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Characterization of a real-time tracer for Isoprene Epoxydiols-derived Secondary Organic Aerosol (IEPOX-SOA) from aerosol mass spectrometer measurements

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Abstract

Substantial amounts of secondary organic aerosol (SOA) can be formed from isoprene epoxydiols (IEPOX), which are oxidation products of isoprene mainly under low-NO conditions. Total IEPOX-SOA, which may include SOA formed from other parallel isoprene low-NO oxidation pathways, was quantified by applying Positive Matrix Factorization (PMF) to aerosol mass spectrometer (AMS) measurements. The IEPOX-SOA fractions of OA in multiple field studies across several continents are summarized here and show consistent patterns with the concentration of gas-phase IEPOX simulated by the GEOS-Chem chemical transport model. During the SOAS study, 78 % of IEPOX-SOA is accounted for the measured molecular tracers, making it the highest level of molecular identification of an ambient SOA component to our knowledge. Enhanced signal at $C_5H_6O^+$ (m/z 82) is found in PMF-resolved IEPOX-SOA spectra. To investigate the suitability of this ion as a tracer for IEPOX-SOA, we examine $f_{C_5H_6O}$ ($f_{C_5H_6O} = C_5H_6O^+/\mathrm{OA}$) across multiple field, chamber and source datasets. A background of $\sim 1.7 \pm 0.1$ ‰ is observed in studies strongly influenced by urban, biomass-burning and other anthropogenic primary organic aerosol (POA). Higher background values of 3.1 ± 0.8 ‰ are found in studies strongly influenced by monoterpene emissions. The average laboratory monoterpene SOA value (5.5 ± 2.0 ‰) is 4 times lower than the average for IEPOX-SOA (22 ± 7 ‰). Locations strongly influenced by isoprene emissions under low-NO levels had higher $f_{C_5H_6O}$ ($\sim 6.5 \pm 2.2$ ‰ on average) than other sites, consistent with the expected IEPOX-SOA formation in those studies. $f_{C_5H_6O}$ in IEPOX-SOA is always elevated (12–40 ‰) but varies substantially between locations, which is shown to reflect large variations in its detailed molecular composition. The low $f_{C_5H_6O}$ (< 3 ‰) observed in non IEPOX-derived isoprene-SOA indicates that this tracer ion is specifically enhanced from IEPOX-SOA, and is not a tracer for all SOA from isoprene. We introduce a graphical diagnostic to study the presence and aging of IEPOX-SOA as a "triangle plot" of f_{CO_2} vs. $f_{C_5H_6O}$. Finally, we develop a simplified method to estimate ambient IEPOX-SOA mass concentrations, which is shown to per-

form well compared to the full PMF method. The uncertainty of the tracer method is up to a factor of ~ 2 if the $f_{C_5H_6O}$ of the local IEPOX-SOA is not available. When only unit mass resolution data is available, as with the aerosol chemical speciation monitor (ACSM), all methods may perform less well because of increased interferences from other ions at m/z 82. This study clarifies the strengths and limitations of the different AMS methods for detection of IEPOX-SOA and will enable improved characterization of this OA component.

1 Introduction

Isoprene (2-methyl-1,3-butadiene, C_5H_8) emitted by vegetation is the most abundant non-methane hydrocarbon emitted to the Earth's atmosphere (~ 440–600 Tg C year^{-1}) (Guenther et al., 2012). It is estimated to contribute substantially to the global secondary organic aerosol (SOA) budget (Guenther et al., 2012; Paulot et al., 2009b). Higher SOA yields from isoprene are observed under low-NO_x conditions (Surratt et al., 2010). Under low-NO conditions, i.e. when a substantial fraction of the peroxy radicals do not react with NO, gas-phase isoprene epoxydiols (IEPOX) are produced with high yield through a HO_x-mediated mechanism (Paulot et al., 2009b). Subsequently, IEPOX can be taken up by acidic aerosols (Gaston et al., 2014), where IEPOX-SOA can be formed through acid-catalyzed oxirane ring-opening of IEPOX (Nguyen et al., 2014; Lin et al., 2012; Cole-Filipiak et al., 2010; Eddingsaas et al., 2010), which is thought to be the main pathway to form IEPOX-SOA (Worton et al., 2013; Surratt et al., 2010; Pye et al., 2013). Although the complete molecular composition of IEPOX-SOA has not been elucidated, several molecular species that are part of IEPOX-SOA have been identified through gas chromatography/mass spectrometry (GC/MS), liquid chromatography/mass spectrometry (LC/MS) and particle analysis by laser mass spectrometry (PALMS). They include 2-methyltetrols (and oligomers that contain them) (Surratt et al., 2010; Lin et al., 2014), C_5-alkene triols (Wang et al., 2005), 3-methyltetrahydrofuran-3,4-diols (Lin et al., 2012), and an IEPOX-organosulfate (Froyd et al., 2010; Liao et al.,

2014). These molecular species account for a variable fraction of the IEPOX-SOA reported, e.g., 8 % in a chamber study (Lin et al., 2012) or 26 % in a field study at Look Rock, TN (Budisulistiorini et al., 2015). An estimate of total IEPOX-SOA can also be derived from an IEPOX-SOA molecular tracer(s) via multiplying the tracer concentration by the total IEPOX-SOA to tracer ratio. However, that method is hindered by the limited information on these molecular tracers and the reported variability of IEPOX-SOA to tracer ratios. IEPOX-SOA may include SOA formed from other parallel isoprene low-NO oxidation pathways (Liu et al., 2014; Krechmer et al., 2015). In addition, the IEPOX-SOA molecular tracers are typically measured with slow time resolution (12/24 h).

Multiple field studies, supported by chamber studies, have shown that the total amount of IEPOX-SOA can be obtained by factor analysis of organic spectra from an aerosol mass spectrometer (AMS) or the aerosol chemical speciation monitor (ACSM) (Budisulistiorini et al., 2013; Lin et al., 2012; Nguyen et al., 2014; Robinson et al., 2011). Robinson et al. (2011) first reported an SOA factor with pronounced f_{82} (= m/z 82/OA) in the mass spectra acquired above a forest with high isoprene emissions in Borneo, and hypothesized that the elevated f_{82} may have arisen from methylfuran (C_5H_6O), consistent with $C_5H_6O^+$ being the major ion at m/z 82 in isoprene-influenced areas. Lin et al. (2012) demonstrated that the 3-MeTHF-3,4-diols associated with IEPOX-SOA result in enhanced f_{82} in AMS spectra, presumably through the formation methylfuran-like structures during thermal desorption. Electron-impact ionization of aerosols formed by atomizing a solution containing IEPOX ($C_5H_{10}O_3$) can also yield $C_5H_6O^+$ signals in an AMS via two dehydration reactions (Lin et al., 2012). However, because gas-phase IEPOX has a high volatility, gas-to-particle partitioning of IEPOX into the organic fraction of aerosol is negligible under typical ambient organic concentrations in forest areas (1–10 µg m^{-3}) (Worton et al., 2013).

IEPOX-SOA was estimated to account for 33 % of ambient OA in summertime Atlanta from PMF analysis of ACSM spectra. The source apportionment result was supported by the pronounced f_{82} peak in the factor spectrum and good temporal correlation of the factor with sulfate and 2-methyltetrols (Budisulistiorini et al., 2013). Sulfate is of-

ten strongly correlated with the acidity of an aerosol, and might also play a direct role in the chemistry, e.g. via direct reaction or nucleophilic effects (Liao et al., 2014; Xu et al., 2014; Surratt et al., 2007). While discussing the results of a recent aircraft campaign from Brazil, Allan et al. (2014) also used f_{82} as a tracer for IEPOX-SOA.

If f_{82} in AMS spectra (and/or $f_{C_5H_6O}$ in HR-AMS spectra) is dominated by IEPOX-SOA, f_{82} would be a convenient, high-time-resolution, and potentially quantitative tracer for IEPOX-SOA. Thus, it will be very useful for investigating the impacts of SOA formation from isoprene with AMS/ACSM measurements, which have become increasingly common in recent years including some continental-scale continuous networks (Fröhlich et al., 2015). However, no studies to date have systematically examined whether enhanced f_{82} is unique to IEPOX chemistry or whether it could also be enhanced in other sources. Nor has the range of f_{82} been determined for IEPOX-SOA. Questions also have been raised about the uniqueness of this tracer and potential contributions from monoterpene SOA (Anonymous_referee, 2014).

