples were put in Petri dishes and stored in a −80 °C freezer before analysis. To determine the mass of collected PM, each filter was weighed before and after the collection using a high-sensitivity balance (±10 µg, Mettler Toledo XSE105DU). In Hyytiälä, the PM_1 and $PM_{1-2.5}$ were separately sampled and then combined and extracted together to represent $PM_{2.5}$ samples. The Mainz PM with a cut-size range of 0.056–1.8 µm was taken as a proxy for $PM_{2.5}$. Particle concentrations in aqueous extracts were estimated to be in the range of 200–6000 µg mL^{-1} (Fig. S1 in the Supplement).

2.3 Formation, collection, and extraction of laboratory-generated SOA

To generate SOA from mixed anthropogenic and biogenic precursors, different concentrations of gas-phase naphthalene and β-pinene were mixed and oxidized in a potential aerosol mass (PAM) chamber, i.e., an oxidation flow reactor (OFR) (Kang et al., 2007; Tong et al., 2018). Naphthalene and β-pinene were used as representative SOA precursors in Beijing and Hyytiälä, respectively (Hakola et al., 2012; Huang et al., 2019). The concentrations of gas-phase O_3 and $^{\bullet}OH$ in the PAM chamber were $\sim$ 1 ppm and $\sim 5.0 \times 10^{11}$ cm^{-3} (Tong et al., 2018), respectively. SOA were produced by adjusting the concentration of naphthalene relative to the sum of it with β-pinene (i.e., [naphthalene]/([naphthalene] + [β-pinene])) to be $\sim$ 9 %, $\sim$ 23 %, and $\sim$ 38 % (mass fractions), respectively. The concentrations of naphthalene and β-pinene were 0.2–0.6 and 1.0–2.5 ppm, respectively, which were determined on the basis of a calibration function measured by gas chromatography–mass spectrometry (Tong et al., 2018). The number and size distributions of SOA particles were measured using a scanning mobility particle sizer (SMPS, GRIMM Aerosol Technik GmbH & Co. KG). When the SOA concentration was stable, 47 mm diameter Teflon filters (JVWP04700, Omnipore membrane filter) were used to collect SOA particles, which were extracted into water solutions within 2 min after the sampling. More information about the formation, characterization, collection, and extraction of SOA can be found in previous studies (Tong et al., 2016a, 2017, 2018, 2019).

2.4 Surrogate mixtures

We used cumene hydroperoxide (CHP), humic acid (HA), fulvic acid (FA), and H_2O_2 as model compounds mimicking the redox-active substances in ambient particulate matter (Lin and Yu, 2011; Ma et al., 2018; Tong et al., 2019). The following method was used to prepare HA or FA solutions. First, 0–1000 µg mL^{-1} HA or FA water suspensions

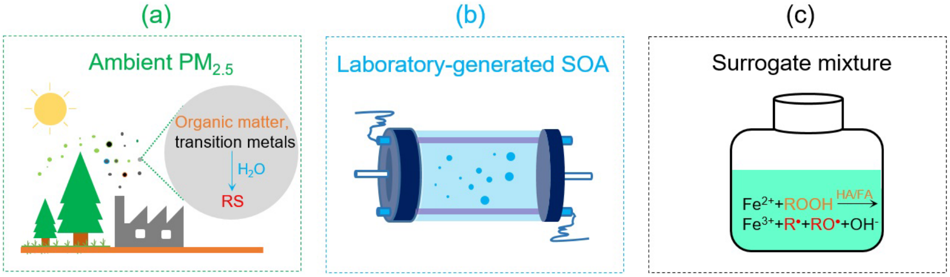

Figure 1. Schematic illustration of the approach used in this research and comparison of the aqueous-phase reactive species (RS) formed in aqueous extracts of ambient fine particulate matter ($PM_{2.5}$), laboratory-generated secondary organic aerosols (SOA), and surrogate mixtures. ROOH: organic hydroperoxide. HA: humic acid. FA: fulvic acid. $R^{\bullet}$ and $RO^{\bullet}$: C- and O-centered organic radicals, respectively.

were made. Then, the suspensions were sonicated for 3 min to accelerate the dissolution of HA or FA. Afterwards, the sonicated suspensions were centrifuged at 6000 rpm (MiniStar, VWR International BVBA) for 2 min. Finally, the supernatants were taken out from the centrifuge tubes with pipettes and stored in glass vials at 4–8 °C before analysis. The HA or FA solutions were prepared fresh each day. To determine the concentrations of dissolved HA or FA, aliquots of the supernatants were dried with a pure N_2 flow (1–2 bar) and weighed with a high-sensitivity balance (±0.01 mg, Mettler Toledo XSE105DU). The concentrations of Fe^{2+}, Cu^{2+}, HA, and H_2O_2 in the surrogate mixtures were 43 µM, 3 µM, 4 $mg\,L^{-1}$, and 7 µM, which were based on the measurement of ambient PM extracts (Fe^{2+} and Cu^{2+}, Sect. 2.8) or the estimated abundance in ambient PM (CHP, HA, FA, and H_2O_2, SI). To explore the influence of HA/FA on Fenton-like reactions, the radical formation in the following aqueous mixtures was also analyzed: CHP + Fe^{2+}, CHP + Cu^{2+}, CHP + Cu^{2+} + HA, and CHP + Cu^{2+} + FA. The concentrations of Fe^{2+}, Cu^{2+}, HA, FA, and H_2O_2 in these solutions were 15–300 µM, 15–300 µM, 0–180 $\mu g\,mL^{-1}$, 0–180 $\mu g\,mL^{-1}$, and 0–300 µM, respectively.

