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Investigating the influences of SO_2 and NH_3 levels on isoprene-derived secondary organic aerosol formation using conditional sampling approaches

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Abstract

Filter-based $PM_{2.5}$ samples were chemically analyzed to investigate secondary organic aerosol (SOA) formation from isoprene in a rural atmosphere of the southeastern US influenced by both anthropogenic sulfur dioxide (SO_2) and ammonia (NH_3) emissions. Daytime $PM_{2.5}$ samples were collected during summer 2010 using conditional sampling approaches based on pre-defined high and low SO_2 or NH_3 thresholds. Known molecular-level tracers for isoprene SOA formation, including 2-methylglyceric acid, 3-methyltetrahydrofuran-3,4-diols, 2-methyltetrols, C_5-alkene triols, dimers, and organosulfate derivatives, were identified and quantified by gas chromatography coupled to electron ionization mass spectrometry (GC/EI-MS) and ultra performance liquid chromatography coupled to electrospray ionization high-resolution quadrupole time-of-flight mass spectrometry (UPLC/ESI-HR-Q-TOFMS). Mass concentrations of six isoprene low-NO_x SOA tracers contributed to 12–19 % of total organic matter (OM) in $PM_{2.5}$ samples collected during the sampling period, indicating the importance of the hydroxyl radical (OH)-initiated oxidation (so-called photooxidation) of isoprene under low-NO_x conditions that leads to SOA formation through reactive uptake of gaseous isoprene epoxydiols (IEPOX) in this region. IEPOX-derived SOA tracers were enhanced under high-SO_2 sampling scenarios, suggesting that SO_2 oxidation increases aerosol acidity of sulfate aerosols needed for enhancing heterogeneous oxirane ring-opening reactions of IEPOX. No clear associations between isoprene SOA formation and high and low NH_3 conditional samples were found. Furthermore, weak correlations between aerosol acidity and mass of IEPOX SOA tracers suggests that IEPOX-derived SOA formation might be modulated by other factors as well in addition to aerosol acidity. Positive correlations between sulfate aerosol loadings and IEPOX-derived SOA tracers for samples collected under all conditions indicates that sulfate aerosol could be a surrogate for surface area in the uptake of IEPOX onto preexisting aerosols.

1 Introduction

Tropospheric fine aerosols ($PM_{2.5}$, with aerodynamic diameter ≤ 2.5 µm) have been recognized to have significant influences on regional air quality, climate change, and human health (Kanakidou et al., 2005; Hallquist et al., 2009). Organic aerosol constituents that usually account for a large fraction (i.e., 20–90 %) of the total $PM_{2.5}$ mass are of particular concern, especially due to their high degree of chemical complexity that results in limited understanding of their sources, sinks, and chemical structure, thus yielding major uncertainties for air quality modeling and human health risk assessment.

Secondary organic aerosol (SOA) that originates from the photochemical oxidation of biogenic volatile organic compounds (BVOCs) is thought to be the largest contributor to the global SOA burden, owing to their large emissions and efficient SOA formation processes (Chung and Seinfeld, 2002; Kanakidou et al., 2005; Henze and Seinfeld, 2006). The atmospheric significance of biogenic secondary organic aerosol (BSOA) has been inferred from recent remote sensing data over the southeastern United States that suggests BVOC emissions combine with anthropogenic pollutants (e.g., SO_2, NO_x, and primary OC emissions) leading to substantial amounts of SOA observed in this region (Goldstein et al., 2009). The enhancement of SOA from BVOCs in this region highlights the need for further research aimed at understanding the attributable sources and detailed mechanisms leading to BSOA formation in order to develop effective control strategies.

Recently, organosulfate formation was reported through reactive uptake of BVOC oxidation products onto acidified sulfate seed aerosols, providing a likely link between anthropogenic pollutants and the enhanced BSOA formation (Iinuma et al., 2007, 2009; Surratt et al., 2007a, 2008). Moreover, the effects of acid-catalyzed enhancement on BSOA formation have also been observed in several laboratory studies (Iinuma et al., 2004; Surratt et al., 2007b; Offenberg et al., 2009; Chan et al., 2011). In the presence of anthropogenic pollutants, such as nitric acid and sulfuric acid produced from the oxidation of NO_x and SO_2, SOA mass yields from isoprene under high- and low-NO_x conditions, respectively, have been shown to increase substantially (i.e., from 1–3 % to 3–30 %) with preexisting acidified sulfate aerosols in the laboratory (Chan et al., 2010a; Surratt et al., 2010). Figure 1 displays the NO_x-dependent isoprene SOA formation mechanisms. Under high-NO_x conditions, isoprene SOA is enhanced with increasing NO_2/NO ratios (Chan et al., 2010a; Surratt et al., 2010). This enhancement is explained by the formation and subsequent photooxidation of methacryloylperoxynitrate (MPAN), which leads to 2-methylglyceric acid (2-MG) formation and its corresponding oligoesters (Surratt et al., 2006, 2010). Notably, 2-MG has been used as one of the isoprene SOA tracer compounds in the organic tracer-based source apportionment method developed by Kleindienst et al. (2007) to estimate the contributions of BVOCs to SOA formation. On the other hand, under low-NO_x (i.e., NO-limited) conditions, isoprene SOA has been observed to be enhanced in the presence of acidified sulfate seed aerosols (mass yield ~ 29 %) over that in the presence of neutral seed aerosols (mass yield ~ 1 %) (Surratt et al., 2010). Increased uptake of gaseous isoprene epoxydiols (IEPOX) by enhanced particle-phase acid-catalyzed oxirane ring-opening reaction rates has been proposed and demonstrated to explain this enhancement (Minerath et al., 2009; Eddingsaas et al., 2010; Surratt et al., 2010; Lin et al., 2012). Identification of known isoprene low-NO_x SOA tracers through reactive uptake of IEPOX onto acidified sulfate seed aerosols also supports this hypothesis (Surratt et al., 2010; Lin et al., 2012). Although clear evidence of acid-catalyzed enhancement for BSOA formation has been shown in laboratory studies, the importance of aerosol acidity on ambient BSOA formation remains unclear owing to the fact that acidified sulfate seed aerosols used in the laboratory studies were usually much more acidic than the acidity measured in ambient aerosols (Edgerton et al., 2007; Tanner et al., 2009). In addition, ambient aerosol acidity is also likely modulated by other environmental factors, such as the atmospheric alkaline species (e.g., NH_3) that leads to the neutralization of acidic aerosols (Huntzicker et al., 1980; McMurry et al., 1983), but the uptake processes and the kinetics in the atmosphere have not been not fully elucidated (Huang et al., 2011; Yao et al., 2011; Liggio et al., 2011).

In the present study, $PM_{2.5}$ samples were collected to investigate the effects of ambient aerosol acidity on BSOA formation in a rural atmosphere under the influences of anthropogenic SO_2 and NH_3 emissions. Filter samples were collected from Yorkville, GA, a rural site located within the Southeastern Aerosol Research and Characterization Study (SEARCH) network during the summer of 2010. This site is characterized by high isoprene emissions during summertime, and is influenced by SO_2 point sources from local coal-fired power plants (Edgerton et al., 2006a), as well as NH_3 emissions from nearby poultry operations (Edgerton et al., 2007). Conditional sampling strategies were employed in this study to collect $PM_{2.5}$ samples under pre-defined environmental thresholds (i.e., the mixing ratios of SO_2 or NH_3) to distinguish the influences of ambient SO_2 and NH_3 levels on ambient aerosol acidity and BSOA formation. More specifically, known isoprene SOA tracers (which include organosulfate derivatives) were chemically characterized by UPLC/ESI-HR-Q-TOFMS and GC/MS techniques to measure SOA constituents at the molecular level. The effects of acid enhancement on BSOA formation were examined by comparing paired samples collected under high and low SO_2 or NH_3 scenarios. Even though some of these BSOA tracers have been previously characterized from $PM_{2.5}$ samples collected from the SEARCH network in a time-integrated manner (Chan et al., 2010b; Gao et al., 2006; Surratt et al., 2007a, 2008), using conditional sampling approaches to collect $PM_{2.5}$ in this study is to our knowledge one of the first attempts to systematically examine if BSOA formation is enhanced or suppressed due to anthropogenic emissions in this region.