In this study, the IEPOX-SOA results reported in various field campaigns are summarized and compared to predicted gas-phase IEPOX concentrations from a global model to help confirm the robustness of the AMS identification of this type of SOA. We then investigate the usefulness and limitations of the IEPOX-SOA tracers $f_{C_5H_6O}$ ($= C_5H_6O^+/OA$) and f_{82} by combining AMS data from multiple field and laboratory studies including a new dataset from the 2013 Southern Oxidant and Aerosol Study (SOAS). We compare the tracer levels in different OA sources (urban, biomass burning and biogenic), characterizing the background levels and interferences on this tracer for both high-resolution (HR) and unit mass resolution (UMR) data. We also provide a simplified method to rapidly estimate IEPOX-SOA from $f_{C_5H_6O}$ and f_{82}. While this method is no substitute for a detailed IEPOX-SOA identification via PMF, it is a simple method to estimate IEPOX-SOA concentrations (or its absence) in real-time from AMS or ACSM measurements or under conditions in real-time, or where PMF analysis is not possible or is difficult to perform.

2 Experimental

We classify the field datasets used in this study into three categories: (1) studies strongly influenced by urban and biomass-burning emissions: Los Angeles area, US and Beijing, China (urban); Changdao island, downwind of China and Barcelona area, Spain (urban downwind); flight data from biomass-burning plumes and continental areas (NW and western, US) in SEAC4RS and DC3 campaigns; and biomass burning lab emissions (FLAME-3 study). (2) Studies strongly influenced by isoprene emissions, including a SE US forest site (SOAS campaign); two pristine and one polluted sites in the Amazon rain forest (Brazil); Borneo rain forest in Malaysia; and flight data from SE US flights from aircraft campaign (SEAC4RS), (3) studies strongly influenced by monoterpene emissions in a pine forest in the Rocky Mountains and a European boreal forest. Locations and additional detailed information about these studies can be found in Fig. 1 and Table 1.

With the exception of SOAS, all of the campaigns included in this analysis have been previously described elsewhere (Table 1). The SOAS campaign took place in a forested area of the SE US during June and July 2013 (Fig. 1) and has several ground sites. The new dataset introduced below was acquired at the SEARCH supersite, Centreville (CTR), AL (32.95° N, 87.13° W). Some results from a different SOAS site (Look Rock, TN) are also discussed later (Budisulistiorini et al., 2015). Relatively high average isoprene and monoterpene concentrations of 3.3 ± 2.4 ppb and 0.7 ± 0.4 ppb, respectively, were observed in SOAS-CTR by on-line GC/MS. Measurements of non-refractory aerosol components of submicron particles (PM_1) were made using an Aerodyne high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS, "AMS" hereafter) (DeCarlo et al., 2006). By applying positive matrix factorization (PMF) to the time series of organic mass spectra (Ulbrich et al., 2009), we separated contributions from IEPOX-SOA and other sources/components of OA. The AMS PMF results used here are very consistent with those from a separate HR-ToF-AMS operated by another group at the same site (Xu et al., 2014). The global gas-phase IEPOX concentrations

in 2013 were modeled at as resolution of $2^{\circ} \times 2.5^{\circ}$ as described in Nguyen et al. (2015). The gas-phase chemistry of isoprene in GEOS-Chem is based on Paulot et al. (2009a, b) as described by Mao et al. (2013).

3 Results and discussion

3.1 IEPOX-SOA in a SE US forest during SOAS, 2013

We use the SOAS-CTR field study (SE US-CTR) as an example for the determination of IEPOX-SOA from AMS data via PMF analysis. The time series and mass spectrum of this component are shown in Fig. 2. A strong correlation is found between AMS IEPOX-SOA and 2-methyltetrols (R = 0.79) and sulfate (R = 0.75) as expected (Xu et al., 2014; Nguyen et al., 2014; Lin et al., 2012; Surratt et al., 2010). The diurnal variation of IEPOX-SOA is also similar to gas-phase IEPOX and isoprene measured in SOAS-CTR. 2-Methyltetrols, measured on-line by GC-EI/MS with the SV-TAG instrument (Isaacman et al., 2014), comprise 26 % of IEPOX-SOA in SOAS-CTR on average, as shown in Fig. 2b. A similar ratio (29 %) is found between 2-Methyltetrols measured by offline analysis of filter samples using GC-EI/MS and LC/MS (Lin et al., 2014) and IEPOX-SOA. Other IEPOX-SOA tracers, such as C_5-alkene triols, IEPOX-organosulfates, and dimers containing them, can also be measured by offline GC-EI/MS and LC/MS (Budisulistiorini et al., 2015; Lin et al., 2014). The total IEPOX-SOA tracers measured in SOAS account for ∼ 78 % of the total IEPOX-SOA mass concentration. This is a remarkably high value compared to the tracer to total SOA ratios for other SOA systems (e.g., SOA from monoterpenes or aromatic hydrocarbons) (Lewandowski et al., 2013) and it is the highest reported in the literature to our knowledge. A total tracers to IEPOX-SOA ratio of 26 % was reported for the Look Rock site in SOAS (SOAS-LR) (Budisulistiorini et al., 2015). Thus, the measured total molecular tracer fraction in total IEPOX-SOA appears to be quite variable (a factor of 3) even if the same or similar techniques are used. Although the calibration methodology between different campaigns may result in some

uncertainties, this value likely changes significantly between different times and locations, potentially due to changes in particle-phase reaction conditions such as sulfate and water concentrations, acidity, and the identity and concentrations of oligomerization partners.

IEPOX-SOA accounts for 17 % of the total OA mass concentration at SOAS-CTR. This is shown in Fig. 1 along with the IEPOX-SOA fraction from several previous studies (Robinson et al., 2011; Chen et al., 2014; Budisulistiorini et al., 2013; Slowik et al., 2011; Hu et al., 2013, 2015; Hayes et al., 2013). Figure 1 also shows the surface gas-phase IEPOX concentrations for July 2013 as simulated with GEOS-Chem. At all sites with at least ∼ 30 ppt predicted average IEPOX concentration, IEPOX-SOA is identified in AMS data. IEPOX-SOA accounts for 6–34 % of total OA in those studies, signifying the importance of IEPOX-SOA for regional and global OA budgets. No IEPOX-SOA factor (or below the PMF detection limit of ∼ 5 %. Ulbrich et al., 2009) was found in areas strongly influenced by urban emissions where high NO concentrations suppress the IEPOX pathway (e.g. Hayes et al., 2013). GEOS-Chem indeed predicts negligible modeled gas-phase IEPOX concentrations in those areas, where isoprene peroxy radicals are expected to react primarily with NO. Some IEPOX can also be formed via high NO chemistry (Jacobs et al., 2014), however this pathway is thought to be much smaller than the low-NO pathway, consistent with the lack of observation of IEPOX-SOA in the polluted studies included here. The fraction of IEPOX-SOA positively correlates with modeled gas-phase IEPOX, as shown in the inset of Fig. 1.

The mass spectrum of IEPOX-SOA during SOAS-CTR is similar to those from other studies as seen in Figs. S1 and S2 (Robinson et al., 2011; Lin et al., 2012; Nguyen et al., 2014; Chen et al., 2014; Budisulistiorini et al., 2013; Xu et al., 2014), and also exhibits a prominent $C_5H_6O^+$ peak at m/z 82. We investigated the correlation between the time series of IEPOX-SOA and each ion in the OA spectra. The temporal variation of ion $C_5H_6O^+$ correlates best (R = 0.96) with that IEPOX-SOA among all OA ions (Table S1), suggesting that it may be the best tracer among all ions for IEPOX-SOA. $C_5H_5O^+$ (m/z 81), $C_4H_5^+$ (m/z 53), $C_4H_6O^+$ (m/z 70) and $C_3H_7O_2^+$ (m/z 75)

also correlate well with IEPOX-SOA in SOAS-CTR and could be potential tracers for IEPOX-SOA. Scatter plots between these four ions and $C_5H_6O^+$ at different campaigns indicates they either have higher background values or lower signal-to-noise compared to $C_5H_6O^+$ (Fig. S3). $f_{C_5H_6O}$ in IEPOX-SOA from SOAS and other field and laboratory studies (Table 1) ranges from 12 to 40 ‰ and have an average value of 22 ± 7 ‰. Note that $C_5H_6O^+$ ion can account for over 95 % of m/z 82 in IEPOX-SOA from SOAS-CTR and other lab studies (Kuwata et al., 2015), hence the average $f_{C_5H_6O}$ values in IEPOX-SOA shown here also includes f_{82} in UMR IEPOX-SOA spectra. These values are substantially higher than those from other types of OA or from locations with little impact from IEPOX-SOA, as discussed below.

