Relationship between chemical composition and oxidative potential of secondary organic aerosol from polycyclic aromatic hydrocarbons

Shunyao Wang[1], Jianhuai Ye[1], Ronald Soong[2], Bing Wu[2], Legeng Yu[1],
André J. Simpson[2], Arthur W.H. Chan[1,*]

[1]Department of Chemical Engineering & Applied Chemistry, University of Toronto

[2] Environmental NMR Centre, Department of Physical and Environmental Sciences,
University of Toronto Scarborough

*Correspondence to: Arthur W.H. Chan (arthurwh.chan@utoronto.ca)

Abstract

Owing to the complex nature and dynamic behaviors of secondary organic aerosol (SOA), its ability to cause oxidative stress (known as oxidative potential, or OP) and adverse health outcomes remain poorly understood. In this work, we probed into linkages between the chemical composition of SOA and its OP, and investigated impacts from various SOA evolution pathways, including atmospheric oligomerization, heterogeneous oxidation and mixing with metal. SOA formed from photooxidation of the two most common polycyclic aromatic hydrocarbons (naphthalene and phenanthrene) were studied as model systems. OP was evaluated using the dithiothreitol (DTT) assay. The oligomer-rich fraction separated by liquid chromatography dominates DTT activity in both SOA systems ($52 \pm 10\%$ for NSOA and $56 \pm 5\%$ for PSOA). Heterogeneous ozonolysis of NSOA was found to enhance its OP, which is consistent with the trend observed in selected individual oxidation products. DTT activities from redox-active organic compounds and metals were found to be not additive. When mixing with highly redox-active metal (Cu), OP of the mixture decreased significantly for 1,2-naphthoquinone ($42 \pm 7\%$), 2,3-dihydroxynaphthalene ($35 \pm 1\%$), NSOA ($50 \pm 6\%$) and PSOA ($43 \pm 4\%$). Evidence from proton nuclear magnetic resonance (^{1}H NMR) spectroscopy illustrates that such OP reduction upon mixing can be ascribed to metal-organic binding interactions. Our results highlight the role of aerosol chemical composition under atmospheric aging processes in determining the OP of SOA, which is needed for a more accurate and explicit prediction of the toxicological impacts from particulate matter.

1 Introduction

25   Exposure to particulate matter (PM) has been associated with various adverse health endpoints,

such as increased risks of myocardial infarction, ischemic heart disease, lung cancer,

exacerbation of asthma, and chronic obstructive pulmonary disease (de Kok et al., 2006; Li et al.,

2003a; Li et al., 2003b; Nel, 2005; Risom et al., 2005; Thurston et al., 2016). As a result,

ambient $PM_{2.5}$ exposure ranks among the top 5 global mortality risk factors (Cohen et al., 2017).

30   Meanwhile, a decreased ambient PM level has been associated with longer life expectancies

(Pope et al., 2009). To establish causal links between aerosol exposure and health endpoints,

cytotoxic and carcinogenic potential has been investigated by epidemiological studies in the past

decades (Brunekreef and Holgate, 2002; Beelen et al., 2014; Lelieveld et al., 2015; Pope et al.,

2002), but the underlying mechanistic pathways by which PM causes adverse health outcomes

35   still remain poorly understood.

Oxidative stress has been proposed as one of the main mechanisms for PM toxicity in recent

years, and is caused by oxidative potential (OP) (Li et al., 2003b). OP is exhibited as the capacity

of inhaled PM to induce oxidative stress, the redox imbalance generated through consumption of

antioxidants and production of reactive oxygen species (ROS) (Antiñolo et al., 2015; Shen et al.,

40   2011; Shiraiwa et al., 2012). ROS include a variety of oxidants such as superoxide ($O_2^{\cdot-}$),

hydroxyl radical (•OH) and hydrogen peroxide (HOOH), which could either be introduced into

human body directly from inhaled PM or generated by targeted cells (Nel et al., 1998; Pöschl and

Shiraiwa, 2015; Rhee, 2006; Verma et al., 2015b). The generation of ROS during multiphase

interactions between air pollutants and human respiratory tract is closely related to the chemical

45   composition, since the combination of various pollutants may influence chemical reactivity as

well as bioavailability of PM while having synergistic or nonlinear influences on its OP (Antiñolo et al., 2015; Charrier et al., 2015; Fang et al., 2015; Shiraiwa et al., 2012; Xiong et al., 2017).

OP of both organic and inorganic PM components have been evaluated by both cellular and

50   acellular assays. *In vitro* cellular assays were conducted by detecting biological endpoints of the exposure, including heme oxygenase-1 (HO-1) and other cytokines as well as macrophage related biomarker expressions (Krapf et al., 2017; Li et al., 2003b). On the other hand, acellular assays use specific chemicals, such as dithiothreitol (DTT), ascorbate (AA) and glutathione (GSH), as surrogates of low-molecular weight (MW) antioxidants (Fang et al., 2016; Godri et al.,

55   2011; McWhinney et al., 2013). Among acellular assays, the DTT assay quantifies OP by measuring the DTT depletion rate over a fixed time interval, which mimics the physiological process of electron transfer from biological antioxidants to dissolved O_2 (Cho et al., 2005). DTT assay is one of the most commonly used OP evaluation methods, since DTT is a potent surrogate for the total thio-pools (glutathione and protein thiols) while this assay can be conducted under

60   biologically relevant conditions (37 °C, pH= 7.4) with relatively simple procedures (Cleland , 1964; Hansen et al., 2009; McWhinney et al., 2011). OP levels measured by this assay have been found to correlate well with cellular ROS expression as well as several airway inflammation biomarkers, such as HO-1, tumor necrosis factor- α (TNF- α) and fractional exhaled nitric oxide (FE_NO) (Delfino et al., 2013; Li et al., 2003b; Tuet et al., 2017).

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Secondary organic aerosol (SOA) from atmospheric oxidation of gaseous precursors comprises a major fraction of submicron particulate matter. To date, The DTT assay has been applied in a few studies to evaluate the OP of both laboratory and ambient SOA (McWhinney et al., 2013;

Tuet et al., 2017b; Verma et al., 2015a). However, owing to the complex and dynamic property

70   of SOA, there is limited understanding of the relationship between detailed SOA composition

and its OP (Charrier and Anastasio, 2012; Pöschl and Shiraiwa, 2015; Tuet et al., 2017b). Tuet et

al. (2017b) studied the DTT activity of chamber-generated SOA from both biogenic and

anthropogenic VOCs under various conditions, showing that naphthalene SOA (NSOA) has the

highest OP. Previous work (Anti ñolo et al., 2015; Bolton et al., 2000; Charrier and Anastasio,

75   2012; Cho et al., 2005; Jiang et al., 2017; Tuet et al., 2017b) indicated while polycyclic aromatic

hydrocarbons (PAHs) are unreactive towards DTT while their oxidation products, such as

quinones, can be highly redox-active. Quinones can be directly emitted from traffic or formed

from secondary oxidation (Cho et al., 2004; McWhinney et al., 2013), and are able to consume

antioxidants in a catalytic cycle (Fig. 1) (Bolton et al., 2000; Valavanidis et al., 2005).

80   McWhinney et al. (2013) found three quinones (1,2- naphthoquinone, 1,4-naphthoquinone and 5-

hydroxy-1,4-naphthoquinone) in NSOA could only account 30 $\pm$ 5% for the observed OP of

NSOA, and the source of the remaining DTT activity remains unknown. Peroxides, which are

the major contributors to the OP of isoprene SOA (Jiang et al., 2017; Lin et al., 2016; Surratt et

al., 2010), may also be abundant in NSOA (Kautzman et al., 2010), but their contribution to the

85   OP of NSOA has not been evaluated. In addition, the composition of SOA may evolve upon

atmospheric aging. Previous study (Verma et al., 2009) found ambient samples collected in the

afternoon had a larger fraction of water soluble organic carbon and higher OP, suggesting the

photochemical aging effects. There may also be correlations between the average carbon

oxidation state ($\overline{OS}c$) and OP of SOA at different stages of oxidation (Tuet et al., 2017a).

90   Moreover, mixing between organics and metals was also found to change the OP of specific

components in SOA (Xiong et al., 2017), but the mechanisms remain the tip of iceberg.

Here, we focused on understanding how the composition of PAH-derived SOA is related to its strong OP (Tuet et al., 2017b). Specific questions we aim to address in this work are: what are the compounds within SOA that are important for DTT activity? How does the OP change upon atmospheric aging processes, including oligomerization, heterogeneous oxidation, and mixing with transition metals (Gao et al., 2004; Rudich et al., 2007)? In this work, SOA from photooxidation of naphthalene and phenanthrene were studied as model systems, and compared to SOA from ozonolysis of α-pinene and limonene. The relative OP contributions of peroxides and high-MW oligomers were evaluated. Effects of aerosol aging on OP was evaluated by examining the OP of individual oxidation products known to be present in NSOA, and the OP of NSOA samples that were further oxidized in the condensed phase. Lastly, the impacts of SOA mixing with metal was explored by mixing SOA or redox-active SOA components with Cu (II), a transition metal which has been identified with the highest OP in ambient particles (Charrier and Anastasio, 2012). Additivity of OP revealed by DTT assay was investigated, and the mechanisms of Cu-organic interactions were examined in detail using proton nuclear magnetic resonance spectroscopy (^{1}H NMR).

2   Methods

2.1 Flow tube experiments

SOA was produced in a custom-built 10 L quartz flow tube. Details about the flow tube conditions have been described in previous work (Ye et al., 2016; Ye et al., 2017). Prior to each experiment, the flow tube was flushed with purified compressed air at a flow rate of 20 L min^{-1} for over 24 hours.

To produce SOA from naphthalene or phenanthrene, solid PAH was placed in a heated container (80 °C), and the sublimed vapor was carried into the flow tube in a 0.2 L min^{-1} flow of purified compressed air. O_3 and water vapor were also added into the flow tube. O_3 was produced by passing 0.5 L min^{-1} oxygen (99.6%, Linde, Mississauga, Canada) through an UV O_3 generator

120   (No. 97006601, UVP, Cambridge, UK). Water vapor was produced by bubbling purified air through a custom-made humidifier with a flow rate of 1.3 L min^{-1}. Residence time inside the flow tube was maintained around 5 min. The flow tube was housed inside an aluminum enclosure, which was equipped with 254 nm UV lamps (UVP, Cambridge, UK). The photolysis of O_3 produces O (^{1}D), which react with water vapor to produce •OH and initiate photooxidation

125   of naphthalene/phenanthrene as well as SOA formation. During naphthalene/phenanthrene photooxidation, O_3 concentration inside the flow tube was controlled around 1 ppm. In addition, blank experiments were conducted under the same conditions, without injecting any hydrocarbons.