2.5 Quantification of radicals by EPR

5-*tert*-Butoxycarbonyl-5-methyl-1-pyrroline-*N*-oxide (BMPO) was used as a spin-trapping agent for detecting different types of radicals formed in the extracts of PM. Ambient PM or laboratory-generated SOA were extracted from Teflon filters into 10 mM BMPO neutral saline or water solutions by vortex shaking for ∼ 15 min (with Heidolph Reax 1). Around one-fourth of each ambient PM filter or a whole SOA-loaded filter was used for extraction. It was assumed that most of the short-lived radicals reacted with BMPO to form stable adducts during the extraction process.

A continuous-wave electron paramagnetic resonance (CW-EPR) X-band spectrometer (EMXplus-10/12; Bruker Corporation) was applied for the identification and quantification of radical adducts (Tong et al., 2016a, 2017, 2018, 2019). In order to increase the signal-to-noise ratio of EPR spectra, some of the extracts were concentrated by a factor of 5–20 through 15–20 min of drying under a 1–2 bar pure N_2 flow. The EPR spectra of BMPO–radical adducts were recorded by setting the following operating parameters: a microwave frequency of 9.84 GHz, a microwave power of 0.017 mW (20 dB), a receiver gain of 40 dB, a modulation amplitude of 1 G, a scan number of 50, a sweep width of 100 G, a modulation frequency of 100 kHz, a conversion time of 11 ms, and a time constant of 10 ms.

To average the EPR spectra of different $PM_{2.5}$ extracts for each site, the magnetic field values of each spectrum were transformed to *g*-values. Then we used the Bruker software Xenon to do the averaging, irrespective of the concentrations of $PM_{2.5}$ in the extracts. The spin-counting method embedded in Xenon was applied to quantify radical adducts. The spin-counting method was calibrated using the standard compound 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPOL). To obtain the relative yields of $^{\bullet}OH$, $O_2^{\bullet -}$, and C- and O-centered organic radicals, EPR spectra were simulated and fitted using the Xenon software before deconvolution (Arangio et al., 2016; Tong et al., 2018). The spin numbers of assigned species accounted for over 95 % of all the radical adducts observed on average, based on the peak area ratios of the corresponding species. EPR spectra with low signal-to-noise ratios introduce uncertainty into the parameters describing the lineshapes of peaks representing radical adducts (Tseitlin et al., 2012), causing a total quantification uncertainty of 0–19 % for different types of radicals ($^{\bullet}OH$, $O_2^{\bullet -}$, C- and O-centered organic radicals, etc.). The hyperfine coupling constants used for spectrum fitting are shown in Table S2. More information on the hyperfine coupling constants of different types of BMPO–radical adducts can be found in previous studies (Zhao et al., 2001; Arangio et al., 2016).

2.6 Measurement of H_2O_2 yields

We extracted ambient $PM_{2.5}$ from one-fourth of each Teflon filter into 1 mL ultrapure water or neutral saline by stirring it with a vortex shaker for ∼ 15 min. Afterwards, the extracts were centrifuged at 9000 rpm (Eppendorf Minispin) for 3 min to remove the insoluble particles. Finally, the concentration of H_2O_2 in the supernatant was measured using the MAK165 assay kit (Yan et al., 2017; Tong et al., 2018). 50 µL of supernatant and 50 µL of a Master Mix solution containing horseradish peroxidase and Amplex Red substrate were mixed in a 96-well plate. The horseradish peroxidase catalyzed the oxidation of Amplex Red by H_2O_2 to form fluorescent resorufin (Wang et al., 2017), which was consequently quantified using a microplate reader (Synergy®NEO, BioTek, excitation at 540 nm and emission at 590 nm) after 30 min of incubation. The concentration of H_2O_2 in aqueous PM extracts was determined using an H_2O_2 calibration curve based on standard H_2O_2 solutions, and was corrected using blank measurements (Tong et al., 2018).

2.7 Mass spectrometry of organic compounds

Using a Q-Exactive Orbitrap mass spectrometer (Thermo Fisher Scientific, MA, USA) coupled with an ultra-high-performance liquid chromatography (UHPLC) system (Dionex UltiMate 3000, Thermo Scientific, Germany) (K. Wang et al., 2018, 2019; Tong et al., 2019), we characterized the HOM and aromatic compounds in Hyytiälä, Mainz, and Beijing winter fine PM samples in negative ionization mode. We processed the MS spectra and UHPLC chromatograms of measured samples through a non-target screening approach using the commercially available software SIEVE® (Thermo Fisher Scientific, MA, USA). Then, we blank corrected the signals with peak intensities $> 1 \times 10^5$. Afterwards, we used the following criteria to assign molecular formulae and filter out the irrational ones: (a) the numbers of atoms of C, H, O, N, S, and Cl should be in the ranges of 1–39, 1–72, 0–20, 0–7, 0–4, and 0–2, respectively; (b) the atomic ratios H/C, O/C, N/C, S/C, and Cl/C should be in the ranges of 0.3–3, 0–3, 0–1.3, 0–0.8, and 0–0.8, respectively.

