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Limited formation of isoprene epoxydiols–derived secondary organic aerosol (IEPOX-SOA) under NO_x-rich environments in Eastern China

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Key points

- First real-time characterization of IEPOX-SOA in Eastern China
- The formation of IEPOX-SOA under NO_x-rich environments is limited
- Source analysis elucidated the interactions between biogenic and anthropogenic emissions

Abstract

Secondary organic aerosol (SOA) derived from isoprene epoxydiols (IEPOX) have potential impacts on regional air quality and climate, yet is poorly characterized under NO_x-rich ambient environments. We report the first real-time characterization of IEPOX-derived SOA (IEPOX-SOA) in Eastern China in summer 2013 using comprehensive ambient measurements, along with model analysis. The ratio of IEPOX-SOA to isoprene high-NO_x SOA precursors, e.g., methyl vinyl ketone and methacrolein, and the reactive uptake potential of IEPOX were lower than those generally observed in regions with prevailing biogenic emissions, low NO_x levels and high particle acidity, elucidating the suppression of IEPOX-SOA formation under NO_x-rich environments. IEPOX-SOA showed high potential source regions to the south with large biogenic emissions, illustrating that the interactions between biogenic and anthropogenic emissions might have played an important role in affecting the formation of IEPOX-SOA in polluted environments in Eastern China.

1. Introduction

Isoprene (2-methyl-1,3-butadiene, C₅H₈) is the most abundant non-methane hydrocarbon compound emitted in the Earth's atmosphere [Guenther *et al.*, 2012]. Oxidation of isoprene can form secondary organic aerosol (SOA), which has potential impacts on human health [Y-H Lin *et al.*, 2016], air quality [von Schneidemesser *et al.*, 2011], and regional climate [Guenther *et al.*, 2012]. Isoprene epoxydiols (IEPOX), a key gas-phase oxidation product of isoprene, plays an especially significant role in ambient isoprene SOA formation [Surratt *et al.*, 2010]. For example, IEPOX-SOA can account for more than 30 % of total organic aerosol (OA) in the Amazonian forest [Chen *et al.*, 2015] and the southeastern US [Budisulistiorini *et al.*, 2013; Hu *et al.*, 2015]. Although IEPOX-derived SOA has been widely identified in isoprene-rich environments [Hu *et al.*, 2015], e.g., the densely forested regions [Chen *et al.*, 2015], there is still a great challenge to improve modeling frameworks for evaluating its influence on air quality and climate change, due to the lack of observed IEPOX-SOA under polluted urban environments.

The hydroperoxyl radicals (HO_2) pathway has been recognized as a dominant mechanism to form IEPOX-SOA through acid-catalyzed multiphase chemistry under low- NO_x conditions [Archibald *et al.*, 2011; Surratt *et al.*, 2010]. The formation of IEPOX-SOA via HO_2 -pathway can be shifted to the NO and NO_2 pathway under high- NO_x conditions, producing gas-phase methyl vinyl (MVK) and methacrolein (MACR), the first-generation photo-oxidation products of isoprene [Surratt *et al.*, 2010; Surratt *et al.*, 2006]. Further oxidation of MACR leads to the formation of either methacrylic acid epoxide (MAE) [Y-H Lin *et al.*, 2013a] or hydroxymethyl-methyl- α -lactone (HMML) [Nguyen *et al.*, 2015]. There is a direct chemical evidence for MAE in the gas phase [Y H Lin *et al.*, 2013b] although its reactive uptake chemistry is fairly slow under acidic conditions [Riedel *et al.*, 2015]. Nguyen *et al.* [2015] recently suggested that HMML likely leads to the formation of most SOA from isoprene under high- NO_x conditions. The isoprene-SOA related tracers, e.g., C_5 -alkene triols, 2-methylglyceric acid, and 2-methyltetrols (MTLs), have been mainly detected so far via filter-based analytical approaches [Ding *et al.*, 2016; Rattanavaraha *et al.*, 2016]. Recent studies conducted with Aerodyne aerosol mass spectrometer (AMS) [Canagaratna *et al.*, 2007] and/or aerosol chemical speciation monitor (ACSM) [Ng *et al.*, 2011], followed by positive matrix factorization (PMF) analysis [Paatero and Tapper, 1994], have been shown to be capable of quantifying IEPOX-SOA [Budisulistiorini *et al.*, 2013; Hu *et al.*, 2015]. However, despite extensive efforts in characterization of IEPOX-SOA formation chemistry in IEPOX-rich areas, only few studies have been conducted in densely anthropogenic-dominated emission regions with high NO_x levels, especially in East Asia.

Eastern China has been suffering from severe fine particle pollution during the past decade [Guo *et al.*, 2014; R J Huang *et al.*, 2014]. The contribution of SOA to fine particles was found to be substantial in this region, mainly due to high anthropogenic emissions and rapid formation of secondary aerosols [Sun *et al.*, 2014; Y Zhang *et al.*, 2015a]. Recent studies also showed significant influences of biogenic emissions on air quality in this region [Geng *et al.*, 2011]. Therefore, this region provides a unique environment to investigate the interaction between anthropogenic activities and biogenic emissions, and its impacts on atmospheric IEPOX-SOA chemistry. In this study, an ACSM was deployed in a polluted urban city (i.e., Nanjing in Eastern China) in summer 2013 for real-time characterization of aerosol particle composition and sources. Here we report the identification and quantification of an IEPOX-SOA factor via PMF analysis of OA spectra, and investigate the potential of the IEPOX reactive kinetics uptake on particles influenced by anthropogenic emissions using an

acid-catalyzed mechanism model [Eddingsaas *et al.*, 2010]. Also, the potential sources of IEPOX-SOA are illustrated using potential source contribution function (PSCF) [Polissar *et al.*, 2001] and non-parametric wind regression (NWR) [Henry *et al.*, 2009] analysis.

