The effects of isoprene and NO_x on secondary organic aerosols formed through reversible and irreversible uptake to aerosol water

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Abstract. Isoprene oxidation produces water-soluble organic gases capable of partitioning to aerosol liquid water. The formation of secondary organic aerosols through such aqueous pathways (aqSOA) can take place either reversibly or irreversibly; however, the split between these fractions in the atmosphere is highly uncertain. The aim of this study was to characterize the reversibility of aqSOA formed from isoprene at a location in the eastern United States under substantial influence from both anthropogenic and biogenic emissions. The reversible and irreversible uptake of water-soluble organic gases to aerosol water was characterized in Baltimore, MD using measurements of particulate water-soluble organic carbon ($WSOC_p$) in alternating dry and ambient configurations. $WSOC_p$ evaporation with drying was observed systematically throughout the late spring and summer, indicating reversible aqSOA formation during these times. We show through time lag analyses that $WSOC_p$ concentrations, including the $WSOC_p$ that evaporates with drying, peak 6 h to 11 h after isoprene concentrations, with maxima at a time lag of 9 h. The absolute reversible aqSOA concentrations, as well as the relative amount of reversible aqSOA, increased with decreasing NO_x/isoprene ratios, suggesting that isoprene epoxydiol (IEPOX) or other low-NO_x oxidation products may be responsible for these effects. The observed relationships with NO_x and isoprene suggest that this process occurs widely in the atmosphere, and is likely more important in other locations characterized by higher isoprene and/or lower NO_x levels. This work underscores the importance of accounting for both reversible and irreversible uptake of isoprene oxidation products to aqueous particles.

1 Introduction

Isoprene (2-methyl-1,3-butadiene, C_5H_8) is the most abundant non-methane organic compound emitted globally (Guenther et al., 2012). Isoprene oxidation stimulates tropospheric ozone production and contributes substantially to secondary organic aerosol (SOA) formation, thus impacting air quality and climate (Henze and Seinfeld, 2006; Pfister et al., 2008). In the southeastern United States, isoprene is likely the dominant SOA precursor during summer (Ying et al., 2015; Kim et al., 2015). The oxidation products of isoprene include compounds that partition to aerosol liquid water (ALW), such as isoprene epoxydiol (IEPOX), glyoxal, and methylglyoxal. These species do not partition to dry particles (Kroll et al., 2005; Nguyen et al., 2014), so their condensed phase products are called aqueous SOA (aqSOA) (Ervens et al., 2011). IEPOX uptake also depends on the inorganic composition and acidity of the seed particles (Surratt et al., 2010; Gaston et al., 2014; Budisulistiorini et al., 2017; Lin et al., 2012; Riedel et al., 2015). A body of work indicates that the uptake of water-soluble organic gases into atmospheric waters (clouds, fogs, and aerosol water) is an important pathway for SOA formation (Ervens et al., 2011). Isoprene oxidation products can also form SOA in the absence of aerosol water (Surratt et al., 2006; Nguyen et al., 2014), though the majority of regional-scale isoprene SOA is currently thought to form through aqueous pathways (Marais et al., 2016). Isoprene emissions show strong seasonal variations in most locations (Guenther et al., 2012), suggesting that aqSOA formation is similarly seasonal in nature. Indeed, SOA formed from IEPOX shows a pronounced seasonal signature in the southeastern U.S. that is consistent with isoprene emissions (Budisulistiorini et al., 2016; Xu et al., 2015).

Although substantial evidence from laboratory, modeling, and ambient studies indicates the importance of aqSOA formation, many uncertainties remain in understanding this pathway on a mechanistic level (McNeill, 2015). A significant uncertainty is the fate of aqSOA under conditions of water evaporation, such as in a cloud cycle or with diurnal changes in ambient relative humidity (RH). The formation of aqSOA is initiated by the equilibrium (and thus, reversible) partitioning of water-soluble organic gases to liquid water (McNeill, 2015). In the aqueous phase, the dissolved organics can undergo reversible reactions such as hydration and oligomerization (De Haan et al., 2009) or irreversible reactions such as acid catalysis, reaction with inorganics, or radical reactions (e.g. (Ervens et al., 2014; Ortiz-Montalvo et al., 2014; Lee et al., 2013)). The former process implies that at least some of the dissolved organics will repartition back to the gas phase when water evaporates, while the latter process can form low-volatility products that remain in the particle phase even after the evaporation of water. Most clouds are non-precipitating (Pruppacher, 1986) and ALW changes throughout the day with changing RH (Nguyen et al., 2014; Khlystov et al., 2005). Thus, determining whether the uptake is reversible or irreversible is critical in understanding the fate of many oxidized organics in the atmosphere. While ambient studies provide evidence for both reversible and irreversible aqSOA formation (El-Sayed et al., 2016; El-Sayed et al., 2015), the reasons underlying these differences are still unclear.

It is important to note that we define aqSOA as all organics present in the condensed phase through partitioning to liquid water, regardless of whether the uptake is reversible or irreversible. Although some definitions of aqSOA only include the organic material that is taken up into liquid water and remains in the particle phase after water evaporation (e.g. (Ervens et al., 2011)), we favor a more comprehensive definition since the organics contribute to aerosol effects on health and optical properties when they are in the condensed phase. Our definition is consistent with the treatment of other semi-volatile aerosol species such as ammonium nitrate. It is, however, important to distinguish reversible and irreversible aqSOA since the atmospheric lifetime of these compounds may differ significantly depending on their phase (Nguyen et al., 2015). Therefore, we define the low-volatility products that remain in the particle phase after the evaporation of liquid water as “irreversible aqSOA”, and the organic compounds taken up in liquid water that repartition back to the gas phase with water evaporation as “reversible aqSOA”.

Nitrogen oxides ($NO_x \equiv NO + NO_2$) may be one factor affecting the reversibility of isoprene aqSOA. NO_x plays a critical role in the oxidation of volatile organic compounds (VOCs). This includes a major effect on the chemical pathway of isoprene oxidation, and on the resulting SOA yield (Kroll and Seinfeld, 2008; Ervens et al., 2008). NO_x affects the volatility, oxidation state, and aging of isoprene-derived SOA (Xu et al., 2014). Recent modeling studies predict that isoprene oxidation in the eastern U.S. is split almost equally between high- and low-NO_x pathways (Travis et al., 2016). Laboratory studies show significant evaporation of aqueous isoprene SOA particles when dried, indicating reversible aqSOA (Wong et al., 2015). This is consistent with the understanding of aqSOA formed from individual isoprene oxidation products, thought to be predominantly IEPOX and glyoxal (Sareen et al., 2017). During the summer, model predictions suggest that glyoxal production from isoprene occurs almost equally through low- and high-NO_x pathways in the eastern U.S. (Chan Miller et al., 2017). Glyoxal is taken up to ALW reversibly and irreversibly (Ortiz-Montalvo et al., 2012; Galloway et al., 2009). IEPOX is formed predominantly through the low-NO_x pathway (Paulot et al., 2009; Surratt et al., 2010), and its uptake to ALW could be reversible or irreversible (Nguyen et al., 2014; Riedel et al., 2015). Therefore, potential differences in reversible aqSOA associated with NO_x may be due to differences in IEPOX production under these chemical regimes. The aim of this study was to characterize the effects of isoprene and NO_x on aqSOA formed reversibly and irreversibly at a site in the eastern U.S. heavily impacted by biogenic and anthropogenic emissions.

