Reactive oxygen species from secondary organic aerosol decomposition in water

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Secondary organic aerosols (SOA) account for a major fraction of fine air particulate matter and have a strong influence on climate and public health (Jimenez et al., 2009; Huang et al., 2014). Evolution of SOA is one of the largest uncertainties in the current understanding of air quality, climate and public health (Kanakidou et al., 2005). With regard to SOA health effects, substantial amounts of reactive oxygen species (ROS) including organic radicals are detected in ambient and laboratory-generated SOA (Venkatachari and Hopke, 2008; Fuller et al., 2014; Kramer et al., 2016; Anglada et al., 2015). Despite intensive research, multiphase chemical reactions of SOA in the atmosphere and upon interaction with the human respiratory tract are not well understood (Pöschl and Shiraiwa, 2015).

In this study, we used a continuous wave electron paramagnetic resonance (CW-EPR) spectrometer and spin-counting technique for measuring ROS formed by laboratory-generated SOA and field-collected fine particles (180-320 nm in diameter). We found that OH and organic radicals were formed by decomposition of laboratory-generated SOA and field-collected fine particles upon interactions with water and iron ions under dark conditions (Tong et al., 2016). The production efficiency of OH and organic radicals by SOA from different precursors can be explained by the decomposition of organic hydroperoxides, which account for the predominant fraction of terpene SOA (Docherty et al., 2005; Ehn et al., 2014). The molar OH yield from SOA formed by ozonolysis of terpenes (α-pinene, β-pinene, and limonene) is ~0.1% upon extraction with pure water and increases to ~1.5% in the presence of Fe^{2+} ions due to Fenton-like reactions. Upon extraction of SOA samples from OH photooxidation of isoprene, we also detected OH yield around ~0.1%, increasing upon addition of Fe^{2+}. The possibility of ROS formation from organic hydroperoxide in water was confirmed by experiments using *tert*-butyl hydroperoxide.

In addition to ROS formation in water, we also quantified the production efficiency of ROS (H_2O_2, OH, superoxide) by laboratory-generated SOA in phosphate buffered saline solutions, surrogate lung lining fluid, and human alveolar basal epithelial cells culturing media. We found that ROS production efficiency of SOA depends on both the SOA composition and extracting solution (pH and components etc.), which can lead different cell responses finally.

Our findings imply that the chemical reactivity and aging of SOA particles is strongly enhanced upon interaction with water and iron. In cloud droplets under dark conditions, SOA decomposition can compete with the classical H_2O_2 Fenton reaction as the source of OH radicals. Also in the human respiratory tract, the inhalation and deposition of SOA particles may lead to a substantial release of ROS, which may contribute to oxidative stress and play an important role in the adverse health effects of atmospheric aerosols (Fig. 1).
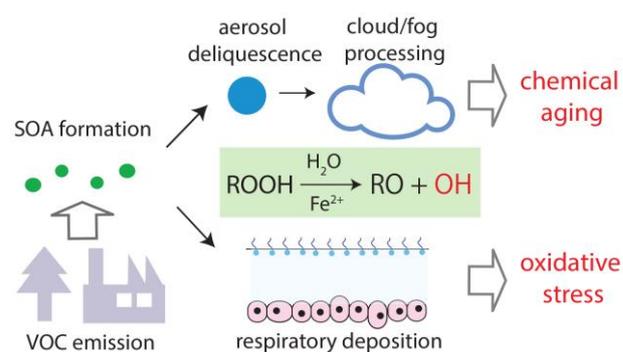

Fig. 1. Implications of OH formation by SOA. Formation of OH radicals upon decomposition of organic hydroperoxides (ROOH) in secondary organic aerosol leads to rapid chemical aging of SOA particles upon deliquescence and cloud or fog processing in the atmosphere as well as oxidative stress upon inhalation and deposition in the human respiratory tract. Fenton-like reactions of iron with ROOH from SOA can occur both in atmospheric particles and in the lung lining fluid.

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