3.2 $f_{C_5H_6O}$ in areas with strong influence from urban and biomass burning emissions

We next examine whether POA or SOA from field studies in areas strongly influenced by urban and biomass-burning emissions and without substantial predicted gas-phase IEPOX concentrations or IEPOX-SOA contributions can lead to enhanced $f_{C_5H_6O}$. Figure 3a shows the distribution of $f_{C_5H_6O}$ in this category of studies peaks at 1.7 ± 0.1 ‰ (range 0.02–3.5 ‰). Data from continental air masses sampled from aircraft over the western and northwest US (where isoprene emissions are low) are shown in Fig. 3b and show a similar range as the polluted ground sites.

Biomass burning emissions and plumes sampled over multiple studies show a similar range to the pollution studies, with some slightly higher values. The peak of the distribution of $f_{C_5H_6O}$ from fresh biomass-burning smoke across many different biomasses during the FLAME-3 study is 2.0 ‰. During the SEAC4RS aircraft campaign, many biomass burning plumes were sampled, where OA concentrations varied over a wide range (several tens to more than one thousand $\mu g\,m^{-3}$). The average $f_{C_5H_6O}$ across these biomass-burning plumes was 1.75 ‰ with low variability (~ 20 %), see Fig. S4.

We also explore whether other anthropogenic POA emission sources could elevate $f_{C_5H_6O}$ above the observed background levels of ~ 1.7 ‰. Figure 3c shows $f_{C_5H_6O}$ for

POA spectra from vehicle exhaust, cooking, coal combustion, and multiple pure chemical standards (e.g., some alcohols; di- or poly acids) (Canagaratna et al., 2015). Almost all the values are below 2 ‰, with exceptions for one type of cooking POA at 3 ‰, the polyol xylitol (4.2 ‰), and some acids (> 4.8 ‰, as shown in Fig. 3d). All the tracers resulting in elevated $f_{C_5H_6O}$ contain multiple hydroxyl groups, and may result in furan-like structures via facile dehydration reactions (Canagaratna et al., 2015). Xylitol has been proposed as a tracer of toluene SOA (Hu et al., 2008). It has a similar structure to 2-methyltetrols, with 5–OH groups instead of 4. In the AMS, xylitol may form the methylfuran structure through dehydration reactions like 2-methytetrols. However, $f_{C_5H_6O}$ in other toluene SOA tracers in our dataset show background levels of $f_{C_5H_6O}$ (< 2 ‰). Given the small fraction of xylitol in toluene SOA (Hu et al., 2008), xylitol is unlikely to increase $f_{C_5H_6O}$ in anthropogenic SOA, consistent with our results.

In summary, in the absence of strong impacts from biogenic SOA, the AMS high resolution ion $C_5H_6O^+$ has a clear and stable background, spanning a small range (0.02–3.5 ‰) with an peak around 1.7 ± 0.1 ‰, about an order of magnitude lower than the average value (22 ± 7 ‰) for IEPOX-SOA.

3.3 Enhancements of $f_{C_5H_6O}$ in areas strongly influenced by isoprene emissions

GEOS-Chem predicts much higher surface gas-phase IEPOX concentrations over the SE US and Amazon rainforest than those in temperate urban areas (Fig. 1). This is expected from high isoprene concentrations (e.g. 3.3 ppb in SOAS-CTR and 4 ppb in the Amazon) under low average NO concentrations (~ 0.1 ppb) (Karl et al., 2009; Ebben et al., 2011). Probability distributions of $f_{C_5H_6O}$ during both campaigns are shown in Fig. 4a, and are very similar with averages of 5–6 ‰ (range 2.5–11 ‰). The Amazon forest downwind of Manaus and a Borneo tropical forest study show even higher averages of 7 and 10 ‰, respectively (Robinson et al., 2011; de Sá et al., 2015). During the SEAC4RS aircraft campaign, the average $f_{C_5H_6O}$ (4.4 ± 1.6 ‰) from all SE US flights is also enhanced compared to levels observed in the northwest and western US conti-

nental air masses (1.7 ± 0.3 ‰) where isoprene emissions are much smaller (Guenther et al., 2012). Thus, campaigns in locations strongly influenced by isoprene emissions under lower NO conditions show systematically higher $f_{C_5H_6O}$ values (with an average peak of 6.5 ± 2.2 ‰) than background levels found in other locations (1.7 ‰). The fact that $f_{C_5H_6O}$ of total ambient OA (6.5 ± 2.2 ‰) in these studies is lower than the values in IEPOX-SOA (22 ± 7 ‰) is expected, since ambient datasets also include OA from other sources, and confirms that IEPOX-SOA is not an overwhelmingly dominant OA source at most of those locations (see Fig. S5).

3.4 Values of $f_{C_5H_6O}$ in laboratory studies of non IEPOX-derived isoprene SOA

We also investigate $f_{C_5H_6O}$ in laboratory SOA from isoprene in Fig. 4a. For SOA produced by chamber isoprene photooxidation under high NO_x conditions, low $f_{C_5H_6O}$ (< 2 ‰) within the background level is observed (Chen et al., 2011; Kroll et al., 2006). SOA from oxidation of isoprene hydroxyhydroperoxide (ISOPOOH, a product of low-NO oxidation of isoprene) under low-NO conditions, when formed under conditions are not favorable for the reactive uptake of IEPOX into aerosols also has low $f_{C_5H_6O}$ of 2 ‰ (Krechmer et al., 2015). Low values of $f_{C_5H_6O}$ (< 3 ‰) are also observed in SOA from isoprene + NO_3 radical reactions without acid seeds (Ng et al., 2008). The low $f_{C_5H_6O}$ (< 3 ‰) observed in non IEPOX-derived isoprene SOA indicate that $f_{C_5H_6O}$ is specifically enhanced from IEPOX-SOA, and is not a tracer for all SOA from isoprene.

3.5 Enhancements of $f_{C_5H_6O}$ in areas strongly influenced by monoterpene emissions

The BEACHON-RoMBAS campaign was carried out in a Rocky Mountain pine forest with high monoterpene emissions that account for 34 % in daytime and 66 % at night of the total VOC mixing ratios (on average peaking at 0.15 ppb during day and 0.7 ppb at night) (Fry et al., 2013) but lower isoprene emissions (peaking at 0.35 ppb during daytime) (Karl et al., 2014; Kaser et al., 2013). One-third of the RO_2 radicals

react via the low-NO route (i.e. via $RO_2 + HO_2$) at this site (Fry et al., 2013). The isoprene/monoterpene ratio at the Rocky Mountain site is 0.48, and is ~ 10–20 times lower than this ratio (4.7) in SOAS-CTR and (8.3) in Amazon studies (Chen et al., 2014), suggesting that $f_{C_5H_6O}$ may be near background levels because of the very low potential contribution of IEPOX-SOA at the Rocky Mountain site. However, the average $f_{C_5H_6O}$ at the Rocky Mountain site is 3.7 ± 0.5 ‰ (Fig. 4a), which although lower than the average $f_{C_5H_6O}$ (6.5 ‰) found in the SE US-CTR, Amazon and Borneo forests, it is still twice the background $f_{C_5H_6O}$ values of 1.7 ‰ observed in pollution and smoke-dominated locations.

Three circumstances may lead to such an enhanced $f_{C_5H_6O}$ at the Rocky Mountain site, which we examine here. (1) A small amount of IEPOX-SOA may be formed from the limited isoprene present at the Rocky Mountain site and surrounding region. However, the average isoprene concentration in this pine forest area is only 0.2 ppb, which is around 16 times less than that (3.3 ppb) at the SE US site in SOAS. The conditions at the Rocky Mountain site were less favorable for IEPOX-SOA formation due to a higher fraction (70 % in daytime) of the RO_2 radicals reacting with NO and less acidic aerosols (Levin et al., 2014; Fry et al., 2013). Thus we can estimate an upper limit contribution of IEPOX-SOA to the $f_{C_5H_6O}$ tracer at the Rocky Mountain site assuming the same ratio of IEPOX-SOA to isoprene in both campaigns. In this case, we would expect $f_{C_5H_6O}$ at the Rocky Mountain site to be the background level (1.7 ‰) plus 1/16th of the enhancement above the background observed in SOAS (5 ‰ – 1.7 ‰ = 3.3 ‰) multiplied by the ratio of OA concentrations at both sites (4.8 $\mu g\,m^{-3}$ in SE US site vs. 1.8 $\mu g\,m^{-3}$ in Rocky Mountain site). This calculation results in an expected upper limit $f_{C_5H_6O}$ ~ 2.25 ‰ at the Rocky Mountain site due to the IEPOX-SOA contribution. This estimate is much lower than the observed average 3.7 ‰. Thus the elevated $f_{C_5H_6O}$ in Rocky Mountain pine forest is very unlikely to be due to IEPOX-SOA.