2 Methods

2.1 WSOC measurements

Ambient measurements were carried out across all four seasons in Baltimore, MD (Table 1). The experimental setup has been described in detail elsewhere (El-Sayed et al., 2016; El-Sayed et al., 2015). Briefly, water-soluble organic carbon was measured in the gas phase ($WSOC_g$) using a mist chamber (MC), and in the particle phase ($WSOC_p$) using a Particle-into-liquid sampler (PILS, Brechtel Manufacturing), both coupled to a total organic carbon (TOC) analyzer (Model 900 Turbo, GE Analytical) operated in Turbo mode. The $WSOC_p$ measurement was alternated between an ambient channel ($WSOC_p$) and a ‘dried’ channel ($WSOC_{p,dry}$) using an automated 3-way valve (Brechtel Manufacturing). The $WSOC_p$ sample was at ambient RH while the $WSOC_{p,dry}$ sample passed through a silica gel diffusion dryer (Table S1). Both the $WSOC_p$ and the $WSOC_{p,dry}$ samples pass through a parallel-plate carbon denuder (Sunset Laboratories) prior to sampling in the PILS. This reduces gas-phase interferences, which are minor in the PILS (Sullivan et al., 2004), and prevents the re-condensation of volatilized organic gases that evaporate in the dryer. Although some gas-phase organics may be lost to the silica gel (Faust et al., 2017), potentially perturbing the gas-particle equilibrium for the dry channel, sampling both channels through the carbon denuder should minimize such differences. Further, based upon the timescales of ambient organic aerosol (OA) equilibration (minutes-to-hours) (Saha et al., 2017), it is highly unlikely that stripping gas-phase compounds would produce any appreciable OA evaporation with only the 7 s residence time encountered in our system. The diffusion dryer does not implement heating, so differences in the $WSOC_p$ concentrations between the two channels are due to $WSOC_p$ evaporation that results from ALW evaporation. Note that the $WSOC_{p,dry}$ channel has not been designed to dry particles completely to efflorescence (El-Sayed et al., 2016). $WSOC_p$ losses through the 3-way valve and through the dried channel are less than 1 % (mass concentration basis) (El-Sayed et al., 2016): no corrections to the data were applied. A ratio of OM/OC=2.1 was used to convert aerosol organic carbon (OC) into organic mass (OM), based upon characterizations of $WSOC_p$ in the eastern U.S. (Xu et al., 2017a).

$WSOC_p$ is operationally defined based upon the solubilites of the organics, themselves, and the level of dilution employed for the analysis (Psichoudaki and Pandis, 2013). In the eastern U.S., the $WSOC_p$ measurement is often used as a surrogate for SOA, especially during summer (Weber et al., 2007). The measurement includes SOA formed through absorptive partitioning and through aqueous-mediated pathways (aqSOA). We consider any $WSOC_p$ that evaporates with drying to be reversible aqSOA, since this material exists in the condensed phase because of the aerosol water and partitions back to the gas phase when the water evaporates.

The $WSOC_{p,dry}$ measurement system employs a total drying time of ≈7 s. The residence time for equilibrium to take place in evaporating water/organic droplets is dependent on the specific organics as well as the aerosol inorganic chemical composition. Longer drying times may increase the amount of evaporated aqSOA in our system, indicating that our measurements provide a conservative (low) bound estimate on the concentration of reversible aqSOA and on the $WSOC_{p,dry}/WSOC_p$ ratio (El-Sayed et al., 2016).

The fully-automated online system was housed in a temperature-controlled environmental enclosure (EKTO, Inc.) placed on the rooftop of the Engineering Building at the University of Maryland, Baltimore County (UMBC). The three samples: $WSOC_g$, $WSOC_p$ and $WSOC_{p,dry}$ were repeatedly measured in a 14-min cycle with sampling times of 4 min, 5 min and 5 min, respectively. Dynamic blanks were measured regularly throughout each ambient sampling period. Factory calibrations of the TOC Analyzer were regularly checked with sucrose solutions prepared to bracket the range of concentrations observed during ambient sampling.

2.2 VOC and NO_x measurements

Isoprene measurements from the Essex Photochemical Assessment Monitoring Stations (PAMS) (AQS ID# 240053001) were provided by Maryland Department of the Environment (MDE). The Essex site represents the PAMS station closest to UMBC (≈20 km distance). Isoprene was measured by MDE every six days from September to May, and hourly during the summer (June, July and August). The hourly isoprene measurements were automated following EPA method 142, using cryogenic preconcentration for sample collection followed by analysis via gas chromatography with flame ionization detection (GC-FID, Perkin Elmer Clarus 500). Hourly measurements of NO_x were also carried out by MDE at the Essex site following method 74 (chemiluminescence). Data were acquired from the U.S. Environmental Protection Agency (https://aqs.epa.gov/api).

A key assumption employed in this analysis is that the WSOC measurements made at UMBC are representative of conditions at Essex, the location of the NO_x and isoprene measurements. Aerosol concentrations in the Baltimore-Washington region are spatially uniform over tens of kilometers (Beyersdorf et al., 2016). Further, $WSOC_p$ concentrations in the eastern U.S. exhibit small spatial variations across urban-to-rural gradients during the summertime (Weber et al., 2007). These prior analyses showed that aerosol concentrations, and in particular WSOC, were not dependent on wind direction. Isoprene emissions in the eastern U.S. are regional in nature, due to the expansive coverage of broadleaf forests (Pye et al., 2013; Guenther et al., 2012). NO_x emissions are spatially segregated from those of isoprene, and are far more localized. However, the isoprene-NO_x chemical regime (high-or low-NO_x) in the eastern U.S. is generally well-represented with model resolution of 28 x 28 km, suggesting that the chemistry occurring on small scales, such as in individual power plant plumes, does not significantly affect the regional isoprene-NO_x regime (Yu et al., 2016). NO_x concentrations at Essex (20 km ENE of UMBC) and HU-Beltsville (35 km SSW of UMBC) are strongly correlated (R = 0.89, Fig. S1), likely due to the overwhelming contribution of mobile source emissions along the heavily-traveled I-95 corridor to the region (Anderson et al., 2014). Together, this supports our analysis into the effects of isoprene and NO_x on reversible aqSOA using the measurements described above.

3 Results

An overview of the seasonal sampling periods is given in Table 1. Measurements were taken from 3 to 4 weeks on average during each of the four seasons. Note that the spring season has been divided into early (23 April to 8 May) and late (9 May to 14 May) periods due to the differences in the $WSOC_p$ results observed during these times. The $WSOC_p$ measurements have been reported to be a good surrogate of the total SOA in the atmosphere (Weber et al., 2007; Kondo et al., 2007), which includes aqSOA as well as SOA formed through traditional gas-phase partitioning (Donahue et al., 2009). The formation of aqSOA has been observed throughout the year, except for the early spring season. This observation was based on the relationship between the fraction of total WSOC in the particle phase, F_p ($F_p = WSOC_p/(WSOC_p + WSOC_g)$) as a function of RH in combination with seasonal ALW analyses (Hennigan et al., 2008). The individual results for the fall and summer have been previously reported (El-Sayed et al., 2016; 2015). A synthesis of aqSOA formation across all seasons is the subject of ongoing analysis.

3.1 Reversibility of aqSOA formation by season

Previous studies conducted by our group have provided evidence for both irreversible (El-Sayed et al., 2015) and reversible (El-Sayed et al., 2016) aqSOA formation during the fall and summer seasons, respectively. Figure 1 shows the $WSOC_{p,dry}/WSOC_p$ ratio across all of the seasons. A ratio of unity indicates that drying did not impact $WSOC_p$ while a ratio less than unity indicates that particle drying caused the evaporation of some $WSOC_p$, and thus was considered reversible aqSOA (El-Sayed et al., 2016). Figure 1 shows that the $WSOC_{p,dry}/WSOC_p$ ratio was unity during the fall and winter, indicating that the $WSOC_p$ remained in the condensed phase upon drying. Therefore, the aqSOA formation that was observed occurred irreversibly (El-Sayed et al., 2015). In the early spring, the $WSOC_{p,dry}/WSOC_p$ ratio was also unity, but this was expected since no F_p-RH enhancement was observed and no significant aqSOA was observed during this period. Beginning in the late spring and continuing into the summer, the $WSOC_{p,dry}/WSOC_p$ ratio was systematically lower than unity. During both seasons, we observed systematic evaporation of some $WSOC_p$ as a result of the ALW evaporation. In the late spring, the $WSOC_{p,dry}/WSOC_p$ ratio was 0.92, on average, and decreased further during the summer where it reached an average of 0.87 (El-Sayed et al., 2016). This observation indicates that at least some of the aqSOA formation occurring in the late spring and summer seasons was reversible. $WSOC_p$ evaporation was higher during the night than during the day (Fig. S2), likely due to higher RH levels and higher ALW at night (Guo et al., 2015).