The HOM were defined as compounds with the general formula $C_xH_yO_z$, including monomers with $x = 8$–10, $y =$ 12–16, $z = 6$–12, and $z/x > 0.7$ and dimers with $x = 17$–20, $y = 26$–32, and $z = 8$–18 (Ehn et al., 2014; Tröstl et al., 2016; Tong et al., 2019). Aromatics in this study were defined as compounds with an aromaticity index (AI) > 0.5 and an aromaticity equivalent (X_c) > 2.5, with the parameters accounting for the fraction of oxygen and sulfur atoms of a compound involved in π-bond structures set to 1 (Koch and Dittmar, 2006; Yassine et al., 2014; Tong et al., 2016b). Beyond this, the relative abundance of HOM or aromatic compounds was defined to be the summed chromatographic area of HOM or aromatics divided by the summed chromatographic area of all assigned organic compounds, with $< 30\,\%$ of all detected organic compounds not assigned (K. Wang et al., 2018).

2.8 Determination of water-soluble transition metal concentrations

Based on the same extraction method as the H_2O_2 analysis described in Sect. 2.6, the concentrations of five selected water-soluble transition metal species (Fe, Cu, Mn, Ni, and V) in the supernatants of $PM_{2.5}$ extracts were quantified using an inductively coupled plasma mass spectrometer (ICP-MS, Agilent 7900). These five transition metal species were chosen for analysis due to their prominent concentrations and high oxidative potential (Charrier and Anastasio, 2012). A calibration curve for ICP-MS analysis was made by measuring standard multielement stock solutions (custom grade, Inorganic Ventures). An aliquot of the supernatants was diluted and acidified using a mixture of nitric acid (5 %) and hydrofluoric acid (1 %), and was brought to a volume of 5 mL before analysis. The measured transition metal concentrations were blank corrected and are shown in corresponding figures. The detection limit of the ICP-MS analysis performed in this study was typically $< 40\,\mathrm{ng\,L^{-1}}$. The $PM_{2.5}$ samples collected on 2, 7, 9, and 12 June 2017 in Hyytiälä, those collected on 22, 26, and 28 August and 25 September, 25 October, and 14 November in 2017 in Mainz, and all the 12 $PM_{2.5}$ samples taken in winter in Beijing were used for transition metal analysis. The temporal evolutions of water-soluble transition metal concentrations in water extracts of Mainz $PM_{2.5}$ were also determined, and we found that the total ion concentrations of Fe, Cu, Mn, Ni, and V showed rapid rises during the first 15 min (Fig. S2a) but much slower rises afterwards (Fig. S2b).

3 Results and discussion

3.1 Aqueous-phase radical formation from ambient $PM_{2.5}$

Figure 2a shows averaged EPR spectra of BMPO–radical adducts in neutral saline extracts of $PM_{2.5}$ samples from Hyytiälä, Mainz, and Beijing (Table S1). Each spectrum is composed of multiple peaks attributable to different types of BMPO–radical adducts. The dotted vertical lines with different colors indicate peaks attributable to adducts of BMPO with $^{\bullet}OH$ (green), $O_2^{\bullet -}$ (orange), and C- and O-centered organic radicals (blue and purple, respectively) (Zhao et al., 2001; Arangio et al., 2016). The spectrum of Hyytiälä $PM_{2.5}$ is dominated by peaks attributable to C-centered radicals, the spectrum of Mainz $PM_{2.5}$ exhibits strong peaks attributable to C-centered radicals and $^{\bullet}OH$, and the spectrum of Beijing winter $PM_{2.5}$ is dominated by four peaks attributable to $^{\bullet}OH$.

Figure 2b shows the relative fractions (RF_{spin}) of $^{\bullet}OH$, $O_2^{\bullet -}$, and C- and O-centered organic radicals averaged over multiple samples from each site. The mean RFs of C- and O-centered organic radicals were found to decrease upon shifting from clean forest air samples (Hyytiälä, 66 % and

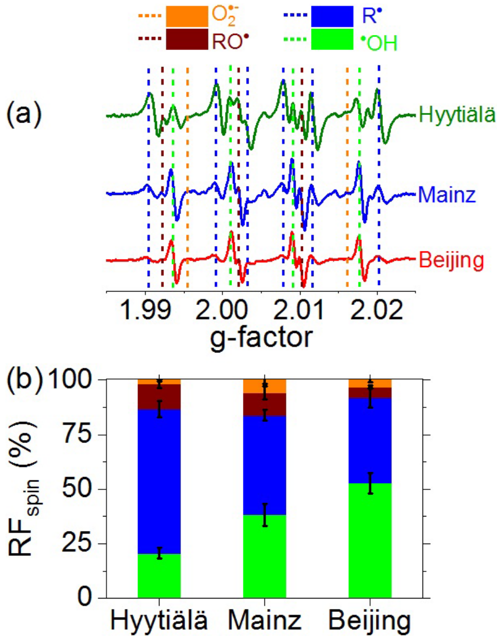

Figure 2. **(a)** Electron paramagnetic resonance (EPR) spectra and **(b)** relative fractions of unpaired electrons (RF_{spin}) attributed to different types of radicals formed in aqueous extracts of ambient $PM_{2.5}$ from Hyytiälä, Mainz, and Beijing. Dotted vertical lines in **(a)** indicate the peak positions of different radical adducts. The spectral intensities in **(a)** and RF_{spin} values in **(b)** represent arithmetic mean values, while the error bars in **(b)** represent standard errors (6–13 samples per location).