2 Experimental section

2.1 Collection of $PM_{2.5}$ by conditional sampling

$PM_{2.5}$ samples were collected from Yorkville (YRK), GA, a rural site located ~55 km west northwest of Atlanta, GA within the SEARCH network during summer 2010. The detailed site descriptions are provided in the SEARCH overview papers (Hansen et al., 2003; Edgerton et al., 2005, 2006b). In the present work, paired quartz filter samples were collected by conditional sampling approaches based on the measured SO_2 or NH_3 mixing ratios. Concentration thresholds were set to: (1) distinguish the influences of SO_2 or NH_3 levels on ambient aerosol acidity and isoprene SOA formation; (2) ensure that sufficient material was collected for chemical analysis; and (3) avoid motor burnout by activating the samplers too frequently. The pre-defined high and low SO_2 or NH_3 thresholds were determined by the review of historical ambient data at the sampling site. For SO_2, data from June–August 2009 were analyzed and the thresholds were set to correspond to the lowest 40 % and highest 40 % of observed 1-min concentrations. We focused on 2009 because installation of emission controls on nearby power plants caused concentrations subsequent to 2008 to be significantly lower than 2008 and before. For NH_3, we analyzed the same months of data for three consecutive years (2007–2009) and set thresholds to correspond approximately to the lowest 20 % and highest 40 % of observed 1-min values.

2.1.1 SO_2 conditional sampling

SO_2 conditional samples were collected from 25 June 2010 until 14 July 2010 between 09:00 and 18:59 local standard time. Two Tisch Environmental (Cleves, OH) Model TE-6070V-2.5 high-volume $PM_{2.5}$ air samplers were operated side-by-side to collect aerosol samples at a flow rate of 1 $m^3\,min^{-1}$ during the day (09:00–18:59 LT). One high-volume $PM_{2.5}$ sampler was designated as the high-SO_2 sampler, which was only turned on to collect $PM_{2.5}$ samples when the measured SO_2 mixing ratio was ≥ 0.5 ppbv. The second high-volume $PM_{2.5}$ sampler was only turned on to collect aerosol samples when the SO_2 mixing ratio was ≤ 0.25 ppbv, and this sampler was designated as the low-SO_2 sampler. SO_2 was measured with 1-min time resolution using a Thermo-Environmental (Franklin, MA) Model 43c pulsed fluorescence SO_2 analyzer.

2.1.2 NH_3 conditional sampling

NH_3 conditional samples were collected from 29 July 2010 until 6 August 2010. The same conditional sampling approaches described above were employed to collect $PM_{2.5}$ samples based on the NH_3 mixing ratios during the day (09:00–18:59 LT). High-NH_3 sampler only collected $PM_{2.5}$ samples when the NH_3 mixing ratios were ≥ 2 ppbv, while low-NH_3 sampler only collected aerosol samples when the NH_3 mixing ratios were ≤ 1 ppbv. NH_3 was measured with 1-min time resolution via continuous denuder difference with a Thermo-Environmental Model 42c chemiluminescence NO-NO_x analyzer. The NO-NO_x analyzer was modified to measure NH_3 as described in Saylor et al. (2010).

Available collocated measurements and meteorological data during the conditional sampling periods are summarized in Table 1.

2.2 Filter extractions and chemical analyses for isoprene SOA tracers

Known isoprene SOA tracers, including 2-methyltetrols (Claeys et al., 2004), C_5-alkene triols (Wang et al., 2005), 3-methyltetrahydrofuran-3,4-diols (3-MeTHF-3,4-diols) (Lin et al., 2012; Zhang et al., 2012), IEPOX-derived dimers (Surratt et al., 2006), and 2-MG (Edney et al., 2005) were characterized by GC/MS with prior trimethylsilylation using electron ionization (EI). A fraction of each 8 × 10-inch quartz filter (1/4) was extracted in pre-cleaned scintillation vials with 20 mL high-purity methanol (LC-MS CHROMASOLV-grade, Sigma-Aldrich) under 45 min of sonication. The filter extracts were filtered through 0.2 µm PTFE syringe filters (Pall Life Science, Acrodisc®) to remove suspended quartz filter fibers and insoluble particles, and subsequently blown to dryness under a gentle N_2 stream at room temperature. Residues of the filter extracts were immediately trimethylsilylated by reacting with 100 µL of BSTFA + TMCS (99 : 1 v/v, Supelco) and 50 µL of pyridine (anhydrous, 99.8 %, Sigma-Aldrich) at 70 °C for 1 h. The derivatized samples were analyzed by GC/MS within 24 h after trimethylsilylation. GC/MS analysis was performed using a Hewlett-Packard (HP) 5890 Series II Gas Chromatograph coupled to a HP 5971A Mass Selective Detector. An *EconoCap*™-*EC*™-*5* Capillary Column (30 m × 0.25 mm i.d.; 0.25 µm film thickness) was used to separate the trimethylsilyl (TMS) derivatives before MS detection. 1 µL of each derivatized sample was injected onto the GC column. Operating conditions and the temperature program of the GC/MS were as described previously by Surratt et al. (2010). Isoprene SOA tracers were quantified with the following base peak ion fragments: *m/z* 219 for 2-methyltetrols, *m/z* 231 for C_5-alkene triols, *m/z* 262 for 3-MeTHF-3,4-diols, *m/z* 335 for dimers, and *m/z* 219 for 2-MG. *Meso*-erythritol (≥99 %, Sigma), a structurally similar analog of 2-methyltetrols, was used as a surrogate standard to quantify 2-methyltetrols, C_5-alkene triols, dimers, and 2-MG in the filter samples. The base ion fragment of *m/z* 217 was used for *meso*-erythritol for quantification. 3-MeTHF-3,4-diols were quantified using synthesized authentic standards. The details of the synthesis procedures are reported in Zhang et al. (2012).

Characterization of organosulfate derivatives was performed using ultra performance liquid chromatography interfaced to a high-resolution quadrupole time-of-flight mass spectrometer (Agilent 6500 Series) equipped with an electrospray ionization source (UPLC/ESI-HR-Q-TOFMS) operated in the negative (–) ion mode. A Waters ACQUITY UPLC HSS T3 column (2.1 × 100 mm, 1.8 µm particle size) was used for chromatographic separations. Detailed UPLC/(–)ESI-HR-Q-TOFMS operating conditions can be found in Zhang et al. (2011). Quartz filter samples for UPLC/(–)ESI-HR-Q-TOFMS analyses were extracted in the same manner as those for GC/MS analyses. After the filter extracts were blown dry, the extract residues were reconstituted with 150 µL of a 50 : 50 (v/v) solvent mixture of methanol containing 0.1 % acetic acid (LC-MS CHROMASOLV-grade, Sigma-Aldrich) and water containing 0.1 % acetic acid (LC-MS CHROMASOLV-grade, Sigma-Aldrich). 5 µL of each sample was injected onto the UPLC column eluted with solvent of the same composition. Isoprene-derived organosulfate species reported previously by Surratt et al. (2008) were identified and quantified. The elemental composition of target compounds was assigned based on accurate mass data. The errors of accurate mass fittings were within ± 1 mDa. Owing to the lack of authentic standards, sodium propyl sulfate (electronic grade, City Chemical LLC) was used to quantify all isoprene-derived organsulfates, since this surrogate standard eluted in the same region as these compounds. The detection limit of sodium propyl sulfate on UPLC/(–)ESI-HR-TOFMS was 0.1 ng μL^{-1}, determined by signal-to-noise ratios of 3 : 1.

The efficiency of the extraction protocols was evaluated by spiking 5 replicates of pre-baked blank quartz filters with quantifying standards. Extraction efficiencies (62–82 %) are taken into account for SOA constituents that were quantified in the field samples.