We attribute the observed $WSOC_p$ evaporation during the late spring and summer seasons to aqSOA that partitions reversibly to ALW. The physical properties that affect SOA formed through absorptive partitioning (what

Ervens et al. (2011) call gasSOA) and SOA formed through an aqueous mediated pathway (aqSOA) are fundamentally different (vapor pressure and gas solubility in water, respectively). Note that ALW can affect SOA formed through traditional absorptive partitioning by increasing the total concentration and decreasing the average molecular weight of the absorbing OM phase (Seinfeld and Pankow, 2003). Models predict that this phenomenon enhances SOA concentrations in the eastern U.S. (Pankow et al., 2015; Jathar et al., 2016) and that drying the particles will result in the evaporation of some semi-volatile SOA compounds in response to this perturbation (Pankow, 2010). However, the effect of ALW on gas-particle partitioning is more pronounced at low organic concentrations (1 to 2 $\mu g\ m^{-3}$), and its sensitivity becomes less profound at higher OA levels (Pankow, 2010). Previous results from our group showed the opposite effect: evaporated $WSOC_p$ concentrations increased significantly with an increase in OA concentrations (El-Sayed et al., 2016). Further, the semi-volatile organic compounds most influenced by this water effect are predicted to be the less oxidized, fresh SOA (Pankow, 2010). $WSOC_p$ is more strongly correlated with the LV-OOA (low-volatility oxygenated organic aerosol) factor identified by the Aerodyne aerosol mass spectrometer (AMS) compared to the SV-OOA (semi-volatile OOA) factor (Sun et al., 2011; Xu et al., 2017b; Kondo et al., 2007). This suggests that the evaporation of $WSOC_p$ was not due to the overall effects on OA partitioning (Jathar et al., 2016), but was due to the reversible partitioning of water-soluble organic gases to aerosol water. In the following sections, we characterize the reasons underlying the seasonal differences in $WSOC_{p,dry}/WSOC_p$ shown in Fig. 1.

3.2 Climatology of isoprene

Isoprene oxidation products are thought to be the most important precursors to aqSOA formation (Marais et al., 2016). Figure 2 shows the average annual climatology of isoprene in Baltimore, MD. These measurements were made at the MDE Essex site, a location ≈20 km from UMBC where the WSOC measurements were conducted. In the eastern U.S., isoprene emissions are regional (Palmer et al., 2003); therefore, data from the Essex site will show consistent trends with those at UMBC. Isoprene concentrations in Baltimore tend to be very low in the winter and early spring seasons, with average monthly values of ≈0.2 ppbC ($nmol\ mol^{-1}$), but they start to rise sharply at the beginning of May, and remain elevated (though variable) during the summer season. This is highly consistent with previously measured seasonal isoprene emissions in other parts of the eastern U.S. (Goldstein et al., 1998). Isoprene concentrations decrease dramatically in September (average decrease of 70 % from 1 Sept to 30 Sept), and then remain low through the winter.

3.3 Effect of isoprene on reversible aqSOA

During the late spring, the onset of reversible aqSOA formation corresponds to the dramatic increase in isoprene concentrations (Fig. 2). Observations of the AMS IEPOX factor (Budisulistiorini et al., 2016) and chemical markers for isoprene SOA (Kleindienst et al., 2007) show similarly sharp transitions in the spring and fall in the southeastern U.S. The highest reversible aqSOA levels were observed during the summer when isoprene emissions were at their maximum. Other VOCs, such as monoterpenes, also contribute to SOA in the eastern U.S. (Xu et al., 2015), but monoterpene and isoprene SOA tracers show distinctly different temporal patterns in the eastern U.S. Isoprene SOA peaks during the summer, but monoterpene SOA tracers exhibit similar (or lower) concentrations in the summer compared to other seasons (Kleindienst et al., 2007; Ding et al., 2008). Further, monoterpene SOA is typically associated with semi-volatile and less-oxidized OA factors in the AMS analysis (Xu et al., 2015; Jimenez et al., 2009) but $WSOC_p$ is poorly correlated with these factors (Timonen et al., 2013; Xu et al., 2016). On the basis of these prior studies and the results in Figures 1 and 2, we attribute the reversible aqSOA in Baltimore to isoprene.

Due to the magnitude of regional isoprene emissions and its predicted contribution to SOA, we would expect relationships between isoprene and both $WSOC_g$ and $WSOC_p$ concentrations. However, simple correlations between isoprene and WSOC are not expected, due to dramatic differences in their atmospheric lifetimes. Under typical summertime conditions, the oxidation of isoprene to form $WSOC_g$ will take a few hours (Hodzic et al., 2014). These oxidation products can undergo further reactions to form lower volatility compounds that partition to the aerosol phase contributing to $WSOC_p$, a process that is expected to take several hours (Ng et al., 2006; Atkinson and Arey, 2003).

The relationship between isoprene and WSOC (both $WSOC_p$ and $WSOC_g$) was characterized for the summer, when hourly isoprene data were available. To account for the differences in the expected timeframe for transformation of isoprene into $WSOC_g$ and $WSOC_p$, we analyzed the WSOC concentrations as a function of isoprene with a variable time lag. We investigated the relationship between the isoprene concentrations at time t and the WSOC concentrations at t + n, where n is the time lag, which was systematically varied from (0 to 13) h. For example, a 1 h time lag indicates that the isoprene concentrations at t are compared to the WSOC concentrations measured t + 1 h after those of isoprene. An offset of zero indicates that the timing of the WSOC measurements is aligned with the timing of the isoprene measurements. During each hour, there were 4 to 5 $WSOC_p$ and $WSOC_g$ measurements corresponding to one isoprene sample; therefore, hourly averages of WSOC were calculated to provide a consistent basis for analysis.

First, the isoprene-$WSOC_g$ relationship was analyzed for time lags in the range of (0 to 6) h (Fig. 3). The $WSOC_g$ data were binned based on the corresponding isoprene concentrations; each marker represents the median of the $WSOC_g$ concentration within each isoprene concentration bin. At (0 to 2) h time lags, no relationship was observed between isoprene and $WSOC_g$. This was anticipated because isoprene has a typical atmospheric lifetime of (1 to 2) hours against oxidation by OH (Atkinson and Arey, 2003). However, with a time lag of 3 h, an increase in isoprene concentrations was coincident with an increase in $WSOC_g$ concentrations. This effect was observed for time lags up to 5 h, as illustrated by the solid blue lines in Fig. 3. Across the entire summer, a 5 ppbC (nmol mol^{-1}) increase in isoprene concentrations was associated with a median increase of 2.0 μg-C m^{-3} in $WSOC_g$. When the time lag between isoprene and $WSOC_g$ was more than 5 h, there was no longer a relationship between isoprene and $WSOC_g$ concentrations. This observation highlights the effect of isoprene on the formation of water-soluble organic gases. Isoprene and $WSOC_g$ showed similar diurnal profiles during the summer, especially when the time lag was considered (Fig. S3). Overall, this suggests that fresh isoprene emissions take about (3 to 5) h to form $WSOC_g$ in an urban environment during typical summertime conditions. Note that the measurement of $WSOC_g$ only includes compounds with effective Henry's law constants above $\approx 10^3$ M atm^{-1} ($\approx 10^1$ mol m^{-3} Pa^{-1}) (Spaulding et al., 2002), so the MC does not efficiently sample many first-generation isoprene oxidation products, such as methacrolein ($K_H = 4 \times 10^0$ M atm^{-1}, or 4×10^{-2} mol m^{-3} Pa^{-1}) or methyl vinyl ketone ($K_H = 4 \times 10^1$ M atm^{-1}, or 4×10^{-1} mol m^{-3} Pa^{-1}) (Sander, 2015).