11 %, respectively) to polluted urban air samples (Mainz, 46 % and 10 %; Beijing, 39 % and 5 %, respectively). The high yield of C-centered radicals can be explained by the rapid trapping of C-centered organic radicals ($R^{\bullet}$) by BMPO in the liquid phase (De Araujo et al., 2006). In the aqueous extracts, we applied a large excess of BMPO (10 mM of BMPO vs. ∼ 1 µM of trapped radicals), and the estimated pseudo-first-order rate coefficient for $R^{\bullet}$ reacting with BMPO ($9 \times 10^5\ s^{-1}$, Tong et al., 2018) is much higher than the estimated $R^{\bullet}$ recombination rate coefficient (2.4×10^3, Simic et al., 1969; Tong et al., 2018). Moreover, rearrangement reactions in water can convert $RO^{\bullet}$ into $R^{\bullet}$ (Chevallier et al., 2004), which may warrant further investigation. The detected organic radicals are likely to comprise different molecular sizes and structures, as supported by our recent observations of organic radicals with up to 20 carbon atoms (C1–C20) formed by laboratory-generated SOA in water (Tong et al., 2018). The mean RF of $^{\bullet}OH$ was found to increase from clean forest air samples (Hyytiälä, 21 %) to polluted urban air samples (Mainz 38 %, Beijing 53 %). The mean RF of $O_2^{\bullet -}$ varied in the range of 2–6 %, showing no clear trend considering the standard errors indicated in Fig. 2b.

The formation of organic radicals, $^{\bullet}OH$, $O_2^{\bullet -}$, and H_2O_2 can be attributed to Fenton-like reactions and the redox chemistry of organic and inorganic particulate matter, including environmentally persistent free radicals (EPFR), highly oxygenated organic molecules (HOM), humic-like substances (HULIS), and transition metal ions (Chevallier et al., 2004; Valavanidis et al., 2005; Li et al., 2008; Page et al., 2012; Gehling et al., 2014; Tong et al., 2016a, 2017, 2018, 2019; Qiu et al., 2020; Arangio et al., 2016). We speculate that hydrolytic or thermal decomposition of ROOH may play a major role in the formation of RS by $PM_{2.5}$ from remote forest locations such as Hyytiälä, where large fractions of peroxide-containing HOM have been detected (Mutzel et al., 2015; Tröstl et al., 2016; Tong et al., 2019; Pye et al., 2019; Roldin et al., 2019; Bianchi et al., 2019). ROOH can generate $^{\bullet}OH$ and O-centered organic radicals through decomposition ($ROOH \rightarrow RO^{\bullet} + {}^{\bullet}OH$) and Fenton-like reactions ($Fe^{2+} + ROOH \rightarrow Fe^{3+} + RO^{\bullet} + OH^-$; $Fe^{2+} + ROOH \rightarrow Fe^{3+} + RO^- + OH^{\bullet}$) (Tong et al., 2016a). Interconversion of $RO^{\bullet}$, $R^{\bullet}$, and $ROO^{\bullet}$ radicals can lead to the formation of $O_2^{\bullet -}$ and H_2O_2 (Chevallier et al., 2004; Tong et al., 2018), which can further react with Fe^{2+} to form $^{\bullet}OH$ ($Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^-$). In $PM_{2.5}$ from urban areas, transition metal ions and HULIS are expected to play a major role in aqueous-phase formation and the interconversion of $^{\bullet}OH$, $O_2^{\bullet -}$, and H_2O_2 (Lloyd et al., 1997; Valavanidis et al., 2000; Zheng et al., 2013; Hayyan et al., 2016; Lakey et al., 2016; Tan et al., 2016; Kuang et al., 2017; Ma et al., 2018; Li et al., 2019).

Environmentally persistent free radicals (EPFR) are known to preexist in $PM_{2.5}$ at mass-specific concentration levels of ∼ 0.2 to ∼ 2 pmol μg^{-1}, which are an order of magnitude higher than the typical mass-specific aqueous-phase radical yields of ∼ 0.02 to ∼ 0.2 pmol μg^{-1} (Arangio et al., 2016; Vejerano et al., 2018; Tong et al., 2019; Chen et al., 2020). While some EPFR may be insoluble in water (Chen et al., 2018), others may directly contribute to the C-centered and O-centered radicals trapped by BMPO or may participate in redox reactions yielding $^{\bullet}OH$ and $O_2^{\bullet -}$ radicals (Khachatryan et al., 2011; Arangio et al., 2016). The latter have such short chemical lifetimes that they must have formed upon the dissolution of the investigated samples immediately prior to trapping by BMPO.

The experiments and data presented in this study provide exploratory perspectives on the pathways for the formation and interconversion of reactive species formed by $PM_{2.5}$ in the aqueous phase, including highly reactive radicals and less reactive reservoir species such as H_2O_2, as discussed below. Quantitative assessment, mechanistic elucidation, and a full understanding will require further comprehensive experimental investigations and model calculations.