2.3 Inorganic ion measurements

Continuous sulfate (SO_4^{2-}), nitrate (NO_3^-), and ammonium (NH_4^+) measurements were made during the sampling periods at the site using continuous particle analyzers; detailed instrumental setup and operating conditions of these analyzers have been described elsewhere (Edgerton et al., 2006b). Briefly, continuous SO_4^{2-} measurements were made using a variation of the Harvard School of Public Health approach. A high temperature (> 850 °C) stainless steel tube was used to reduce particle SO_4^{2-} to SO_2. Then SO_2 was measured by a Thermo-Environmental Instruments Model 43s or 43ctl high-sensitivity, pulsed ultraviolet fluorescence SO_2 analyzer. Continuous NO_3^- and NH_4^+ measurements were made using a three-channel continuous differencing approach developed by ARA, Inc. Air samples were drawn through the inlet and series of denuders coated with sodium carbonate and citric acid followed by an activated carbon honeycomb denuder to remove interferents, and then the flow was split into three analytical channels that converted different nitrogen species to NO depending on temperature. Channel 1 (CH1) measured the baseline gas-phase NO_y for the analyzer by passing the air through a 2-µm Teflon filter, followed by a KCl-coated filter and a molybdenum (Mo) mesh catalyst heated to 350 °C. Channel 2 (CH2) measured the baseline NO_y plus particle-bound NO_3^- by passing air through Mo converter at 350 °C without filtration. Channel 3 (CH3) measured NH_4^+ plus baseline NO_y and particle-bound NO_3^- by flowing air through ceramic tube containing platinum (Pt) catalyst heated to 600 °C, followed by another Mo converter at 350 °C. NO_3^- and NH_4^+ concentrations were calculated as CH2-CH1 and CH3-CH2, respectively. Continuous inorganic data were processed in a time-weighted manner to represent the real-time aerosol inorganic conditions to estimate ambient aerosol acidity.

Filter-based inorganic measurements were also performed by analyzing a 37-mm filter punch from each quartz filter sample. Filter samples were extracted with 15 mL Millipore 18.2 Megohm Ultrapure DI H_2O. A Dionex ICS-3000 Ion Chromatography System was used to quantify SO_4^{2-}, NO_3^-, and NH_4^+ concentrations in filter extracts. The anion channel included a Dionex AG18 guard column, a Dionex AS18 analytical column and 10 mM KOH eluent. The cation channel included a Dionex CG16 guard column, a Dionex CS16 analytical column and 18 mM methanesulfonic acid eluent. The ICS-3000 was calibrated with NIST-traceable multi-element standards covering the range of observed concentrations. Sample injection volumes were 1.0 mL and peak area was used for quantification. Analytical detection limits were in the range of 2–3 $\mu g\,L^{-1}$ and analytical uncertainties were $< 5\,\%$. Measured concentrations were compared with continuous inorganic measurements to evaluate the changes of inorganic composition during sample storage.

2.4 Calculation of aerosol acidity

Ambient aerosol acidity of the collected $PM_{2.5}$ samples was estimated by calculating the degree of stoichiometric neutralization, defined as the molar ratios of NH_4^+ to the sum of SO_4^{2-} and NO_3^-, assuming aerosol SO_4^{2-} and NO_3^- were only associated with NH_4^+ and H^+. Acidic aerosols are characterized by having a neutralization degree less than unity. The neutralization degree greater than unity implies the samples are fully neutralized.

$$\text{Neutralization Degree} = [NH_4^+]/(2 \times [SO_4^{2-}] + [NO_3^-]) \tag{1}$$

In addition, an on-line version of the extended aerosol thermodynamics model (E-AIM II: H^+-NH_4^+-SO_4^{2-}-NO_3^--H_2O) was used to estimate aerosol acidity by calculating the in situ aerosol pH in the particle aqueous phase (Clegg et al., 1998). Inputs of free $[H^+]$ were calculated based on charge balance from measured NH_4^+, SO_4^{2-}, and NO_3^- concentrations. Temperature and relative humidity (RH) parameters were obtained from the measurements at the sampling site.

$$[H^+]_{\text{free}} = (2 \times [SO_4^{2-}] + [NO_3^-]) - [NH_4^+] \tag{2}$$

Modeling outputs of activity coefficient and moles of H^+_{aq} in the aqueous phase, and the total volume of aqueous phase in the aerosol per m^3 air in the thermodynamic equilibrium were used to calculate in situ aerosol pH.

$$\text{pH} = -\log[\gamma_{H^+\,aq} \times n_{H^+\,aq}/(V_{aq}/1000)] \tag{3}$$

$\gamma_{H^+\,aq}$: activity coefficient of H^+_{aq}
$n_{H^+\,aq}$: moles of H^+_{aq}
V_{aq}: total volume of the aqueous phase (cm^3).

3 Results and discussion

3.1 Identification and quantification of isoprene SOA tracers at YRK

UPLC/(–)ESI-HR-Q-TOFMS and GC/EI-MS with prior trimethylsilylation were used to identify and quantify isoprene SOA tracers in the $PM_{2.5}$ samples collected from the YRK site. Figure 2 shows a typical base peak chromatogram (BPC) from UPLC/(–)ESI-HR-Q-TOFMS analysis, and a typical total ion chromatogram (TIC) from GC/EI-MS analysis for a representative $PM_{2.5}$ sample collected on 27 June 2010 under the high-SO_2 sampling scenario. Overall, most of the major peaks identified from the filter samples could be attributed to BSOA tracers, which have been confirmed by prior chamber studies (Surratt et al., 2008, 2010; Lin et al., 2012). The IEPOX-derived organosulfate ($[M–H]^-$ ion at *m/z* 215) was the most abundant compound detected by the UPLC/(–)ESI-HR-Q-TOFMS technique. Other base peak ions displayed in the BPC correspond to monoterpene-derived organosulfates (e.g., $[M–H]^-$ ions at *m/z* 239, 279, and 281) (Surratt et al., 2008), nitrooxy (or nitrated) organosulfates derived from both isoprene (e.g., $[M–H]^-$ ion at *m/z* 260) and monoterpenes (e.g., $[M–H]^-$ ions at *m/z* 294 and 296) (Surratt et al., 2008), and terpenoic acids (e.g., $[M–H]^-$ ions at *m/z* 157 and 187) (Yasmeen et al., 2011). For the TIC from GC/EI-MS analysis, the most abundant peak (labeled as Peak 1) was identified as silanol, trimethyl-, sulfate (2 : 1) based on the NIST MS library search. This peak, which likely originates from the extracted particle sulfate content after trimethylsilylation, was also observed by Jaoui et al. (2012) in the samples collected from chamber studies under conditions of pre-seeded ammonium sulfate aerosol, and SO_2 oxidation that forms sulfuric acid. Other major peaks detected could be attributed to isoprene low-NO_x SOA tracers, including 3-MeTHF-3,4-diols (two isomers grouped as Peak 2), C_5-alkene triols (three isomers grouped as Peak 3), 2-methyltetrols (two isomers grouped Peak 4). Strong signal intensity of C_5-alkene triols and 2-methyltetrols in the TIC, as well as the IEPOX-derived organosulfate in the BPC from the UPLC/(–)ESI-HR-Q-TOFMS technique, shows the atmospheric significance of IEPOX chemistry leading to SOA formation in this region.

SOA tracer compounds were quantified with authentic or surrogate standards. Field blanks were collected during the field study, and subsequently analyzed to subtract background signals from all aerosol samples for quantification. The average mass concentrations of isoprene low-NO_x and high-NO_x SOA tracers measured under high- and low-SO_2 conditions in this study are shown in Table 2. For high SO_2

conditional samples, the average mass concentration of isoprene low-NO_x tracers, including 2-methyltetrols, C_5-alkene triols, 3-MeTHF-3,4-diols, as well as IEPOX-derived organosulfate (*m/z* 215), were higher than those of the corresponding paired low SO_2 conditional samples ($p = 0.012$). The differences of isoprene high-NO_x (MPAN-derived) SOA tracers between high- and low-SO_2 conditions were not as significant ($p = 0.754$). This observation provides evidence for isoprene SOA formation from IEPOX chemistry being enhanced under a high-SO_2 environment. The enhancement of isoprene SOA formation, especially for the identified isoprene low-NO_x SOA tracers, can be explained by the oxidation of SO_2 producing sulfuric acid that provides aerosol acidity to enhance the rate of heterogeneous oxirane ring-opening reactions when the gas-phase IEPOX is taken up by preexisting acidic aerosol surfaces (Edney et al., 2005; Surratt et al., 2010; Lin et al., 2012). Moreover, the enhancement of IEPOX chemistry could also be explained by the increased aerosol sulfate concentrations under high-SO_2 conditions (Table 1). The hygroscopic nature of the particle sulfate could have provided a wet aerosol surface that facilitated the IEPOX uptake and lead to SOA formation. In order to clarify the role of SO_2, correlations between aerosol acidity, particle sulfate loadings and isoprene low-NO_x SOA tracers are discussed in subsequent sections of this manuscript.