The relationship between isoprene and evaporated $WSOC_p$ (i.e., reversible aqSOA) was characterized using the same time-lag analysis, extended from n = (0 to 13) h. At time lags less than 5 h, there was no relationship between isoprene and evaporated $WSOC_p$ concentrations (red dotted lines in Fig. 4). However, the amount of evaporated $WSOC_p$ increased with increasing isoprene concentrations when the evaporated $WSOC_p$ time lag was in the range of (6 to 11) h (green solid lines in Fig. 4). The highest response of evaporated $WSOC_p$ to isoprene was found for a time lag of 9 h. At this time lag, an increase of 5 ppbC (nmol C mol^{-1}) in isoprene concentrations led to a median increase of 0.7 $\mu g\ m^{-3}$ in evaporated $WSOC_p$. Beyond the 11 h time lag, no relationship was observed between isoprene and evaporated $WSOC_p$ levels (blue dotted lines in Fig. 4). The average evaporated $WSOC_p$ concentrations showed a similar increase with increasing isoprene, but were even higher than the median levels (Fig. S4). For example, at a 9 h time lag, a 5 ppbC (nmol C mol^{-1}) increase in isoprene corresponded to an average increase in evaporated $WSOC_p$ of 1.6 $\mu g\ m^{-3}$. The (6 to 11) h time lag between isoprene and the evaporated $WSOC_p$ is consistent with the predicted kinetics of IEPOX SOA formation in the eastern U.S. (Budisulistiorini et al., 2017). This observed (6 to 11) h time lag between isoprene and the evaporated $WSOC_p$ is likely due to multi-generational oxidation (Carlton et al., 2009; Hodzic et al., 2014; Paulot et al., 2009). Alternately, it could be that the isoprene oxidation products that partition reversibly to liquid water were formed relatively quickly (< 6 h), but responded to the diurnal cycle in ALW, which peaks in the eastern U.S. in the early morning hours (Guo et al., 2015). The observed delay time could also be the combination of these factors. Consistent with Fig. 3 and Fig. 4, there was also a strong relationship between the $WSOC_g$ concentration and the time-offset evaporated $WSOC_p$ concentration (Fig. S5). The above observations suggest that isoprene is strongly linked with the formation of reversible aqSOA in the eastern U.S. Based on this relationship, we next consider the effect of NO_x on reversible aqSOA formation since NO_x is critical to isoprene oxidation chemistry (Kroll et al., 2006).

Note that we assume that the $WSOC_p$ measurement is a surrogate for SOA (Weber et al., 2007). However, $WSOC_p$ is weakly correlated with lightly-oxygenated components in OA, such as the SV-OOA factor often resolved by the AMS (Timonen et al., 2013). Thus, our analysis would likely be a poor method for some SOA systems, for example α-pinene ozonolysis (Jimenez et al., 2009). As discussed above, the $WSOC_g$ measurement does not efficiently sample compounds with low Henry's law constants, including some first generation isoprene oxidation products (Hodzic et al., 2014). These measurement limitations contribute to the (6 to 11) h and (3 to 5) h time lags for the isoprene associations with evaporated $WSOC_p$ and $WSOC_g$, respectively. For many compounds, multi-generation oxidation contributes significantly to SOA formation (Ng et al., 2006), and this is almost certainly the case for atmospheric SOA (Jimenez et al., 2009). However, shorter lag times may be observed with other instruments sensitive to early-generation oxidation products.

3.4 Effect of NO_x on reversible aqSOA

Figure 5 shows the relationship between evaporated $WSOC_p$ and the NO_x/isoprene ratio during the summer. For this analysis, hourly NO_x/isoprene ratios and the hourly evaporated $WSOC_p$ concentrations with a 9 h time lag were used, since this timing corresponded to the maximum evaporated $WSOC_p$. Blue markers represent the mean of the evaporated $WSOC_p$ concentrations within each NO_x/isoprene bin. Figure 5 shows that the amount of evaporated $WSOC_p$ decreased substantially with an increase in the NO_x/isoprene ratio. At low NO_x/isoprene ratios (less than

0.5 ppb/ppbC, or 0.5 mol mol^{-1} C), the amount of evaporated WSOC$_p$ was at its maximum (average of 1.4 µg m^{-3}), however at NO$_x$/isoprene ratios more than 15 ppb/ppbC (mol mol^{-1} C), the evaporated WSOC$_p$ was as low as 0.2 µg m^{-3}. Generally, the evaporated WSOC$_p$ decreased with the increase in NO$_x$/isoprene ratios, but flattened out beyond NO$_x$/isoprene ratios of ≈5 ppb/ppbC (mol mol^{-1} C).

Similarly, the effect of NO$_x$/isoprene ratios on WSOC$_p$ concentrations during the summer is shown in Fig. 6. As in Fig. 5, the hourly NO$_x$/isoprene ratios were compared against the hourly WSOC$_p$ concentrations at a time lag of 9 h. At NO$_x$/isoprene ratios of less than 0.5 ppb/ppbC (mol mol^{-1} C), the average WSOC$_p$ concentration was ≈5 µg m^{-3}, but it decreased substantially to ≈1.5 µg m^{-3} (almost summertime WSOC$_p$ background levels) at NO$_x$/isoprene ratios above 15 ppb/ppbC (mol mol^{-1} C).

If isoprene is indeed associated with the evaporated WSOC$_p$ that we observed during the late spring and summer, then a logical question is why we did not observe this phenomenon during measurements throughout September (Fig. 1, El-Sayed et al., 2015). Although isoprene emissions decrease dramatically during September, there are still periods with elevated concentrations. Here, we analyze the effects of NO$_x$ and isoprene on the reversibility of isoprene aqSOA by considering the average daily NO$_x$/isoprene ratios during the late spring, summer, and fall. For this analysis, daily averages were used due to the lack of hourly isoprene measurements during the late spring and fall. The relationship between the WSOC$_{p,dry}$/WSOC$_p$ and NO$_x$/isoprene ratios across all three seasons is shown in Fig. 7. Figures 5 and 6 show that the relationships of the NO$_x$/isoprene ratio with WSOC$_p$ and evaporated WSOC$_p$ are qualitatively similar. However, it is clear from Fig. 7 that WSOC$_p$ and the evaporated WSOC$_p$ are affected differently by NO$_x$/isoprene. The days in which average NO$_x$/isoprene ratios were higher than 5 ppb/ppbC (mol mol^{-1} C) were characterized by WSOC$_{p,dry}$/WSOC$_p$ ratios very close to unity, indicating irreversible aqSOA. On the other hand, the days in which NO$_x$/isoprene ratios were lower than 5 ppb/ppbC (mol mol^{-1} C) were all characterized by WSOC$_{p,dry}$/WSOC$_p$ ratios lower than unity, indicating some reversible aqSOA on these days. Further, the WSOC$_{p,dry}$/WSOC$_p$ ratio decreased with decreasing NO$_x$/isoprene ratios under this condition. IEPOX is produced under low-NO$_x$ conditions with very limited formation in NO$_x$ rich environments (Zhang et al., 2017) whereas glyoxal can be produced from both low-and high-NO$_x$ pathways with higher yields at high-NO$_x$ conditions (Chan Miller et al., 2017). Based on our observations, this suggests that IEPOX was more abundant during the late spring and summer and was responsible for the reversible aqSOA formed under the lower NO$_x$/isoprene conditions. These results provide an explanation for the variability in the seasonal occurrence of reversible aqSOA in the eastern U.S.

There is uncertainty in the absolute NO$_x$/isoprene ratio that represents the transition to reversible aqSOA. Although NO$_x$ concentrations at Essex are strongly correlated with those at a site 50 km away (HU-Beltsville), the absolute NO$_x$ concentrations are approximately two times higher at Essex (Fig. S1), due to its closer proximity to downtown Baltimore. Therefore, although Figure 7 suggests that reversible aqSOA formation occurs at NO$_x$/isoprene ratios below 5 ppb/ppbC (mol mol^{-1} C), transitions at lower ratios may be observed in other areas.

