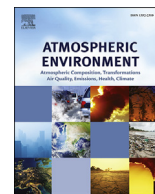




Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

Assessing the oxidative potential of isoprene-derived epoxides and secondary organic aerosol



Amanda J. Kramer, Weruka Rattanavaraha, Zhenfa Zhang, Avram Gold, Jason D. Surratt*, Ying-Hsuan Lin**^{1, 2}

Department of Environmental Sciences and Engineering, Gillings School of Global Public Health, The University of North Carolina at Chapel Hill, Chapel Hill, NC, USA

HIGHLIGHTS

- ROS potential tested for isoprene-, MACR-, IEPOX-, and MAE-derived SOA systems.
- ROS potential tested for synthetic IEPOX, MAE, 2-MT, 2-MG, organosulfates, and ISOPOOH.
- High-NO_x conditions produce SOA that is more oxidizing compared low-NO_x conditions.
- MACR SOA had a higher ROS potential than diesel PM + ozone and daytime diesel PM.
- Organic peroxides could be major contributors to observed oxidative potential.

ARTICLE INFO

Article history:

Received 21 May 2015
 Received in revised form
 7 October 2015
 Accepted 7 October 2015
 Available online 20 October 2015

Keywords:

PM_{2.5}
 DTT assay
 Oxidative stress
 Health effects

ABSTRACT

Fine particulate matter (PM_{2.5}) is known to contribute to adverse health effects, such as asthma, cardiopulmonary disease, and lung cancer. Secondary organic aerosol (SOA) is a major component of PM_{2.5} and can be enhanced by atmospheric oxidation of biogenic volatile organic compounds in the presence of anthropogenic pollutants, such as nitrogen oxides (NO_x) and sulfur dioxide. However, whether biogenic SOA contributes to adverse health effects remains unclear. The objective of this study was to assess the potential of isoprene-derived epoxides and SOA for generating reactive oxygen species (ROS) in light of the recent recognition that atmospheric oxidation of isoprene in the presence of acidic sulfate aerosol is a major contributor to the global SOA burden. The dithiothreitol (DTT) assay was used to characterize the ROS generation by the isoprene-derived epoxides, *trans*-β-isoprene epoxydiol (*trans*-β-IEPOX) and methacrylic acid epoxide (MAE), and their hydrolysis products, the 2-methyltetrol diastereomers (2-MT), 2-methylglyceric acid (2-MG), their organosulfate derivatives, as well as an isoprene-derived hydroxyhydroperoxide (ISOPOOH). In addition, ROS generation potential was evaluated for total SOA produced from photooxidation of isoprene and methacrolein (MACR) as well as from the reactive uptake of *trans*-β-IEPOX and MAE onto acidified sulfate aerosol. The high-NO_x regime, which yields 2-MG-, MAE- and MACR-derived SOA has a higher ROS generation potential than the low-NO_x regime, which yields 2-MT, IEPOX- and isoprene-derived SOA. ISOPOOH has an ROS generation potential similar to 1,4-naphthoquinone (1,4-NQ), suggesting a significant contribution of aerosol-phase organic peroxides to PM oxidative potential. MAE- and MACR-derived SOA show equal or greater ROS generation potential than reported in studies on diesel exhaust PM, highlighting the importance of a comprehensive investigation of the toxicity of isoprene-derived SOA.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Fine particulate matter (PM_{2.5}) is an ensemble of suspended particles 2.5 microns or smaller in diameter and has been shown to contribute to adverse health effects, including asthma, cardiopulmonary disease, and lung cancer (Brunekreef and Holgate, 2002;

* Corresponding author.

** Corresponding author.

E-mail addresses: surratt@unc.edu (J.D. Surratt), yhslin@umich.edu (Y.-H. Lin).

¹ Michigan Society of Fellows, University of Michigan, Ann Arbor, MI, USA.

² Department of Chemistry, University of Michigan, Ann Arbor, MI, USA.