2. Experiment

2.1 Sampling site and measurements

All the measurements were conducted on the roof of a six-story building (approximately 18 m above the ground) at Jiangsu Environment Monitoring Center in urban Nanjing (32°03' N, 118°46' E). This sampling site is extensively described in supporting information (Sect. S1). Briefly, it is a typical urban site mainly influenced by anthropogenic activities, such as traffic and cooking emissions [Y J Zhang *et al.*, 2015b]. Some industries [Wang *et al.*, 2016], like power, iron-steel, and oil refineries, are located approximately 15 - 25 km to the north and south. The spatial distributions of isoprene emissions (Fig. S1) suggest that the sampling site is subject to influences from mixed anthropogenic and biogenic emissions. The non-refractory submicron aerosol (NR-PM₁) species, including OA, sulfate, nitrate, ammonium and chloride, were measured on-line using the ACSM with a ~30 min time resolution. A more detailed description of the ACSM can be found elsewhere [Ng *et al.*, 2011; Sun *et al.*, 2012]. The oxidation products of isoprene, MVK and MACR, were measured every hour using an on-line Gas Chromatography-MS/Flame Ionization Detector (GC-MS/FID) system that has been described by Yuan *et al.* [2012]. Particle number size distributions from ~13 nm to 600 nm were measured using a scanning mobility particle sizer that consists of a differential mobility analyzer (TSI Model 3081) and a condensation particle counter (TSI Model 3775). Gaseous species, including NO-NO₂-NO_x (model 42i), O₃ (model 49i), and SO₂ (model 43i), were measured using collocated Thermo Scientific gas analyzers. Gas-phase ammonia (NH₃) was measured by a Monitor for Aerosols and Gases in Air (MARGA). The total PM₁ and PM_{2.5} mass concentrations were measured using two Met One systems (BAM-1020). In addition, meteorological parameters, such as temperature (*T*), relative humidity (RH), wind speed (WS), and wind direction (WD), were obtained from a meteorological station at the same location. A summary of the meteorological conditions is given in Table S1.

2.2 Data analysis.

The ACSM data were analyzed by standard data analysis software [Allan *et al.*, 2004] written in IGOR Pro. The collection efficiency (CE) values used for the ACSM data analysis were based on the composition-dependent $CE = \max(0.45, 0.0833 + 0.9167 \times \text{ANMF})$ [Middlebrook *et al.*, 2012], in which ANMF is the mass fraction of NH_4NO_3 in $\text{PM}_{1.0}$. Ionization efficiency (IE) and relative ionization efficiencies (RIEs) were calibrated with pure ammonium nitrate (see Sect. S1) following the procedures in Ng *et al.* [2011]. The satisfactory inter-comparison results between NR- $\text{PM}_{1.0}$ and total $\text{PM}_{1.0}$ and $\text{PM}_{2.5}$ can be found in Figure S3.

PMF with ME-2 algorithm was performed on the ACSM OA mass spectra, and the results were then carefully evaluated using the Source Finder (SoFi) toolkit [Canonaco *et al.*, 2013]. Four OA factors were identified, including three oxygenated factors, i.e., IEPOX-SOA, a less oxidized oxygenated OA (LO-OOA), and a more oxidized OOA (MO-OOA), and a primary OA factor (hydrocarbon-like OA, HOA). The detailed reasons for the selection of this 4-factor solution can be found in Supporting Information (Sect. S2).

Particle liquid water content (LWC) associated with inorganic species, and particle acidity (pH) were predicted using a thermodynamic model (ISORROPIA-II) [Fountoukis and Nenes, 2007], along with the “forward mode” for metastable aerosol. A modified resistor model [Gaston *et al.*, 2014] based on acid-catalyzed mechanism [Eddingsaas *et al.*, 2010] was applied for modeling the potential of IEPOX reactive uptake (γ_{IEPOX}) and the first-order reaction rate constant in the aqueous phase (k_{aq}). More details are given in Supporting Information (Sect. S3).

48-h backward trajectories were obtained from the Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model [Draxler, 2003], developed by National Oceanic and Atmospheric Administration (NOAA)/Air Resources Laboratory (ARL), for simulating air mass arrivals at 100 m altitude (a.g.l.) with 1 h resolution. PSCF and NWR analysis in this study were using the ZeFir toolkit [Petit *et al.*, 2017]. PSCF was performed on the combined measurements and the corresponding air masses histories from HYSPLIT outputs (see details in section S3). NWR was also performed on OA factors, NR- $\text{PM}_{1.0}$ species, and gas-phase tracers. In brief, NWR is a source-to-receptor model to estimate wind-dependent sources of atmospheric pollutants. The percent of a given pollutant which is originated from a specific wind sector can be identified and quantified using kernel smoothing methods [Henry *et al.*, 2009].

3. Results and discussion

Figure 1 shows the temporal variations of meteorological parameters (T , RH, WD, and air masses history), gas-phase species (O_3 , NO_2 , isoprene, and MVK+MACR), and IEPOX-SOA and sulfate. The average mixing ratio of NO_x is 21.4 ppb, which is about 20 times higher than that (0.1 – 2 ppb) at Look Rock, Tennessee in the southeastern US where high IEPOX-SOA concentrations were reported [Budisulistiorini *et al.*, 2015]. Also, the average NR- PM_{10} mass loading is approximately 3 times higher, indicating an environment with substantial anthropogenic emissions in this study. The three OOA factors dominate OA for the entire study, on average accounting for 78.0% of the total OA mass. This is consistent with the results from a previous study in Shanghai, a megacity near Nanjing, showing a predominance of SOA over primary aerosols during the summer season [X F Huang *et al.*, 2012]. The average IEPOX-SOA concentration is $0.33 \pm 0.19 \mu\text{g}/\text{m}^3$ for the entire study, accounting for 3.8% of the total OA. Compared to the IEPOX-rich regions, such as Yorkville ($4 \mu\text{g}/\text{m}^3$), Georgia ($3 \mu\text{g}/\text{m}^3$), and Jefferson ($2 \mu\text{g}/\text{m}^3$) in the southeastern US [Xu *et al.*, 2015a], IEPOX-SOA shows a much smaller average concentration under polluted urban environments in Eastern China.

The formation of isoprene peroxy radicals (ISOPOO) is derived from isoprene reaction with OH radical, but their fate is dominated by NO- HO_2 conditions in the atmosphere [Liu *et al.*, 2016; Paulot *et al.*, 2009]. ISOPOO mainly reacts with NO and produces NO_2 and MVK and MACR under NO-dominant conditions [Liu *et al.*, 2016; Surratt *et al.*, 2010]. It can also react with HO_2 radicals to dominantly produce hydroxyhydroperoxides (ISOPOOH) [Paulot *et al.*, 2009]. As shown in Figure 2a, IEPOX-SOA, as well as O_x and MVK+MACR concentrations are increasing with the $[NO_2]/[NO]$ ratio, implying that enhanced O_3 and/or OH concentrations might increase both isoprene oxidation products via HO_2 and NO pathways. Some contributions of MACR and MVK could come from decomposition of other products (such as ISOPOOH) [St. Clair *et al.*, 2016], which might be another potential reason for the positive relationship between MVK + MACR and IEPOX-SOA. However, the formation of IEPOX via RO_2+HO_2 pathway could be suppressed due to the high ambient NO loadings. In addition, Jacobs *et al.* [2014] demonstrated that further oxidation of the first-generation isoprene hydroxynitrates in the presence of high NO yielded much lower IEPOX than that from the oxidation of low- NO_x ISOPOOH products [Paulot *et al.*, 2009]. Thus RO_2+NO pathway might also produce IEPOX under high NO_x conditions, and thereby to form a very small fraction of ambient IEPOX-SOA [Jacobs *et al.*, 2014; Xu *et al.*, 2016].