4 Atmospheric Implications

These results represent the first observations to characterize the seasonal occurrence of reversible aqSOA formation. The results suggest an important effect on aerosol measurements that implement drying, which may not measure (or may incompletely measure) reversible aqSOA. Our results suggest that this is especially relevant in areas with high isoprene emissions. For example, Zhang et al. (2012) observed substantial loss of $WSOC_p$ (≈30 % on average) from Federal Reference Method (FRM) filters in the southeastern U.S. It is likely that reversible aqSOA contributed to this measurement artifact, although direct comparisons to our $WSOC_{p,dry}$ measurement would be needed to test this hypothesis. These compounds are important, since they contribute to aerosol effects – visibility, aerosol optical depth (AOD), health, climate – when they are in the condensed phase.

We hypothesize that the evaporation of $WSOC_p$ observed with drying during the late spring and summer is due to the reversible partitioning of IEPOX to aerosol water, or to other low-NO_x isoprene oxidation products such as multifunctional hydroperoxides (Liu et al., 2016a; Krechmer et al., 2015; Riva et al., 2016). This is supported by strong associations between the evaporated $WSOC_p$ and isoprene concentrations using the time lag analysis. It is further supported by the decreasing $WSOC_{p,dry}/WSOC_p$ ratios with decreasing NO_x/isoprene ratios. Note that Sareen et al. (2017) predict very low dissolved IEPOX in the eastern U.S. during summer (< 0.01 µg m^{-3}), suggesting reversibly formed reaction products are the dominant contributors to reversible aqSOA.

Laboratory studies have found reversible and irreversible uptake of IEPOX to aqueous particles (Nguyen et al., 2014; Riedel et al., 2015). However, ambient studies generally suggest that IEPOX-SOA has very low volatility (Lopez-Hilfiker et al., 2016; Hu et al., 2016). This could be due to challenges measuring the reversible aqSOA by the methods used to derive volatilities. For example, it is unclear how the instruments employed by Lopez-Hilfiker et al. (2016) and Hu et al. (2016) respond to reversible IEPOX reaction products present in the aqueous phase. It could also be that the evaporated $WSOC_p$ we observe is contributed by other low-NO_x isoprene oxidation products. Approximately 30 % of isoprene-SOA generated under NO_x-free conditions partitioned reversibly to aerosol water, but the molecular identities of the reversible aqSOA were not determined (Wong et al., 2015). Although the experiments of Wong et al. (2015) were performed in a chemical regime where IEPOX formation is favored, it did not contribute to the SOA in their experiments due to high OH levels. Given the absence of IEPOX-SOA in the experiments of Wong et al. (2015), the atmospheric relevance of their results needs further review. The uptake of other, non-IEPOX, low-NO_x oxidation products may explain such observations (Liu et al., 2016b; Riva et al., 2016; Krechmer et al., 2015; Liu et al., 2016a). Overall, identifying the molecular composition of the reversible aqSOA that is associated with low-NO_x isoprene oxidation will require targeted field measurements.

The effect of water evaporation on $WSOC_p$ also has important implications for the representation of SOA formation in models. The results in Fig. 1 show that ≈10 to 15 % of the total $WSOC_p$ evaporates with drying during the late spring and summer, on average. This suggests that the fraction of aqSOA that is formed reversibly is much higher than 15%, since the measurement of $WSOC_p$ includes aqSOA and compounds formed through traditional SOA partitioning (e.g., (Donahue et al., 2009)). Further, the fraction of $WSOC_p$ that evaporates with drying is variable, with values of up to 60 % for individual measurements (El-Sayed et al., 2016). Models that include aqSOA and aerosol multiphase chemistry can improve predictions of OA (e.g., (Carlton et al., 2008;Marais et al., 2016)). A complication of model evaluations is that comparisons of modeled OA concentrations to ambient measurements may be problematic if the measurements, themselves, are subject to the bias discussed above. For this reason, accounting for both reversible and irreversible uptake of water-soluble organic gases to liquid water is critical (McNeill, 2015). Our observations, supported by laboratory studies (Faust et al., 2017), suggest that treatment of aqSOA as an irreversible uptake process is not consistent with actual phenomena occurring in the atmosphere, especially in the eastern U.S. Although likely due to a different mechanism, Liu et al. (2016b) and Riva et al. (2017) also showed that isoprene oxidation forms semi-volatile compounds that re-partition back to the gas phase after forming SOA.

The lifetime of organic compounds in the atmosphere is strongly dependent on their phase (Pye et al., 2017). Oxygenated organic compounds in the gas-phase often have much shorter lifetimes than particle-phase organics due to significantly higher dry deposition velocities (Nguyen et al., 2015) and photolysis rates (Fu et al., 2008). The reversible uptake of $WSOC_g$ to aerosol water may effectively shield these species from such loss processes, resulting in enhanced transport. Thus, accounting for the reversible partitioning of water-soluble organic gases to aerosol water would likely improve model predictions of these compounds.

NO_x plays a critical role in the oxidation of VOCs, including effects on the composition and quantity of SOA produced. Herein, we show that NO_x strongly affects the amount and nature of SOA produced in an urban area that is under substantial influence from biogenic emissions. Higher concentrations of $WSOC_p$ were associated with decreasing NO_x/isoprene ratios. The fraction of $WSOC_p$ that evaporated with drying was also inversely related to NO_x/isoprene. In the future, isoprene concentrations are predicted to increase in response to changes in temperature and land use associated with climate change (Heald et al., 2008; Sanderson et al., 2003). The eastern U.S. is currently undergoing a transition from high- to low-NO_x chemical regimes (Travis et al., 2016; Edwards et al., 2017), and NO_x levels are likely to continue decreasing (He et al., 2013). This suggests future NO_x/isoprene ratios will generally decrease across the eastern U.S., as well, resulting in increased production of reversible aqSOA. The current results are from the greater Baltimore metropolitan area; although we observe a range of NO_x concentrations and NO_x/isoprene ratios, these measurements are representative of an urban environment. Thus, we may expect $WSOC_{p,dry}/WSOC_p$ ratios to be even lower in more rural environments impacted by isoprene emissions.

In addition to NO_x, sulfate also strongly affects SOA formation from isoprene through its separate contributions to ALW, particle acidity, and aqueous chemistry (Xu et al., 2015; Nguyen et al., 2014; Surratt et al., 2010). Laboratory studies have not yet elucidated the role of each factor in the reversibility of isoprene SOA, and we do not have sufficient sulfate data to characterize such effects with our analysis. However, it is worth noting that particle acidity is not likely a factor in the relative split between reversible and irreversible aqSOA formed from isoprene. Studies predict that particles in the eastern U.S. are highly acidic throughout the year (Weber et al., 2016; Battaglia et al., 2017; Guo et al., 2016; 2015), and acidity is not a limiting factor in isoprene SOA formation during the summer (Budisulistiorini et al., 2016; Xu et al., 2015). The implication from our observations is that reversible aqSOA from isoprene forms even in the presence of such persistently acidic particles. This further questions the treatment of isoprene SOA as an irreversible uptake process in models.

5 Conclusions

The eastern U.S. is undergoing a transition from a high- to –low-NO_x chemical regime, which has broad implications for nighttime chemistry, ozone production, and SOA formation (Travis et al., 2016; Marais et al., 2016; Edwards et al., 2017). Using a time lag analysis, we show that NO_x/isoprene strongly affects concentrations of SOA in the eastern U.S., including SOA formed through the reversible uptake of water-soluble organic gases to aqueous particles. Lower NO_x leads to a higher fraction of aqueous SOA formed reversibly. Our measurements from an urban area suggest that this process is even more important in other, more rural environments.

Predictions of future NO_x and isoprene emissions in response to regulations, technology, and climate change also suggest that this process may increase in importance going forward. Such an inference is complicated by concurrent reductions in SO_2 emissions in the U.S. and other developed nations. The consequent decreases in sulfate may offset the effects of NO_x reductions on isoprene SOA (de Sá et al., 2017). However, we stress that prior studies into the NO_x-sulfate-isoprene system have not systematically determined how these species affect the reversibility of isoprene SOA. Therefore, while we hypothesize that future decreases in NO_x and increases in isoprene will increase reversible isoprene SOA (or at least the reversible fraction), the role of changing sulfate will also need to be considered. Future laboratory and modeling studies will be needed to address this question directly.