Turner et al., 2011). Adverse health effects can be exacerbated in susceptible populations such as individuals with limited cardio-pulmonary function or the elderly. PM_{2.5} are assumed to be harmful because they are deposited deep in the lungs (Harrison and Yin, 2000) causing airway inflammation and impaired pulmonary function. Both human activity and natural emissions are sources of PM_{2.5}. Secondary organic aerosol (SOA) is a major component of PM_{2.5} produced from the atmospheric oxidation of volatile organic compounds (VOCs), which leads to low-volatility products that undergo gas-to-particle phase partitioning. While PM_{2.5} mass is currently regulated by the United States Environmental Protection Agency as a one of the six criteria air pollutants, regulations do not consider particulate composition. However, investigations into health impacts of exposure to PM_{2.5} increasingly point to the relevance of particulate constituents such as organics in toxicity (Atkinson et al., 2015), although exposure-induced health effects are not well characterized because of the complex composition and formation mechanisms of SOA.

Isoprene (2-methyl-1,3-butadiene, C₅H₈) is the most abundant biogenic VOC emitted into the atmosphere world-wide and is particularly high in concentration in the Southeastern United States during summer (Guenther et al., 2006). Hydroxyl radical (OH)-initiated oxidation of isoprene leads to SOA formation (Claeys et al., 2004; Kroll et al., 2006), and the presence of anthropogenic pollutants, such as nitrogen oxides (NO_x) and sulfur oxides (SO_x) (Edney et al., 2005; Kroll et al., 2006; Surratt et al., 2006, 2010; Chan et al., 2010), enhance isoprene-derived SOA yield and influence its physicochemical characteristics. Since anthropogenic emissions represent the controllable component of SOA, strategies for setting and meeting regulatory standards protective of human health require that influence of anthropogenic pollutants on SOA toxicity be well understood. Isoprene-derived SOA has been estimated to contribute a significant mass fraction of tropospheric PM_{2.5} (Henze and Seinfeld, 2006; Carlton et al., 2009) and for this reason it is important to characterize the toxicity of SOA generated by the interaction of isoprene oxidation products with anthropogenic emissions.

Studies strongly support the hypothesis that PM_{2.5} toxicity is derived from the generation of reactive oxygen species (ROS) in lung cells (Dellinger et al., 2001; Gurgueira et al., 2002; Li et al., 2003). ROS are oxygen-containing compounds, including superoxide anion (O₂⁻), hydrogen peroxide (H₂O₂), and hydroxyl radical (OH), shown to act as powerful oxidants *in vivo* and *in vitro*, causing cell damage referred to collectively as oxidative stress (Glasauer and Chandel, 2013). The prevailing view of the mode of action specific to PM_{2.5} is interaction with the airway epithelial cells and macrophages to generate ROS (Cho et al., 2005), triggering a cascade of events associated with inflammation and apoptosis. A commonly used method to quantify redox activity of a PM_{2.5} sample and its potential to generate ROS is the dithiothreitol (DTT) assay (Li et al., 2009). This assay measures the rate of DTT consumption, which is proportional to the concentration of the catalytically active redox-active species in the sample (Rattanavara et al., 2011). Therefore, the DTT assay measures the potential of a PM_{2.5} sample to evoke oxidative stress.

Previous work has focused on characterizing the oxidizing potential of PM from diesel exhaust, diesel exhaust with ozone (O₃), and polycyclic aromatic hydrocarbons (PAH) (Li et al., 2009; Rattanavara et al., 2011). This study characterizes the ROS generating potential of isoprene-derived epoxides, which are known precursors to isoprene-derived SOA (Surratt et al., 2010; Lin et al., 2013b), and isoprene-derived SOA generated in smog chambers under low- and high-NO_x conditions representative of urban and rural atmospheres (Surratt et al., 2010). The DTT assay was used to measure the oxidizing potential of the following: (1)