(2) The second explanation of high $f_{C_5H_6O}$ observed at Rocky Mountain site is that SOA from monoterpene oxidation (MT-SOA) may have a higher $f_{C_5H_6O}$ than background OA from other sources. Several chamber studies show that MT-SOA, e.g., SOA from

ozonolysis (Chhabra et al., 2011; Chen et al., 2014) or photooxidation (Ng et al., 2007) of α-pinene, or NO_3 reaction with α-pinene, β-pinene and Δ^3-Carene (Fry et al., 2014; Boyd et al., 2015) can result in higher $f_{C_5H_6O}$ (average 5.5 ± 2.0 ‰) than background levels of ~ 1.7 ‰ (Fig. 4a). We note that the average MT-SOA value is still 4 times lower than the average for IEPOX-SOA, and thus they leave some room to separate both contributions. Oxidation of monoterpenes can lead to species with multiple –OH groups, which may result in the production of methylfuran (or ions of similar structure) upon AMS analysis. We do not observe enhanced $f_{C_5H_6O}$ in SOA from sesquiterpene oxidation (< 2 ‰) (Chen et al., 2014). The values of $f_{C_5H_6O}$ in chamber SOA from monoterpenes, together with the finding of a substantial contribution of monoterpenes to SOA at this Rocky Mountain site (Fry et al., 2013) suggest that MT-SOA may explain the values of $f_{C_5H_6O}$ observed there.

Two other field studies support the conclusion that ambient MT-SOA may have slightly enhanced $f_{C_5H_6O}$. Figure 6 shows data from a DC3 aircraft flight in the areas around Missouri and Illinois. Ambient $f_{C_5H_6O}$ increases from background levels (~ 1.7 ‰) to ~ 4.1 ‰ in a highly correlated manner to monoterpene concentration increases. Meanwhile, isoprene and gas-phase IEPOX stay at low levels similar to the rest of the flight, indicating that enhanced $f_{C_5H_6O}$ in the periods with higher MT concentrations should arise from MT-SOA and not IEPOX-SOA. Figure 4a includes AMS measurements at a MT-emission dominated European boreal forest (Hyytiälä in Finland) (Robinson et al., 2011). Average $f_{C_5H_6O}$ is ~ 2.5 ‰ at this site, which is again higher than the background $f_{C_5H_6O}$ value of 1.7 ‰. The slightly lower $f_{C_5H_6O}$ in the Boreal forest vs. the Rocky Mountain site may be partially explained by a small contribution from IEPOX-SOA at the latter (estimated above to increase $f_{C_5H_6O}$ up to 2.25 ‰ at the Rocky Mountain site), as well as by differences of the MT-SOA/OA ratio at both sites (Corrigan et al., 2013) and the relative importance of different MT oxidation pathways.

(3) The enhanced $f_{C_5H_6O}$ at the Rocky Mountain site may have arisen from oxidation products of 2-methyl-3-buten-2-ol (MBO, $C_5H_{10}O$) emitted from pine trees. MBO, with a daytime average of 2 ppb accounts for ~ 50 % of the total VOC mixing ratio during

the day (Karl et al., 2014). MBO has been shown to form aerosol with a 2–7 % yield in chamber studies, which is thought to proceed via the uptake of epoxide intermediates ($C_5H_{10}O_2$ vs. IEPOX $C_5H_{10}O_3$) under acidic aerosol conditions (Zhang et al., 2014; Mael et al., 2014; Zhang et al., 2012). Some aerosol species formed by MBO-derived epoxides have similar structures (e.g., $C_5H_{12}O_3$) to the IEPOX oxidation products in SOA and thus they might contribute to $f_{C_5H_6O}$. No pure MBO-derived epoxides or their oxidation products in the aerosol phase have been measured by AMS so far, to our knowledge.

To attempt to differentiate whether MT-SOA or MBO-SOA dominate the higher $f_{C_5H_6O}$ at the Rocky Mountain site, average diurnal variations of ambient $f_{C_5H_6O}$, monoterpene and isoprene + MBO are plotted in Fig. S6. $f_{C_5H_6O}$ shows a diurnal pattern that increases at night and peaks in the early morning, similar to the diurnal variation of monoterpenes. Monoterpenes continue to be oxidized during nighttime at this site by NO_3 radical and O_3 with a lifetime of ~ 30 min (with 5 ppt of NO_3 and 30 ppb of O_3) (Fry et al., 2013). In contrast only a decrease and later a plateau of $f_{C_5H_6O}$ are observed during the period with high MBO concentration and higher oxidation rate of MBO due to high OH radical in daytime (as MBO reacts slowly with O_3 and NO_3) (Atkinson and Arey, 2003). While MBO-SOA may or may not have $f_{C_5H_6O}$ above background levels, the diurnal variations point to MT-SOA playing a dominant role in $f_{C_5H_6O}$ at this site.

3.6 $f_{C_5H_6O}$ vs. OA oxidation level (f_{CO_2}) "triangle plot" – background studies

In AMS spectra, the CO_2^+ ion is a marker of aging and oxidation processes (Ng et al., 2011a; Alfarra et al., 2004). To evaluate whether oxidation plays a role on the observed $f_{C_5H_6O}$ for different types of OA, in this section we use plots of f_{CO_2}(= CO_2^+/OA) vs. $f_{C_5H_6O}$ as a graphical diagnostic of this process, similar to graphical diagnostics ("triangle plots") used for other purposes with AMS data (Ng et al., 2011a; Cubison et al., 2011). For studies strongly influenced by urban and biomass-burning emissions in Fig. 3d we observe a wide range of f_{CO_2} values from 0.001 to 0.3 (= 30 % or 300 ‰). The wide range of f_{CO_2} is due to variable fractions of POA and SOA (mixing effect) and

a variable oxidation level of POA and SOA (oxidation effect) in the different studies. In fact, to our knowledge, these studies encompass the values of f_{CO_2} observed in all ambient AMS studies to date (Ng et al., 2011a). Several studies when urban and forest air, or biomass burning smoke were aged by intense OH oxidation with an oxidation flow reactor (OFR) (Kang et al., 2007; Ortega et al., 2013; Li et al., 2013) are also included. However, despite the wide range of f_{CO_2}, $f_{C_5H_6O}$ changes little, staying in the range 0.02–3.5 ‰, and with little apparent dependence on f_{CO_2} for the ambient studies. A linear regression to quantiles from this dataset results in an intercept of 1.7 ‰ and a very weak decrease with increasing f_{CO_2}. A stronger decrease is observed when aging urban air (Los Angeles) by intense OH exposure in flow reactor, as shown in Fig. 3d.

Ambient f_{CO_2} at the Rocky Mountain forest site shows a moderate oxidation level (0.1–0.15), similar to the SE US-CTR (Fig. 5). $f_{C_5H_6O}$ in the Rocky mountain site decreases linearly when f_{CO_2} increases. During the Rocky Mountain study, the intense OH aging of ambient air in a flow reactor shows a continuation of the trend observed for the ambient data, where $f_{C_5H_6O}$ decreases as f_{CO_2} increases. A linear regression to the combined ambient and OFR datasets ($f_{C_5H_6O} = -0.013 \times f_{CO_2} + 0.0054$) will be used below to estimate background $f_{C_5H_6O}$ in areas with strong monoterpene and low isoprene emissions.

$f_{C_5H_6O}$ in ambient SOA from other studies catalogued in the HR-AMS spectral database are also shown in Fig. 5. Most urban oxygenated OA (OOA) are within background $f_{C_5H_6O}$ (average 1.7 ‰; range: 0.02–3.5 ‰), which is consistent with the $f_{C_5H_6O}$ (< 3 ‰) in lab aromatic SOA and other urban OA in Fig. 5. However, some ambient SOA spectra do show higher $f_{C_5H_6O}$ (3–10 ‰) than the background $f_{C_5H_6O}$ (0.02–3.5 ‰), which we will discuss in the next section.

3.7 $f_{C_5H_6O}$ vs. OA oxidation level (f_{CO_2}) – IEPOX-SOA influenced studies

f_{CO_2} vs. $f_{C_5H_6O}$ in studies impacted by IEPOX-SOA are shown in Fig. 5. Consistent with the distributions discussed above, the bulk of points from these areas all show

distinctively enhanced $f_{C_5H_6O}$ when compared to background $f_{C_5H_6O}$ points of similarly moderate or higher oxidation levels. The $f_{C_5H_6O}$ measurements with lower f_{CO_2} values are more broadly distributed than the $f_{C_5H_6O}$ points with higher f_{CO_2} values in SE US-CTR, SEAC4RS, Borneo forest and Amazon forest down Manaus campaigns. However, increased $f_{C_5H_6O}$ with higher f_{CO_2} was observed in the Amazon. Both oxidation and mixing of airmasses with different OA can influence these observations. $f_{C_5H_6O}$ in IEPOX-SOA usually will decrease with oxidative aging. E.g., $f_{C_5H_6O}$ from the SOAS oxidation flow reactor decreases continuously as OA becomes more oxidized than ambient OA in SOAS-CTR (f_{CO_2} increases from 0.15 to 0.3). Airmass mixing effects are more complex. Depending on the f_{CO_2} of OA in the airmasses mixed with, $f_{C_5H_6O}$ in IEPOX-SOA-rich air can show positive, neutral or negative trends with increasing f_{CO_2}. E.g., in pristine Amazon forest, points with lower f_{CO_2} (< 0.08) have low $f_{C_5H_6O}$ are thought to be mainly caused by advection of POA from occasional local pollution.