The average mass concentrations of isoprene SOA tracers measured under high- and low-NH_3 conditions are shown in Table 3. Organosulfate species, such as the IEPOX-derived organosulfate (*m/z* 215), the organosulfate derivative of the IEPOX-derived dimers (*m/z* 333), and MPAN-derived organosulfate (*m/z* 199) were more abundant under low-NH_3 conditions. Other tracer compounds, however, have higher mass concentrations detected under high-NH_3 conditions, which might coincide with the higher average solar radiation under high NH_3 conditional sampling (Table 1). Figure 3 shows correlations between isoprene-derived organosulfates. Interestingly, strong correlations between the IEPOX-derived organosulfate (*m/z* 215) and the organosulfate derivatives of the IEPOX-derived dimers (*m/z* 333) ($r = 0.83$) support the common pathway and formation mechanisms of these two tracers as shown in Fig. 1.

In addition, strong correlations ($r = 0.71$) were observed between the IEPOX-derived organosulfate (*m/z* 215) and the MPAN-derived organosulfate (*m/z* 199), suggesting similar formation behaviors or limiting factors, since these two species are known to form from different NO_x-dependent pathways as shown in Fig. 1. Notably, the detected isoprene low-NO_x SOA tracers were higher during the NH_3 conditional sampling period (late July to early August) than the SO_2 conditional sampling period (late June to mid-July), likely due to the change of meteorological conditions. For example, a higher average temperature during the NH_3 conditional sampling period might lead to higher isoprene emissions, as well as faster photochemical processes for isoprene SOA formation. In contrast, the isoprene high-NO_x SOA tracers remained constant between the two sampling periods. This could be explained by the NO-limited isoprene SOA formation pathway that occurs once the NO levels in the environment are consumed, resulting in the low-NO_x (RO_2+HO_2) chemistry becoming the dominant pathway in the atmosphere, while isoprene is still continuously emitted during daytime.

Temporal variations of isoprene low-NO_x and high-NO_x SOA tracers compared to OM are shown in Figs. 4 and 5, respectively. On most days, IEPOX- and MPAN-derived SOA tracers track well with the OM mass loadings. The *r*-values range from 0.40–0.68 for IEPOX-derived SOA tracers and 0.17–0.69 for MPAN-derived SOA tracers. Weak correlations occur only under high NH_3 conditional sampling events for both IEPOX- and MPAN-derived SOA tracers. It is worth noting that the sum of IEPOX-derived SOA tracers contributed substantially (12–19 %) to the total organic matter (OM) in the $PM_{2.5}$ samples collected at this site, showing the atmospheric abundance of the isoprene low-NO_x (or IEPOX-derived) SOA that originates from a single source and pathway (Tables 2 and 3). OM was estimated as OC × 1.8 here for summertime aerosols (Simon et al., 2011). To examine whether or not the differences of isoprene SOA formation between high and low SO_2 or NH_3 conditional sampling protocols were significant, paired-t-tests were performed. The results of the paired-t-tests indicate that the enhancement of IEPOX-derived SOA is statistically significant ($p = 0.012$) under high-SO_2 conditions. No significant enhancement of the sum of isoprene SOA tracers was observed for high or low NH_3 conditional samples ($p = 0.830$).

3.2 Comparisons of continuous inorganic measurements to filter-based IC data

Figure 6 shows comparisons of continuous inorganic measurement to filter-based measurements in this study. Time-weighted average of continuous inorganic data was compared to the IC data from filter samples. Strong correlations were observed for particle NH_4^+ ($r = 0.85$) and SO_4^{2-} ($r = 0.79$) concentrations from the two data sets. The correlation for particle NO_3^- concentrations was ($r = 0.49$) weak, possibly due to low concentrations throughout the study and artifacts in both the filter and continuous measurements.

3.3 Ambient aerosol acidity and isoprene SOA tracers

To estimate aerosol acidity of collected $PM_{2.5}$ samples, the degree of neutralization was calculated as the molar ratio of ammonium to the sum of sulfate and nitrate ($[NH_4^+]/(2 \times [SO_4^{2-}] + [NO_3^-])$). Acidic aerosols are characterized with neutralization degrees less than unity, while neutralization degrees greater than unity imply the samples are neutralized. Figure 7 compares the degree of neutralization for $PM_{2.5}$ samples collected in this study calculated from on-line continuous inorganic measurements and filter-based IC data. In general, most of the aerosol samples have been fully neutralized. However, the frequency distribution from filter-based data shows that most of the samples had the neutralization degree close to unity, while data from continuous inorganic measurements had a more broad distribution. Since filter samples could have absorbed the ambient acidic or basic gases that lead to neutralization of aerosol samples over time during the sampling period, to capture the more representative aerosol acidity, continuous inorganic data were used for further data analysis.

Figure 8 shows the distribution of aerosol samples grouping based on sampling conditions. SO_2 conditional samples are acidic, while NH_3 conditional samples are more neutralized. Figure 9 shows the result from E-AIM II modeling. In situ aerosol pH can only be calculated in very few cases due to the neutralized characteristics of aerosol samples. In addition, some of the samples, although not fully neutralized, were modeled as no liquid water content (LWC) under given RH conditions. Thus, aerosol pH could not be calculated for those samples either. As a result, in situ aerosol pH could be modeled from only 3 samples (out of 50), and the average was found to be 1.71, ranging from 1.69 to 1.75.

Figures 10 and 11 show the correlations between the neutralization degree and the sum of isoprene low-NO_x (or IEPOX-derived) and high-NO_x (or MPAN-derived) SOA tracers, respectively. For IEPOX-derived SOA, the results show that the tracer compounds were weakly enhanced with less-neutralized aerosols, but no clear associations were observed for NH_3 conditional samples. For MPAN-derived SOA, no clear associations were observed for either SO_2 or NH_3 conditional samples. This could be due to most of the aerosol samples being fully neutralized. However, it is worth noting that prior chamber work has shown that under high-NO_x conditions no enhancement in SOA mass was observed due to the presence of acidified sulfate seed aerosol where as under low-NO_x conditions SOA mass was enhanced due to the presence of acidified sulfate seed aerosol (Surratt et al., 2006). Furthermore, it was suspected that the time scale for our field sampling approach might not be long enough in order to capture SO_2 conversion to SO_4^{2-}. Moreover, the aerosol samples could have formed upwind of the sampling site, and thus, were associated to a more aged and regional (background) aerosol type. Distinguishing weak correlations from meteorological effects on measured isoprene SOA levels is challenging, since the isoprene SOA might have been formed upwind, but not formed locally. Our findings are in agreement with Tanner et al. (2009), who previously reported that at the YRK site no consistent positive correlations were found between changes in OC or TC levels and aerosol acidity, which was estimated by nitrate-corrected ammonium-to-sulfate ratios, even with time lag up to 6 h. Aerosol acidity at this site is relatively low due to nearby agricultural sources of NH_3. In addition, recent research by Liggio et al. (2011) reported that the rate of aerosol neutralization by NH_3 uptake is significantly reduced in the presence of ambient organic gases on time scales ∼10 min to several hours, while acidic aerosol mixed with organic-free air and NH_3 was neutralized on a time scale < 1 min. This reduction in NH_3 uptake was concurrent with an increase in the amount of particle-phase organics. Thus, our NH_3 conditional sampling approaches might not be able to capture the neutralization effects on aerosol acidity and isoprene SOA formation, since this would not be an instantaneous process.

3.4 Particle sulfate loadings and isoprene SOA tracers

Figures 12 and 13 show correlations between isoprene low-NO_x and high-NO_x SOA tracers and the particle sulfate loadings, with $r = 0.51$–0.58 for IEPOX-derived SOA tracers and $r = 0.34$–0.36 for MPAN-derived SOA tracers, respectively. Figure 14 shows correlations between the sum of isoprene SOA tracers (combining IEPOX- and MPAN-derived SOA) and particle SO_4^{2-} loadings for all $PM_{2.5}$ samples collected during SO_2 conditional sampling period ($r = 0.44$) and the NH_3 conditional sampling period ($r = 0.58$) in this study. Positive correlations were observed for all conditions. These condition-independent correlations may suggest that aerosol sulfate could serve as the surface area that facilitates the reactive uptake IEPOX onto preexisting aerosols. Although acidified sulfate aerosol has been demonstrated to enhance isoprene SOA formation (Surratt et al., 2007b, 2010), laboratory studies are lacking that systematically examine the effect of varying surface area of pre-existing aerosol on isoprene SOA formation as a function of liquid water content, aerosol acidity, and chemical composition. More work is needed to understand if this is a surface- or bulk-limited process and how this changes with environmental conditions.