130   Two types of SOA from monoterpene ozonolysis were also synthesized under similar conditions. α-pinene (Sigma-Aldrich, 98%) or limonene (Sigma-Aldrich, 97%) was pre-dissolved in cyclohexane (Sigma-Aldrich, 99.5%) with volumetric ratio of 1:500 or 1:1500, respectively. At these ratios, the reaction rates between •OH and cyclohexane are at least a hundred time higher than that of SOA precursors (Atkinson and Arey, 2003; Keywood et al., 2004). The experimental

135   solution was injected continuously into purified air flow by a syringe (1000 mL, Hamilton) installed on a syringe pump (KDS Legato100) to achieve an initial concentration of 588 ± 16 ppb or 298 ± 24 ppb of α-pinene or limonene, respectively. O_3 was produced by passing oxygen

through the O_3 generator at a flow rate of 0.2 L min^{-1} or 0.3 L min^{-1} for α-pinene or limonene, respectively, such that the O_3 concentrations were at least 5 times higher than α-pinene or

140   limonene. Both experiments were conducted in the same flow tube without irradiation of UV lights.

Temperature and relative humidity were monitored by an Omega HX94C RH/T transmitter. The concentrations of SOA precursors at the inlet and outlet of the flow tube were measured by a gas

145   chromatography-flame ionization detector (GC-FID, Model 8610C, SRI Instruments Inc., LV, USA) equipped with a Tenax® TA trap. Size distribution and volume concentration of SOA at the flow tube reactor outlet were monitored using a custom-built scanning mobility particle sizer (SMPS), which was composed of a differential mobility analyzer column (DMA, Model 3081, TSI, Shoreview, MN, USA) with flow controls and a condensation particle counter (CPC, Model

150   3772, TSI, Shoreview, MN, USA). The SMPS data were inverted to particle size distributions using custom code written in Igor Pro (Wavemetrics, Portland, OR, USA). By assuming a particle density of 1.25 g cm^{-3} for monoterpene SOA (Kostenidou et al., 2007; Shilling et al., 2009) and 1.55 g cm^{-3} for PAH SOA (Chan et al., 2009; McWhinney et al., 2011), volume concentrations of particle were converted into mass concentrations and integrated as a function

155   of sample collection time and flow rates to obtain the total mass of collected SOA.

2.2 SOA sampling and extraction

All SOA samples were collected on 47 mm prebaked (500 ℃, 24 h) quartz fiber filters (Pall, Ann Arbor, MI, USA) in a stainless-steel filter holder after reaching a steady state yield, and then

160   wrapped in prebaked aluminum foil before being stored in sterile petri dishes sealed with

Parafilm M® at -20 °C. Within 3 days of collection, the filters were extracted in methanol (HPLC grade, 99.9%, Sigma Aldrich, St. Louis, MO, USA), by ultra-sonication at room temperature for more than 3 minutes. After sonication, insoluble materials were filtered by a PTFE (polytetrafluoroethylene) syringe filters (Fisherbrand™) with pore size of 0.22 μm. Chemical

165   analysis and DTT activities of the filter extracts were conducted within hours after extraction. As negative control, filter samples were also collected during blank experiments and extracted in the same manner.

2.3 DTT assay

170   OP of SOA and selected quinone/peroxide standards were quantified by the depletion rate of DTT, an antioxidant surrogate that can be consumed by oxidative components in PM (Kumagai et al., 2002). The protocols used in this work are adapted from those of McWhinney et al. (2011; 2013). The SOA extracts were first evaporated to complete dryness in a 5.0 L min^{-1} of N_2 using a blow-off system (N-EVAP, Organomation, USA). Phosphate buffer (0.1 M, pH 7.4) was then

175   added to dissolve the SOA to achieve a concentration of 0.2 mM. For quinones, copper (II) sulfate and peroxides, each pure compound was weighed and dissolved in 0.1 M phosphate buffer. The concentration of quinones and copper (II) sulfate solutions was 1 μM, and the concentration of each peroxide solution was 120 μM. The specific solution was then added into multiple wells in a 96-well UV plate (Greiner Bio-One, Kremsmünster, AT) with 160 μL per

180   well, and immediately covered with adhesive plate sealer (EdgeBio, Gaithersburg, USA). The plate was then placed in a UV-Vis spectrophotometer (Spectramax 190, Molecular Devices Corporation, Sunnyvale, CA) for incubation. The incubation temperature was maintained at 37 °C inside the spectrophotometer to mimic human physiological conditions. 0.02 mL DTT (0.2

mM) was then added into each well to initiate the redox-reactions. At each time point, 0.02 mL

185   of 5, 5'-dithiobis (2-nitrobenzoic acid) (DTNB) (2 mM) was added, which immediately

consumed all the remaining DTT to form a yellow product, 2-nitro-5-thiobenzoic acid (TNB)

(Fig.S1). DTNB was added in excess (10 times) of DTT for a rapid and complete consumption of

the remaining DTT. The initial DTT concentration was determined in order to maintain an

eventual consumption of around 50% (Fig. S2c, d) for PAH derived SOA. TNB was quantified

190   by the light absorption at a wavelength of 412 nm, which was further converted to the DTT

amount by calibration curve (Fig. S2b) in order to obtain the DTT decay rate. The reaction was

quenched by adding DTNB at different wells at different times (all containing the same initial

mixture), allowing for quantification of the DTT decay rate over a 30-minute time interval (every

5 minutes for the first 10 minutes and then every 10 minutes). Blank control and the calibration

195   curve for DTT quantification are shown in Fig. S2. SOA methanol extractions were blown off by

various extents in order to assess whether the loss of volatile compounds along with the N_2 blow-

off procedure affects the DTT activity of SOA (Fig. S3). Here, we used the total DTT decay rate,

DTT_t (μM DTT min^{-1}), to report the total oxidative capacity, as well as the mass normalized

DTT decay rate, DTT_m (pmol DTT min^{-1} μg^{-1} organics), to report the OP (Charrier et al., 2016;

200   Jiang et al., 2017; Xiong et al., 2017). Detailed information about the chemicals used in this

assay is shown in Section S1.

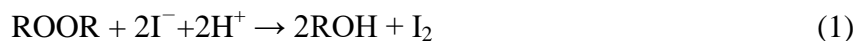
2.4 Quantification of peroxides in SOA

Quantification of total peroxides in the four types of SOA was conducted using the iodometric-

205   spectrophotometric method, which quantifies total aerosol peroxides in all three forms (H_2O_2,

ROOH, ROOR) (Banerjee and Budke, 1964; Docherty et al., 2005):

$$ROOR + 2I^- + 2H^+ \rightarrow 2ROH + I_2 \tag{1}$$

$$I_2 + I^- \rightarrow I_3^- \tag{2}$$

where I^- is oxidized to I_2 by peroxides under acidic conditions, and then complexes with

210   remaining I^- to form I_3^-, a compound with brown color detected spectrophotometrically at a

wavelength of 470 nm. The concentration of each SOA solution was first adjusted to 5mM.

0.02 mL of potassium iodide solution (1 g mL^{-1}, KI dissolved in DI water), which provided the

I^- in Reaction (1), and 0.02 mL of formic acid (Sigma-Aldrich, ≥95%), which maintained the

acidity, were added to 0.16 mL of the SOA solution in each well of a 96-well UV plate. The

215   plate was immediately sealed and incubated for 1 h following the same procedures as in the DTT

assay, and the UV-vis absorbance was measured at 470 nm. After testing for the sensitivities of

various peroxides in KI assay (Fig. S4), and following the previous work by Kautzman et al.

(2010), benzoyl peroxide (Sigma-Aldrich, ≥98%) was chosen to represent peroxides in NSOA

and used as standards for mass calibration in this study. All values are reported as mass fraction

220   of peroxides in the total SOA.

2.5 Heterogeneous oxidation

Heterogeneous oxidation of NSOA was conducted by first cutting a filter with freshly collected

NSOA into halves (within 3 days of flow tube synthesis and stored at -20 ℃). One half of the

225   filter was placed in a sealed container, and an O_3 stream (~3 ppm, from the previously mentioned

O_3 generator) was passed through the filter at a flow rate of 0.2 L min^{-1}. The other half of the

filter was treated in parallel with a 0.2 L min^{-1} flow of N_2 over the same time intervals, to

account for evaporation and/or decomposition of SOA components at room temperature. 3 sets

of experiments were conducted with exposure times of 1 h, 12 h and 24 h where the O_3 exposure

230   can be determined by,

$$O_3 \text{ exposure} = \int_0^t [O_3] \, \mathrm{d}t = \langle O_3 \rangle_t \times t \tag{3}$$

where $\langle O_3 \rangle_t$ is the time averaged O_3 concentration at a total flow rate of 0.2 L min^{-1}. The DTT

activity of each O_3-exposed aerosol sample was normalized to that of the corresponding N_2

exposure group. Changes in organic carbon mass on NSOA filters exposed to O_3/N_2 for 1 h, 12 h

235   and 24 h were also monitored with a thermal optical organic carbon/elemental carbon (OC/EC)

aerosol analyzer instrument (Sunset Laboratory Inc., Tigard, OR, USA). OC/EC content was

measured following the IMPROVE OC/EC protocol (Chow et al., 1993). Blanks were measured

before each run and subtracted from the sample measurements.

240   **2.6 Chromatographic Separation of NSOA**

To identify the relative contributions of monomers and oligomers in N/ PSOA to DTT activity,

the SOA extract was separated using ultra-high performance liquid chromatography (UHPLC),

and analyzed using electrospray ionization/Ion Mobility-Time of Flight Mass Spectrometry

(ESI/IMS-TOF MS, TOFWERK, Switzerland, hereafter referred to as IMS-TOF). SOA

245   methanol extract (30 g L^{-1}) was separated on a reverse phase column (ZORBAX Eclipse Plus

C18, Agilent, USA) with an initial mobile phase of 90% DI water and 10% HPLC methanol at a

flow rate of 0.15 mL min^{-1} (1290 Infinity II, Agilent, USA). The ratio of water to methanol was

gradually adjusted from 9:1 to 1:9 between 25 and 30 min. Separation temperature was set to 30 °C

with a pressure setting of 150 bar. The outlet flow was regulated using a LC-MS post column

250   flow splitters (Supelco, SigmaAldrich, USA) at a ratio of 30:1. The major flow was collected in

two different fractions: the first fraction was collected between 6 and14 min, and the second

fraction was collected between 14 and 33 min for NSOA (3-17 min and 17-28 min for PSOA).

DTT assay was conducted on each fraction to assess their OPs. The minor flow injected into

IMS-TOF was controlled at 5 μL min^{-1} for mass spectrometric analysis in the negative mode.

255

A deactivated fused silica capillary (360 μm OD, 50 μm ID, 50 cm length, New Objective,

Woburn, MA, USA) was used as the sample transfer line between the UHPLC and the IMS-TOF.