The increase of IEPOX-SOA is much higher during high O₃ episode compared to the entire period (Fig. 2a), which could be explained by the formation and subsequent isoprene photooxidation of ISOPOOH, forming IEPOX-SOA via HO₂-pathway. Furthermore, recent works showed that MTLs, a component of IEPOX-SOA for isoprene low-NO_x pathway SOA tracers, can be formed via the reaction of isoprene with O₃ in the presence of acidic aerosols [Rattanavaraha *et al.*, 2016; Riva *et al.*, 2016]. Although it remains unclear to quantify exactly isoprene with O₃ reactions to yield MTLs, the products from these reactions are certainly undergoing acid-catalyzed multiphase chemistry to yield MTLs that could contribute to IEPOX-SOA burden. Although the isoprene mixing ratio in this study is approximately 4 times lower than those in the southeastern US, the average isoprene emission flux seems to be quite similar (~ 1.7-1.9 mg m⁻² hr⁻¹) for both area, as obtained from the model (Fig. S11). The average ratio of [MVK+MACR]/[Isoprene] is 1.31 in this study, which is approximately 3 times than that in the southeastern US (Fig. S12) [Xiong *et al.*, 2015]. However, the [IEPOX-SOA]/[MVK+MACR] is nearly 5 times lower than that under relatively low-NO_x environments during summertime 2013 in the southeastern US [Budisulistiorini *et al.*, 2015; Xiong *et al.*, 2015; Xu *et al.*, 2015a]. This is likely due to the rapid oxidation processes of isoprene to largely yield NO_x-pathway isoprene oxidation products under NO_x-rich environments. For example, once isoprene emitted into the atmosphere, it can be rapidly oxidized by OH radical [Paulot *et al.*, 2009], and forms MVK and MACR [Liu *et al.*, 2016; Surratt *et al.*, 2010; Surratt *et al.*, 2006]. These results suggest that RO₂ + NO reaction pathway might dominate the isoprene SOA chemistry under NO_x-rich environments in Eastern China although both regimes of RO₂ + HO₂ and RO₂ + NO are prevalent. This may also constrain the conversion efficiency of isoprene to gas-phase IEPOX, leading to an impediment of IEPOX-SOA formation.

To investigate the effects of particle LWC, particle acidity (H⁺_(aq)), and sulfate on IEPOX-SOA formation, a multivariate linear regression analysis was performed following the procedures in Xu *et al.* [2015a] (Table S2). Sulfate presents a statistically significant positive relationship ($P < 0.0001$) with IEPOX-SOA, and IEPOX-SOA is correlated well with the total particle surface area ($r = 0.78$, Fig. 3a). We also note that the ratio of IEPOX-SOA to MVK+MACR is enhanced during periods with higher sulfate loadings (Fig. 2b). These results suggest that IEPOX-SOA formation in urban Nanjing is likely mediated by pre-existing sulfate particles (i.e., nucleophile and/or salting-in effect) which may facilitate the ring-opening reactions of IEPOX and provide particle area required for IEPOX reactive

uptake [Y-H Lin *et al.*, 2012; Xu *et al.*, 2015a]. However, the efficiency of IEPOX-SOA formation might be lower than that in the southeastern US [Xu *et al.* 2015a] as indicated by the more than 10 times lower regression slope (0.03 vs. 0.42). Interestingly, particle water shows a statistically significant relationship ($P < 0.0001$) with IEPOX-SOA, but with a negative regression coefficient (-0.005) (Table S2). As shown in Fig. 4, k_{aq} , indicative of aqueous-phase reaction rate constant of IEPOX [Eddingsaas *et al.*, 2010; Gaston *et al.*, 2014], shows a negative relationship with particle LWC, supporting that particle water may reduce aqueous-phase reaction rate by decreasing aerosol acidity and nucleophile e.g., $\text{SO}_4^{2-}(\text{aq})$, concentrations and suppressing the IEPOX kinetic uptake due to the weaker ionic strength and salting-in effect [Xu *et al.*, 2015a]. Thus, particle water increases in this study still keep within limits of IEPOX-SOA formation.

$\text{H}^+(\text{aq})$ does not show a statistically significant correlation with IEPOX-SOA (Table S2), likely due to the fact that aerosol acidity doesn't vary as much as sulfate loadings (Fig. S13). This result is consistent with previous field observations made in the southeastern US [Budisulistiorini *et al.*, 2015; Y H Lin *et al.*, 2013b; Rattanavaraha *et al.*, 2016; Xu *et al.*, 2015a]. The average concentrations of bisulfate HSO_4^- and $\text{H}^+(\text{aq})$ are 0.02 mol/L and 0.01 mol/L (corresponding to an average pH = 2.6), respectively, indicating significant lower particle acidity levels compared with those in the southeastern US [Hu *et al.*, 2015]. This could be due to the neutralization effect by the abundant ammonium (Fig. S4). As shown in Fig. 3b, IEPOX-SOA shows independent variations on LWC and $\text{H}^+(\text{aq})$, but was strongly associated sulfate variations, which is consistent with the results reported by Xu *et al.* [2015a]. This might be due to the competition between IEPOX uptake to particles and subsequent aqueous-phase reactions [Xu *et al.*, 2016]. For example, Gaston *et al.* (2014) found that the reactive uptake of *trans*- β -IEPOX is driven by ring-opening chemistry under the condition of $\text{pH} \geq 1$, but not acid catalysis. In addition, aerosol acidity ($\text{pH} < 2$) is needed to make IEPOX uptake competitive with other potential atmospheric loss process of IEPOX [Gaston *et al.*, 2014], such as $\text{IEPOX} + \text{OH}$ [Bates *et al.*, 2014] or IEPOX deposition [Eddingsaas *et al.*, 2010]. Therefore, the results above further support that the IEPOX-SOA formation is likely dominantly affected by the sulfate particles rather than particle acidity and/or particle water in this study.

