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Oxidative potential of secondary organic aerosols produced from photooxidation of different hydrocarbons using outdoor chamber under ambient sunlight

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HIGHLIGHTS

- Toluene SOA and isoprene SOA yielded much higher DTT response than 1,3,5-trimethylbenzene SOA and α-pinene SOA.
- Toluene SOA and isoprene SOA are more important than α-pinene SOA in urban air in terms of the oxidative potential.
- Toluene SOA induce more IL-8 expression than 1,3,5-trimethylbenzene SOA.

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ABSTRACT

The oxidative potential of various secondary organic aerosols (SOA) was measured using dithiothreitol (DTT) assay to understand how organic aerosols react with cellular materials. SOA was produced *via* the photooxidation of four different hydrocarbons (toluene, 1,3,5-trimethylbenzene, isoprene and α-pinene) in the presence of NO_x using a large outdoor photochemical smog chamber. The DTT consumption rate was normalized by the aerosol mass, which is expressed as DTT_{mass}. Toluene SOA and isoprene SOA yielded higher DTT_{mass} than 1,3,5-trimethylbenzene SOA or α-pinene SOA. In order to discover the correlation between the molecular structure and oxidative potential, the DTT responses of selected model compounds were also measured. Among them, conjugated aldehydes, quinones, and H_2O_2 showed considerable DTT response. To investigate the correlation between DTT response and cell responses *in vitro*, the expression of biological markers, i.e. IL-6, IL-8, and HMOX-1 were studied using small airway epithelial cells. Higher cellular expression of IL-8 was observed with toluene SOA exposure compared to 1,3,5-trimethylbenzene SOA exposure, which aligned with the results from DTT assay. Our study also suggests that within the urban atmosphere, the contribution of toluene SOA and isoprene SOA to the oxidative potential of ambient SOA will be more significant than that of α-pinene SOA.

1. Introduction

Hydrocarbons (HCs) that are emitted from anthropogenic activities or plants enter a NO_x cycle and are atmospherically oxidized to produce both carbon dioxide and semivolatile oxygenated products (Hallquist et al., 2009; Aumont et al., 2005). Secondary organic aerosols (SOA) are generated from these semivolatile products *via* a gas-particle partitioning process or self-nucleation (Hallquist et al., 2009; Jang et al., 2006). They comprise a major fraction of organic aerosol in atmospheric $PM_{2.5}$ (Gelencsér et al., 2007). For example, Gelencsér et al. reported that in the source apportionment of $PM_{2.5}$, secondary organic carbon from five sites in Europe made up 70%–86% of total organic carbon during the summer season, and 21%–68% during the winter season (Gelencsér et al., 2007). Exposure to $PM_{2.5}$ is associated with a number of adverse respiratory and cardiovascular health effects (e.g., respiratory disease) (HEI Perspectives, 2002). Such particulates, including SOA, can be transported deeply into the respiratory tract (e.g., alveolar region) and potentially cause cellular and tissue

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damage (HEI Perspectives, 2002; Li et al., 2003). The high fraction of SOA in particulate matter (PM) suggests that SOA may be a significant contributor to the observed adverse health effects.

The biological responses of cells have been frequently studied to investigate the health effects of SOA. Both *in vitro* and *in vivo* studies suggest that SOA exposure increased the release of biological markers, such as interleukin-8 (IL-8), heme oxygenase-1 (HMOX-1), cyclooxygenase-2, tumor necrosis factor-α (Jang et al., 2006; Gaschen et al., 2010; Sunil et al., 2007; McDonald et al., 2012). For example, Jang et al. reported that exposure to SOA produced from the ozone reaction with biogenic hydrocarbons (e.g., α-pinene and terpinolene) led to the increase of IL-8 expression in human lung epithelial cells (BEAS-2B) *in vitro* (Jang et al., 2006). Gaschen et al. also showed that the α-pinene SOA that was collected after 6-h photooxidation, significantly increased the IL-8 response in pig primary airway epithelial cells (Gaschen et al., 2010).

It is widely known that some biological responses are triggered by oxidative stress (Li et al., 2003; Paszti-Gere et al., 2012) that is induced by reactive oxygen species (ROS) (e.g., ·OH, $O_2^{\cdot-}$, H_2O_2, ROOH) (Simon et al., 2000) or *via* the interaction of biosystems with unsaturated aldehydes (e.g., acrolein) (Yoshida et al., 2009). ROS can be generated by the reaction between cell components and air pollutants, such as quinones, polycyclic aromatic hydrocarbons (PAHs), and metals (Squadrito et al., 2001). For example, quinones can catalyze the formation of H_2O_2 and $O_2^{\cdot-}$ by transferring electrons from NADPH to oxygen (Squadrito et al., 2001). The chemical metal-cell interaction (e.g., Fe, Cr, etc.) also leads to the generation of $O_2^{\cdot-}$ and ·OH *via* Fenton chemistry (Li et al., 2003; Verma et al., 2009). However, the role of SOA in producing oxidative stress is poorly understood for several reasons. First, the complexity of oxidation mechanisms of various hydrocarbons makes it difficult to clarify the atmospheric processes of SOA formation (Hallquist et al., 2009). Second, SOA contains complex multifunctional products, such as carbonyls, alcohols, carboxylic acids, organonitrates, organosulfates, epoxides, peroxides, quinones, etc. (Im et al., 2014). Third, the correlation between cellular ROS production and pollutants is difficult to decipher due to the transformative nature of pollutants in biosystems. For example, some polycyclic aromatic hydrocarbons can be transformed into quinones in biosystems to become redox active (Penning et al., 1999).