The ESI source was equipped with an uncoated SilicaTip Emitter (360 μm OD, 50 μm ID, 50 μm

tip ID, New Objective, Woburn, MA, US). Charged SOA droplets generated from the tip of the

260   emitter were transferred through a desolvation region by a 1 L min^{-1} N_2 flow at room temperature,

and ions produced from the evaporated droplets were introduced into the drift tube for ion

mobility separation. The IMS drift voltage was set to –1.2 kV for the negative mode. The

separation temperature was set to 80 ± 1 ℃ with an operation pressure setting of 1.2 bar for the

whole mass spectrometer. After separation in the ion mobility region, the ion m/z is measured by

265   high-resolution time-of-flight mass spectrometry within an m/z range of 40 to 800. Resolution

(m/dm$_{50}$) of the time-of-flight mass spectrometer is typically 3500–4000 FWHM at m/z 250

(Groessl et al., 2015; Krechmer et al., 2016). Spectra recording and data processing of the current

study were performed using routines written in Igor Pro (6.37, Wavemetrics, OR, USA):

"Acquility" (version 2.1.0, http://www.tofwerk.com/acquility) for raw data acquisition and

270   "Tofware" (version 2.5.3, www.tofwerk.com/tofware) for post processing.

2.7 ^{1}H NMR spectroscopy

^{1}H NMR spectroscopy was used to further investigate the mechanism behind the OP reduction

upon mixing specific organics and transition metals (Simpson et al., 2011;Simpson and Simpson,

275   2014; Smith and van Eck, 1999). NMR measurements were performed on a Bruker Avance III

NMR spectrometer (11.7 T), equipped with a 4-channel liquid state (^{1}H, ^{13}C, ^{15}N, ^{2}H) inverse

detection probe (QXI) fitted with an actively shielded Z gradient. Typical parameters used for

1D ^{1}H experiments were: a 9.5 μs ^{1}H pulse, 64k acquisition points, 14 ppm spectral width and 8

transients were collected, with a total of 5.7 s between scans. Before NMR analysis, each sample

280   was dissolved into deuterium oxide (D_2O, Cambridge Isotope Laboratories, 99.96%) and

dimethyl sulfoxide (DMSO, Fisher Scientific, 99.9%) at a ratio of 9:1. Here we used D_2O as a

lock reagent by suppressing it through pre-saturation.

In order to monitor the duration for the nuclear spin magnetization returning to an equilibrium

285   state, NMR relaxation times T1 (longitudinal direction), T2 (transverse direction) were analyzed.

T1 of the sample was measured through the standard inversion recovery experiment. The delay

periods used for T1 measurements ramped from 0.001 s to 15 s in 16 increments with a delay of

60 s between scans, which represented $> 5 \times$ T1 time to permit full signal recovery. For each

delay period, 16 transients were collected. The T2 of the sample was measured through the

290   standard Carr-Purcell-Meiboom-Gill (CPMG) sequence. The delay periods used for T2

measurements ramped from 1.2 ms to 614 ms in 16 increments with a delay of 60 s between

scans, which represented > 5 x T1 time to permit full signal recovery. For each delay period, 16

transients were collected. A total of 16 free induction decays were collected for each of the

relaxation experiments, and relaxation time calculations were done on Bruker Dynamics Centre

295   (v2.4.5) using mono-exponential fitting functions (Eq. 3 and 4 below).

$$f(t) = I_0 \times [1 - 2e^{-t/T1}] \tag{4}$$

$$f(t) = I_0 \times e^{-t/T2} \tag{5}$$

Eq. (4) and Eq. (5) are the fitting functions for T1 and T2, respectively, where I_0 is the thermal

equilibrium state of the overall proton nuclear spin magnetization; t is the variable delay time.

300   All the ^{1}H NMR spectra were collected using TopSpin (Bruker, v3.2). Post-NMR-data

processing was conducted in MestReNova (Mestrelab Resesarch, v11.0.4) and Origin

(OriginLab, v9).

2.8 Statistical analysis

305   Data in this study were interpreted as mean $\pm$ standard error of the mean (SEM, n=3), and

significance analyses among DTT activities were performed by Student's t-test with a 95%

confidence interval. A statistical value of $p < 0.05$ was considered significant.

3 Results and discussion

310   **3.1 DTT activity of laboratory generated SOA**

Here, we chose two types of SOA derived from PAHs, naphthalene and phenanthrene, as the

model SOA systems. The OP of NSOA has been shown to be the highest among various types of

SOA previously studied (Tuet et al., 2017a;Tuet et al., 2017b). At the same time, both NSOA

and PSOA contain quinones which are known to be highly redox active and exhibit high OP

315   (Cho et al., 2004; McWhinney et al., 2013). As a comparison, α-pinene and limonene SOA from

ozonolysis were chosen to represent biogenic SOA derived from monoterpenes. Experimental

conditions and SOA yield information are summarized in Table 1.

The mass-normalized DTT decay rate, DTT_m, was applied here for OP evaluation (Fig. 2).

320   Similar DTT_m have been reported for NSOA, with values of 118 pmol min^{-1}μg^{-1} by McWhinney

et al. (2013) and 110 pmol min^{-1} µg^{-1} by Tuet et al. (2017b) for NSOA generated from chamber photooxidation under dry conditions. The DTT$_m$ of α-pinene SOA of 19.1 $\pm$ 2.5 pmol min^{-1} µg^{-1} in this study is also consistent with those reported by Tuet et al. (2017b) and Jiang et al. (2017). The similar values among the different studies highlight the reproducibility of results from the DTT assay. To the best of our knowledge, the OP of PSOA and limonene SOA from this study are the first ones reported in the literature. Both SOA derived from PAHs yield a higher OP than the two types of monoterpene SOA. The similarities in OP between limonene and a-pinene SOA (cyclic monoterpenes), and between naphthalene and phenanthrene SOA (PAHs) observed in this study further confirms the hypothesis proposed by Tuet et al. (2017b) that the intrinsic OP of SOA is closely related to the molecular skeleton of the precursor.

One of the reasons for the high OP exhibited by PAH-derived SOA is the abundance of redox-active quinone moieties in SOA compounds (Lee and Lane, 2009). The cytotoxic and carcinogenic effects from quinone-like compounds are well recognized in the field of biochemistry (Bolton et al., 2000; Valavanidis et al., 2005), and the toxicity of PM has been attributed to the presence of quinones. Charrier and Anastasio (2012) have found the OP of several quinones are comparable to transition metals in ambient particles. The importance of quinone-like components to OP was also evaluated by examining the changes in DTT activity in response to the presence of 2,4-dimethylimidazole, which has been shown to be the co-catalyst of the quinone redox cycle (Jiang et al., 2017). However, McWhinney et al. (2013) quantified three quinones in NSOA using GC/MS and found that these quinones can only account for 30% of the total NSOA DTT response. The remaining DTT activity may arise from other quinone-like compounds that have not been identified, or from other oxidation products in NSOA. Given this

knowledge gap, we examine the potential roles of peroxides, oligomers and other more

345   oxygenated products that may explain the high DTT activities of NSOA in the next sections.

3.2 OP contribution from peroxides

One of the main hypothesis in this study is that organic peroxides contribute to OP. Organic

peroxides have been identified to be major components in both laboratory and ambient OA

350   (Jokinen et al., 2014; Lin et al., 2016; Surratt et al., 2010; Zhang et al., 2015; Zhang et al., 2017).

They can play important roles in forming high-MW oligomers (Docherty et al., 2005) and highly

oxygenated molecules (Mentel et al., 2015). Recent studies have shown that peroxides may also

be important for OP. Kramer et al. (2016) suggested that isoprene-derived

hydroxyhydroperoxide (ISOPOOH) is an essential contributor to the OP of isoprene SOA,

355   consistent with the results of bulk peroxide measurements using 4-nitrophenylboronic acid assay

(NPBA assay) by Jiang et al. (2017). Since peroxides have been proposed to be a major

component in NSOA (Kautzman et al., 2010), it is essential to determine whether or not these

peroxides can account for the remaining OP contribution (McWhinney et al., 2013).

360   Here we compare the NSOA and α-pinene SOA systems to determine the role of peroxides in OP.

The KI assay is known to be sensitive to all types of SOA peroxides (ROOR, ROOH and HOOH)

(Banerjee and Budke, 1964), and we confirmed its sensitivity by conducting calibrations with 4

different peroxides (Fig. S4). Similar KI response factors were observed with hydrogen peroxide,

cumene hydroperoxide, tert-butyl peroxide and benzoyl peroxide. Since it is likely that the

365   peroxides in NSOA have one aromatic ring are mostly in the form of ROOR (Kautzman et al.,

2010), we used benzoyl peroxide as the mass calibration standard. The mass fraction of

peroxides and DTT_m of each SOA system are shown in Table 2. A high percentage of peroxide (40-100%) was observed in α-pinene SOA, which was consistent with the results (47%) in the study by Docherty et al. (2005). Meanwhile, a very low percentage of peroxides (<3%) was

370   found in NSOA system, a result that is inconsistent with previous work (>20%) by Kautzman et al. (2010). The difference in measured peroxide content is most likely due to the difference in the UV light source. Kautzman et al. (2010) and McWhinney et al. (2013) used H_2O_2 photolysis under black lights (~350 nm), whereas in our study 254 nm UV lamps were used to photolyze O_3 and generate O (^{1}D). Organic peroxides in SOA are known to be photo-labile (Banerjee and

375   Budke, 1964; Krapf et al., 2016; Wang et al., 2011) and had likely decomposed rapidly under the shorter UV wavelengths used in our studies. Despite the differences in light conditions and peroxide content, the DTT_m measured for NSOA in this study is consistent with those measured in two separate studies (McWhinney et al., 2013; Tuet et al., 2017). Also, the DTT_m of NSOA was found to be significantly higher than that of α-pinene SOA, which contains a large fraction

380   of peroxides. Therefore, from our work, there is no evidence showing that peroxides contribute significantly to the high DTT_m observed in NSOA. Even if organic peroxides were present at a mass fraction of around 20%, as reported by Kautzman et al., (2010), we expect these peroxides would react with DTT at a similar rate as benzoyl peroxide, which has a similar structure that the proposed peroxides. The DTT_m of benzoyl peroxide (ROOR-type) is 37 pmol min^{-1}ug^{-1}, which is

385   around 3 times lower than the DTT_m of NSOA. It should also be noted that organic hydroperoxides are the major OP contributors for biogenic SOA, such as isoprene and monoterpene SOA (Jiang et al., 2017). One of the potential mechanisms is the formation of hydroxyl radicals from the decomposition of organic hydroperoxides in water (Tong et al., 2016).

For the NSOA system, our results suggest that other non-peroxide species are likely to serve as
390   major contributors to OP.

3.3 OP of oligomers in NSOA

Atmospheric OA also undergoes extensive oligomerization, forming high-MW compounds that
have profound impacts on SOA physicochemical properties (Hallquist et al., 2009; Rudich et al.,
395   2007; Trump and Donahue, 2014;Wang et al., 2011). Laboratory photooxidation of aromatic
compounds produces a substantial fraction of oligomers in the SOA (Kalberer et al., 2004) and
these oligomers may be highly functionalized (Gao et al., 2004; Tolocka et al., 2004;). IMS-TOF
analysis reveals that a substantial fraction of the signals in NSOA and PSOA are located in the
high m/z range, which are associated with high-MW oligomeric products. Since previous studies
400   have largely focused on monomeric quinones (such as 1,2-naphthoquinone or 9,10-
phenanthrenequinone), the contribution of high-MW products to OP have not been studied and
may explain the "missing" OP contributors.