The average value of γ_{IEPOX} is 1.57×10^{-4} ranging from 1.03×10^{-5} to 5.10×10^{-4} , which is overall consistent with those from laboratory experiments ($2 - 6.5 \times 10^{-4}$) [Gaston *et al.*, 2014; Riedel *et al.*, 2015] with ammonium sulfate as aerosol seeds. However, these values are approximately two orders of magnitude lower than those under high particle acidity conditions (e.g., bisulfate as seeds) [Gaston *et al.*, 2014; Riedel *et al.*, 2015] and in sulfur-rich plumes [Xu *et al.*, 2016]. Therefore, the lower γ_{IEPOX} might be mainly due to the correspondingly lower particle acidity in this study. The pseudo-first-order heterogeneous reaction rate efficient (k_{het}) for IEPOX uptake on particles depends on γ_{IEPOX} and particle surface area [Gaston *et al.*, 2014]. The average k_{het} is 7.12×10^{-8} in this study, which is significantly lower than that was reported in the sulfur-rich plumes [Xu *et al.*, 2016]. These results indicate that aqueous-phase reaction is not sufficiently fast due to low particle acidity and low probability of IEPOX reactive uptake in this study. To quantitatively evaluate the effects of particle acidity on k_{het} , we further calculated k_{het} ($k_{\text{het, new}}$) using a new γ_{IEPOX} by increasing the $\text{H}^+_{(\text{aq})}$ concentration by a factor of 10 (Fig. 4), a value close to that in the power-plant plumes in Scherer in the southeastern US [Xu *et al.*, 2016]. We found that approximately 90% ($= [(k_{\text{het, new}} - k_{\text{het}}) / k_{\text{het, new}}] \times 100$) of the k_{het} enhancement can be explained by the increase of particle acidity. Therefore, our results illustrate that the reactive uptake chemistry might be one of the major factors in the suppression of IEPOX-SOA formation under polluted environments in Eastern China. In addition, a very recent study also found the limited formation of IEPOX-SOA under high NO plumes near Manaus, Brazil in the Amazon [de Sá *et al.*, 2016], which is consistent with our conclusions.

As shown in Figure 5, IEPOX-SOA shows an evident wind sector gradient, with the highest concentrations in association with winds from the south. Such wind sector dependence of IEPOX-SOA is remarkably consistent with the spatial distribution of biogenic emissions in Eastern China (Fig. S1). Moreover, the high potential source areas for IEPOX-SOA, mainly located at the south of Nanjing, were consistent with those with high isoprene loadings (Fig. S1) and gas-phase IEPOX in Eastern China [Hu *et al.*, 2015]. In addition, gas-phase MVK+MACR also shows similar wind sector dependence (Fig. S15) and potential sources areas (Fig. S16) as IEPOX-SOA. In contrast, anthropogenic emissions related gas-phase species, such as SO_2 and NO_2 , present different wind sector gradients (Fig. S15). For example, SO_2 shows a more regional character with high concentration associated with winds from the north-northwest and the south-southwest. The wide potential source areas for sulfate (mostly formed by cloud processing of SO_2) also indicate a regional origin

[Sun *et al.*, 2014]. These results suggest that mixing of biogenic and anthropogenic air masses during regional transport of biogenic emissions from their emissions-rich regions impacts the formation of IEPOX-SOA under polluted urban environments.

4. Implications

We have identified an IEPOX-SOA factor in polluted environments in Eastern China. Our results showed that the IEPOX-SOA formation was more sensitive to ring-opening chemistry mediated by aerosol sulfate along with enhanced particle surface area rather than acid catalysis chemistry, and the suppression of IEPOX-SOA formation was mainly caused by the low IEPOX reactive uptake rate and the NO-dominant gas-phase chemistry with less production of IEPOX-SOA precursors. Considering that IEPOX-SOA shows a considerable contribution to OA in the global Earth, and might have potential impacts on radiative forcing and human health, a long-term characterization of IEPOX-SOA in highly polluted environment is urgently needed. Our results also show that regional climate models need to consider the impacts of anthropogenic NO_x, SO₂ and NH₃ on the isoprene SOA formation via low-NO_x pathway in highly polluted environments to have a better evaluation of the radiative forcing of IEPOX-SOA.

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References

- Allan, J. D., et al. (2004), A generalised method for the extraction of chemically resolved mass spectra from Aerodyne aerosol mass spectrometer data, *J. Aerosol Sci.*, 35(7), 909-922, doi:10.1016/j.jaerosci.2004.02.007.
- Archibald, A. T., et al. (2011), Impacts of HO_x regeneration and recycling in the oxidation of isoprene: Consequences for the composition of past, present and future atmospheres, *Geophys. Res. Lett.*, 38(5), doi:10.1029/2010GL046520.
- Bates, K. H., J. D. Crouse, J. M. St. Clair, N. B. Bennett, T. B. Nguyen, J. H. Seinfeld, B. M. Stoltz, and P. O. Wennberg (2014), Gas Phase Production and Loss of Isoprene Epoxydiols, *The Journal of Physical Chemistry A*, 118(7), 1237-1246, doi:10.1021/jp4107958.
- Budisulistiorini, S. H., et al. (2013), Real-time continuous characterization of secondary organic aerosol derived from isoprene epoxydiols in downtown Atlanta, Georgia, using the Aerodyne Aerosol Chemical Speciation Monitor, *Environ. Sci. Technol.*, 47(11), 5686-5694, doi:10.1021/es400023n.
- Budisulistiorini, S. H., et al. (2015), Examining the effects of anthropogenic emissions on isoprene-derived secondary organic aerosol formation during the 2013 Southern Oxidant and Aerosol Study (SOAS) at the Look Rock, Tennessee ground site, *Atmos. Chem. Phys.*, 15(15), 8871-8888, doi:10.5194/acp-15-8871-2015.
- Canagaratna, M. R., et al. (2007), Chemical and microphysical characterization of ambient aerosols with the aerodyne aerosol mass spectrometer, *Mass Spectrom. Rev.*, 26(2), 185-222, doi:10.1002/mas.20115.
- Canonaco, F., M. Crippa, J. G. Slowik, U. Baltensperger, and A. S. H. Prévôt (2013), SoFi, an IGOR-based interface for the efficient use of the generalized multilinear engine (ME-2) for the source apportionment: ME-2 application to aerosol mass spectrometer data, *Atmos. Meas. Technol.*, 6(12), 3649-3661, doi:10.5194/amt-6-3649-2013.
- Chen, Q., et al. (2015), Submicron particle mass concentrations and sources in the Amazonian wet season (AMAZE-08), *Atmos. Chem. Phys.*, 15(7), 3687-3701, doi:10.5194/acp-15-3687-2015.
- de Sá, S. S., et al. (2016), Influence of urban pollution on the production of organic particulate matter from isoprene epoxydiols in central Amazonia, *Atmos. Chem. Phys. Discuss.*, 2016, 1-58, doi:10.5194/acp-2016-1020.
- Ding, X., Q.-F. He, R.-Q. Shen, Q.-Q. Yu, Y.-Q. Zhang, J.-Y. Xin, T.-X. Wen, and X.-M.