The overall trend for the ambient measurements in studies strongly influenced by isoprene emissions (Fig. 5) is that those points cluster in a triangle shape and $f_{C_5H_6O}$ decreases as f_{CO_2} increases. This "triangle shape" indicates that in most of campaigns of this study shows the local OA with IEPOX-SOA contributions is influenced by the ambient oxidation processes or mixing with more aged aerosols.

Finally, points with higher $f_{C_5H_6O}$ in OA or OOA/aged OA are labeled with numbers in Fig. 5. The sources of those labeled points are summarized in Table S2. OA from those studies are all partially influenced by biogenic emissions. For example, during measurements of ambient OA in the Central Valley of California (number 2), high isoprene emissions and acidic particles were observed (Dunlea et al., 2009), suggesting that potential IEPOX-SOA formed in this area may explain the higher $f_{C_5H_6O}$ in ambient OA there.

3.8 Best estimate of $f_{C_5H_6O}$ in IEPOX-SOA

IEPOX-SOA from different field campaigns and chamber studies lay towards the right and on the bottom half of Fig. 5. IEPOX-SOA from chamber studies show systemati-

cally lower f_{CO_2} than ambient studies. This is likely explained by the lack of additional aging in the laboratory studies, because all the lab IEPOX-SOA were measured directly after uptake gas-phase IEPOX onto acidic aerosol without undergoing substantial additional oxidation.

A wide range (12–40 ‰) of $f_{C_5H_6O}$ is observed with an average of 22 ± 7 ‰ in ambient and lab IEPOX-SOA. $f_{C_5H_6O}$ in IEPOX-SOA did not show a trend vs. f_{CO_2} in IEPOX-SOA. The IEPOX-SOA molecular tracer 3-MeTHF-3,4-diols has been shown to enhance the $f_{C_5H_6O}$ in OA (Fig. 5) (Lin et al., 2012; Canagaratna et al., 2015). Except 3-MeTHF-3,4-diols, none of the other pure IEPOX-derived polyols standards have been atomized and injected into the AMS system so far, to our knowledge. We suspect other polyols such as 2-methyltetrols may also lead to such an enhancement through dehydration reactions in the AMS vaporizer leading to methylfuran-type structures. The diversity of $f_{C_5H_6O}$ in IEPOX-SOA in different studies is related with the variable content of specific IEPOX-SOA molecular species that enhance $f_{C_5H_6O}$ differently. The fractions of molecular IEPOX-SOA species in total IEPOX-SOA is plotted vs. $f_{C_5H_6O}$ in IEPOX-SOA in four different studies in Fig. 7. A strong correlation is observed between the fraction of IEPOX-derived 2-methyltetrols and $f_{C_5H_6O}$ in IEPOX-SOA. A similar trend is observed between IEPOX-derived C_5-alkene triols and $f_{C_5H_6O}$ in IEPOX-SOA, and also with total IEPOX-SOA tracers. The strong simultaneous variation of both quantities indicates that the diversity of $f_{C_5H_6O}$ in IEPOX-SOA is very likely explained by the variability of the molecules comprising IEPOX-SOA among different studies.

During one day in SOAS (26 June 2013), IEPOX-SOA comprised 80–90 % of total OA (Fig. S7), possibly due to high sulfate concentrations favoring IEPOX-SOA formation. $f_{C_5H_6O}$ reached 25 ‰, which is similar to the 22 ‰ for the PMF-resolved IEPOX-SOA from this study, and consistent with a slightly lower value for the average vs. freshest ambient IEPOX-SOA. Among the chamber studies, the study of reactive uptake of isoprene-oxidation products into an acidic seed is most similar to the full chemistry in real ambient environments (Liu et al., 2014), and reports similar $f_{C_5H_6O}$ values (19 ‰).

Hence, we propose an average $f_{C_5H_6O}$ (21 ‰) from both studies as the typical value of fresh IEPOX-SOA.

3.9 Proposed method for real-time estimation of IEPOX-SOA

So far, PMF of AMS spectra is the only demonstrated method for quantifying total IEPOX-SOA concentrations. However, the PMF method is labor-intensive and requires significant expertise, and may fail to resolve a certain factor when present in lower mass fractions (< 5 %). A simpler, real-time method to estimate IEPOX-SOA would be useful in many studies, including during ground-based and aircraft campaigns.

We propose an estimation method for IEPOX-SOA based on the mass concentration of its tracer ion $C_5H_6O^+$. To do this, we express the mass concentration of $C_5H_6O^+$ as

$$C_5H_6O^+_{total} = C_5H_6O^+_{IEPOX\text{-}SOA,\ ambient} + C_5H_6O^+_{background}. \quad (1)$$

Where, $C_5H_6O^+_{total}$ is measured total $C_5H_6O^+$ signal in AMS; $C_5H_6O_{IEPOX\text{-}SOA,\ ambient}$ and $C_5H_6O^+_{background}$ are the $C_5H_6O^+$ signals contributed by IEPOX-SOA in ambient OA and other background OA (non IEPOX-SOA). Note that in the AMS, the "mass concentration" of an ion is used to represent the mass of the species whose detection resulted in the observed ion current of that ion, based on the properties of electron ionization (Jimenez et al., 2003).

Then, $C_5H_6O_{IEPOX\text{-}SOA,\ ambient}$ and $C_5H_6O^+_{background}$ can be calculated as:

$$C_5H_6O^+_{IEPOX\text{-}SOA,\ ambient} = \text{IEPOX-SOA} \times f_{C_5H_6O_{IEPOX\text{-}SOA}}. \quad (2)$$

$$C_5H_6O^+_{background} = (OA_{mass} - \text{IEPOX-SOA}) \times f_{C_5H_6O_{background}}. \quad (3)$$

Where, $f_{C_5H_6O_{IEPOX\text{-}SOA}}$ is the fractional contribution of $C_5H_6O^+$ to the total ion signal in the spectra of IEPOX-SOA from lab generated IEPOX-SOA or PMF-resolved IEPOX-SOA factors. $f_{C_5H_6O_{background}}$ is the background $f_{C_5H_6O}$ in other non-IEPOX-SOA, e.g., values from OA strongly influenced by urban and biomass burning emissions.

Then, by combining Eqs. (1)–(3), we can express $C_5H_6O^+_{total}$ as:

$$C_5H_6O^+_{total} = \text{IEPOX-SOA} \times f_{C_5H_6O_{\text{IEPOX-SOA}}} + (\text{OA} - \text{IEPOX-SOA}) \times f_{C_5H_6O_{\text{background}}}. \quad (4)$$

Finally, IEPOX-SOA can be estimated as:

$$\text{IEPOX-SOA} = \frac{C_5H_6O^+_{total} - \text{OA} \times f_{C_5H_6O_{\text{background}}}}{f_{C_5H_6O_{\text{IEPOX-SOA}}} - f_{C_5H_6O_{\text{background}}}}. \quad (5)$$

In Eq. (5), $C_5H_6O^+_{total}$ and OA mass are measured directly by AMS. $f_{C_5H_6O_{\text{background}}}$ and $f_{C_5H_6O_{\text{IEPOX-SOA}}}$ are two parameters that must be determined by other means.

As discussed above, the background value in the absence of a substantial impact of MT-SOA is ~ 1.7 ‰. In studies influenced by monoterpene emissions, the background value may be elevated by MT-SOA. $f_{C_5H_6O}$ at the Rocky Mountain site estimated by $f_{C_5H_6O} = (0.41 - f_{CO_2}) \times 0.013$ (Fig. 5) will be used as $f_{C_5H_6O_{\text{background}}}$ for areas with strong MT-SOA contributions. There is some uncertainty in this value, due to possible contributions of a small amount of IEPOX-SOA, MBO-SOA, and other OA sources at this site. An alternative estimate as $f_{C_5H_6O_{\text{background}}}$ from area with strong monoterpene emissions would be ~ 1.7 ‰ + 3 × MT_{avg} (ppb), which is also approximately consistent with our ambient data, but may have higher uncertainty. Further characterization of the background $f_{C_5H_6O}$ in areas with MT-SOA impact is of interest for future studies. As discussed above, we use average $f_{C_5H_6O_{\text{IEPOX-SOA}}}$ = 22 ‰ in Eq. (3) as a representative value of ambient IEPOX-SOA.