The oxidative potential has been proposed as an important parameter in quantifying the capability of air pollutants to oxidize cellular materials (Janssen et al., 2014). Dithiothreitol (DTT), a surrogate compound for biological reducing agents (e.g., NAPDH), has been widely used to measure the oxidative ability of air pollutants (Li et al., 2003; Verma et al., 2009; Fang et al., 2014; Janssen et al., 2014). For example, Li et al. have applied the DTT assay to the oxidative potential measurement of diesel exhaust particles (Li et al., 2003). Janssen et al. also measured the oxidative potential of PM at different types of sampling sites using the DTT assay (Janssen et al., 2014). Furthermore, Fang et al. developed a semi-automated system that can quantify the oxidative potential of aerosols accurately and efficiently (Fang et al., 2014).

In this study, the DTT response of various SOA was measured to understand the SOA-cell interaction. SOA was produced from the photooxidation of four different HCs in the presence of NO_x using a large outdoor smog chamber. For anthropogenic HCs, toluene and 1,3,5-trimethylbenzene (135-TMB) were chosen due to their high concentrations in the urban atmosphere (Jia et al., 2008). For biogenic HCs, isoprene and α-pinene were chosen for the following reasons. The isoprene emission rate is the highest of all non-methane hydrocarbons (600 Tg/yr) (Carlton et al., 2009). α-Pinene is the most abundant terpene and has a high SOA yield (Odum et al., 1996; Greenberg et al., 2004). Chamber generated SOA was collected efficiently by a Particle-Into-Liquid Sampler (PILS) technique within a small amount of water. The resulting liquid sample was then applied to DTT assay to study the oxidative potential of SOA. In order to investigate the correlation between DTT response and cell responses *in vitro*, cytotoxicity and biological markers including interleukin-6 (IL-6), IL-8 and HMOX-1 were analyzed in the human small airway epithelial cells (SAEC) *in vitro* after exposure to toluene SOA and 135-TMB SOA.

2. Materials and methods

2.1. Chemicals

Toluene (ACS, 99.5%), 135-TMB (99%, extra pure) and hydrogen peroxide (50 wt% aqueous solution) were obtained from Acros Organics (NJ, USA). Isoprene (99%), α-pinene (98%), CCl_4 (99.9%), sodium nitrite (ACS, ≥97%), sulfuric acid (ACS, 95–98%), potassium phosphate buffer (0.1 M), 9,10-phenanthraquinone (PQN) (99%), 1,2-naphthoquinone (1,2-NQN) (97%), 1,4-naphthoquinone (1,4-NQN) (97%), and glyoxal (40% aqueous solution) were obtained from Sigma-Aldrich (St. Louis, MO, USA). Dithiothreitol (99%), Tris base (99.8–100.1%), dimethyl sulfoxide (DMSO, 99%), 5,5′-dithiobis-(2-nitrobenzoic acid) (DTNB, 99%), trichloroacetic acid (TCA, 99%), DI water (ACS, ASTM Type I) were purchased from Thermo Fisher Scientific (Pittsburgh, PA, USA). Acrolein (97%, stabilized by hydroquinone) and methacrolein (96%, stabilized by hydroquinone) were purchased from Alfa Aesar (Ward Hill, MA, USA). Acetaldehyde (ACS reagent grade) was obtained from MP biomaterials (Solon, OH, USA).

2.2. SOA outdoor chamber experiment

SOA was produced *via* the photochemical reactions of HCs (toluene, 135-TMB, isoprene, and α-pinene) in the presence of NO_x in the University of Florida Atmospheric PHotochemical Outdoor Reactor (UF-APHOR) dual chambers (52 m^3 for each chamber) that are located on the roof of the Black Hall at the University of Florida, Gainesville, Florida (Section S1 in Supporting Information (SI)). Before each experiment, the chamber was flushed by the clean air from the air purifier system (GC Series, IQAir Inc.) for 2 days. The background particle mass concentration was below 1 μg/m^3. The particle size distribution of SOA in the chamber was monitored by a scanning mobility particle sizer (SMPS). The number concentration was converted to mass concentration by multiplying by the SOA density, which is 1.3 g/cm^3 for α-pinene SOA and 1.4 g/cm^3 for other three SOA (Im et al., 2014; Ng et al., 2007). The mass concentration of organic carbon (OC) was monitored by a semi-continuous Organic carbon/Element carbon (OC/EC) aerosol analyzer. The organic matter (OM) concentration is determined by multiplying OC by the [OM]/[OC] ratio, which is 1.6 for α-pinene and 2.0 for other three types of SOA (Aiken et al., 2008; Kleindienst et al., 2007). The chamber experiment conditions that produced various organic aerosols are listed in Table 1. Details of the chamber experiment procedures and instruments are provided in Sections S1 in SI. SOA particles were efficiently collected within a small amount of deionized (DI) water using a PILS (Metrohm, Riverview, FL) technique. We placed an activated charcoal denuder upstream of the PILS to remove the gas phase compounds (Section S2 in SI). For experiments without charcoal denuder, an acidic denuder and a basic denuder were placed upstream of the PILS to remove NH_3 and gaseous inorganic acid, respectively. They can also partially remove some gaseous polar organic compounds.

2.3. Collection of wood smoke particles

Commercial hickory hardwood was burned in a stove under