We hypothesize that IEPOX uptake to aqueous particles is responsible for the reversible aqSOA, but other low-NO_x isoprene oxidation products are possible, as well (Wong et al., 2015). We quantify reversible aqSOA through observations of $WSOC_p$ evaporation that results from drying. Ultimately, molecular composition measurements made concurrently with our WSOC system are required to identify the chemical species responsible for this phenomenon. The evaporation of $WSOC_p$ with drying occurred systematically during the late spring and summer, and was linked to isoprene and NO_x. This has importance for a wide range of aerosol measurements that implement drying. It also has importance for modeling multi-phase SOA formation, as simplified treatment of irreversible uptake does not represent actual atmospheric processes.

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Table 1. Seasonal sampling periods in Baltimore, MD.

Season	Sampling Period
Fall	3 – 30 September 2014
Winter	4 February – 23 March 2015
Early spring	23 April – 8 May 2015
Late spring	9 May – 14 May 2015
Summer	6 July – 14 August 2015

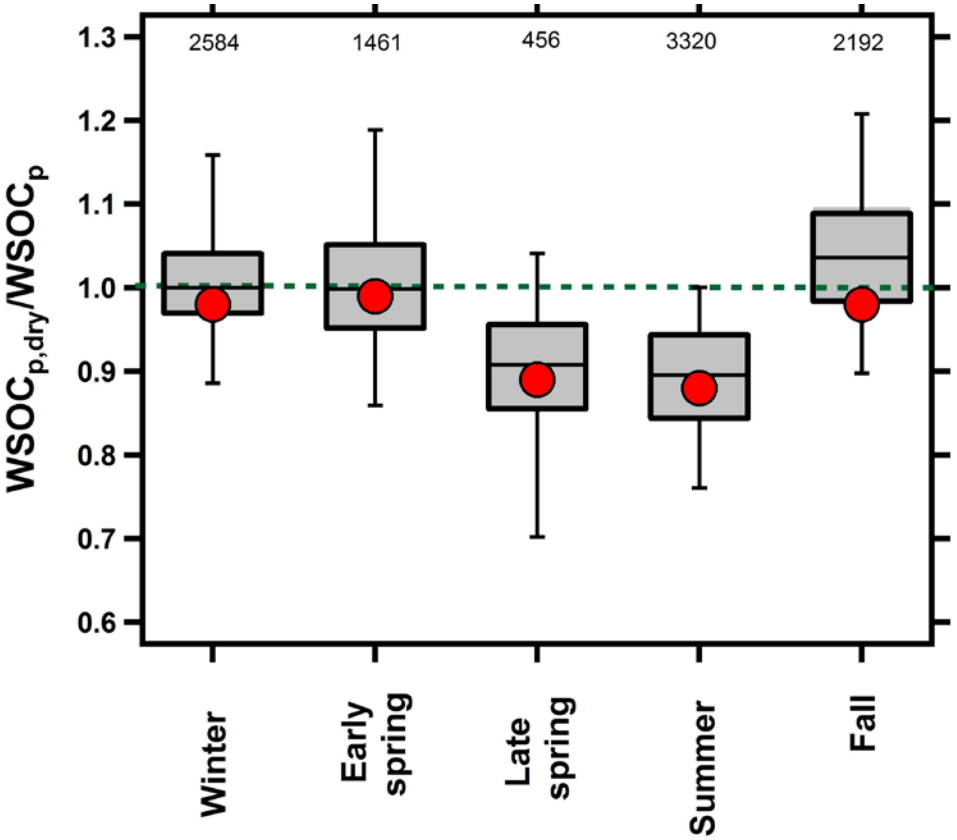

Figure 1: Boxplot of the overall seasonal WSOC$_{p,dry}$/WSOC$_p$ ratios. For each bin, mean (red marker), median (horizontal black line), 25th and 75th percentiles (lower and upper box values), as well as 5th and 95th percentiles (vertical lines) are shown. The dotted green line at unity is shown for visual reference. Numbers at the top represent the number of paired WSOC$_{p,dry}$/WSOC$_p$ measurements within each season.

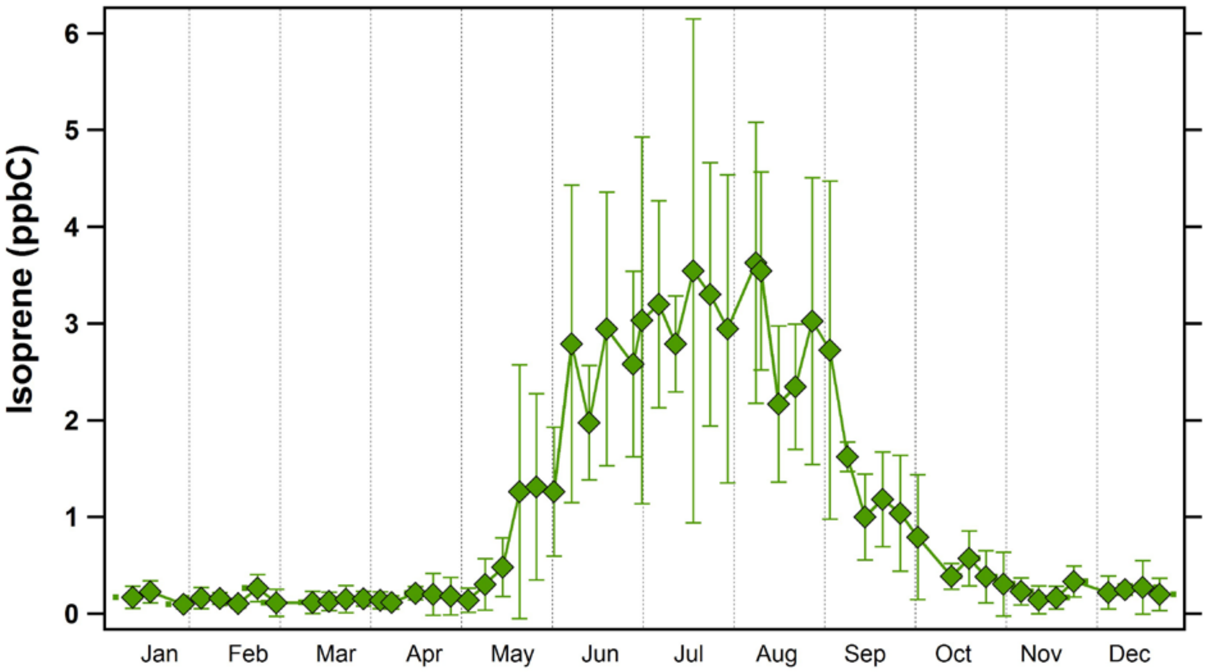

Figure 2: Annual climatology of isoprene concentrations in Essex, MD (2011 to 2015). Symbols represent average concentrations (in ppbC or nmol C mol^{-1}) while error bars represent ± 1σ.