epoxide SOA precursors, *trans*-β-isoprene epoxydiol (*trans*-β-IEPOX) and methacrylic acid epoxide (MAE); the epoxide hydrolysis products, 2-methyltetrol diastereomers (2-MT) (Claeys et al., 2004; Lin et al., 2012) and 2-methylglyceric acid (2-MG) (Edney et al., 2005; Lin et al., 2013b); their organosulfate derivatives (Surratt et al., 2010; Lin et al., 2013b) and a surrogate for isoprene-derived organic peroxides reported to be a significant component of SOA (Surratt et al., 2006) (2) the complete SOA generated from the photochemical oxidation of isoprene and methacrolein (MACR) in outdoor chamber studies, and (3) the complete IEPOX- and MAE-derived SOA from indoor chamber reactive uptake studies. The results are presented as DTT activity and are also converted to a normalized index of oxidant generation (NIOG) for comparison of the oxidative potential of isoprene-derived epoxides and SOA with that of PM_{2.5} samples from various sources reported in previous studies.

2. Materials and methods

2.1. Isoprene-derived epoxides, epoxide hydrolysis products, and the isoprene-derived hydroxyhydroperoxide

Trans-β-IEPOX (Lin et al., 2012; Zhang et al., 2012), MAE (Lin et al., 2013b), 2-MT, 2-MG (Budisulistiorini et al., 2015), the organosulfate derivatives (Budisulistiorini et al., 2015), and an isoprene-derived hydroxyhydroperoxide (ISOPOOH, 2-hydroperoxy-2-methylbut-3-en-1-ol) (Krechmer et al., 2015) were synthesized in-house (Budisulistiorini et al., 2015). Compounds were characterized by ¹H and ¹³C nuclear magnetic resonance (NMR) spectroscopy. Purity of these compounds were assessed by gas chromatography/electron ionization-quadrupole mass spectrometry (GC/EI-MS) analysis with prior trimethylsilylation, and ultra-performance liquid-chromatography coupled to electrospray ionization quadrupole time-of flight mass spectrometry (UPLC/ESI-QTOFMS). Purity was confirmed to be >99% for all compounds. Stock solutions were diluted to 100 μg μL⁻¹ before analyses by the DTT method. Standard solutions of the synthetic epoxides IEPOX and MAE, which are sensitive to hydrolysis, were made up and stored in the aprotic solvent ethyl acetate. Ethyl acetate was evaporated using a gentle N₂ (g) stream prior to analysis because it is immiscible in aqueous buffer solutions used in the DTT assay. For other pure compounds, including 2-MT, 2-MG, 2-MT_OS, 2-MG_OS and ISOPOOH, they were dissolved in methanol and could be added directly into the aqueous DTT assay buffer.

2.2. Outdoor chamber experiments

Outdoor smog chamber experiments were performed in a 120-m³ triangular cross-section Teflon chamber located on the roof of the Gillings School of Global Public Health at the University of North Carolina (UNC) at Chapel Hill. The operation of chamber facilities has been described in detail previously (Ebersviller et al., 2012). Photochemical experiments were carried out in the presence of natural sunlight. The chamber was flushed with HEPA (high-efficiency particulate arresting)-filtered ambient air to replace at least five chamber volumes prior to each experiment. Chamber background particles were continuously monitored using a differential mobility analyzer (DMA; Brechtel Manufacturing, Inc., Model 2002) coupled to a mixing condensation particle counter (MCPC; Brechtel Manufacturing, Inc., Model 1710). An on-line gas chromatograph (GC; Varian CP-3800) equipped with a flame ionization detector (FID) was used to measure SOA precursors (isoprene and MACR). The gas-sampling line feeding the instrument traveled from the floor of the chamber, through the roof of the building directly to the GC/FID instrument in the laboratory below.

Download English Version:

<https://daneshyari.com/en/article/6336646>

Download Persian Version:

<https://daneshyari.com/article/6336646>

[Daneshyari.com](https://daneshyari.com)