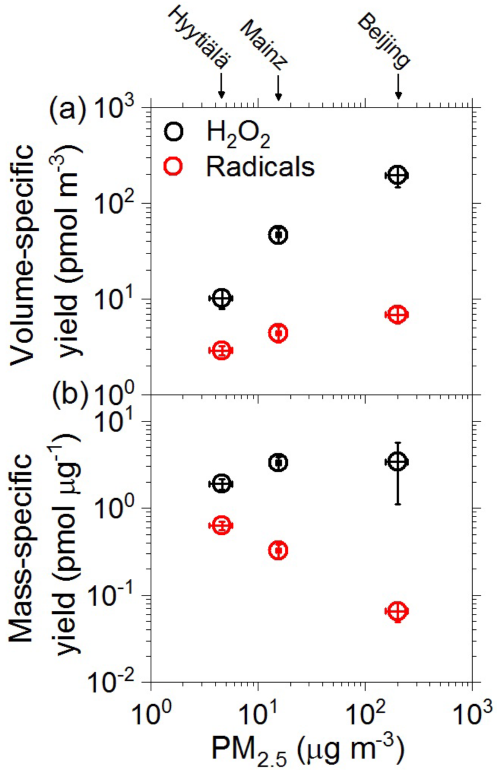

Figure 3. (a) Air sample volume-specific yields and **(b)** mass-specific yields of aqueous-phase radicals (red circles) and H_2O_2 (black circles) formed in aqueous extracts of ambient $PM_{2.5}$ from Hyytiälä, Mainz, and Beijing plotted against $PM_{2.5}$ mass concentration. The error bars represent standard errors of the mean (4–12 samples per location).

3.2 Yields of aqueous-phase radicals and H_2O_2 from ambient $PM_{2.5}$

Figure 3 shows the average air volume-specific yields and $PM_{2.5}$ mass-specific yields of aqueous-phase reactive species (RS), including radicals and H_2O_2, plotted against the $PM_{2.5}$ mass concentrations observed during the sampling periods in Hyytiälä, Mainz, and Beijing, respectively. The volume-specific yields refer to the sampled air volume and are given in units of pmol m^{-3}. They represent the absolute amounts of RS that are formed when the particulate matter is deposited in an aqueous phase such as cloud water or epithelial lining fluid, where they can contribute to atmospheric multiphase chemistry and to oxidative stress and adverse health effects of PM, respectively (Lakey et al., 2016; Tong et al., 2018). The mass-specific yields are normalized to the sampled mass of $PM_{2.5}$ and given in units of pmol µg^{-1}. They represent the relative amounts of aqueous RS formed per mass unit of $PM_{2.5}$, enabling a direct comparison of the relative reactivities and aqueous RS-forming potentials of the fine particulate matter from different sampling sites.

As illustrated in Fig. 3a, the $PM_{2.5}$ concentration was more than an order of magnitude lower in samples from Hyytiälä than in those from Beijing (∼ 5 and ∼ 200 µg m^{-3}, respectively), and the volume-specific yields of aqueous-phase H_2O_2 exhibited a similarly large difference (∼ 10 and ∼ 200 µg m^{-3}, respectively), while the volume-specific yields of aqueous-phase radicals exhibited a much smaller difference (∼ 3 and ∼ 7 pmol m^{-3}, respectively; Tables S1, S4, and S5). The strong increase in H_2O_2 with increasing $PM_{2.5}$ concentration is consistent with earlier studies identifying a wide range of redox-active organic and inorganic aerosol components that can produce H_2O_2 in the aqueous phase (Gunz and Hoffmann, 1990; Anastasio et al., 1994; Zuo and Deng, 1997; Arellanes et al., 2006; Chung et al., 2006; Hua et al., 2008; Möller, 2009; Wang et al., 2010, 2012; Anglada et al., 2015; Herrmann et al., 2015; Lakey et al., 2016; Tong et al., 2018; Bianco et al., 2020).

As illustrated in Fig. 3b, the average mass-specific yields of aqueous-phase H_2O_2 were similar for the investigated urban and forest $PM_{2.5}$ samples (around 2–4 pmol µg^{-1}). In contrast, the mass-specific yield of aqueous-phase radicals was highest for the forest samples (∼ 0.6 pmol µg^{-1}) and decreased steeply with increasing $PM_{2.5}$ mass concentration for the urban samples (∼ 0.3 pmol µg^{-1} for Mainz, ∼ 0.06 pmol µg^{-1} for Beijing). Accordingly, the relative fraction of radicals compared to H_2O_2 formed and detected in the aqueous phase decreased from 22 % for the $PM_{2.5}$ samples from Hyytiälä to 8 % for those from Mainz and 3 % for those from Beijing. In other words, the aqueous H_2O_2-forming potential per mass unit of $PM_{2.5}$ was roughly the same for all investigated samples, whereas the aqueous radical-forming potential varied widely between the different samples.

The observed negative correlation with $PM_{2.5}$ mass concentration suggests that the mass-specific yield of aqueous-phase radicals from fine particulate matter may be influenced by the sample load and concentration in aqueous extracts, e.g., through enhanced recombination of radicals at elevated concentration. However, experiments performed at different dilutions, i.e., with varying aqueous extract volumes and concentrations, suggest that observed differences in radical-forming potential were not just due to different sample loads but were influenced by differences in the chemical compositions and reactivities of the investigated $PM_{2.5}$ samples (Fig. S1d and e). For example, the particularly high mass-specific yields of total radicals and C-centered radicals in the aqueous phase appear to be associated with particularly high mass fractions of organic matter in $PM_{2.5}$ from Hyytiälä (∼ 70 %, Jimenez et al., 2009; Maenhaut et al., 2011).