3.10 Application of the real-time estimation method of IEPOX-SOA

To test the proposed estimation method, we use SE US forest (SOAS) data as an example in Fig. 8, applying both background estimates (urban and biomass burning, and monoterpene emissions). Since there are high monoterpene concentrations (~ 1 ppb during the night) in SOAS, we expect the MT-influenced background to be more

accurate. The IEPOX-SOA estimated by subtracting the MT-SOA background (IEPOX-SOA_{MT}) is indeed better correlated with PMF-resolved IEPOX-SOA (R = 0.99) than that (R = 0.96) when the urban and biomass-burning background is applied (IEPOX-$SOA_{urb\&bb}$). The intercept of regression line between IEPOX-SOA_{MT} and PMF-resolved IEPOX-SOA is zero, indicating the background of IEPOX-SOA contributed by MT-SOA is clearly deducted.

The regression slope between IEPOX-SOA_{MT} and IEPOX-SOA_{PMF} is 0.95, suggesting that $C_5H_6O^+$ in SE US CTR site (SOAS) may be slightly overcorrected by minimizing $C_5H_6O^+$ from monoterpene emissions. This underestimation may be associated with higher MT-SOA contribution to $C_5H_6O^+$ in Rocky Mountain pine forest site than SE US forest site, or interference from IEPOX-SOA/MBO-SOA at the Rocky Mountain site. IEPOX-$SOA_{urb\&bb}$ is 1.26 times higher than PMF-resolved IEPOX-SOA. Thus, as expected IEPOX-SOA_{MT} and IEPOX-$SOA_{urb\&bb}$ provide lower and upper limits of estimated IEPOX-SOA.

Among all the datasets introduced in this study, the SOAS-CTR dataset should be the best case scenario since $f_{C_5H_6O_{\text{IEPOX-SOA}}}$ = 22 ‰ is coincidently the same value in the spectrum of PMF-resolved IEPOX-SOA in SOAS-CTR and a large fraction (17 %) of IEPOX-SOA existed in SOAS-CTR as well. Given the spread of values of $f_{C_5H_6O_{\text{IEPOX-SOA}}}$ (12–40 ‰) in different studies, if no additional local IEPOX-SOA spectrum is available for a given site, the estimation from this method should be within a factor of ~ 2 of the actual concentration. Further information concerning the estimation method using unit mass resolution m/z 82 (or f_{82}) can be found in the Appendix.

4 Conclusions

To investigate if the ion $C_5H_6O^+$ (at m/z 82) in AMS spectra is a good tracer for IEPOX-SOA, tens of field and lab studies are combined and compared, including the SOAS 2013 campaign in the SE US. The results show that $f_{C_5H_6O}$ is clearly elevated when IEPOX-SOA is present, and thus has potential usefulness as a tracer of this aerosol

type. The average $f_{C_5H_6O}$ in chamber generated and ambient PMF resolved IEPOX-SOA is 22 ± 7 ‰ (range 12–40 ‰). No dependence of $f_{C_5H_6O}$ on oxidation level (f_{CO_2}) of IEPOX-SOA was found. Background $f_{C_5H_6O}$ in OA strongly influenced by urban or biomass-burning emissions or pure anthropogenic POAs averages 1.7 ± 0.1 ‰ (range 0.02–3.5 ‰).

In ambient OA that is strongly influenced by isoprene emissions under lower NO, we observe systematically higher $f_{C_5H_6O}$ (with an average of ~ 6.5 ± 2.2 ‰), consistent with presence of IEPOX-SOA. Low tracer values ($f_{C_5H_6O}$ < 3 ‰) are observed in non IEPOX-derived isoprene-SOA, indicating that the tracer ion is specifically enhanced from IEPOX-SOA, and is not a tracer for all SOA from isoprene.

Higher background values of $f_{C_5H_6O}$ (3.1 ± 0.8 ‰ in average) were found in area strongly impacted by monoterpene emissions. $f_{C_5H_6O}$ in pure monoterpene SOA is 5.5 ± 2.0 ‰, which are substantially lower than for IEPOX-SOA, and thus they leave some room to separate both contributions. A background of $f_{C_5H_6O}$ as a function of f_{CO_2} in monoterpene emissions is determined by linear regressing the $f_{C_5H_6O}$ and f_{CO_2} at a Rocky Mountain pine forest site.

A simplified method to estimate IEPOX-SOA based on measured ambient $C_5H_6O^+$, CO_2^+ and OA in AMS is proposed. Good correlations (R > 0.96) between estimated IEPOX-SOA and PMF-resolved IEPOX-SOA are obtained for SOAS, confirming the potential usefulness of this estimation method. Given the observed variability in IEPOX-SOA composition, the method is expected to be within a factor of ~ 2 of the true concentration if no additional information about the local IEPOX-SOA is available for a given study. When only unit mass resolution data is available as in ACSM data, all methods may perform less well because of increased interferences from other ions at m/z 82.

Appendix:

In addition to the preceding high resolution $C_5H_6O^+$ data analysis, we also investigated unit mass resolution (UMR) m/z 82 as a tracer of IEPOX-SOA. In addition to $C_5H_6O^+$

(m/z 82.0419), the reduced ion $C_6H_{10}^+$ and oxygenated ion $C_4H_2O_2^+$ often contribute signal to UMR m/z 82. The average background level of f_{82} (= m/z 82/OA) is from 4.3±0.9 ‰ (0.01 to 10 ‰) in studies strongly influenced by urban, biomass-burning and other anthropogenic POA, as shown in Fig. A1a–c. This value is higher than the high-resolution $f_{C_5H_6O}$ background (1.7 ‰) in the same studies. Background f_{82} increases when OA is fresher (lower f_{44}, f_{44} = m/z 44/OA) as shown in Fig. A1d, and can be estimated as $f_{82} = 5.5 \times 10^{-3} - 8.2 \times 10^{-3} \times f_{44}$ in areas strongly impacted by urban and biomass-burning emissions. The uncertainty of calculated f_{82} can be as high as 30 % in the lower fresh OA plumes by considering the uncertainties from quantile average and linear regression. There are also some pure chemical species that exhibit high f_{82} values, as shown in Fig. A1c. These species include docosanol, eicosanol and oleic acid. However, none of these pure chemical species alone contributes substantially to ambient aerosol.

The probability density distributions of f_{82} in studies strongly influenced by isoprene emissions are shown in Fig. A2a. The peaks (~ 8.7 ± 2.5 ‰) are similar in SE US, pristine, polluted Amazon forest, Borneo forest to high resolution $f_{C_5H_6O}$ (~ 6.5±2.2 ‰), indicating $C_5H_6O^+$ is the dominant ion at UMR m/z 82 in these studies. Compared to the studies with strong urban and biomass-burning emissions, clear enhancements of f_{82} in studies strongly influenced by isoprene emissions are still observed, but with less contrast than for in high resolution datasets (Figs. A2 and A3).

Figure A2a also shows the probability density distributions of f_{82} at Rocky Mountain and European boreal forests (strongly influenced by monoterpene emissions). Those distributions peak at ~ 5 ‰, which are within the range (0.01–10 ‰) of f_{82} in aerosols strongly influenced by urban and biomass-burning emissions. In the lab studies, most of f_{82} (average 6.7 ± 2.2 ‰; range 4–11 ‰) observed in the spectra of MT-SOA are also comparable to background f_{82} levels (average 4.3 ± 0.9 ‰; range 0.01–10 ‰), and tend to be in the higher f_{82} region from urban and biomass-burning emissions. A linear regression line of f_{44} vs f_{82} for the Rocky Mountain site ($f_{82} = 7.7 \times 10^{-3} - 0.019 \times f_{44}$)

is used to estimate the background f_{82} from areas strongly influenced by monoterpene emissions.