To evaluate OP of high-MW products in NSOA and PSOA, solutions of SOA extract were
405   separated in a C18 reverse phase column into two major fractions. As shown in Fig. 4, when
analyzed by IMS-TOF, the first fraction was found to contain relatively higher signals at m/z
associated with monomers, and the second fraction contain products with higher signals located
in a higher m/z range. It should be noted that complete separation could not be achieved in this
work. Other techniques, such as size exclusion chromatography (Di Lorenzo and Young,
410   2016;Di Lorenzo et al., 2017), may yield better separation based on molecular weights, but may
not be able to resolve compounds in the relative low molecular weight range in the current study.

Nonetheless, the first fraction can be qualitatively described as a "monomer-rich" fraction, and the second fraction can be regarded as an "oligomer-rich" fraction (Fig. 4, Fig. 5a, b). The DTT assay was then conducted on both of the original SOA solution as well as the two separated

415   fractions. Since the amount of organic material in each fraction is not known, we use the total DTT activity (DTT_t, in μM min^{-1}) to qualitatively compare the oxidative capacities of the two fractions.

As shown in Fig. 5, both the monomer-rich and oligomer-rich fractions are reactive towards DTT.

420   Compared to the DTT_t of NSOA before LC separation, relative DTT_t of monomer-rich fraction and the oligomer-rich fraction were $16 \pm 3\%$ and $56 \pm 10\%$, respectively (Fig. 5c). For PSOA, relative DTT_t from monomer-rich fraction and oligomer-rich fraction were $40 \pm 8\%$ and $50 \pm 5\%$, respectively (Fig. 5d). In both systems, the oligomer-rich fraction caused a more rapid decay in DTT than the monomer-rich fraction even with a lower summed ion signal of low-MW

425   constituents (Fig. 5a, b for NSOA and PSOA, respectively). These qualitative results suggest that while the current focus of health studies has been focused on monomeric quinones, other higher-MW products may be important for the OP of NSOA and PSOA. Specific molecular characteristics of these high-MW OP contributors are currently unknown, and understanding them will be the subject of future research. It is very likely that the oligomers also contain redox-

430   active quinone functional groups, such as those formed on the surface of oxidized soot (Antiñolo et al., 2015), and are therefore important for OP.

3.4 OP from heterogeneous oxidation

In addition to its complexity, the composition of SOA is also highly dynamic and evolves upon atmospheric oxidation (Jimenez et al., 2009). Heterogeneous oxidation in the particle phase is one of the major pathways in aerosol aging (George and Abbatt, 2010;Rudich et al., 2007) and can increase oxygen content during the functionalization processes. McWhinney et al. (2013) attributed 21% of the NSOA's DTT activity to two quinone isomers (1,2-NQN and 1,4-NQN) in NSOA while found a higher DTT contribution (30%) when they took 5-hydroxy-1,4-naphthoquinone (5-OH-1,4-NQN) into consideration. Thus, we expect that oxygenated derivatives produced upon heterogeneous oxidation may also contribute to the OP of SOA, and the OP of SOA could be enhanced by heterogeneous oxidation.

We first examined the changes in OP with additional functional groups in known organic compounds. As shown in Fig. 6, two pairs of organic compounds in NSOA were chosen: 1,4-NQN, and 5-OH-1,4-NQN were used to study quinone-like compounds while naphthol (NPL) and 1,3-dihydroxy naphthalene (1,3-DHN) were used to compare phenol-like compounds. The $\overline{OS}$c of those four components were calculated (Kroll et al., 2011), as shown in Fig.6. Our results demonstrated a higher DTT_m for standards with higher oxidation states. For each addition of an OH group to the selected molecule, the OP increases. OP of an aromatic compound is therefore shown here to be associated with its degree of oxygenation and is demonstrated here fundamentally using individual organic compounds.

More broadly, oxidation also increases the degree of oxygenation in the bulk aerosol phase, and increases OP. Here we conducted heterogeneous oxidation by exposing filter-collected SOA to

O$_3$/ N$_2$ with the same flow rate. The N$_2$ exposure group is used as the control group in order to

isolate the effects of evaporation and/or decomposition at room temperature from those of

460 heterogeneous O$_3$ oxidation. For each of the exposure (1 h, 12 h, 24 h), the DTT$_t$ of O$_3$ exposure

group was normalized by the DTT$_t$ of the corresponding N$_2$ exposure group (Fig.7a). OC loss

was determined by thermal optical OC/EC analysis, and was observed to be 17% and 13% for

the O$_3$ and N$_2$ exposure groups after 24 hours, respectively (Fig.7b). Generally, DTT$_t$ of NSOA

filter under O$_3$ exposure was higher than that of N$_2$ exposure. The study of Anti ñolo et al. (2015)

465 also showed an increased redox activity of soot accompanied by an increased amount of

oxygenated derivatives (quinone) under heterogeneous oxidation. However, the enhanced

oxidative capacity from heterogeneous ozonolysis appeared to decrease with longer exposure to

O$_3$ (Fig.7a), which we hypothesize may result from functionalization as well as fragmentation of

organic molecules during heterogeneous oxidation (Kroll et al., 2009). This can be further

470 confirmed with the observed changes in the different OC fractions, as shown in Fig. S5. Within

the 24 h exposure, the volatile fractions (OC1 and OC2) of the O$_3$ exposed group increased while

the less volatile fractions (OC3 and OC4) decreased compared to the N$_2$ group, which suggested

the decomposition of high-MW (low volatility) species into low-MW (high volatility)

compounds. Previous work has also shown fragmentation can play a dominant role in a late stage

475 of heterogeneous oxidation (Kroll et al., 2011). The overall increased volatility may lead to

evaporation of smaller redox-active molecules and decrease the DTT$_t$ compared to the N$_2$

exposure group. It should also be noted that the O$_3$ concentrations to which NSOA are exposed

here are about 100 times higher than typical ambient levels (Finlayson-Pitts and Pitts Jr, 1999).

Assuming heterogeneous oxidation mechanisms are linear and an ambient O$_3$ concentration of 30

480 ppb, O$_3$ exposure for 1 h, 12 h, and 24 h under our experimental conditions represent 4, 50, 100

days of aging in the atmosphere. Therefore, we anticipate an overall enhancement in OP under ambient conditions. Though similar observations have been made in soot (Antiñolo et al., 2015) and diesel exhausted particles (McWhinney et al., 2013), this enhancement in OP by heterogeneous oxidation is shown here for the first time in SOA particles.

485

3.5 OP changes upon mixing with Cu

Ambient PM forming from mixed sources is frequently composed of both organics and metals. To date, both organics (quinone) and transition metals (Cu, Fe, Mn, etc.) have been shown to be redox-active (Charrier and Anastasio, 2012; Xiong et al., 2017). Metals in ambient particles can

490 range from insoluble substances to soluble cations, leading to various health outcomes after deposition onto the human respiratory tract (Gojova et al., 2007; Oberdörster et al., 2005).

Based on the chemical composition and the assumption that DTT activities of quinones and transition metals are additive, previous studies have attempted to reconstruct the overall OP in

495 ambient particles based on the chemical composition (Charrier and Anastasio, 2012;Charrier et al., 2015). However, addition of a transition-metal chelator did not result in significant changes in the expression of inflammatory biomarkers (Donaldson et al., 2001), suggesting that oxidative activities from different transition metals may not be additive. In our study, significant reductions in OP were observed for PSOA ($43 \pm 4\%$) and NSOA ($50 \pm 6\%$), when they were

500 mixed with Cu (II) (Fig. 8a). Conversely, no significant OP reduction was observed when α-pinene or limonene SOA was mixed with Cu (II). To further investigate the cause of this reduction, we examined the OP of 1,2-NQN, 1,4-NQN, 1,3-DHN and 2,3-DHN and the effects from mixing with Cu (II). Significant OP reductions for 1,2-NQN ($42 \pm 7\%$) and 2,3-DHN

(35 ± 1%) (Fig. 8b) were observed, but no such changes were observed with 1,4-NQN or 1,3-

505   DHN upon metal mixing. It should be noted that a mixture of phenanthrenequinone and Cu (II)

did not show a significant reduction in DTT activity in a study by Charrier and Anastasio (2012)

while it is likely that the DTT measurements may be affected by the inefficiency of the quench

regent, trichloroacetic acid (Curbo et al., 2013). Furthermore, an increased level of OP reduction

was observed when an increasing amount of Cu (II) were mixed with the same amount of 1,2-

510   NQN (Fig. S7). Based on the observation that OP reduction occurs only when there are

neighboring oxygenated functional groups, we hypothesize that the OP reduction is related to

formation of covalent bonds between the electron-deficient Cu (II) and the electron-donating

polar functional groups. The formation of quinone-copper complexes have been demonstrated

previously (Dooley et al., 1990; Klinman, 1996), and may be responsible for reducing the overall

515   OP.

To understand the underlying mechanism, ^{1}H NMR spectroscopy was used to monitor the

formation of the organic-Cu complex. ^{1}H NMR has previously been applied to study the binding

between metals and organics (Peana et al., 2015; Syme and Viles, 2006). The relaxometry (T2)

520   of NSOA illustrated in Fig. 9 shows a decreasing trend on average for T2 relaxation time when

Cu (II) was added to the system. Such decrease in relaxation time indicates interactions between

copper and SOA components. In general, protons adjacent to and within aliphatic hydroxyl

groups resonate between 3-5 ppm, while aromatic groups and double bonds arise between 5-9

ppm. Before the addition of copper, NSOA T2 relaxation time show a range of values consistent

525   with a complex material with a diversity of functional groups and dynamics. It was after the

addition of copper, both of the aliphatic hydroxyl and aromatic region showed a decrease in T2

and inherit roughly similar relaxation values. This suggested copper is able to influence a wide range of SOA components, with both structural categories (aliphatic hydroxyl and aromatic) involved in copper binding to some extent. Due to the complexity in the SOA NMR spectra, it is

530   still currently challenging to specifically identify binding between individual NSOA components and Cu. To further investigate the binding reactions, ^{1}H NMR measurements were made for the compounds present in NSOA, as previously mentioned, in the presence and absence of Cu, as shown in Fig. 10. Significant interactions between Cu and 1,2-NQN are evidenced by the broadened peak shapes (Fig. 10a), caused by the coordination of adjacent oxygen groups with the

535   copper ion, which has also been well documented in previous studies with similar compounds (Inoue and Gokel, 1990;Schmidt et al., 1990;Tolman, 1977). Protons proximal to the binding sites are more significantly broadened, while protons further away are less affected. Conversely, mixing of 1, 4-NQN with Cu led to little changes in peak shape, indicating the lack of any interactions with copper, as shown in Fig. 10b. Similar phenomena were also observed with

540   another pair of isomers (2,3-DHN and 1,3-DHN). As shown in Fig.10c, 2, 3-DHN shows a clear change in peak shape indicating that these hydroxyl moieties on adjacent carbons are very important for copper coordination. On the other hand, the 1, 3-DHN structure shows very little peak broadening when mixed with copper.