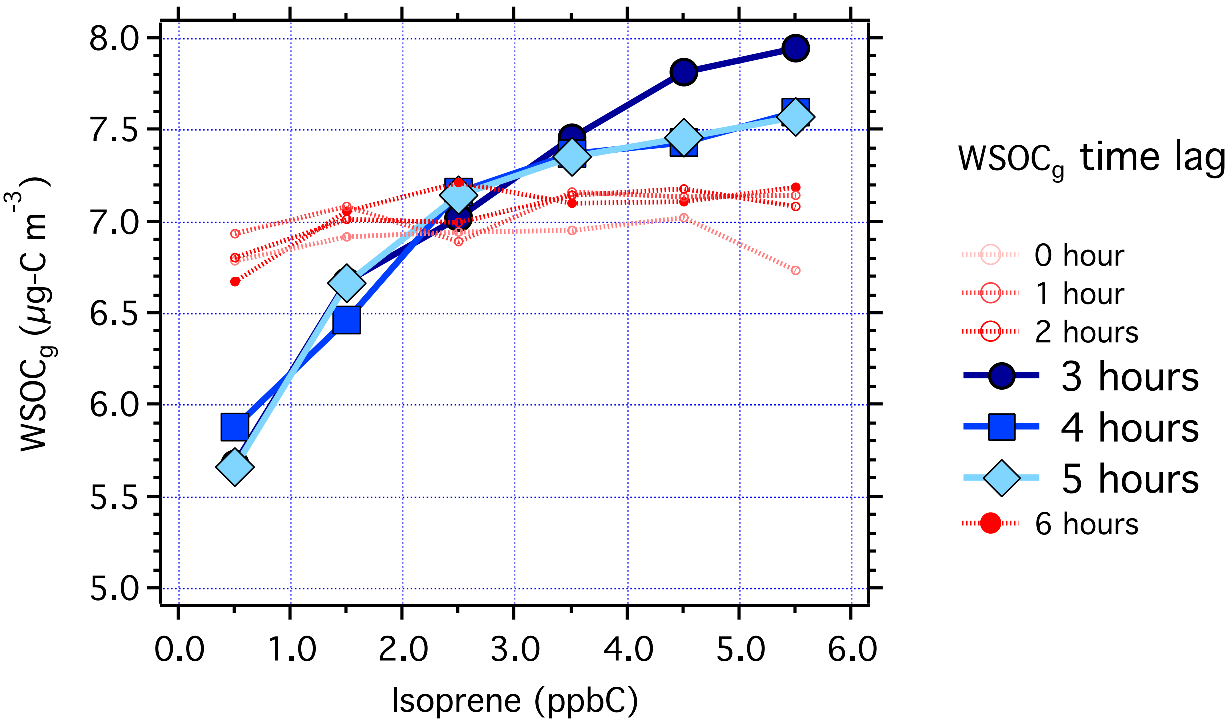

Figure 3: Median WSOC$_g$ concentrations as a function of isoprene concentrations (in ppbC or nmol C mol^{-1}) at different WSOC$_g$ time lags during the summer. The following isoprene concentrations bins were defined: < 1 ppbC, (1 to 2) ppbC, (2 to 3) ppbC, (3 to 4) ppbC, (4 to 5) ppbC, and > 5 ppbC. Scatter and box plots showing individual data are presented in Fig. S6.

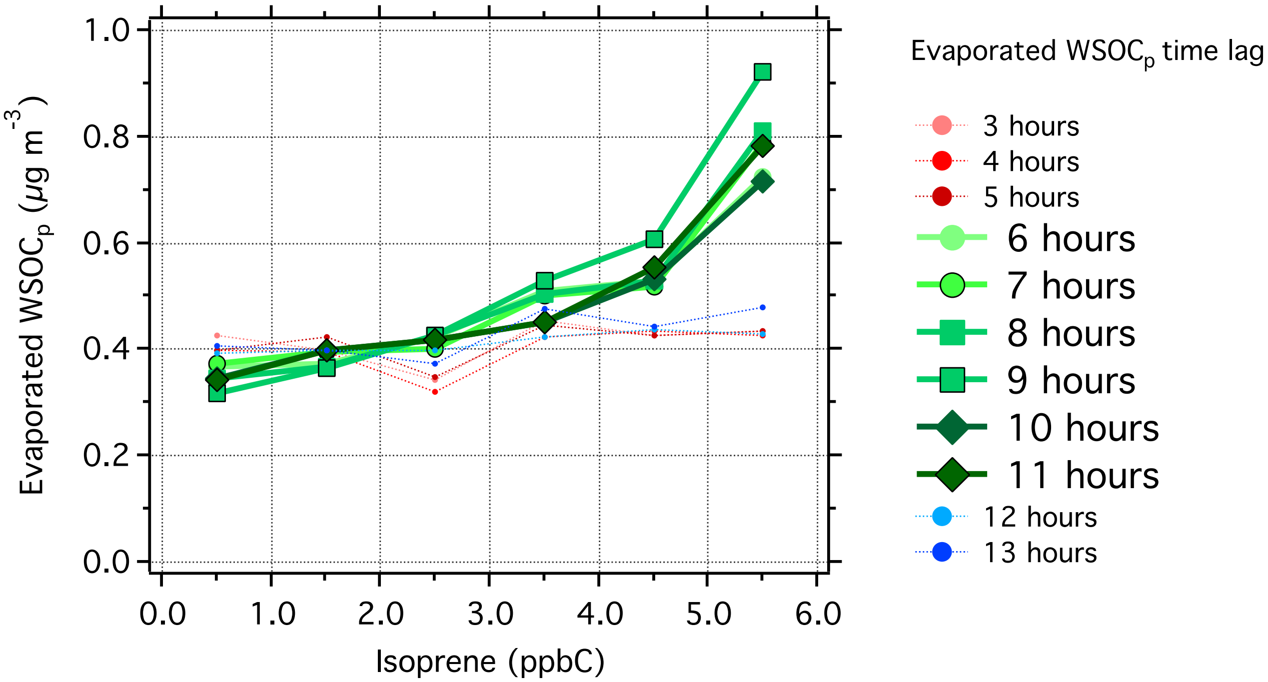

Figure 4: Median evaporated WSOC$_p$ concentrations as a function of isoprene concentrations (ppbC or nmol C mol^{-1}) at different evaporated WSOC$_p$ time lags during the summer. Scatter and box plots showing individual data are presented in Fig. S6.

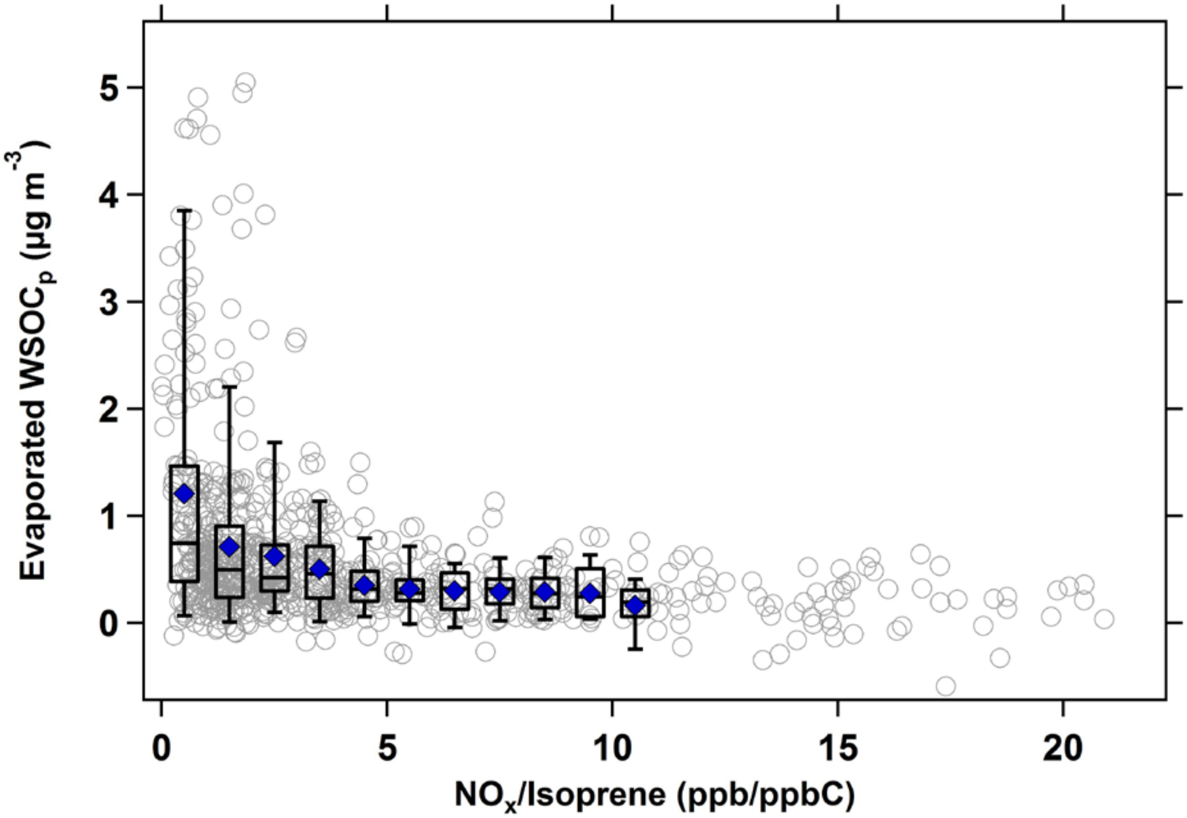

Figure 5: Scatter and box plots of evaporated WSOC$_p$ (9 h time lag) as a function of NO$_x$/isoprene ratio (ppb/ppbC or mol mol^{-1} C) in the summer. Bins were defined: (0 to 1) ppb/ppb-C (0 to 1 mol/mol C), (1 to 2) ppb/ppb-C, (2 to 3) ppb/ppb-C, (3 to 4) ppb/ppb-C, (4 to 5) ppb/ppb-C, (5 to 6) ppb/ppb-C, (6 to 7) ppb/ppb-C, (7 to 8) ppb/ppb-C, (8 to 9) ppb/ppb-C, (9 to 10) ppb/ppb-C, > 10 ppb/ppb-C. Bins were chosen to include at least 50 datapoints. For each bin, mean (blue marker), median (horizontal black line), 25th and 75th percentiles (lower and upper box values), as well as 5th and 95th percentiles (vertical lines) are shown.