In summary, elevated f_{82} in studies with high isoprene-emissions is observed. Pronounced f_{82} should be a key feature of IEPOX-SOA spectra. Thus IEPOX-SOA can be estimated as Eq. (A1) here:

$$\text{IEPOX-SOA} = \frac{m82_{\text{total}} - m82_{\text{background}}}{f_{82_{\text{IEPOX-SOA}}} - f_{82_{\text{background}}}} = \frac{m82_{\text{total}} - \text{OA}_{\text{mass}} \times f_{82_{\text{background}}}}{f_{82_{\text{IEPOX-SOA}}} - f_{82_{\text{background}}}}, \quad \text{(A1)}$$

where $f_{82_{\text{IEPOX-SOA}}}$ is 22 ‰ as obtained average (Fig. A3). In Eq. (4), $f_{82_{\text{background}}}$ can be calculated as a function of f_{44} in studies strongly influenced by urban and biomass-burning emissions ($f_{82} = 5.5 \times 10^{-3} - 8.2 \times 10^{-3} \times f_{44}$) or monoterpene emissions ($f_{82} = 7.7 \times 10^{-3} - 0.019 \times f_{44}$), as discussed earlier. $m82_{\text{total}}$ and OA_{mass} are the measured ambient m/z 82 and OA mass concentrations by AMS. Because f_{82} in MT-SOA and OA from urban and biomass-burning emissions cannot be separated, only one background value of f_{82} will be used in the UMR method.

To test this UMR empirical method, we apply Eq. (A1) to SOAS-CTR dataset, see Fig. A4. The estimated IEPOX-SOA in SOAS-CTR from both background corrections (urban + biomass burning vs. monoterpene) both correlates well with PMF-resolved IEPOX-SOA with $R = 0.97$ and $R = 0.98$, respectively. The regression slopes between estimated fresh IEPOX-SOA vs. IEPOX-SOA PMF factor are 1.11 and 0.94, which are within 15 % of 1 : 1 line. The deviation of estimated IEPOX-SOA from UMR by subtracting the background of MT-SOA influences is similar to that from HR in the SOAS dataset, indicating the UMR-based IEPOX-SOA estimation may perform as well as HR in areas with high IEPOX-SOA fractions. For areas with small IEPOX-SOA fractions, more uncertainties may exist in UMR calculation, e.g., there are wider variations of background f_{82} from urban and biomass-burning emissions with oxidation level, whereas a smaller and less variable background of $f_{C_5H_6O}$ is found in HR. Overall, m/z 82 in unit mass resolution data is also useful to estimate IEPOX-SOA. The different

methods to estimate IEPOX-SOA may perform less well because of increased interferences from other ions at m/z 82, however at locations with very high fractions of IEPOX-SOA such as SOAS-CTR, the UMR-based method performs well.

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Table 1. Datasets used in this study[a]. Ranges or average plus SD of $f_{C_5H_6O}$ (high resolution) and f_{82} (unit mass resolution) in different studies are also included.

Name of datasets	Time period	Site locations and descriptions	Campaign name	Ranges or average ± SD $f_{C_5H_6O}$ (‰)	Ranges or average ± SD f_{82} (‰)	References
Studies strongly-influenced by isoprene emissions under lower NO						
SE US forest-CTR site	Jun–Jul 2013	Centreville, AL,	SOAS	6.2 ± 2.4	7.6 ± 2.2	(1)
Pristine Amazon forest 2008, Brazil	Feb–Mar 2008	Pristine rain forest site, TT34	AMAZE-08	5.0 ± 2.3	7.9 ± 1.7	(2)
Amazon forest downwind Manaus, Brazil	Feb–Mar 2014	T3 site, near Manacapuru	GoAmazon2014/15	6.9 ± 1.6	7.1 ± 1.0	(3)
Pristine Amazon forest 2014, Brazil	Aug–Dec 2014	T0 site, ~ 150 km northeast of Manaus	GoAmazon, 2014/15	N/A	5.6 ± 1.7	(4)
SE US	Aug–Sep 2013	Aircraft measurement:	SEAC4RS	4.3 ± 1.6	N/A	(5)
Borneo forest, Malaysia	Jun–Jul 2008	Rain forest GAW station, Sabah, Malaysia	OP3	10 ± 0.3	12.4 ± 0.4	(6)
Atlanta, US	Aug–Sep 2011	JST site, Atlanta, Georgia, US		N/A	N/A	(7)
Harrow, Canada	Jun–Jul 2007	Harrow site, rural sites surrounded by farmland, Canada	BAQSMET	N/A	N/A	(8)
Bear Creek, Canada	Jun–Jul 2007	Bear Creek site, wetlands area surrounded by farmland, Canada	BAQSMET	N/A	N/A	(8)
Studies strongly-influenced by monoterpene emissions						
Rocky mountain pine forest, CO, USA	Jul–Aug 2011	Manitou Experimental Forest Observatory, CO,	BEACHON-RoMBAS	3.7 ± 0.5	5.1 ± 0.5	(9)
European Boreal forest, Finland	2008–2009	Hyytiala site in Pine forest, Finland	EUCAARI campaign	2.5 ± 0.1 [b]	4.8 ± 0.1 [b]	(10)
Studies mixed-influenced by isoprene and monoterpene emissions						
North American temperate, US	Aug–Sep 2007	Blodgett Forest Ameriflux Site, CA, US	BEARPEX	4.0 ± < 0.1 [b]	4.0 ± < 0.1 [b]	(10)
Studies strongly-influenced by urban emissions						
Los Angeles area, CA, USA	May–Jun 2010	Pasadena, US	CalNex	1.6 ± 0.2	3.6 ± 0.5	(11)
Beijing, China	Nov–Dec 2010	Peking University, in NW of Beijing city, China	N/A	1.5 ± 0.3	4.6 ± 0.7	(12)
Changdao island, Downwind of China	Mar–Apr 2011	Changdao island, China	CAPTAIN	1.6 ± 0.2	3.8 ± 0.5	(13)
Barcelona area, Spain	Feb–Mar 2009	Montseny, Spain	DAURE	1.6 ± 0.2	4.8 ± 0.9	(14)
Studies of biomass-burning smokes						
BB Chamber study	Sep–Oct 2009	Missoula, MO, USA	FLAME-3	1.9 ± 0.6	5.9 ± 1.4	(15)
Biomass burning plumes	Aug–Sep 2013	All over US, aircraft measurement	SEAC4RS	1.8 ± 0.5	N/A	(5)
Biomass burning plumes	May–Jun 2011	All over US, aircraft measurement	DC-3	1.8 ± 0.4	N/A	(16)

Table 1. Continued.

Name of datasets	Time period	Site locations and descriptions	Campaign name	Ranges or average ± SD $f_{C_5H_6O}$ (‰)	Ranges or average ± SD f_{82} (‰)	References
Continental plumes						
NW US	Aug–Sep 2013	Aircraft measurement	SEAC4RS	1.7 ± 0.3	N/A	(15)
Western US	May–Jun 2011	Aircraft measurement	DC-3	1.9 ± 0.6	N/A	(16)
OA from specific sources						
IEPOX-SOA from ambient PMF factors and chamber studies.				22 ± 7	22 ± 7	(17)
Isoprene derived non-IEPOX SOA (reaction with OH under conditions of high NO or low NO without seed not favorable for the reactive-uptake of IEPOX, reaction with NO3 without seed)				< 3	< 3	(18)
Monoterpene-derived SOA				5.5 ± 2.0	6.7 ± 2.0	(19)
Other SOA (not from isoprene and mononterpene)				2.2 ± 0.9	6.1 ± 2.1	(20)
Cooking				1.5 ± 0.8	8.2 ± 1.1	(21)
Coal combustion				1.4–2.0	N/A	(22)
Vehicle emission				1.1 ± 0.6	5.1 ± 1.1	(23)
Biomass burning				2.3 ± 0.7	4.3 ± 1.5	(24)
Pure chemical species				0.7 ± 1.0	4.0 ± 5.5	(25)

[a] HR-ToF-AMS was used for all the campaigns except the Atlanta, US and Pristine Amazon forest 2014, Brazil using ACSM.
[b] Standard error.
(1) This study; (2) Chen et al. (2014); (3) de Sá et al. (2015); (4) Carbone et al. (2015); (5) Toon (2015); (6) Robinson et al. (2011); (7) Budisulistiorini et al. (2013); (8) Slowik et al. (2011); (9) Ortega et al. (2014); (10) Robinson et al. (2011); (11) Hayes et al. (2013); (12) Hu et al. (2015); (13) Hu et al. (2013); (14) Minguillón et al. (2011); (15) Ortega et al. (2013); (16) Barth et al. (2014); (17) Chhabra et al. (2011); Budisulistiorini et al. (2013); Chen et al. (2014); Liu et al. (2014); Robinson et al. (2011); Kuwata et al. (2015); (18) Ng et al. (2008); Kroll et al. (2006); Krechmer et al. (2015); (19) Boyd et al. (2015); Chen et al. (2014); Bahreini et al. (2005); (20) Bahreini et al. (2005); Liggio et al. (2005); Chhabra et al. (2011); Loza et al. (2012); (21) Mohr et al. (2012) (2009); Hu et al. (2015); He et al. (2010); Huang et al. (2010); Crippa et al. (2013); Lanz et al. (2007); (22) Hu et al. (2015) (2013); (23) Sage et al. (2008); Mohr et al. (2012); Setyan et al. (2012); Aiken et al. (2009); Docherty et al. (2011); Saarikoski et al. (2012); Canagaratna et al. (2004); Mohr et al. (2009); Lanz et al. (2007); Chang et al. (2011); Crippa et al. (2013); Hersey et al. (2011); Coggon et al. (2012); Ng et al. (2011b); (24) Hu et al. (2015) (2013); Aiken et al. (2009); Mohr et al. (2012); Saarikoski et al. (2012); Weimer et al. (2008); Schneider et al. (2011); He et al. (2010); Schneider et al. (2006); Ng et al. (2011b); Crippa et al. (2013); (25) Aiken et al. (2009); Dzepina et al. (2007); Takegawa et al. (2007); Katrib et al. (2004); Alfarra (2004); Schneider et al. (2011); Phinney et al. (2006); Li et al. (2011).