545   Such binding evidence was further supported by NMR relaxation data (Fig. 11). As copper is paramagnetic, it is an effective relaxation agent, and protons brought into its proximity undergo faster T1 and T2 relaxation that manifest themselves as spectral broadening in 1D NMR (Fig. 10). For the epitope maps, the largest circles indicate the least interactions with copper. For both T1 and T2 data (Fig. 11, Table S1), protons adjacent to the binding sites a and f (pronto peak

550   assignment based on Fig.10a, Fig.S6) underwent significant changes in relaxation indicating the

metal coordinating to the neighboring oxygen groups. Proton e changed less as it is located

further away from the copper binding site. While copper has a relatively mild effect on protons b

and d, a significant reduction in T1 and T2 for proton c was observed. Such interesting

phenomenon is due to the increased nuclear Overhauser effect (NOE) from the b and d sites. In

555   the absence of binding, protons b and d would in part relax via NOE with protons a and e, which

relax rapidly due to the copper binding. As such protons b and d can no longer lose

magnetization via an Overhauser effect owing to a and e. Instead, they pass magnetization to

position c which underwent enhanced level of relaxation as a result. The NOE effect for ring

systems with similar structure has also been demonstrated by several previous publications

560   (Kowalewski and Maler, 2006; Rehmann and Barton, 1990). It should be noted that the increased

level of OP depletion is accompanied by an increased ratio of Cu to 1,2-NQN (Fig. S4a), the

degree of broadening in the 1D NMR proton peaks becomes more significant (Fig. S4b), and the

relaxation times T1, T2 decreases (Fig. 11). All these observations together illustrate that the

reduction of OP is proportional to the binding between Cu and organics, and further supports the

565   mechanism behind OP depletion in the DTT assay. Based on the conclusions from the individual

organic standards, the overall decrease in relaxation times for NSOA mixing with Cu (shown in

Fig. 9) likely indicates that Cu (II) are binding with NSOA components, limiting the redox

activities and OP of both the Cu (II) ions and the redox-active NSOA components.

570   **4   Implications**

Oxidative stress caused by ROS production and antioxidant consumption is one of the most

commonly studied mechanisms for PM toxicity (Nel, 2005;Rhee, 2006;Manke et al., 2013). Here

we performed OP evaluation of two SOA formed from PAHs (naphthalene, phenanthrene) by the

DTT assay, and investigated the linkages between SOA OP and chemical composition upon

575   various atmospheric aging processes. SOA derived from ozonolysis of monoterpenes (α-pinene,

limonene) have a lower DTT_m than that of the two PAHs derived SOA, which could be attributed

to the high redox-active quinone-like components. This is also consistent with the previous

hypothesis that OP of SOA is highly dependent on the identity of its precursor (Tuet et al.,

2017a). To further link SOA OP to its chemical composition, this study also explored the

580   possible impacts from atmospheric aging processes so as to provide mechanistic understanding

for ambient observations.

Over the span of atmospheric lifetime, the mass and chemical composition of SOA can be

affected by aging processes (Kroll et al., 2009; Lim et al., 2017). The aerosol aging processes

585   that we studied here include oligomerization, heterogeneous oxidation and metal mixing. Apart

from quinones that are well known to exhibit high OP in aerosol samples, OP contributions from

peroxides in our NSOA system are likely to be insignificant. Rather, oxygenated derivatives

were shown here to contribute greater OP than their precursors in our study of selected organic

individuals, and heterogeneous oxidation of NSOA was shown to lead to greater OP as well.

590   Moreover, DTT activities of the monomer-rich and oligomer-rich fractions in NSOA separated

by liquid chromatography showed oligomers are OP contributors in SOA. While organic

peroxides have been proved to be very labile components with half-lives of minutes at room

temperature (Krapf et al., 2016), SOA oligomers are relatively stable and highly oxygenated with

their ratio of total organic molecular weight per organic carbon weight (OM/OC) similar to that

595   of atmospheric humic-like substances (HULIS) (Altieri et al., 2008). Consistent with OP

contributions from oxygenated components enriched HULIS fraction in ambient PM (Verma et al., 2015b), this study also shows evidence for OP contributors from atmospheric aging products of PAH-derived SOA, indicating major organic PM OP contributors could be less volatile than previously thought, and may more readily remain in the particle phase under atmospheric aging.

600   Nevertheless, future work should focus on improving separation methods, allowing for more precise measurements of OP from SOA oligomeric constituents.

A reduction in OP was observed when mixing NSOA/PSOA with Cu (II), resulting in a non-additive effect. However, no such reduction was observed in α-pinene SOA or limonene SOA.

605   Using ^{1}H NMR spectroscopy, we demonstrate that the reduction in OP is likely caused by binding between Cu (II) and redox active organic compounds. Both the peak broadening in 1D NMR spectra and shorter relaxation times are observed for compounds that exhibited OP reduction (1,2-NQN, 2,3-DHN) upon Cu (II) mixing. Additionally, the greater amount of Cu (II) mixed in, the enhanced OP reduction and the decrease in relaxation times showed up. While it is

610   still challenging to determine which NSOA components are binding with Cu (II), the overall relaxation time also decreased when NSOA was mixed with Cu (II), indicating binding between Cu (II) and various NSOA components. Based on our work, previously recognized redox-active organic and inorganic components in ambient particles (Charrier and Anastasio, 2012; McWhinney et al., 2011; Monks et al., 1992; Turski and Thiele, 2009) may bind with each other

615   once mixed during atmospheric aging processes (external) or within the physiological environment of the human body (internal). Similarly, Hems et al. (2017) found a suppression of OH generation (Photo-Fenton reaction) occurred, and attributed the decrease to the formation of metal-SOA complex. Although current studies demonstrate such metal-SOA binding leads to a

lower OP, other studies (Gonzalez et al., 2017; Yu et al., 2018) have found an increased level of

620 OH radicals through the formation of Fe (Ⅱ)-HULIS complex. These synergistic /antagonistic

metal-organic interactions are relevant to multiple health outcomes. Figuring out the dominant

interactions under atmospherically/ physically relevant conditions may provide hints for

alleviating the health impact of ambient particles. In the future, a more detailed understanding of

SOA binding with metal components and the effects on the oxidative health outcomes will be

625 essential. It should also be noted that the DTT assay alone may not be entirely representative of

physiological ROS variations (Tuet et al., 2017a; Xiong et al., 2017). More *in vitro* and *in vivo*

work should be performed in establishing the relationship between chemical composition and the

OP of aerosol.

630 ASSOCIATED CONTENT

Supporting Information.

AUTHOR INFORMATION

Corresponding Author

635 * Address: 200 College Street, Toronto, ON, M5S 3E5

Email: arthurwh.chan@utoronto.ca

Phone: +1 (416)-978-2602

Notes
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Table 1. Flow tube experimental conditions

Compund	Reaction[a]	ΔHC ppb	$Y^{b,c}$ %	RH
limonene	ozonolysis	251 ± 23	25 ± 3.9	$14 \pm 1\%$
α-pinene	ozonolysis	304 ± 17	19 ± 4.2	$14 \pm 1\%$
naphthalene	photooxidation	6436 ± 402	28 ± 6.7	$57 \pm 5\%$
phenanthrene	photooxidation	4050 ± 578	12 ± 2.6	$57 \pm 5\%$

a. Temperature in all experiments is around room temperature (22-25 °C).
b. SOA mass yields were calculated without particle wall loss correction.
c. SOA density in this study was assumed to be 1.25 g cm^{-3} for monoterpene SOA (Shilling et al., 2009), and 1.55 g cm^{-3} for PAHs SOA(Chan et al., 2009).