Figure 4 shows how the relative fractions (RF_{spin}) of C-centered radicals and $^{\bullet}OH$ in the aqueous phase varied with the abundances of HOM, aromatic compounds, and water-soluble transition metal ions in the investigated $PM_{2.5}$ samples (Hyytiälä and Mainz) or $PM_{2.5}$ collected at different times (Beijing). As illustrated in Fig. 4a, C-centered radicals exhibited a pronounced increase with increasing

HOM, whereas $^{\bullet}$OH radicals showed a near-linear decrease. The observed increase in C-centered radicals with HOM is consistent with earlier studies indicating that peroxide-containing HOM may play an important role in organic radical formation (Tong et al., 2016a, 2019). In contrast, the C-centered radicals decreased with increasing abundance of aromatic compounds (Fig. 4b). This is consistent with the ability of certain aromatic compounds such as quinones and semiquinones to enhance redox cycling and the formation of $^{\bullet}$OH radicals, in analogy to Fenton reactions (Chung et al., 2006; Zhang and Tao, 2009; Khachatryan et al., 2011; Elser et al., 2016; Fan et al., 2016; Lakey et al., 2016; An et al., 2019). As illustrated in Fig. 4c, C-centered radicals exhibited a pronounced decrease with transition metal ions, whereas $^{\bullet}$OH radicals exhibited a near-linear increase. These findings are consistent with the role of transition metal ions in Fenton-like reactions that efficiently convert H_2O_2 and hydroperoxides into $^{\bullet}$OH radicals, and with studies reporting that metal–organic interactions may alter the oxidative potential particulate matter under atmospheric and physiological conditions (Zuo and Hoigne, 1992; Lakey et al., 2016; Singh and Gupta, 2016; Cheng et al., 2017; S. Wang et al., 2018; Wei et al., 2019; Lin and Yu, 2020). To gain further insights into the complex interactions of organic particulate matter, transition metal ions, and reactive species in the aqueous phase, we performed experiments with laboratory-generated secondary organic aerosols and surrogate mixtures of atmospherically relevant substance classes, as detailed in the following sections.

3.3 Aqueous-phase radical yields of laboratory-generated SOA

To investigate the influences of biogenic and anthropogenic secondary organic aerosols (SOA) on aqueous-phase radical formation, we performed experiments with SOA from naphthalene and β-pinene oxidized by O_3 and $^{\bullet}$OH in a PAM chamber (Sect. 2.3).

As illustrated in Fig. 5a, we found a steep nonlinear increase in the mass-specific radical yield with increasing precursor mass fraction of β-pinene from $\sim 2\,\mathrm{pmol\,\mu g^{-1}}$ for pure naphthalene SOA to $\sim 8\,\mathrm{pmol\,\mu g^{-1}}$ for pure β-pinene SOA, which is consistent with related earlier investigations that found higher radical yields for biogenic SOA compared to anthropogenic SOA (Tong et al., 2016a, 2017, 2018, 2019).

Figure 5b shows that β-pinene SOA mainly generates $^{\bullet}$OH ($\sim$ 86 %), whereas naphthalene SOA and mixtures of naphthalene and β-pinene SOA mainly generate $^{\bullet}O_2^-$ (60 %–77 %) and C-centered radicals (18 %–34 %). Substantial formation of $^{\bullet}O_2^-$ by terpene SOA is consistent with a recent study showing that $O_2^{\bullet -}$ is formed via $^{\bullet}$OH oxidation of primary or secondary alcohols followed by unimolecular decomposition of α-hydroxyperoxyl radicals (Wei et al., 2021). The small RF of $^{\bullet}$OH generated by naphthalene SOA may appear to contrast with the high RF of $^{\bullet}$OH generated from $PM_{2.5}$ from Beijing, which contains substantial amounts of aromatics (Fig. 4b). Note, however, that the composition of $PM_{2.5}$ from Beijing is much more complex than that of laboratory-generated naphthalene SOA. For example, Fenton-like reactions of transition metal ions are expected to generate $^{\bullet}$OH in ambient $PM_{2.5}$ (Kehrer, 2000; Tong et al., 2016a), whereas the laboratory-generated SOA does not contain significant amounts of transition metals.

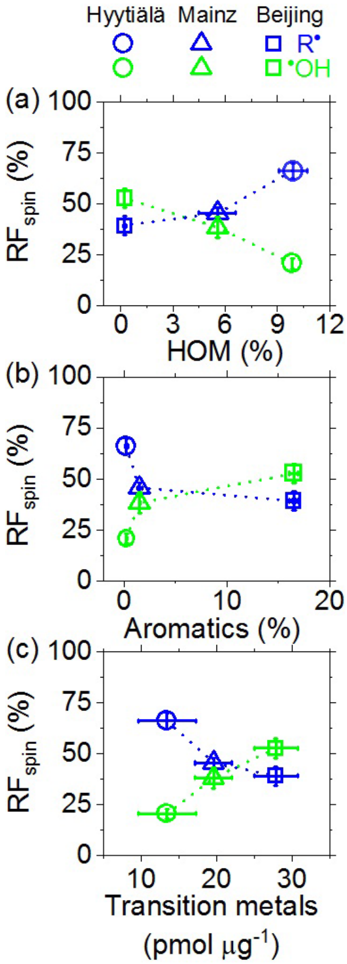

Figure 4. Relative fractions (RF_{spin}) of aqueous-phase C-centered ($R^{\bullet}$) and $^{\bullet}$OH radicals plotted against the relative abundances of **(a)** highly oxygenated organic molecules (HOM), **(b)** aromatics, and **(c)** water-soluble transition metals in ambient $PM_{2.5}$ from Hyytiälä, Mainz, and Beijing. The relative abundances of HOM and aromatics in **(a)**–**(b)** represent the summed chromatographic area of HOM or aromatics divided by the summed chromatographic area of all assigned organic compounds. The abundances of HOM shown in **(a)** were taken from a recent companion study (Tong et al., 2019). The error bars represent standard errors of the mean (4–12 samples per location). The dashed lines are included to guide the eye.