- Wang (2016), Spatial and seasonal variations of isoprene secondary organic aerosol in China: Significant impact of biomass burning during winter, *Sci. Rep.*, 6, 20411.
- Draxler, R. R., Rolph, G.D., (2003), HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model Access via NOAA ARL READY Website. NOAA Air Resources Laboratory, Silver Spring, MD. <http://www.arl.noaa.gov/ready/hysplit4.html>.
- Eddingsaas, N. C., D. G. VanderVelde, and P. O. Wennberg (2010), Kinetics and Products of the Acid-Catalyzed Ring-Opening of Atmospherically Relevant Butyl Epoxy Alcohols, *The Journal of Physical Chemistry A*, 114(31), 8106-8113, doi:10.1021/jp103907c.
- Fountoukis, C., and A. Nenes (2007), ISORROPIA II: a computationally efficient thermodynamic equilibrium model for K^+ - Ca^{2+} - Mg^{2+} - NH_4^+ - Na^+ - SO_4^{2-} - NO_3^- - Cl^- - H_2O aerosols, *Atmos. Chem. Phys.*, 7(17), 4639-4659, doi:10.5194/acp-7-4639-2007.
- Gaston, C. J., T. P. Riedel, Z. Zhang, A. Gold, J. D. Surratt, and J. A. Thornton (2014), Reactive Uptake of an Isoprene-Derived Epoxydiol to Submicron Aerosol Particles, *Environ. Sci. Technol.*, 48(19), 11178-11186, doi:10.1021/es5034266.
- Geng, F., X. Tie, A. Guenther, G. Li, J. Cao, and P. Harley (2011), Effect of isoprene emissions from major forests on ozone formation in the city of Shanghai, China, *Atmos. Chem. Phys.*, 11(20), 10449-10459, doi:10.5194/acp-11-10449-2011.
- Guenther, A. B., X. Jiang, C. L. Heald, T. Sakulyanontvittaya, T. Duhl, L. K. Emmons, and X. Wang (2012), The Model of Emissions of Gases and Aerosols from Nature version 2.1 (MEGAN2.1): an extended and updated framework for modeling biogenic emissions, *Geosci. Model Dev.*, 5(6), 1471-1492, doi:10.5194/gmd-5-1471-2012.
- Guo, S., et al. (2014), Elucidating severe urban haze formation in China, *Proc. Natl. Acad. Sci. U.S.A.*, 111(49), 17373-17378, doi:10.1073/pnas.1419604111.
- Henry, R., G. A. Norris, R. Vedantham, and J. R. Turner (2009), Source Region Identification Using Kernel Smoothing, *Environ. Sci. Technol.*, 43(11), 4090-4097, doi:10.1021/es8011723.
- Hu, W. W., et al. (2015), Characterization of a real-time tracer for isoprene epoxydiols-derived secondary organic aerosol (IEPOX-SOA) from aerosol mass spectrometer measurements, *Atmos. Chem. Phys.*, 15(20), 11807-11833, doi:10.5194/acp-15-11807-2015.
- Huang, R. J., et al. (2014), High secondary aerosol contribution to particulate pollution during haze events in China, *Nature*, 514(7521), 218-222, doi:10.1038/nature13774.

- Huang, X. F., L. Y. He, L. Xue, T. L. Sun, L. W. Zeng, Z. H. Gong, M. Hu, and T. Zhu (2012), Highly time-resolved chemical characterization of atmospheric fine particles during 2010 Shanghai World Expo, *Atmos. Chem. Phys.*, *12*(11), 4897-4907, doi:10.5194/acp-12-4897-2012.
- Jacobs, M. I., W. J. Burke, and M. J. Elrod (2014), Kinetics of the reactions of isoprene-derived hydroxynitrates: gas phase epoxide formation and solution phase hydrolysis, *Atmos. Chem. Phys.*, *14*(17), 8933-8946, doi:10.5194/acp-14-8933-2014.
- Lin, Y.-H., M. Arashiro, E. Martin, Y. Chen, Z. Zhang, K. G. Sexton, A. Gold, I. Jaspers, R. C. Fry, and J. D. Surratt (2016), Isoprene-Derived Secondary Organic Aerosol Induces the Expression of Oxidative Stress Response Genes in Human Lung Cells, *Environ. Sci. Technol. Lett.*, *3*(6), 250-254, doi:10.1021/acs.estlett.6b00151.
- Lin, Y.-H., et al. (2013a), Epoxide as a precursor to secondary organic aerosol formation from isoprene photooxidation in the presence of nitrogen oxides, *Proc. Natl. Acad. Sci. U.S.A.*, *110*(17), 6718-6723, doi:10.1073/pnas.1221150110.
- Lin, Y.-H., et al. (2012), Isoprene Epoxydiols as Precursors to Secondary Organic Aerosol Formation: Acid-Catalyzed Reactive Uptake Studies with Authentic Compounds, *Environ. Sci. Technol.*, *46*(1), 250-258, doi:10.1021/es202554c.
- Lin, Y. H., E. M. Knipping, E. S. Edgerton, S. L. Shaw, and J. D. Surratt (2013b), Investigating the influences of SO₂ and NH₃ levels on isoprene-derived secondary organic aerosol formation using conditional sampling approaches, *Atmos. Chem. Phys.*, *13*(16), 8457-8470, doi:10.5194/acp-13-8457-2013.
- Liu, Y., et al. (2016), Isoprene photochemistry over the Amazon rainforest, *Proc. Natl. Acad. Sci. U.S.A.*, *113*(22), 6125-6130, doi:10.1073/pnas.1524136113.
- Middlebrook, A. M., R. Bahreini, J. L. Jimenez, and M. R. Canagaratna (2012), Evaluation of Composition-Dependent Collection Efficiencies for the Aerodyne Aerosol Mass Spectrometer using Field Data, *Aerosol Sci. Technol.*, *46*(3), 258-271, doi:10.1080/02786826.2011.620041.
- Ng, N. L., et al. (2011), An Aerosol Chemical Speciation Monitor (ACSM) for Routine Monitoring of the Composition and Mass Concentrations of Ambient Aerosol, *Aerosol Sci. Technol.*, *45*(7), 780-794, doi:10.1080/02786826.2011.560211.
- Nguyen, T. B., et al. (2015), Mechanism of the hydroxyl radical oxidation of methacryloyl peroxyxynitrate (MPAN) and its pathway toward secondary organic aerosol formation in the atmosphere, *Physical Chemistry Chemical Physics*, *17*(27), 17914-17926,

doi:10.1039/C5CP02001H.