Table 2. SOA peroxide content and OP

Organics	Peroxide percentage %	DTT_m pmol min^{-1} μg^{-1}
Naphthalene SOA	<3	100-129
α-pinene SOA	40-100	10-20
Benzoyl peroxide	100	37
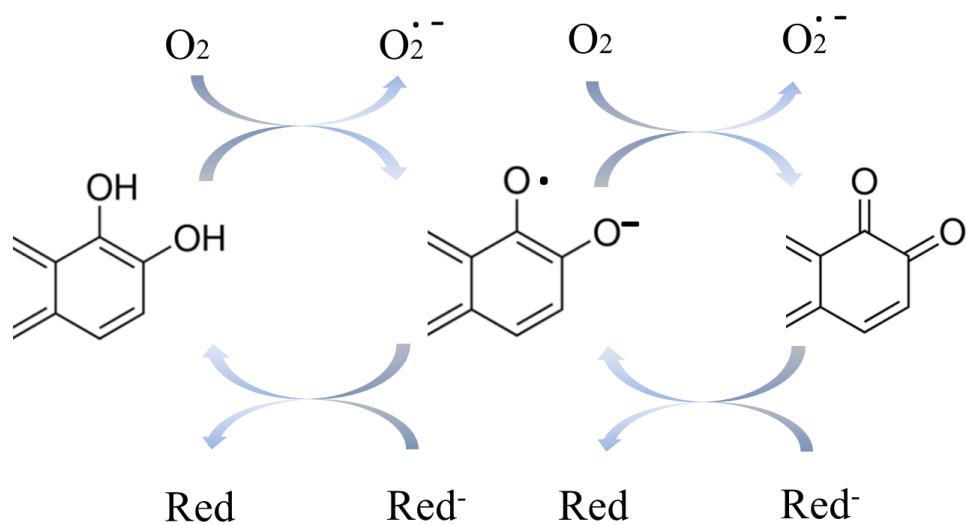
Figure 1. A simplified mechanism of redox cycling of quinone-like substances and formation of superoxide anion radicals. ***Red*** refers to a general reductant. In the redox cycle, regenerated quinone serves as a chemical intermediate to transfer electrons from reductants to oxygen to form superoxide ($O_2{}^{\cdot-}$).
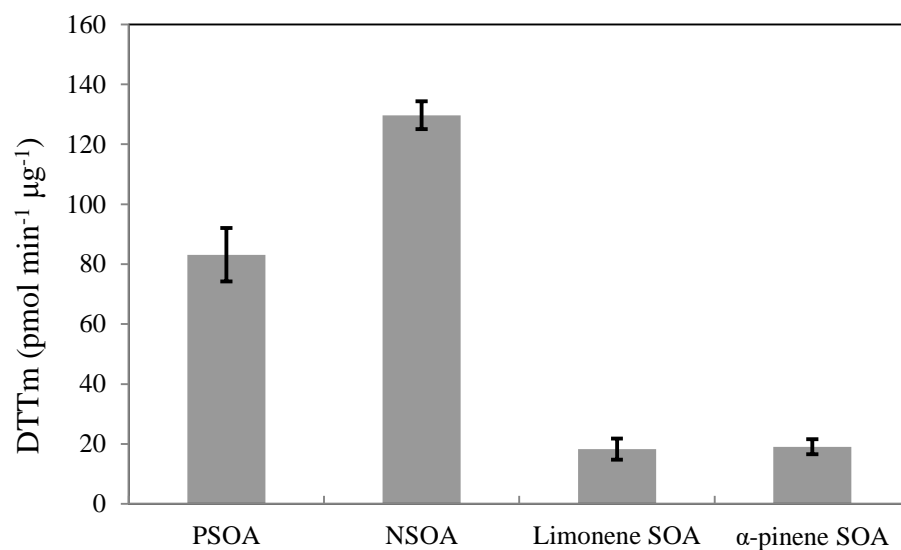
Figure 2. DTT_m (pmol min^{-1} μg^{-1}) for SOA formed from various types of hydrocarbons (phenanthrene, naphthalene, limonene and α-pinene). Each measurement was conducted in triplicates, and the error bar represents the standard error of the mean (SEM).
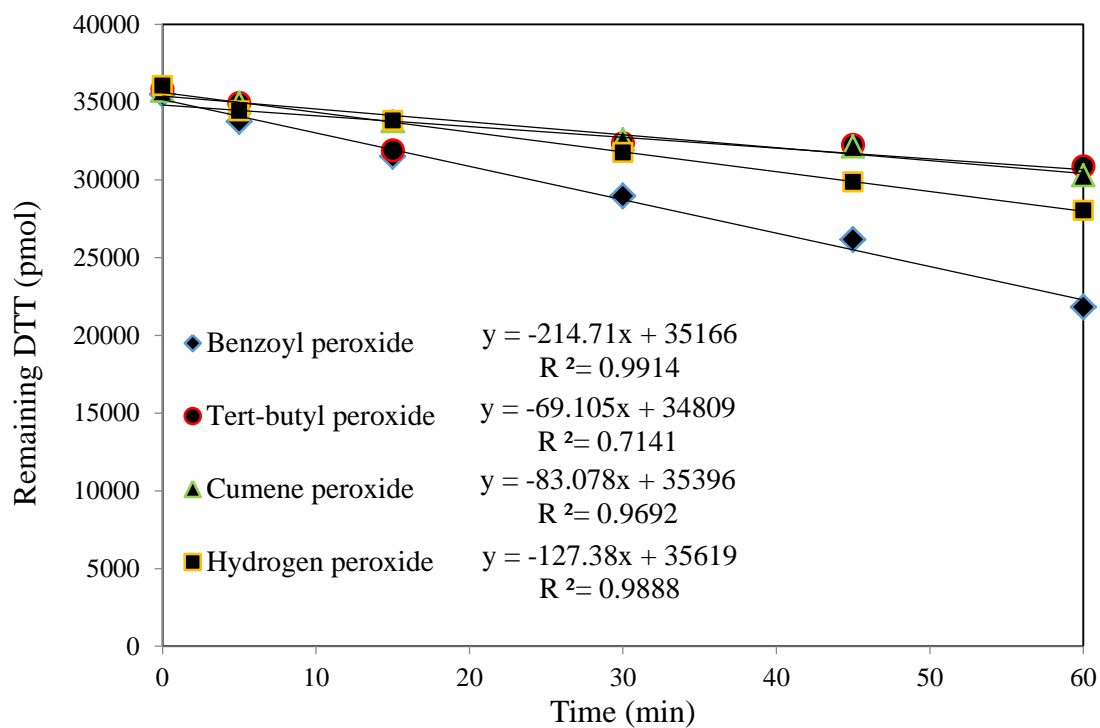
Figure 3. DTT activity of various types of peroxides (hydrogen peroxide, cumene peroxide, tert-Butyl peroxide, benzoyl peroxide). With the same initial concentration of peroxide (120 µM), benzoyl peroxide has the highest DTT activity (converted to DTT_m of 37 pmol min^{-1} ug^{-1}).
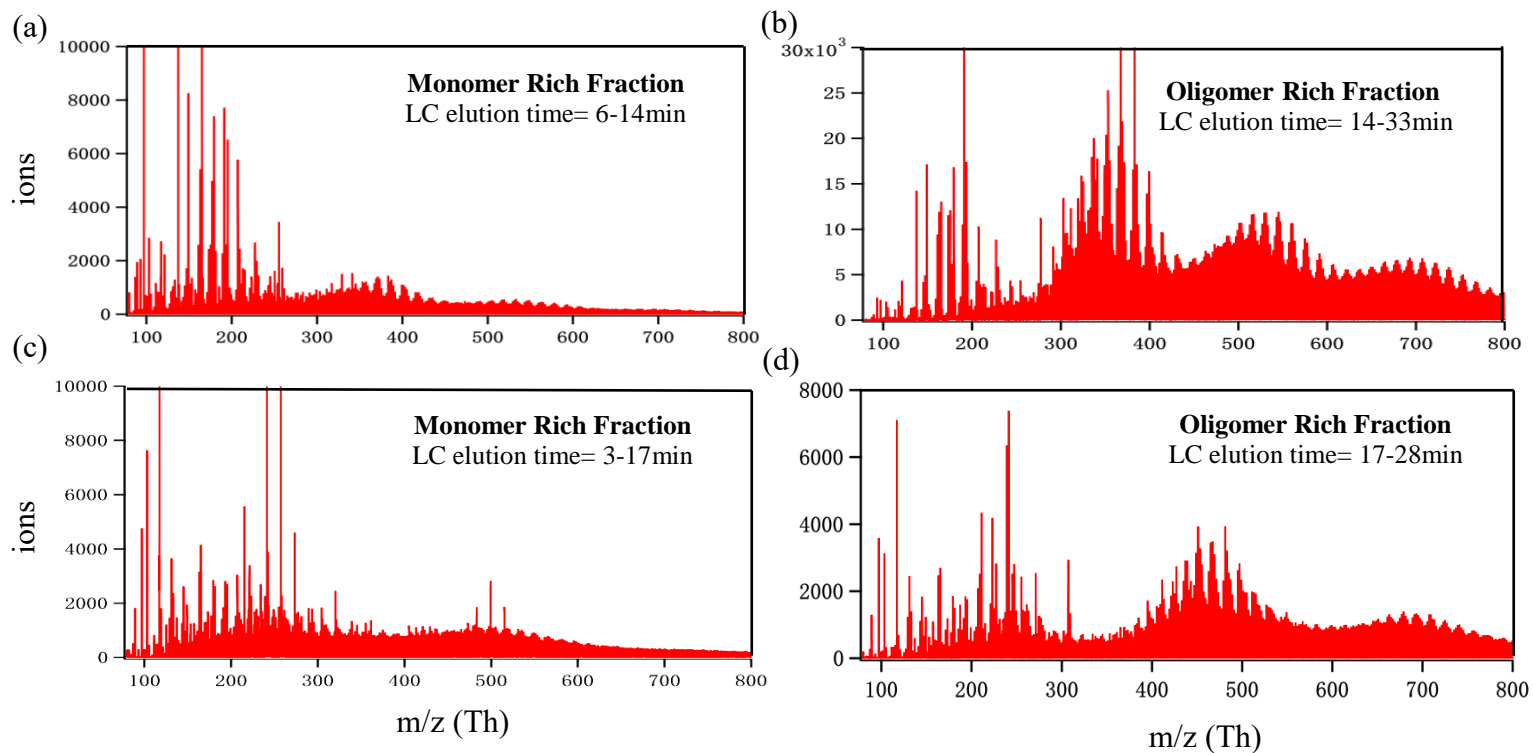
Figure 4. IMS-TOF mass spectra for (a) monomer-rich fraction (b) oligomer-rich fraction in

NSOA and (c) monomer-rich fraction (d) oligomer-rich fraction in PSOA. During a total of 46-

min elution, the majority of NSOA monomers eluted at 6-14 min, and most of the oligomers

eluted at 14-33 min. For PSOA system, the majority of monomers eluted at 3-17 min, and most

