Short communication

Technical note: Detailed characterization of a mist chamber for the collection of water-soluble organic gases

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ABSTRACT

Mist chambers (MC) have been used for decades to sample water-soluble gases in atmospheric studies. Herein, we characterize the use of a mist chamber for the collection of oxygenated organic gases, with a focus on intermediate solubility compounds to better constrain the transition from low-to-high collection efficiency. The investigated compounds span a range in Henry's law constants (K_H, 2.5×10^1 M atm^{-1} to 4.1×10^5 M atm^{-1}) and include moieties abundant in tropospheric gases (carboxylic acids, alcohols, and carbonyls). Under the configuration used here, the MC achieved greater than 90% collection efficiency for compounds with $K_H > 4.9 \times 10^2$ M atm^{-1}. This represents an improvement over prior MC characterizations, likely due to the increased number of intermediate solubility compounds investigated. We apply the MC collection efficiency to simulations of VOC photooxidation. The results indicate that the MC is likely to collect the majority of gas-phase oxidation products for ten different VOCs, with the highest collection efficiency (94%) predicted for the oxidation products of α-pinene under low-NO$_x$ conditions.

1. Introduction

Volatile organic compounds (VOCs) are ubiquitous components in Earth's atmosphere due to their emissions from a wide range of anthropogenic and natural sources. VOCs react with atmospheric oxidants – notably hydroxyl radicals (OH), ozone (O$_3$), and nitrate radicals (NO$_3$) – and can form hundreds of different products from a single precursor (Atkinson and Arey, 2003). The oxidation products (oxygenated VOCs, OVOCs) can partition to the particle phase forming secondary organic aerosols (SOA) if they have sufficiently low volatility (vapor pressure) or sufficiently high solubility in water (Hallquist et al., 2009; Carlton and Turpin, 2013). OVOCs exert numerous effects on human health through their contributions to SOA and O$_3$ formation (Edwards et al., 2014; Lin et al., 2017). Some OVOCs are classified as air toxics: they contribute directly to effects on human health, including an increased risk for cancer (Logue et al., 2011). Oxygenated organic compounds in the condensed phase affect aerosol hygroscopicity and thus cloud condensation nuclei abundance (Ovadnevaite et al., 2017; Trivitayanurak and Adams, 2014). OVOCs also have important implications for climate through their surfactant properties and subsequent impacts on cloud droplet formation (Sareen et al., 2013).

Given the above effects, it is important to measure the atmospheric abundance, as well as the geospatial and temporal variations of oxygenated organic gases. This is challenging, however, since there are thousands of oxygenated organics in the atmosphere, with both primary and secondary sources (Karl et al., 2018; Koss et al., 2018). These compounds span a wide range of chemical and physical properties, including volatility, water solubility, and chemical reactivity (Hodzic et al., 2014). Such diversity in chemical and physical properties severely challenges current analytical methods to comprehensively measure atmospheric organics (Hunter et al., 2017). For example, unidentified gas-phase compounds likely contribute substantially to SOA formation from many sources (Jathar et al., 2014). Such diversity in chemical and physical properties results in highly variable fate, transport, and atmospheric lifetimes of these compounds (Nguyen et al., 2015; Hodzic et al., 2016). Their associated impacts on human health and climate are thus variable.

Due to the vast quantity of atmospheric organic compounds, measurement strategies often focus on characterizing properties of the bulk organics, rather than attempting to comprehensively identify all compounds on a molecular level. Such measurements include the elemental composition (most frequently C, O, and H) of organic aerosols (OA) (Heald et al., 2010), grouping OA into different factors based on mass spectra (Ng et al., 2010), carbon isotopic analysis to identify the source