- Paatero, P., and U. Tapper (1994), Positive matrix factorization: A non-negative factor model with optimal utilization of error estimates of data values, *Environmetrics*, 5(2), 111-126, doi:10.1002/env.3170050203.
- Paulot, F., J. D. Crounse, H. G. Kjaergaard, A. Kürten, J. M. St. Clair, J. H. Seinfeld, and P. O. Wennberg (2009), Unexpected Epoxide Formation in the Gas-Phase Photooxidation of Isoprene, *Science*, 325(5941), 730-733, doi:10.1126/science.1172910.
- Petit, J. E., O. Favez, A. Albinet, and F. Canonaco (2017), A user-friendly tool for comprehensive evaluation of the geographical origins of atmospheric pollution: Wind and trajectory analyses, *Environmental Modelling & Software*, 88, 183-187, doi:<http://dx.doi.org/10.1016/j.envsoft.2016.11.022>.
- Polissar, A. V., P. K. Hopke, and R. L. Poirot (2001), Atmospheric Aerosol over Vermont: Chemical Composition and Sources, *Environ. Sci. Technol.*, 35(23), 4604-4621, doi:10.1021/es0105865.
- Rattanavaraha, W., et al. (2016), Assessing the impact of anthropogenic pollution on isoprene-derived secondary organic aerosol formation in PM_{2.5} collected from the Birmingham, Alabama, ground site during the 2013 Southern Oxidant and Aerosol Study, *Atmos. Chem. Phys.*, 16(8), 4897-4914, doi:10.5194/acp-16-4897-2016.
- Riedel, T. P., Y.-H. Lin, S. H. Budisulistiorini, C. J. Gaston, J. A. Thornton, Z. Zhang, W. Vizuete, A. Gold, and J. D. Surratt (2015), Heterogeneous Reactions of Isoprene-Derived Epoxides: Reaction Probabilities and Molar Secondary Organic Aerosol Yield Estimates, *Environ. Sci. Technol. Lett.*, 2(2), 38-42, doi:10.1021/ez500406f.
- Riva, M., S. H. Budisulistiorini, Z. Zhang, A. Gold, and J. D. Surratt (2016), Chemical characterization of secondary organic aerosol constituents from isoprene ozonolysis in the presence of acidic aerosol, *Atmos. Environ.*, 130, 5-13, doi:<http://dx.doi.org/10.1016/j.atmosenv.2015.06.027>.
- St. Clair, J. M., J. C. Rivera-Rios, J. D. Crounse, E. Praske, M. J. Kim, G. M. Wolfe, F. N. Keutsch, P. O. Wennberg, and T. F. Hanisco (2016), Investigation of a potential HCHO measurement artifact from ISOPOOH, *Atmos. Meas. Tech.*, 9(9), 4561-4568, doi:10.5194/amt-9-4561-2016.
- Sun, Y., Q. Jiang, Z. Wang, P. Fu, J. Li, T. Yang, and Y. Yin (2014), Investigation of the sources and evolution processes of severe haze pollution in Beijing in January 2013, *J.*

- Geophys. Res. Atmos.*, 119(7), 4380-4398, doi:10.1002/2014JD021641.
- Sun, Y., Z. Wang, H. Dong, T. Yang, J. Li, X. Pan, P. Chen, and J. T. Jayne (2012), Characterization of summer organic and inorganic aerosols in Beijing, China with an Aerosol Chemical Speciation Monitor, *Atmos. Environ.*, 51, 250-259, doi:10.1016/j.atmosenv.2012.01.013.
- Surratt, J. D., A. W. H. Chan, N. C. Eddingsaas, M. Chan, C. L. Loza, A. J. Kwan, S. P. Hersey, R. C. Flagan, P. O. Wennberg, and J. H. Seinfeld (2010), Reactive intermediates revealed in secondary organic aerosol formation from isoprene, *Proc. Natl. Acad. Sci. U.S.A.*, 107(15), 6640-6645, doi:10.1073/pnas.0911114107.
- Surratt, J. D., et al. (2006), Chemical Composition of Secondary Organic Aerosol Formed from the Photooxidation of Isoprene, *J. Phys. Chem. A*, 110(31), 9665-9690, doi:10.1021/jp061734m.
- von Schneidemesser, E., P. S. Monks, V. Gros, J. Gauduin, and O. Sanchez (2011), How important is biogenic isoprene in an urban environment? A study in London and Paris, *Geophys. Res. Lett.*, 38(19), doi:10.1029/2011GL048647.
- Wang, J., T. B. Onasch, X. Ge, S. Collier, Q. Zhang, Y. Sun, H. Yu, M. Chen, A. S. H. Prévôt, and D. R. Worsnop (2016), Observation of Fullerene Soot in Eastern China, *Environ. Sci. Technol. Lett.*, 3(4), 121-126, doi:10.1021/acs.estlett.6b00044.
- Xiong, F., et al. (2015), Observation of isoprene hydroxynitrates in the southeastern United States and implications for the fate of NO_x, *Atmos. Chem. Phys.*, 15(19), 11257-11272, doi:10.5194/acp-15-11257-2015.
- Xu, L., et al. (2015a), Effects of anthropogenic emissions on aerosol formation from isoprene and monoterpenes in the southeastern United States, *Proc. Natl. Acad. Sci. U.S.A.*, 112(1), 37-42, doi:10.1073/pnas.1417609112.
- Xu, L., et al. (2016), Enhanced formation of isoprene-derived organic aerosol in sulfur-rich power plant plumes during Southeast Nexus, *Journal of Geophysical Research: Atmospheres*, 121(18), 11,137-111,153, doi:10.1002/2016JD025156.
- Xu, L., S. Suresh, H. Guo, R. J. Weber, and N. L. Ng (2015b), Aerosol characterization over the southeastern United States using high-resolution aerosol mass spectrometry: spatial and seasonal variation of aerosol composition and sources with a focus on organic nitrates, *Atmos. Chem. Phys.*, 15(13), 7307-7336, doi:10.5194/acp-15-7307-2015.
- Zhang, Y., et al. (2015a), Chemical composition, sources and evolution processes of aerosol at an urban site in Yangtze River Delta, China during wintertime, *Atmos. Environ.*, 123,

Part B, 339-349, doi:<http://dx.doi.org/10.1016/j.atmosenv.2015.08.017>.

Zhang, Y. J., et al. (2015b), Insights into characteristics, sources, and evolution of submicron aerosols during harvest seasons in the Yangtze River delta region, China, *Atmos. Chem. Phys.*, *15*(3), 1331-1349, doi:10.5194/acp-15-1331-2015.