of the oligomer- rich fraction eluted at 17-28 min.
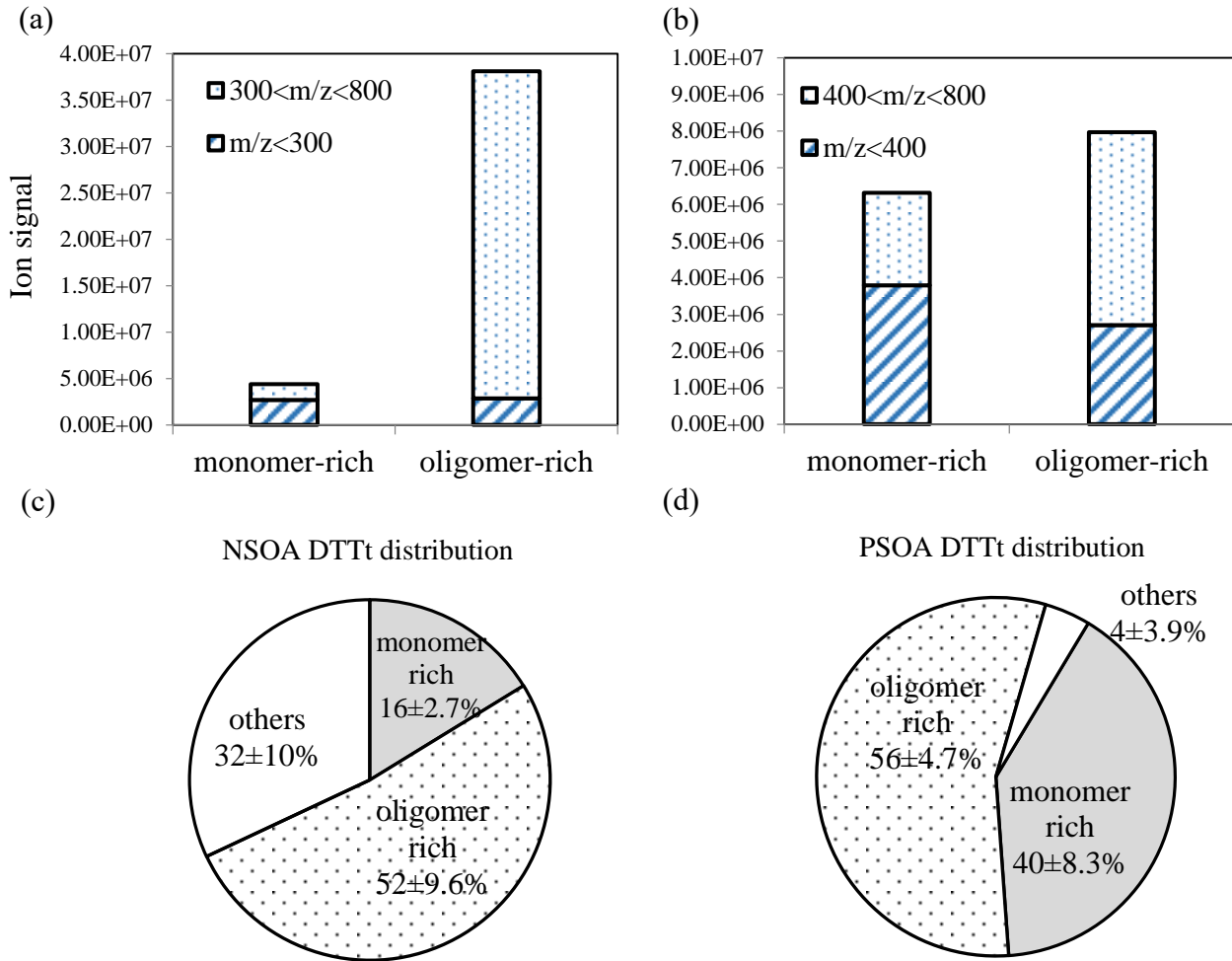
Figure 5. Sum of ion signals for monomers and oligomers in monomer-rich fraction and oligomer-rich fraction for NSOA (a) and PSOA (b) systems. Relative DTT_t from monomer-rich fraction and oligomer-rich fraction in NSOA (c) and PSOA (d) systems. The remaining DTT activity (others, white) is attributed to residual SOA fractions that did not clearly elute out.
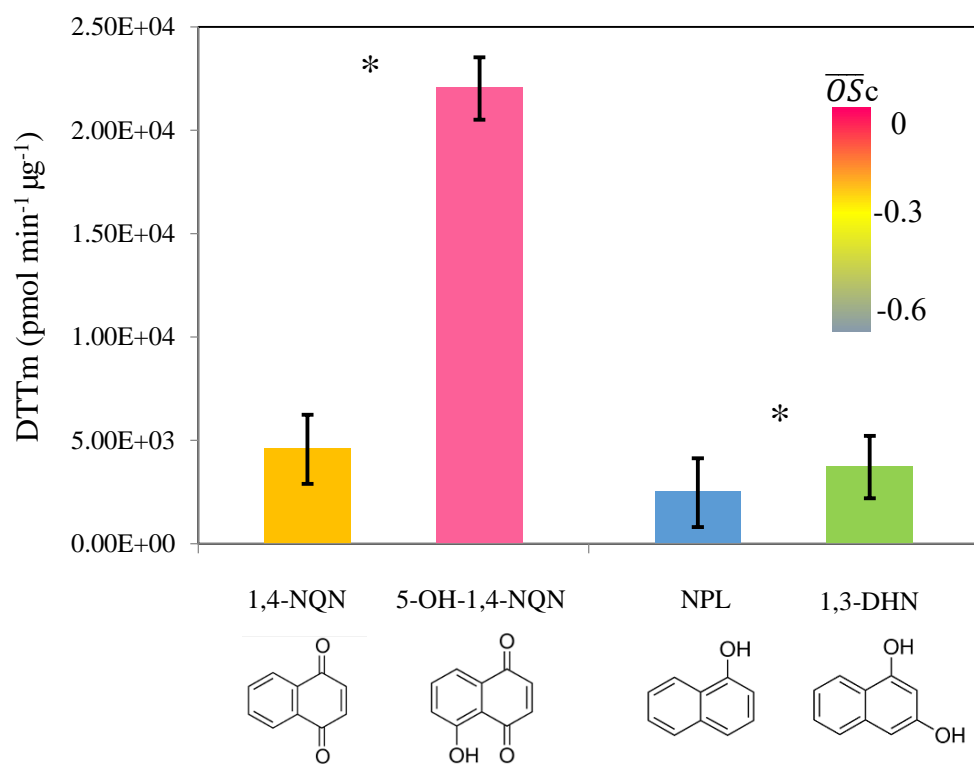
Figure 6. DTT$_m$ for two selected pairs of oxygenated derivatives in NSOA system (1,4-NQN vs. 5-OH 1,4-NQN, NPL vs. 1,3-DHN). Averaged carbon oxidation state ($\overline{OS}c$) of each component is shown in color (color scale shown on top-right). Each measurement was conducted in triplicates, and the error bar here represents the SEM. The asterisk indicates significant difference between each pair of measurements at the 95% confidence level.
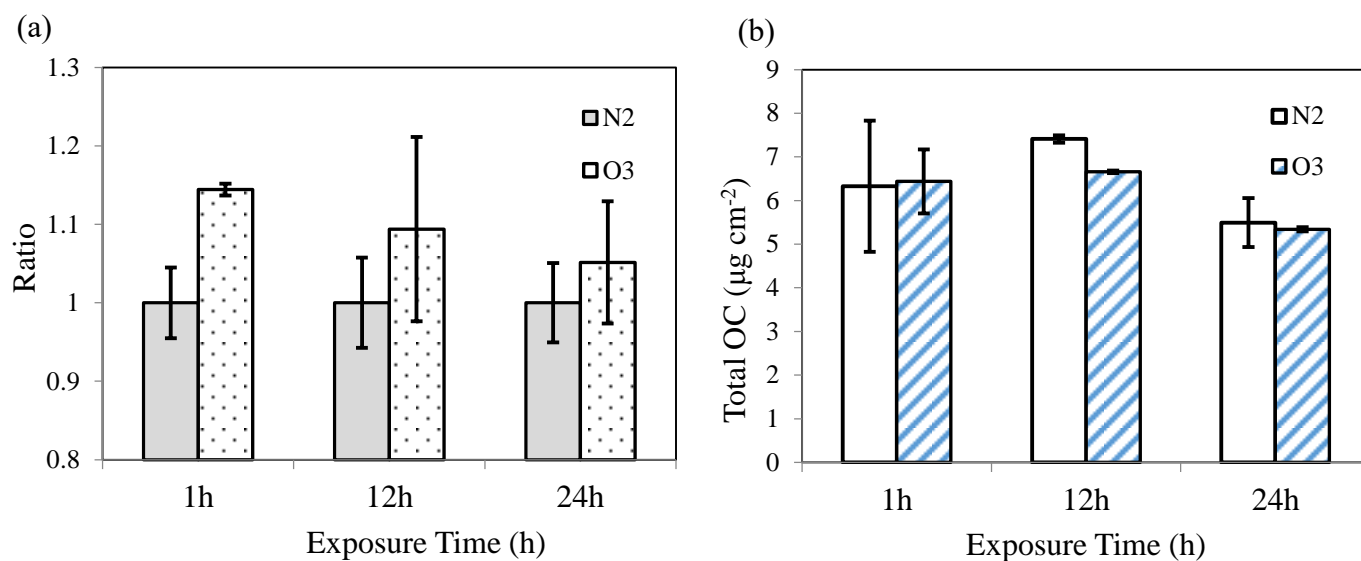
Figure 7. (a) Relative DTT_t for NSOA after O_3 and N_2 exposure. For each of the exposure

duration (1 h, 12 h, 24 h), the DTT_t of O_3 exposure group was normalized by the DTT_t of the

corresponding N_2 exposure group. Generally, DTT_t of NSOA that underwent heterogeneous

ozonolysis was higher than that of the N_2 control. (b) OC/EC measurement results show total OC

mass loss (17% and 13% for O_3 and N_2 exposure, respectively) after 24-hour exposures. Each

measurement was conducted in triplicates, and the error bar represents the SEM.
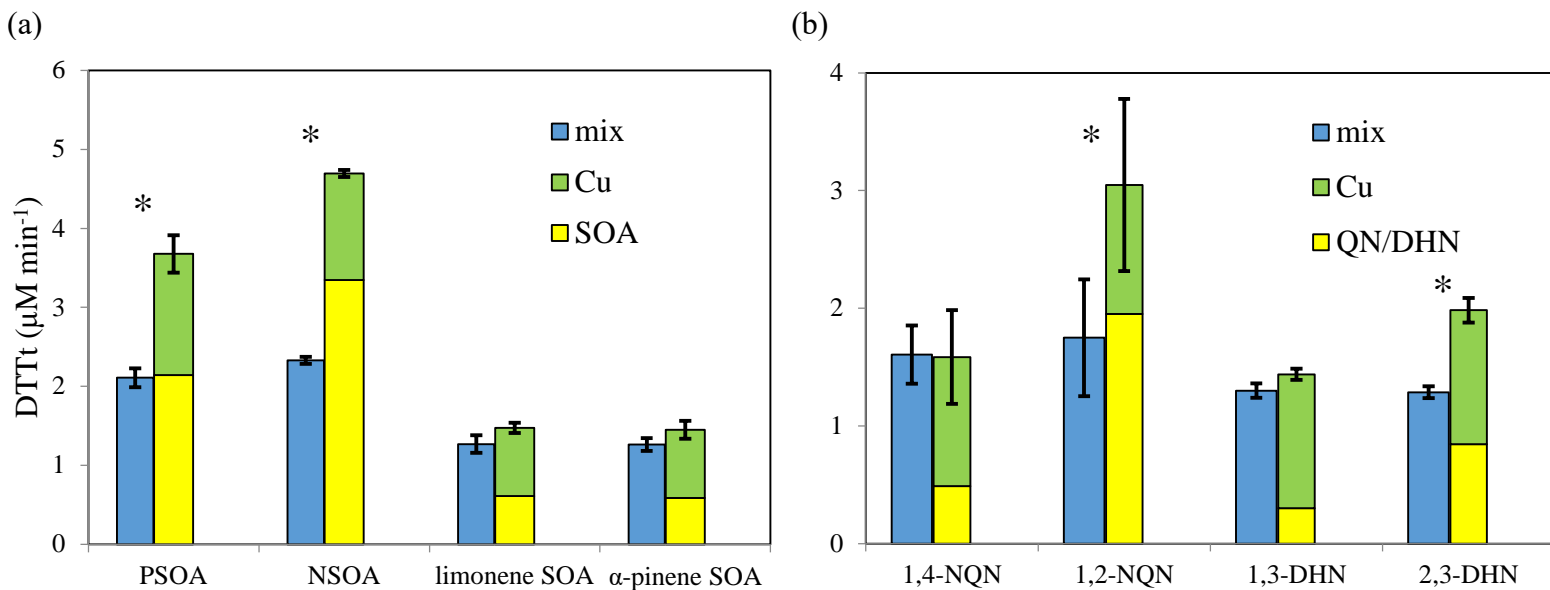
Figure 8. Significant OP depletions were observed when PSOA($43 \pm 4\%$), NSOA($50 \pm 6\%$),