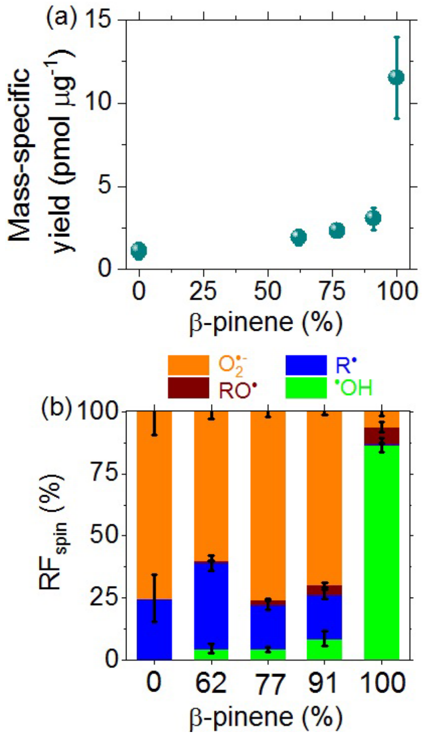

Figure 5. **(a)** Mass-specific yields and **(b)** relative fractions (RF$_{spin}$) of different types of radicals formed upon the aqueous extraction of laboratory-generated SOA from precursor mixtures of β-pinene and naphthalene plotted against the mass fraction of β-pinene (%) in the precursor mixture. The error bars represent standard errors (4–6 samples per data point).

3.4 Aqueous-phase radical yields of surrogate mixtures

To investigate the influences of different types of redox-active components in $PM_{2.5}$ on the total yield of radicals in the aqueous phase and on the relative fractions (RF$_{spin}$) of different types of radicals, we performed experiments with aqueous surrogate mixtures of Fe^{2+}, Cu^{2+}, humic acid (HA), fulvic acid (FA), cumene hydroperoxide (CHP), and H_2O_2 of various concentrations. Figure 6 shows that increasing the concentration of organic hydroperoxide (i.e., CHP here) can lead to a near-linear increase in the total radical concentration in the aqueous phase (Fig. 6a) and to a strong increase in RF$_{spin}$ for C-centered radicals (Fig. 6b). The increase in $R^\bullet$ with CHP is consistent with the high RF$_{spin}$ for C-centered radicals in $PM_{2.5}$ from Hyytiälä (Fig. 2b), which contains a large fraction of HOM (Tong et al., 2019). Increasing the concentration of H_2O_2 also led to a near-linear increase in the total radical concentration in the aqueous phase (Fig. 6c) as well as a strong increase in $^\bullet OH$ (Fig. 6d). The strong increase in aqueous-phase $^\bullet OH$ with H_2O_2 indicates that gas-particle partitioning and multiphase chemical reactions of gas-phase oxidants can substantially influence the generation of radicals and oxidative stress by ambient $PM_{2.5}$.