4 Conclusions

Analyses of $PM_{2.5}$ samples collected from the rural southeastern US by off-line chromatography coupled with mass spectrometry techniques show substantial contributions (12–19 %) of isoprene low-NO_x SOA tracers to organic aerosol mass in this region, revealing the importance for heterogeneous chemistry of IEPOX. Conditional sampling approaches employed in this study indicate that IEPOX-derived SOA formation is enhanced under higher SO_2 conditions ($p = 0.012$). In contrast, conditional sampling did not show significant influence of NH_3 levels on low-NO_x isoprene SOA concentrations. Thus, it is possible that the effects (or degree) of NH_3 neutralization were masked by other confounding factors or atmospheric processes occurring simultaneously. Particle sulfate loadings have moderate positive correlations with the sum of isoprene SOA tracers for all conditions, suggesting a role of surface- or bulk-limited chemistry for isoprene SOA formation.

Weak correlations between isoprene SOA tracers and aerosol acidity suggest there might not be enough time for our sampling approach to observe SO_2 conversion to sulfuric acid that provides aerosol acidity. Evaporation of volatile particle constituents, such as NO_3^-, would affect the estimate of aerosol acidity; however, NO_3^- concentrations were generally too low to make a big difference in the neutralization calculation. In addition, during the volatilization process it remains uncertain if this is primarily HNO_3 or HNO_3 plus NH_3 leaving the filters. The latter would not have any effect on acidity. Very few samples could be modeled using E-AIM II, and thus, our ability to elucidate potential effects of aqueous-phase chemistry on isoprene SOA formation is quite limited. Furthermore, regional-scale transport could have brought isoprene SOA formed upwind that masked the effects of aerosol acidity. Future work is needed to differentiate the effects of enhanced BSOA formation from regional-scale transport and aqueous-phase chemistry.

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Table 1. Summary of average meteorological data and complementary collocated measurements.

Condition	High SO_2	Low SO_2	High NH_3	Low NH_3
Sampling Period	25 Jun 2010–14 Jul 2010		29 Jul 2010–6 Aug 2010	
O_3 (ppb)	46.9 ± 3.0	46.1 ± 2.6	43.4 ± 3.5	48.7 ± 3.5
CO (ppb)	141.8 ± 4.6	145.7 ± 6.6	167.7 ± 10.2	161.1 ± 11.3
SO_2 (ppb)	1.1 ± 0.1	0.2 ± 0.0	0.7 ± 0.3	0.7 ± 0.2
NO (ppb)	0.2 ± 0.0	0.2 ± 0.0	0.3 ± 0.1	0.2 ± 0.0
NO_2 (ppb)	1.2 ± 0.2	1.1 ± 0.2	1.3 ± 0.4	1.5 ± 0.4
NO_y (ppb)	2.8 ± 0.3	2.6 ± 0.3	3.0 ± 0.5	2.9 ± 0.4
HNO_3 (ppb)	0.6 ± 0.0	0.6 ± 0.1	0.6 ± 0.1	0.6 ± 0.1
NH_3 (ppb)	2.2 ± 0.4	2.3 ± 0.4	2.6 ± 0.3	1.4 ± 0.2
NEPH (Mm^{-1})	50.1 ± 3.4	47.6 ± 4.6	71.8 ± 7.4	65.1 ± 9.6
SO_4^{2-} ($\mu g\,m^{-3}$)	4.1 ± 0.4	3.5 ± 0.5	3.3 ± 0.3	3.3 ± 0.3
NO_3 ($\mu g\,m^{-3}$)	0.2 ± 0.0	0.2 ± 0.1	0.3 ± 0.1	0.2 ± 0.1
NH_4^+ ($\mu g\,m^{-3}$)	1.4 ± 0.1	1.3 ± 0.1	1.6 ± 0.2	1.4 ± 0.2
BC ($\mu g\,m^{-3}$)	0.3 ± 0.0	0.3 ± 0.0	0.3 ± 0.0	0.3 ± 0.1
OC ($\mu g\,m^{-3}$)	3.2 ± 0.1	3.1 ± 0.3	3.6 ± 0.2	3.3 ± 0.3
$PM_{2.5}$ ($\mu g\,m^{-3}$)	13.5 ± 0.8	12.2 ± 1.1	16.1 ± 1.2	14.9 ± 2.0
Temp (°C)	27.4 ± 0.4	27.4 ± 0.7	29.3 ± 1.0	29.2 ± 0.6
RH (%)	66.3 ± 2.5	65.7 ± 3.0	67.1 ± 4.8	66.5 ± 3.6
BP (mbar)	969.9 ± 0.7	969.3 ± 0.7	968.4 ± 0.9	967.5 ± 0.7
SR ($W\,m^{-2}$)	526.2 ± 44.1	461.5 ± 42.0	600.8 ± 69.7	290.6 ± 48.5

Table 2. Isoprene SOA tracers quantified in $PM_{2.5}$ samples (ng m^{-3}) collected under high and low SO_2 conditions.

Isoprene low-NO_x SOA tracers (IEPOX-derived SOA tracers)	High SO_2	Low SO_2
2-methyltetrols	316.7 ± 21.5	283.9 ± 33.7
C_5-alkene triols	319.6 ± 32.4	258.8 ± 33.0
3-MeTHF-3,4-diols	11.4 ± 1.4	7.5 ± 1.4
Dimers	1.3 ± 0.3	1.2 ± 0.3
IEPOX-derived organosulfate (*m/z* 215)	107.3 ± 14.8	92.1 ± 19.5
Organosulfate of dimers (*m/z* 333)	2.7 ± 0.5	2.7 ± 0.7
Σ IEPOX SOA tracers/OM[a]	13.3 %	11.9 %
Isoprene high-NO_x SOA tracers (MPAN-derived SOA tracers)		
2-MG	7.4 ± 0.8	8.6 ± 1.5
MPAN-derived organosulfate (*m/z* 199)	11.9 ± 0.9	11.8 ± 2.2
Σ MPAN SOA tracers/OM[b]	0.34 %	0.36 %

[a] Paired-t-test ($n = 16$); $p = 0.012$.
[b] Paired-t-test ($n = 16$); $p = 0.754$.

Table 3. Isoprene SOA tracers quantified in $PM_{2.5}$ samples ($ng\,m^{-3}$) collected under high and low NH_3 conditions.

Isoprene low-NO_x SOA tracers (IEPOX-derived SOA tracers)	High NH_3	Low NH_3
2-methyltetrols	572.7 ± 82.6	414.0 ± 83.6
C_5-alkene triols	524.1 ± 92.6	482.0 ± 133.5
3-MeTHF-3,4-diols	19.0 ± 3.5	14.4 ± 3.8
Dimers	2.1 ± 0.6	2.4 ± 0.9
IEPOX-derived organosulfate (*m/z* 215)	104.3 ± 40.0	196.5 ± 48.9
Organosulfate of dimers (*m/z* 333)	3.1 ± 1.0	4.8 ± 1.5
Σ IEPOX SOA tracers/OM[a]	19.1 %	18.6 %
Isoprene high-NO_x SOA tracers (MPAN-derived SOA tracers)		
2-MG	9.9 ± 1.3	7.6 ± 1.3
MPAN-derived organosulfate (*m/z* 199)	9.9 ± 2.3	13.6 ± 3.2
Σ MPAN SOA tracers/OM[b]	0.31 %	0.37 %

[a] Paired-t-test ($n = 9$); $p = 0.830$.

[b] Paired-t-test ($n = 9$); $p = 0.506$.