1,2-NQN($42 \pm 7\%$) and 2,3-DHN($35 \pm 1\%$) mixed with Cu (II). The asterisk indicates

significant difference between a pair of bars at a 95% confidence level.
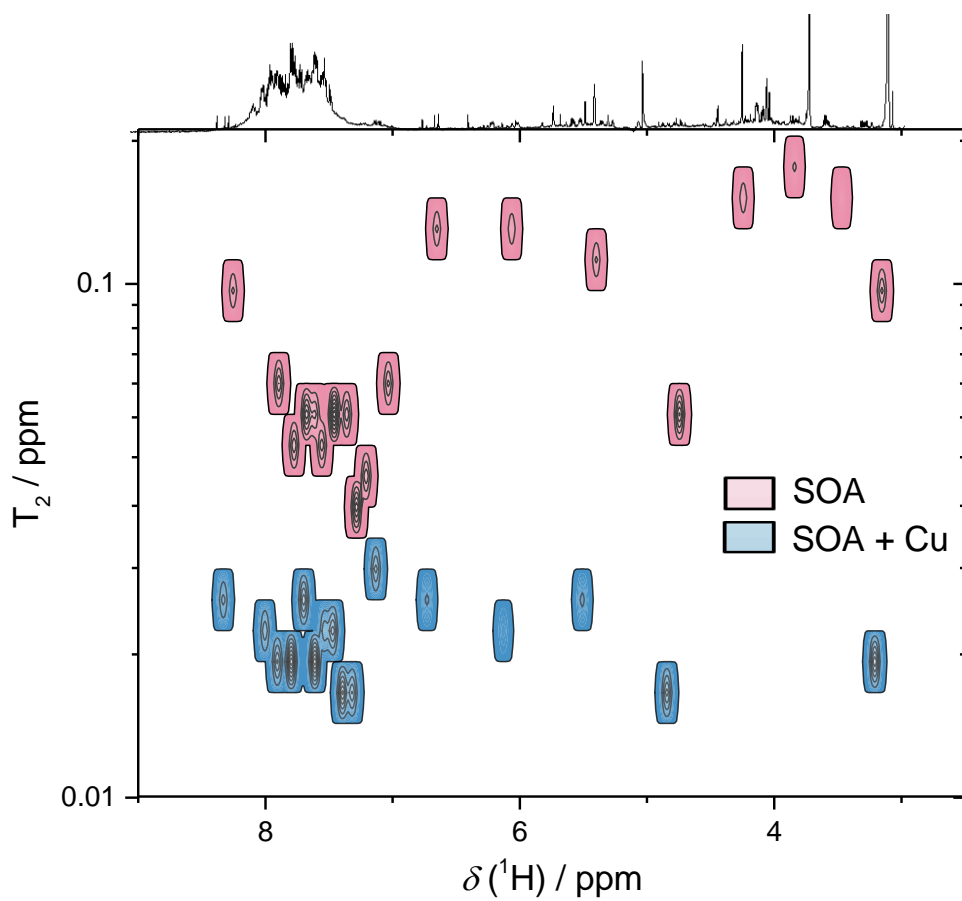
Figure 9. 2D ^{1}H-NMR T2 relaxation contour map for NSOA with (blue) and without copper (red) with 1D NMR projections from the top. A general decreasing trend in T2 is observed here, which indicates interactions (binding) of Cu (II) with many NSOA components.
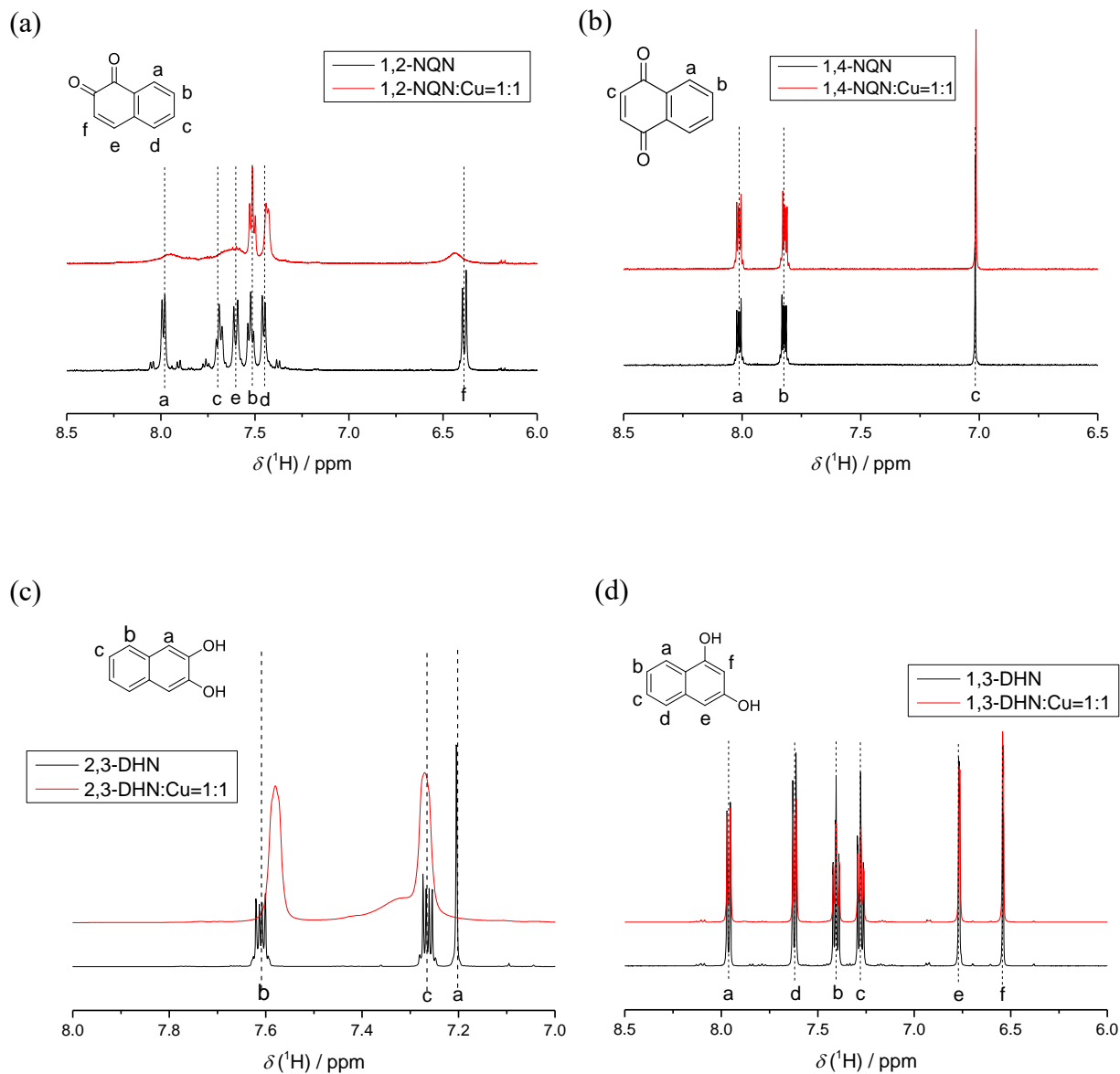
Figure 10. 1 D ^{1}H-NMR spectra of (a) 1,2-NQN (b) 1,4-NQN (c) 2,3-DHN (d)1,3-DHN and their mixture with 1:1 ratio of Cu (II). Both 1,2-NQN and 2,3-DHN show the broadening of ^{1}H-NMR peaks (protons at a, c, e, f and a, b, c for 1,2-NQN and 2,3-DHN, respectively) after mixing with Cu (II).

(a)

(b)
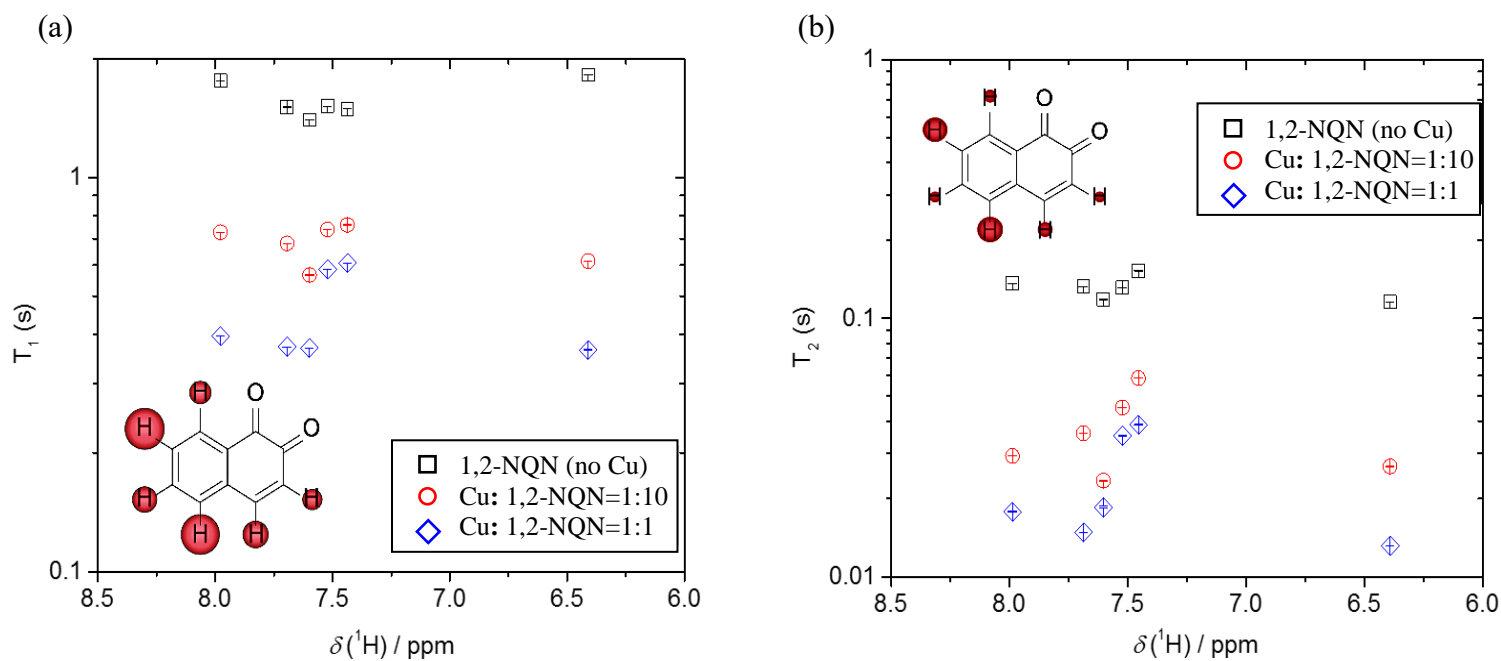
Figure 11. ^{1}H NMR relaxometry analyses for (a) T1, (b) T2 of 1,2-NQN mixed with Cu (II) at different ratios: 1,2-NQN with no Cu (**black**), Cu (II):1,2-NQN = 1:10 (**red**), Cu (II):1,2-NQN =1:1(**blue**). Both T1, T2 decreased when Cu was introduced into the system, indicating a smaller scale of nuclear spin dynamic resulted from organic-metal binding. The molecular epitopes illustrate the influence of Cu (II) binding on individual proton. A smaller sphere shadow on a proton denotes a larger relaxation influence from Cu (II)-organic binding.