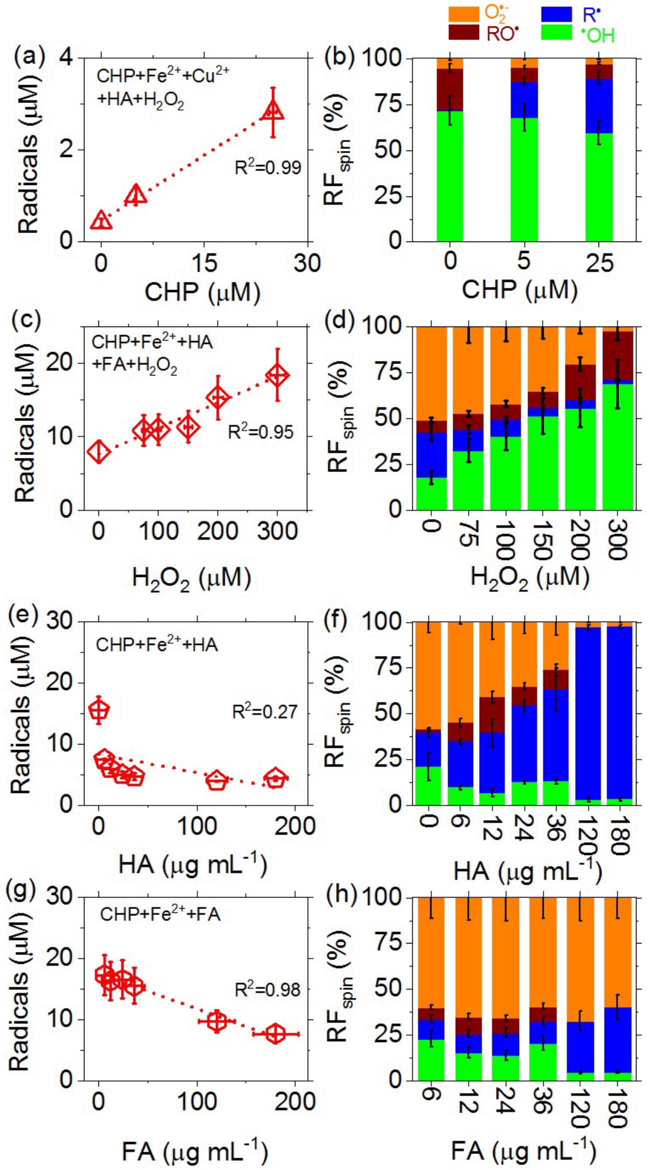

Figure 6. **(a, c, e, g)** Total concentrations and **(b, d, f, h)** relative fractions (RF$_{spin}$) of different types of radicals (spins) observed in aqueous mixtures of Fe^{2+}, Cu^{2+}, humic acid (HA), fulvic acid (FA), cumene hydroperoxide (CHP), and H_2O_2 serving as surrogate species for redox-active components of $PM_{2.5}$. **(a, b)** 0–25 µM CHP, 43 µM Fe^{2+}, 3 µM Cu^{2+}, 4 µg mL^{-1} HA, 7 µM H_2O_2 (CHP + Fe^{2+} + Cu^{2+} + HA + H_2O_2). **(c, d)** 100 µM CHP, 300 µM Fe^{2+}, 100 µg mL^{-1} HA, 80 µg mL^{-1} FA, 0–300 µM H_2O_2. **(e, f)** 100 µM CHP, 300 µM Fe^{2+}, 0–180 µg mL^{-1} HA (CHP + Fe^{2+} + HA). **(g, h)** 100 µM CHP, 300 µM Fe^{2+}, 6–180 µg mL^{-1} FA (CHP + Fe^{2+} + FA). The error bars represent the uncertainties in the EPR signal integration (y axis) and solute concentration (x axis), respectively.

For increasing concentrations of humic acid (HA), we observed a strong nonlinear decrease in total radical concentration in the aqueous phase (Fig. 6e) and a strong increase in RF$_{spin}$ for C-centered radicals (Fig. 6f). The decreasing radical concentration is likely due to the ability of HA to bind/chelate iron and other metal ions (Graber and Rudich, 2006; Laglera and van den Berg, 2009; Scheinhardt et al., 2013; Tang et al., 2014; Yang et al., 2017), which may lead to a suppression of radical formation via Fenton-like reactions. Moreover, humic substances can act as antioxidants and radical scavengers (Aeschbacher et al., 2012). The fractional increase in C-centered radicals reflects the involvement of HA in complex radical chemistry (Shi et al., 2020). Compared to HA, the effects of fulvic acid (FA) were qualitatively similar but quantitatively less pronounced (Fig. 6g and h), which is consistent with earlier studies investigating the metal ion binding capacity and redox chemistry of FA (Wang et al., 1996; Graber and Rudich, 2006; Scheinhardt et al., 2013; Tang et al., 2014; Gonzalez et al., 2017; Yang et al., 2017). The different reactivities of HA and FA are also reflected in the different RF values of $O_2^{\bullet -}$ and C-centered radicals observed at high concentrations of FA and HA (Fig. 6h vs. Fig. 6f) as well as in reaction mixtures with copper instead of iron ions (Fig. S6). Further investigations will be required to resolve the underlying reaction mechanisms and kinetics.

4 Conclusions and implications

In this study, we investigated the formation of aqueous-phase H_2O_2 and radicals by aerosol samples from a remote forest and polluted urban air. The aqueous H_2O_2-forming potential per mass unit of $PM_{2.5}$ was roughly the same for all investigated samples, whereas the mass-specific yields of radicals were lower for sampling sites with higher concentrations of ambient $PM_{2.5}$.

The abundances of water-soluble transition metals in ambient $PM_{2.5}$ were positively correlated with the relative fraction of $^{\bullet}OH$ and negatively correlated with the relative fraction of carbon-centered radicals, which can be attributed to Fenton-like reactions. In contrast, HOM was negatively correlated with the relative fraction of $^{\bullet}OH$ and positively correlated with the relative fraction of carbon-centered radicals, which is consistent with related earlier studies indicating that peroxide-containing HOM may play an important role in organic radical formation (Tong et al., 2016a, 2019).

We found that the relative fractions of different types of radicals formed by ambient $PM_{2.5}$ were comparable to surrogate mixtures comprising transition metal ions, organic hydroperoxide, H_2O_2, and humic or fulvic acids. Our results show that the interplay of transition metal ions (e.g., iron and copper ions), highly oxidized organic molecules (e.g., hydroperoxides), and complexing or scavenging agents (e.g., humic or fulvic acids) leads to nonlinear concentration dependencies in aqueous-phase RS production. A strong dependence on chemical composition was also observed for the aqueous-phase radical yields of laboratory-generated SOA from precursor mixtures of naphthalene and β-pinene.

Overall, our findings show how the composition of $PM_{2.5}$ can influence the amount and nature of aqueous-phase RS, which may explain differences in the chemical reactivity and health effects of particulate matter in clean and polluted air. Further investigations will be required to resolve the influences of biogenic and anthropogenic pollutants on atmospheric chemistry, air quality, and public health in the Anthropocene (Pöschl and Shiraiwa, 2015; Cheng et al., 2016; Shiraiwa et al., 2017; An et al., 2019; Roldin et al., 2019; Daellenbach et al., 2020; Fang et al., 2020; Lelieveld et al., 2020; Lin and Yu, 2020; Pöschl, 2020; Su et al., 2020; Tao et al., 2020; Yun et al., 2020; Zheng et al., 2020; Wang et al., 2021).

Data availability. The dataset for this paper is available upon request from the corresponding author (h.tong@mpic.de, haijie.tong@polyu.edu.hk).

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Author contributions. HT and UP designed the experiment and wrote up the original draft together with FL. CX, SY, and HMJK were involved in the collection of ambient particles. HT, FL, AF, and YZ participated in laboratory measurements and data analysis. All other coauthors contributed to the results, discussion, and manuscript editing.

Competing interests. The authors declare that they have no conflict of interest.

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