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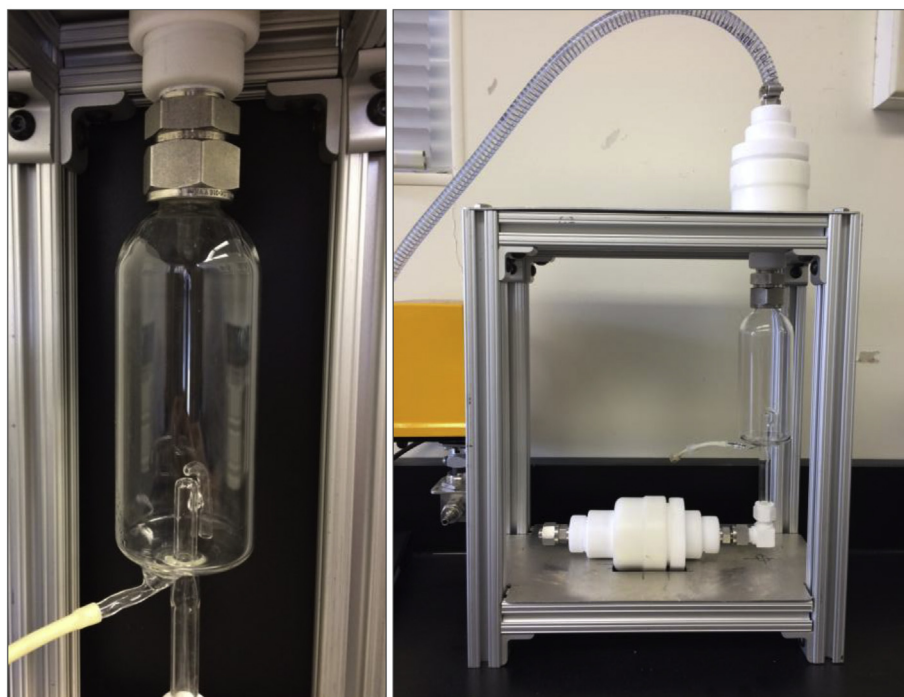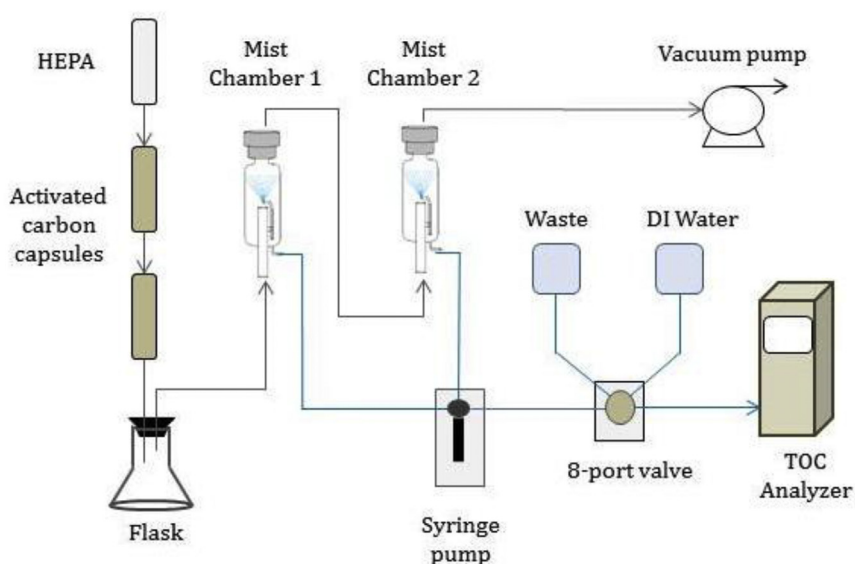E-mail address: hennigan@umbc.edu (C.J. Hennigan).

Fig. 1. Schematic of the experimental setup used to characterize organic compound collection efficiencies in the mist chamber (top); close-up picture of the mist chamber (bottom left); and picture of a single mist chamber in its sampling configuration (bottom right).

of OA as fossil or non-fossil (Weber et al., 2007), binning primary organic emissions by volatility (Zhao et al., 2015), and functional group contributions to OA (Takahama et al., 2011). Another common approach is the measurement of the water-soluble fraction of organic carbon in the gas- and particle phases (WSOC$_g$ and WSOC$_p$, respectively) (Sullivan et al., 2004; Hennigan et al., 2008). The oxidation of organics in the atmosphere typically produces products that are less volatile and more oxygenated than the parent compound (Jimenez et al., 2009). The oxidation process also produces compounds with increasing water solubility (Hodzic et al., 2014). The coupled measurements of WSOC$_p$ and WSOC$_g$ offer important insight into the evolution of organics in the atmosphere, including SOA formed through aqueous pathways (Hennigan et al., 2009; El-Sayed et al., 2018).

Due to the immense chemical complexity of ambient OA, the bulk measurement of WSOC$_p$ has seen widespread, global applications

(Sullivan et al., 2006; Kondo et al., 2007; Duong et al., 2011; Saffari et al., 2014; Timonen et al., 2013; Rastogi et al., 2015; Decesari et al., 2017; Kim et al., 2016; El-Sayed et al., 2018). The WSOC$_p$ method has been the subject of extensive studies into the principles and theory (Psichoudaki and Pandis, 2013) and detailed chemical analyses (Xu et al., 2017; Sullivan and Weber, 2006a; b; Decesari et al., 2001) that underlie the measurement. Recently, there has also been an increase in studies applying the measurement of WSOC$_g$ (Anderson et al., 2008; Hennigan et al., 2009; Zhang et al., 2012; El-Sayed et al., 2015; Sareen et al., 2016). The WSOC$_g$ method has been far less rigorously characterized, even though detailed molecular simulations of VOC oxidation indicate a myriad of water-soluble organic gases that are not measured on a molecular level with current analytical instruments (Hodzic et al., 2014). This provides the motivation for the present work in which we characterize a wet scrubbing mist chamber, which is a critical