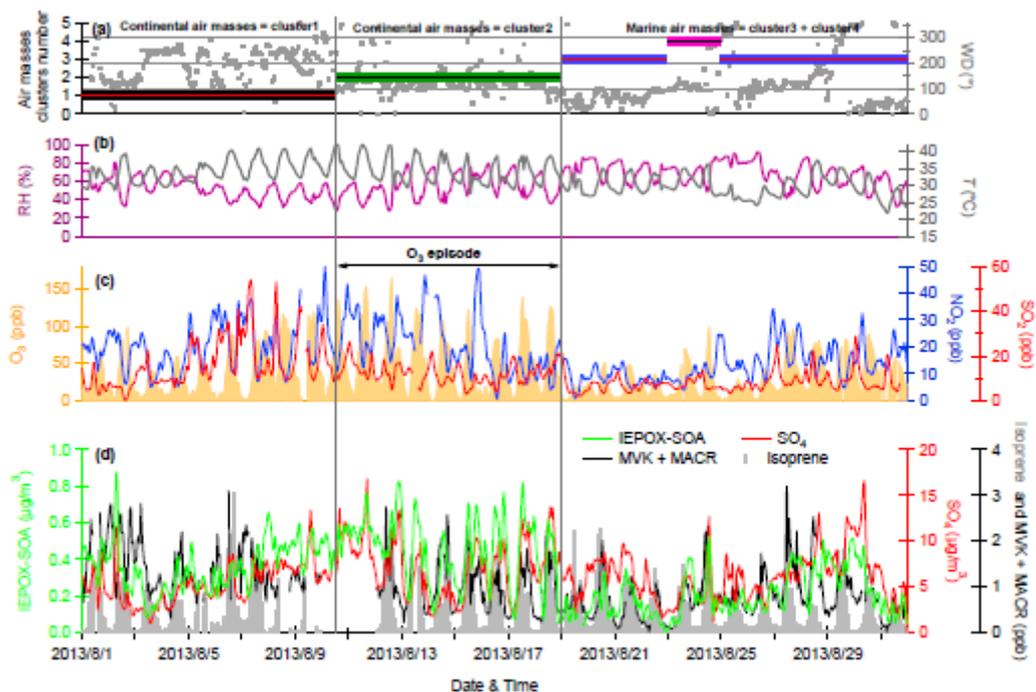


Figure 1. Time series of (a) wind direction (WD) (b) relative humidity (RH) and ambient temperature (T); (c) O_x ($= O_3 + NO_2$), NO_2 , and SO_2 ; and (d) mass concentrations of IEPOX-SOA, sulfate (SO_4), isoprene, and methyl vinyl ketone and methacrolein (MVK+MACR). The air masses during the study period were also classified into four clusters as shown in Figure S2. The missing data of isoprene and MVK+MACR on the Fig. 1d denotes instrument was not sampling ambient air.

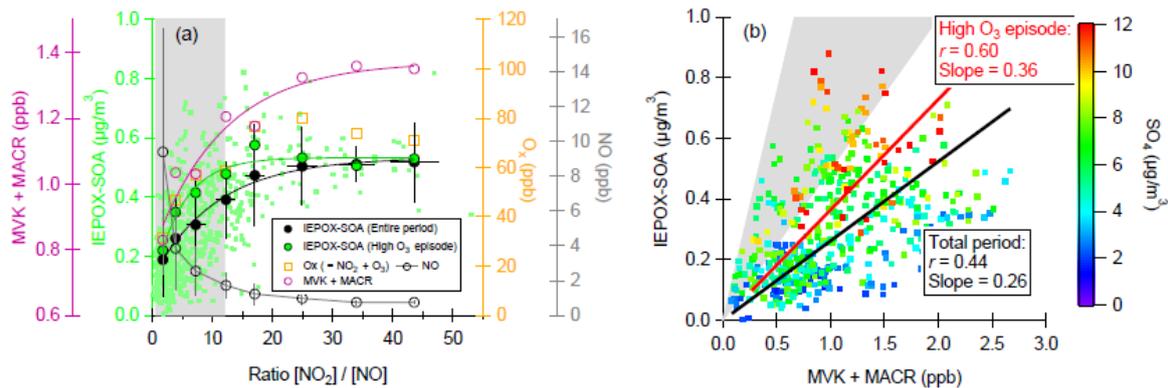


Figure 2. (a) Variations of IEPOX-SOA, MVK+MACR, Ox, and NO as a function of $[\text{NO}_2]/[\text{NO}]$. The gray shaded area (a) represents the typical ratios of $[\text{NO}_2]/[\text{NO}]$ in summer in southeastern US [Rattanavaraha *et al.*, 2016; Xu *et al.*, 2015b]; and (b) IEPOX-SOA versus MVK+MACR, which are color coded by O_x and SO_4 , respectively. The gray shaded area (b) represents the typical ratios of [IEPOX-SOA] to [MVK+MACR] [Budisulistiorini *et al.*, 2015; Xiong *et al.*, 2015; Xu *et al.*, 2015a] under relatively low- NO_x environments in summer 2013 in southeastern US. In addition, the correlations during high O_3 episode marked in Fig. 1 are also shown.

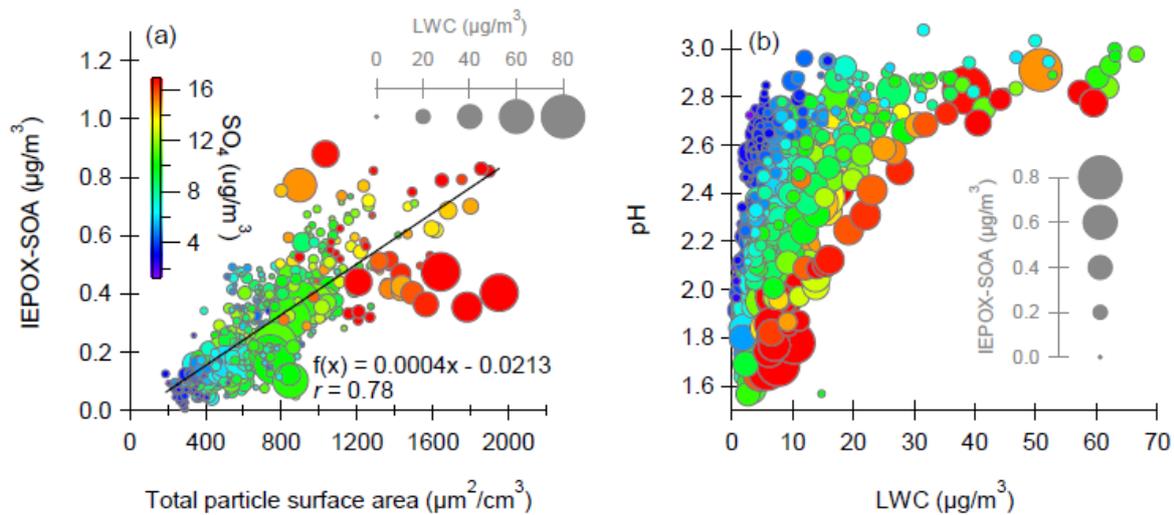


Figure 3. (a) Correlation between IEPOX-SOA and total particle surface area, and (b) relationship between aerosol particle pH and LWC. The data points in (a) and (b) are color coded by SO_4 concentrations, and the marker sizes indicate the values of LWC and IEPOX-SOA, respectively.