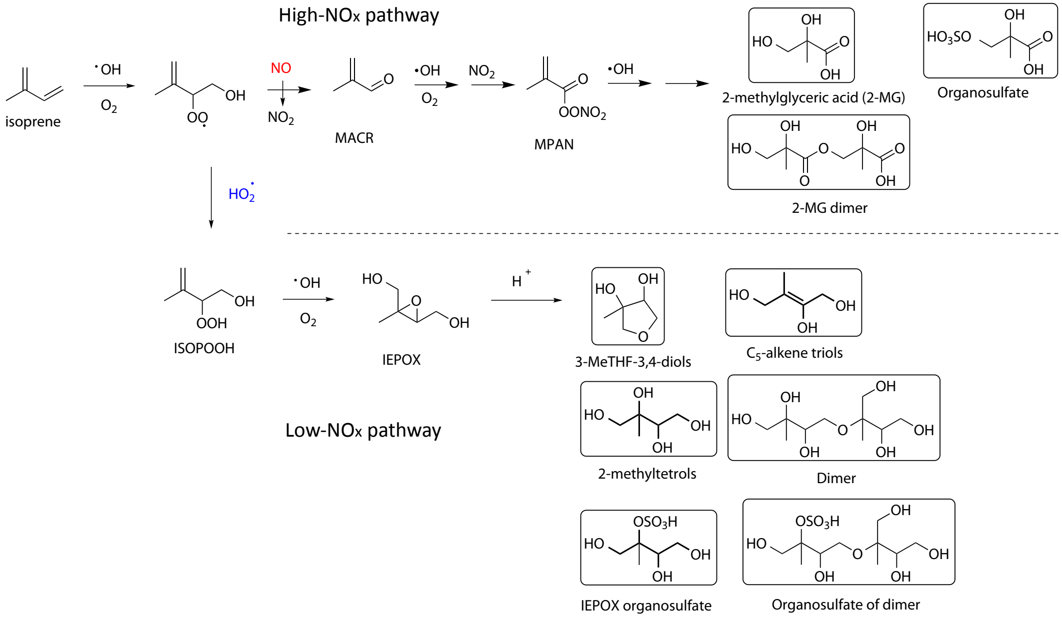
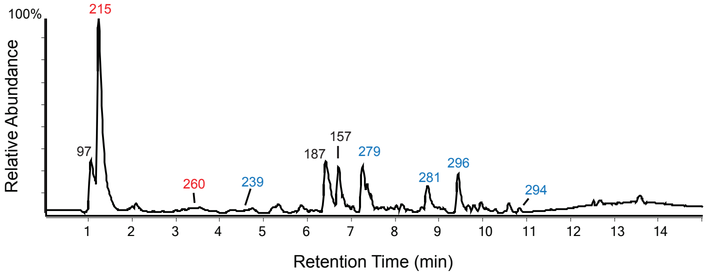


Fig. 1. Proposed chemistry leading to isoprene SOA: NO_x-dependent pathways (Surratt et al., 2010). For simplicity, only the *cis*-*β*-IEPOX isomer is shown for IEPOX in the low-NO_x (or NO-limited) pathway.

(a) UPLC/ESI-HR-Q-TOFMS data



Isoprene-derived Organosulfates

m/z 215: $C_5H_{12}O_7S$

m/z 260: $C_5H_{11}NO_9S$ (nitrated)

Monoterpene-derived Organosulfates

m/z 239: $C_7H_{12}O_7S$

m/z 279: $C_{10}H_{16}O_7S$

m/z 281: $C_{10}H_{18}O_7S$

m/z 294: $C_{10}H_{17}NO_7S$ (nitrated)

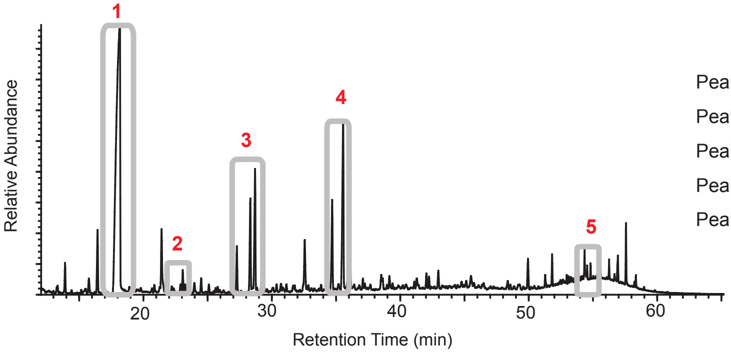
m/z 296: $C_9H_{15}NO_8S$ (nitrated)

Other peaks

m/z 97: sulfate

m/z 187 and *m/z* 157: terpenoid acids

(b) GC/EI-MS analysis with prior trimethylsilylation



Peak 1: sulfate

Peak 2: 3-methyltetrahydrofuran-3,4-diols

Peak 3: C5-alkene triols

Peak 4: 2-methyltetrols

Peak 5: dimers

Fig. 2. Representative **(a)** UPLC/ESI-HR-Q-TOFMS base peak chromatogram and **(b)** GC/EI-MS total ion chromatogram of the $PM_{2.5}$ sample collected at YRK on 27 June 2010 under high-SO_2 conditions, showing isoprene-derived SOA tracers were major SOA constituents detected at this site during summertime.

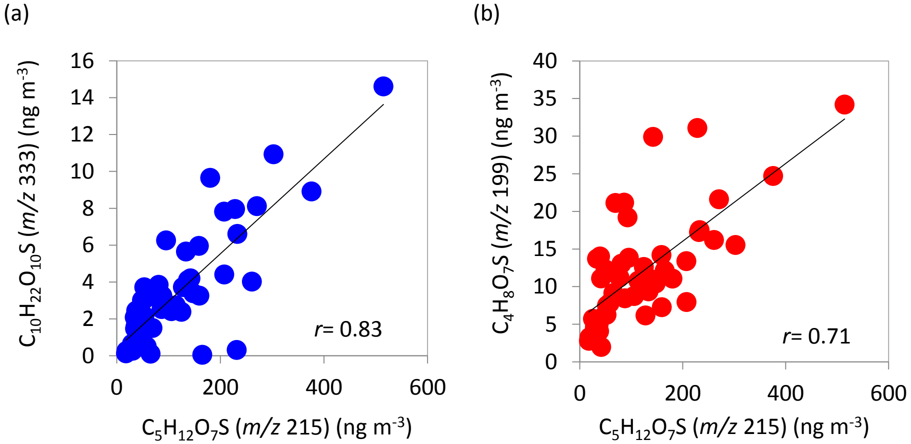


Fig. 3. Correlations between isoprene-derived organosulfates: **(a)** Correlations between IEPOX-derived organosulfate (*m/z* 215) and organosulfate derivatives of IEPOX-derived dimers (*m/z* 333) support the common isoprene low-NO_x pathway and formation mechanisms of these two tracers. **(b)** Correlations between the IEPOX-derived organosulfate (*m/z* 215) and the MPAN-derived organosulfate (*m/z* 199) suggest similar limiting factors for organosulfate formation, as these two species have been known to form from isoprene photooxidation through low-NO_x and high-NO_x pathways, respectively.

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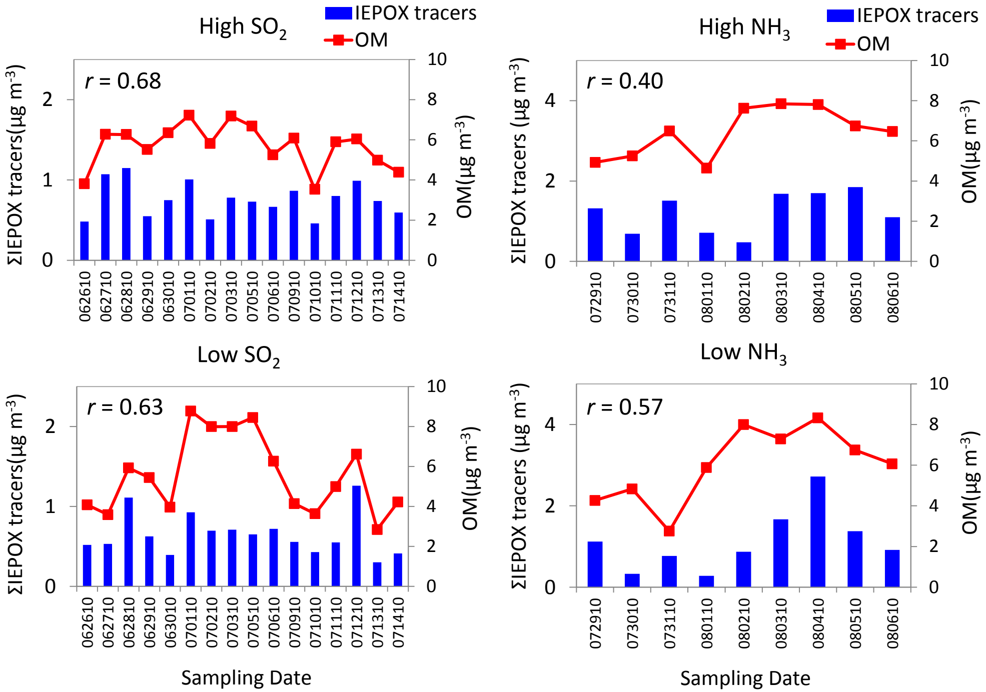

Fig. 4. Temporal variations of low-NO$_x$ SOA tracers and OM.