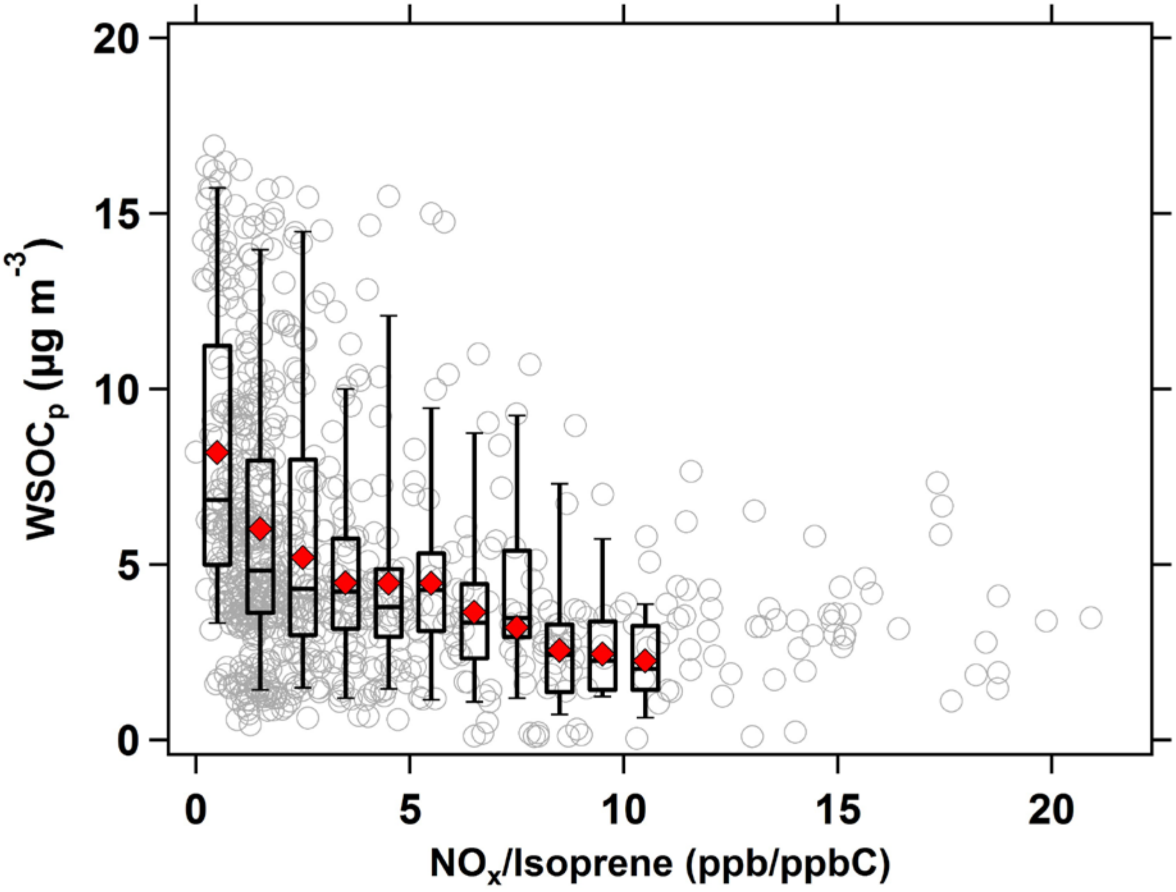

Figure 6: Scatter plot of $WSOC_p$ as a function of NO_x/isoprene ratio (ppb/ppbC or mol mol^{-1} C) in the summer. Symbols and bins are consistent with those defined in Fig. 5.

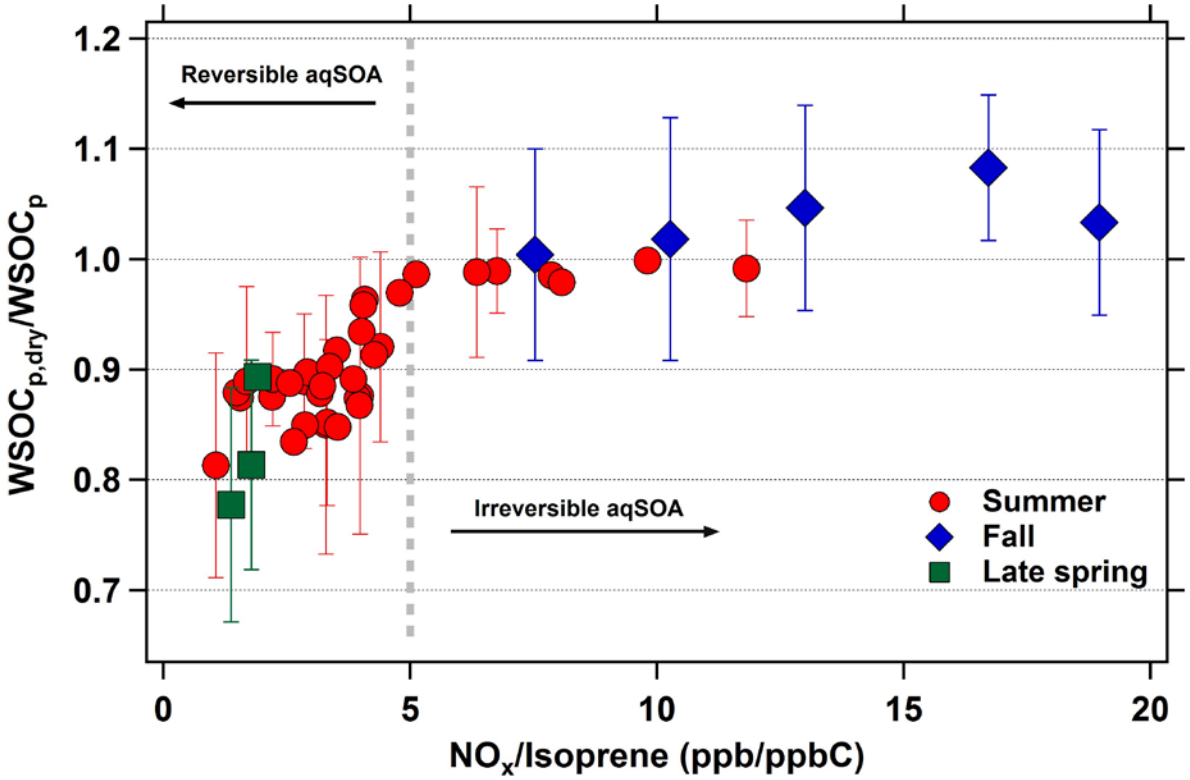

Figure 7: Daily average $WSOC_{p,dry}/WSOC_p$ ratios as a function of daily average NO_x/isoprene ratios (ppb/ppbC or mol mol^{-1} C). Gray dotted line is representative of the transition zone from reversible to irreversible aqSOA conditions. Error bars represent ± 1σ, and are shown for one-third of the data for clarity.