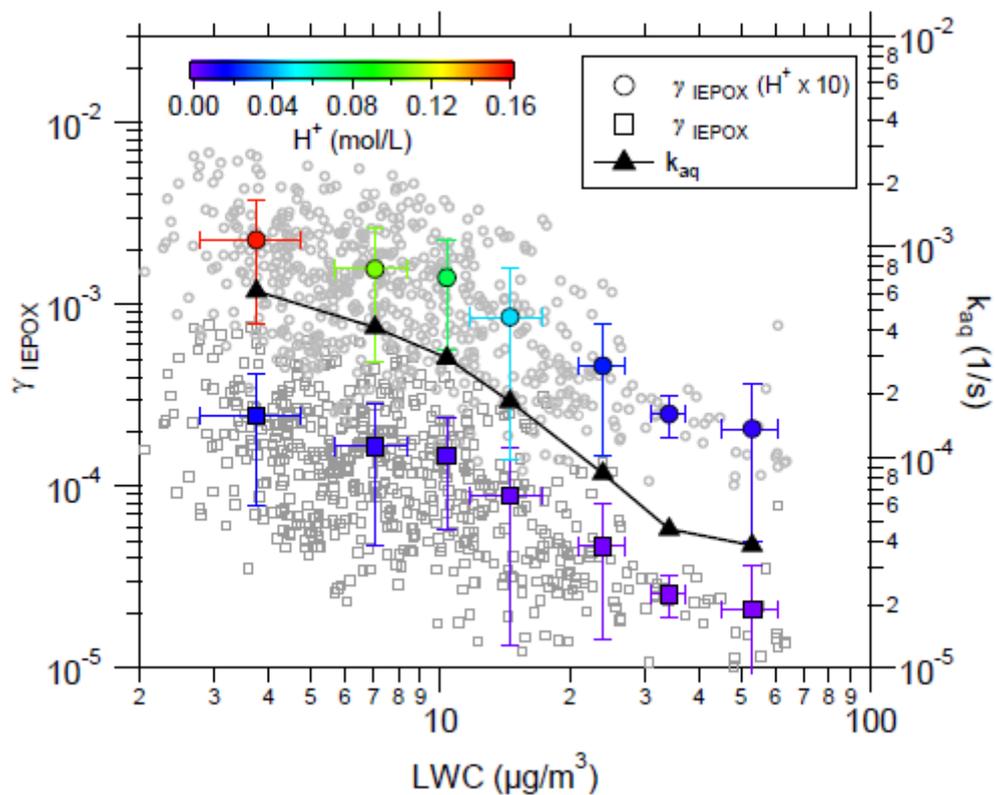


Figure 4. Reactive uptake (γ_{IEPOX}) and heterogeneous reaction rate constant (k_{aq}) of IEPOX as a function of particle LWC. Also, the data points colored by the aerosol acidity (H^+) were averaged into seven bins according to LWC.

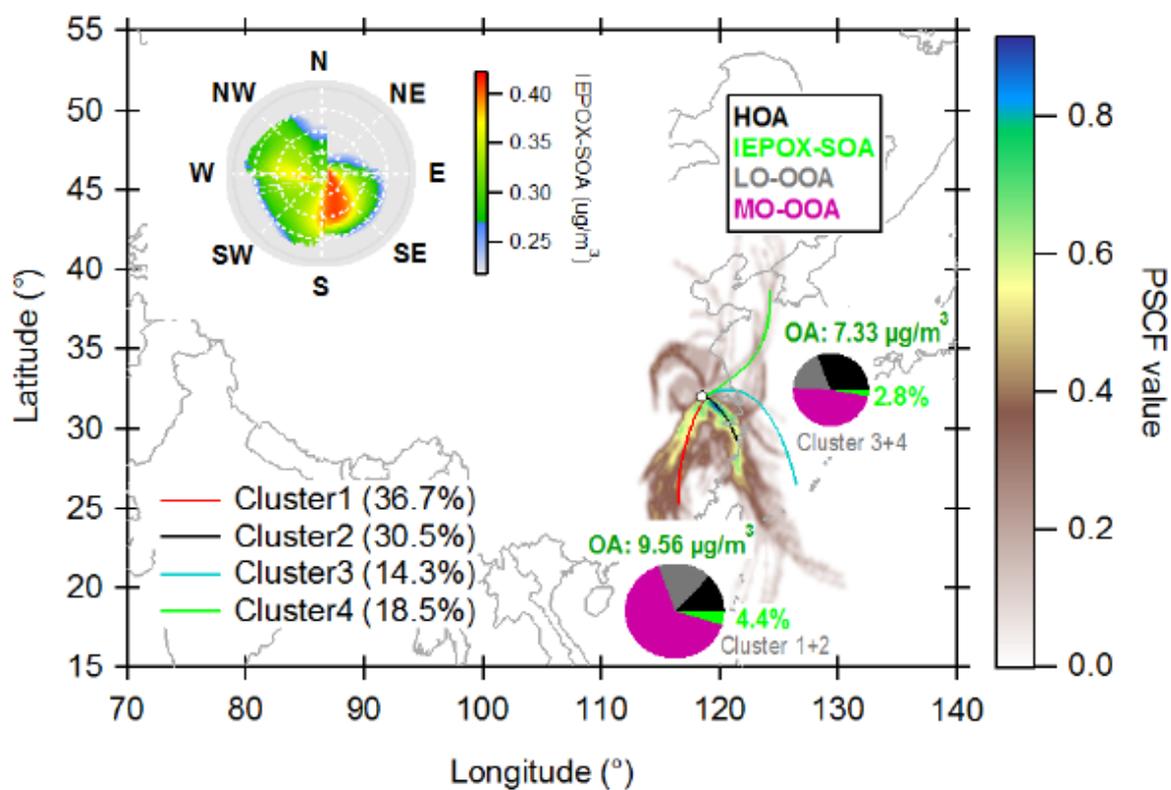


Figure 5. Potential source contribution function (PSCF) and NWR plots of IEPOX-SOA. The two pie charts show the average OA composition for cluster 1 and 2, and cluster 3 and 4.