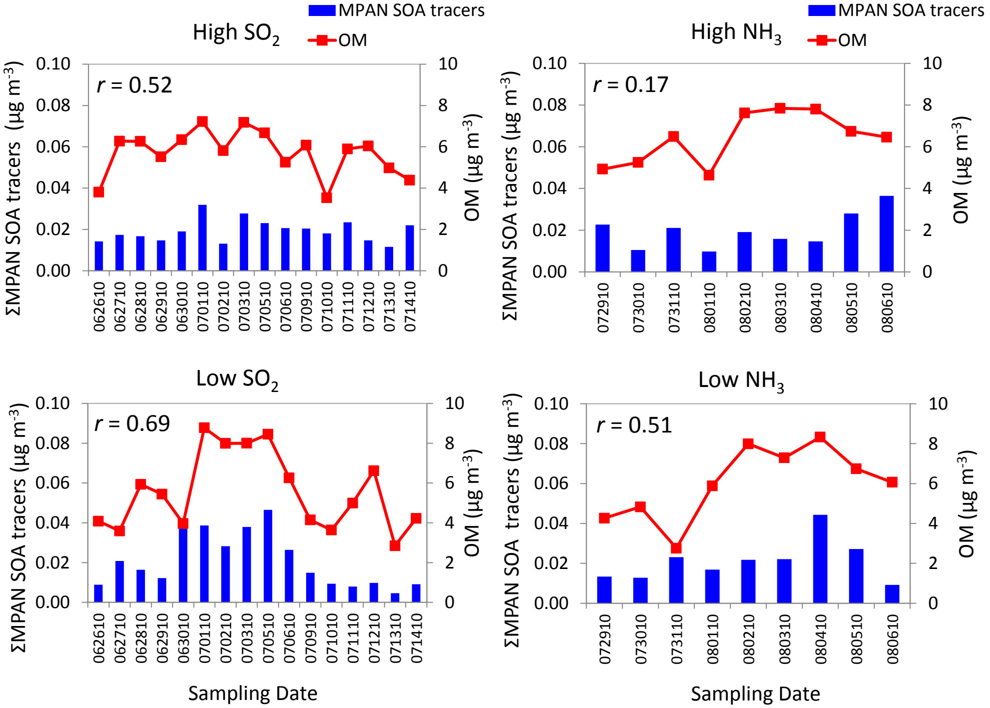

Fig. 5. Temporal variations of isoprene high-NO$_x$ SOA tracers and OM.

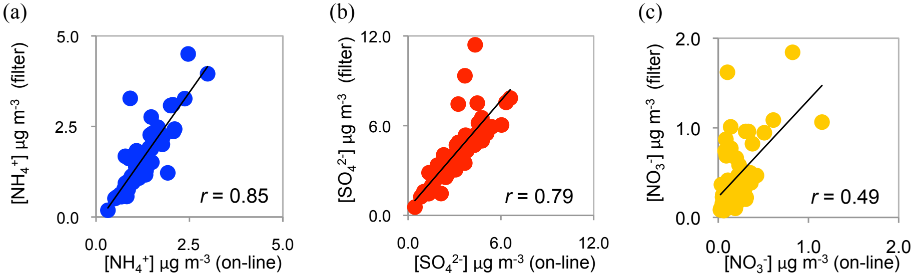

Fig. 6. Comparisons of on-line continuous particle analyzer data and filter-based IC measurements: **(a)** NH_4^+, **(b)** SO_4^{2-}, **(c)** NO_3^-.

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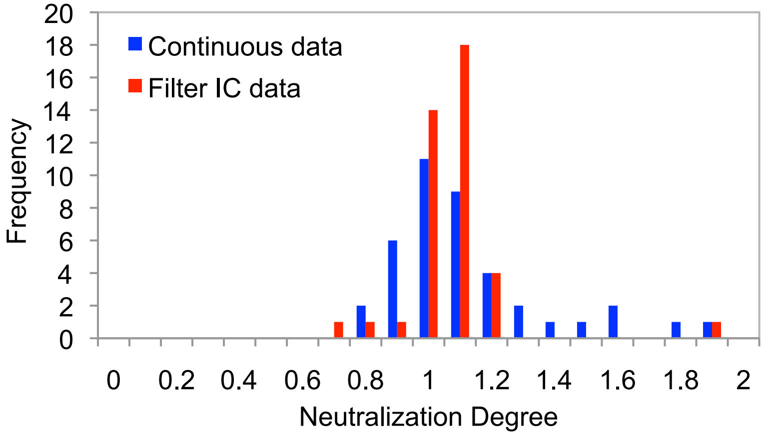

Fig. 7. Frequency distribution of the neutralization degree from aerosol samples calculated by on-line continuous particle analyzer data (blue) and filter-based IC data (red).

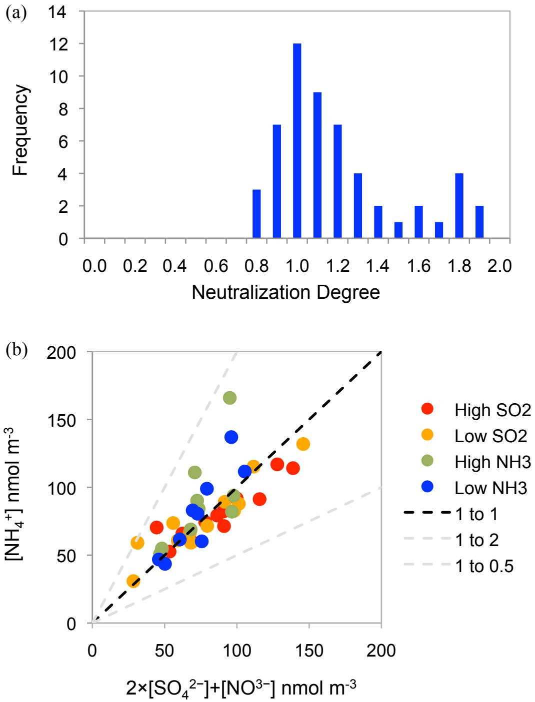

Fig. 8. (a) Frequency distribution of the neutralization degree from aerosol samples **(b)** NH_4^+ to SO_4^{2-} plus NO_3^- ratios.

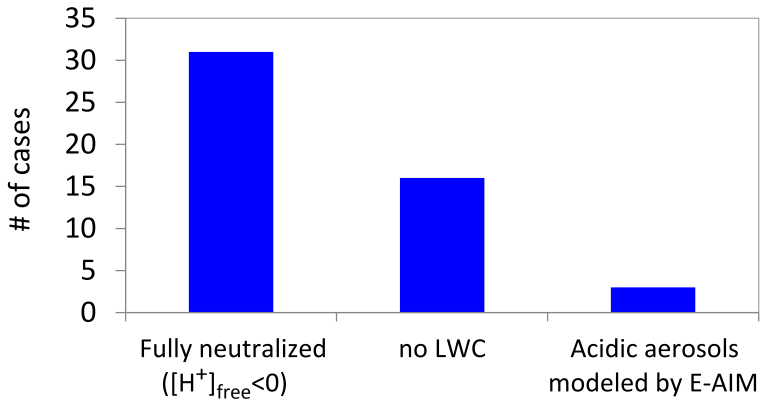

Fig. 9. E-AIM II modeling: in situ aerosol pH can only be calculated in very few cases (3 out of 50) in our samples. 31 aerosol samples were calculated as fully neutralized ($[H^+]_{free} < 0$) that could not be modeled by E-AIM II. 16 samples were modeled as no LWC.

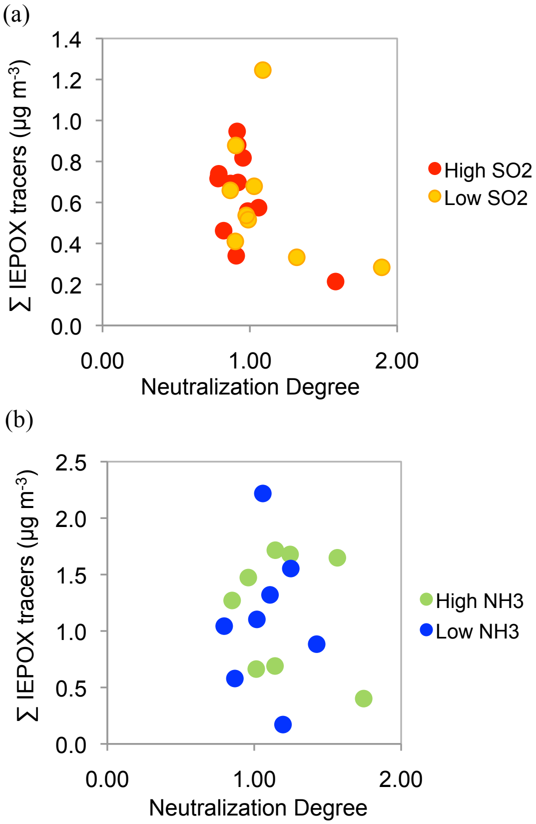

Fig. 10. Effects of aerosol acidity on IEPOX-derived SOA formation: **(a)** SO_2 conditional samples **(b)** NH_3 conditional samples. The sum of IEPOX-derived SOA tracers was enhanced with less-neutralized (i.e., more acidic) aerosols for SO_2 conditional samples, but no clear associations were observed for NH_3 conditional samples.

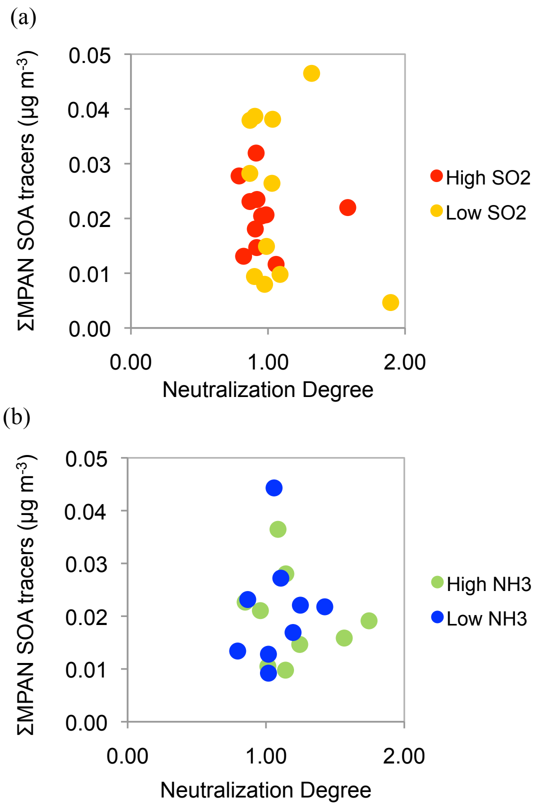

Fig. 11. Effects of aerosol acidity on isoprene high-NO_x SOA formation: **(a)** SO_2 conditional samples **(b)** NH_3 conditional samples. No clear associations between aerosol acidity and the sum of MPAN-derived SOA tracers were observed for either SO_2 or NH_3 conditional samples.

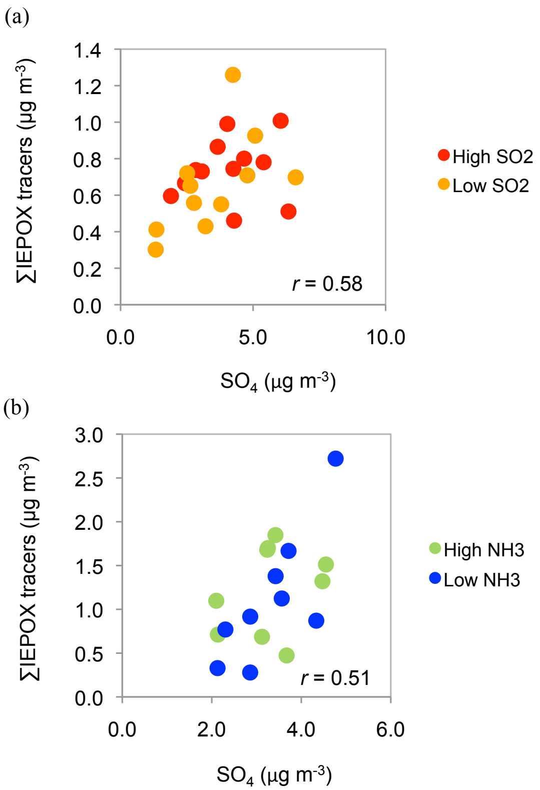

Fig. 12. Correlations between the sum of IEPOX SOA tracers and the particle sulfate loadings: **(a)** SO_2 conditional samples **(b)** NH_3 conditional samples. Positive correlations were observed for both SO_2 and NH_3 conditional samples, indicating a role of particle sulfate loadings for providing surface area that limits the IEPOX uptake and forming SOA tracers.

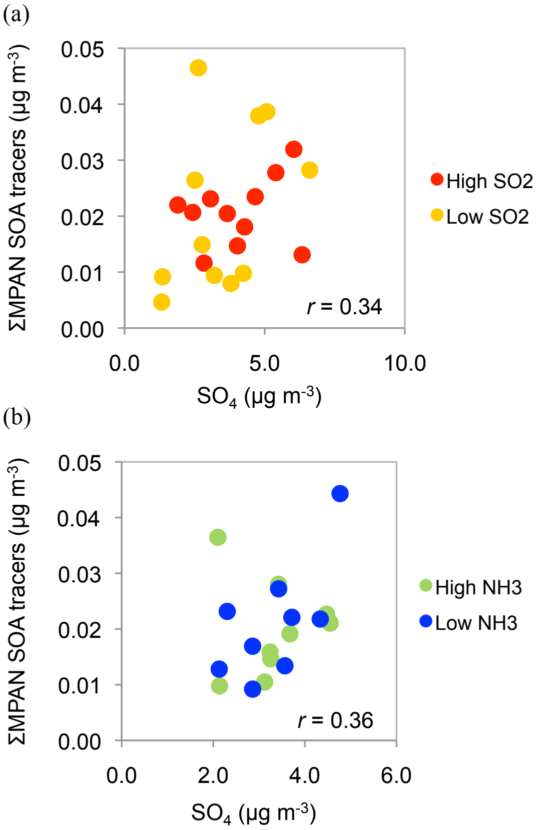

Fig. 13. Correlations between the sum of MPAN-derived SOA tracers and the particle sulfate loadings: **(a)** SO_2 conditional samples **(b)** NH_3 conditional samples. Positive correlations were observed for both SO_2 and NH_3 conditional samples, suggesting surface area could be a limiting factor that modulates isoprene high-NO_x SOA formation.

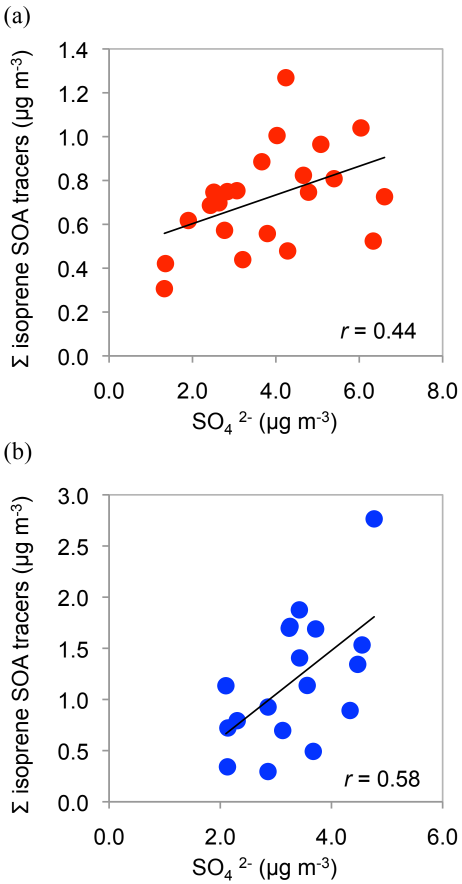

Fig. 14. Correlations between the sum of isoprene SOA tracers (combining IEPOX- and MPAN-derived SOA) and the particle sulfate loadings for all $PM_{2.5}$ samples collected in this study from **(a)** 25 June to 14 July 2010 (SO_2 conditional sampling period) and **(b)** 29 July 2010 to 6 August 2010 (NH_3 conditional sampling period).