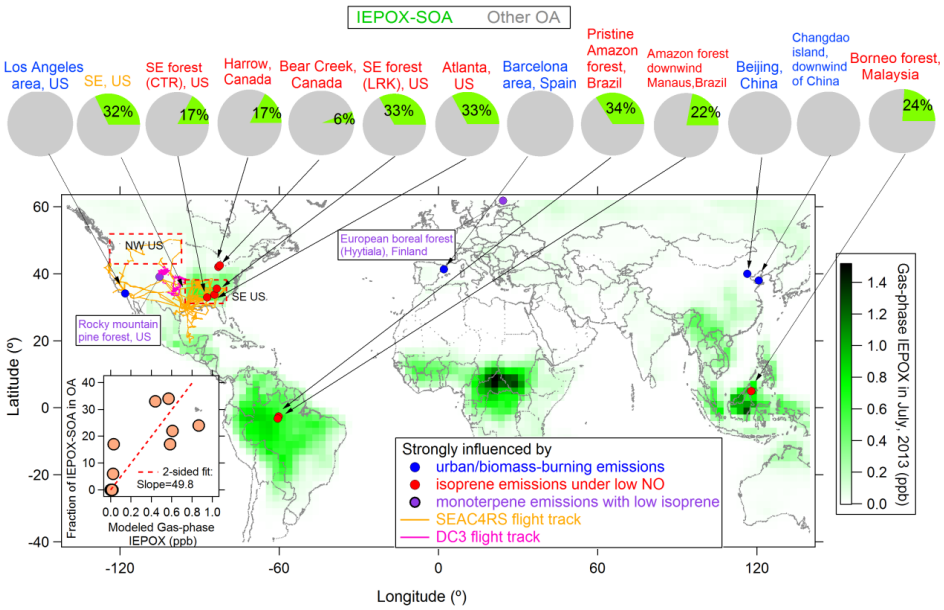

Figure 1. Locations of field campaigns used in this study. The IEPOX-SOA fractions of OA in different studies are shown in the pie charts on the top of graph. Site names are color-coded with site types. Detailed information these studies can be found in Table 1. The green background is color coded with modeled global gas-phase IEPOX concentrations for July 2013 from the GEOS-Chem model. The insert shows as scatter plot of observed average fraction of IEPOX-SOA in OA vs. GEOS-Chem modeled gas-phase IEPOX in various field campaigns.

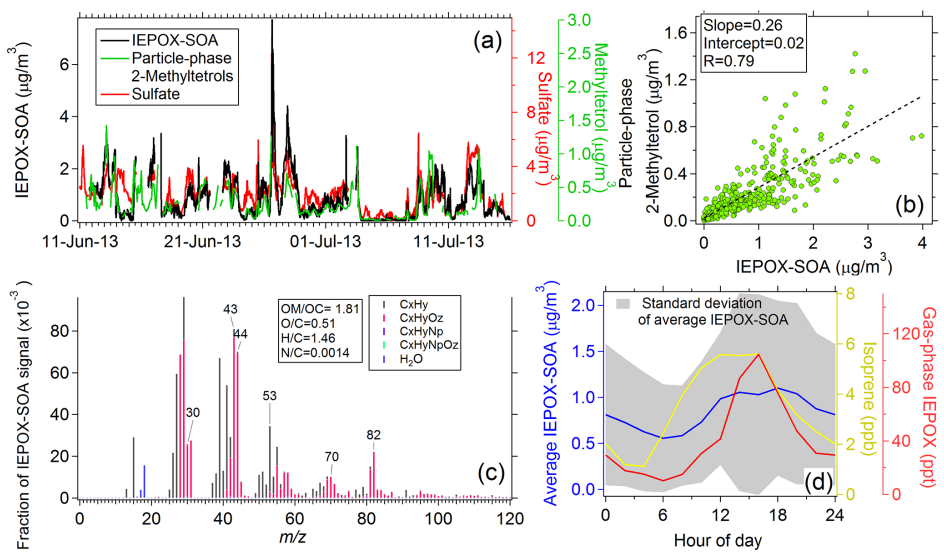

Figure 2. Results from the SOAS campaign in a SE US forested site. **(a)** Time series of IEPOX-SOA PMF factor, sulfate and particle-phase 2-methylterols (a key IEPOX uptake product) from on-line GC/MS. **(b)** Scatter plot between particle-phase 2-methylterols and IEPOX-SOA. **(c)** Mass spectrum of IEPOX-SOA. **(d)** Diurnal cycle of IEPOX-SOA, isoprene and gas-phase IEPOX (the latter measured by CF_3O^- CIMS).

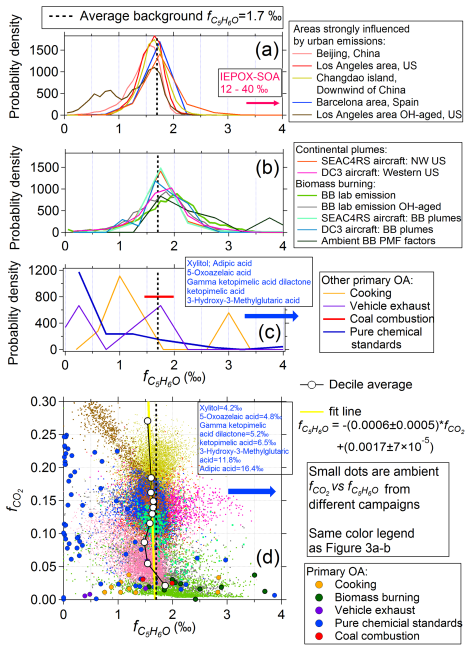

Figure 3. Probability density distributions of $f_{C_5H_6O}$ in studies **(a)** strongly influenced by urban emissions; **(b)** continental air masses sampled from aircraft and biomass-burning emissions; **(c)** other anthropogenic primary OA sources and pure chemical standards. The dashed line (1.7‰) is the average $f_{C_5H_6O}$ in studies shown in (**a** and **b**). **(d)** Scatter plot of f_{CO_2} (f_{CO_2} = CO_2^+/OA) vs. $f_{C_5H_6O}$ for all studies shown in panels **(a–c)**, using the same color scheme. Quantile averages of $f_{C_5H_6O}$ across all studies sorted by f_{CO_2} are also shown, as is a linear regression line to the quantile points.

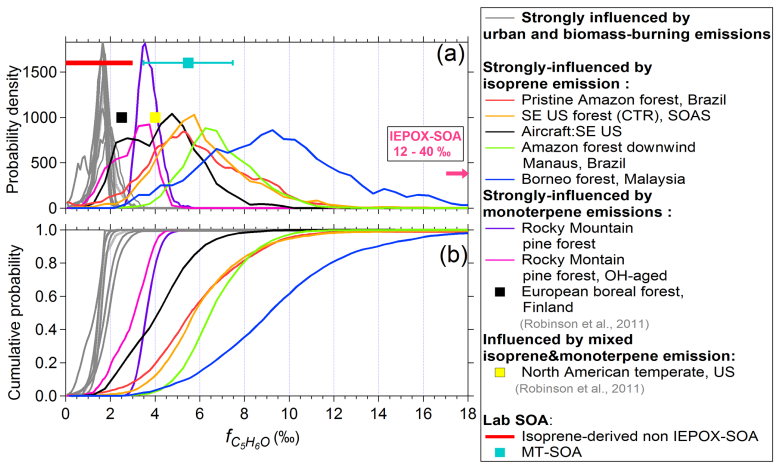

Figure 4. (a) Probability density and **(b)** cumulative probability distributions of $f_{C_5H_6O}$ in studies strongly influenced by isoprene and/or monoterpene emissions. The ranges of $f_{C_5H_6O}$ from other non IEPOX-derived isoprene-SOA and MT-SOA are also shown. The background grey lines are from studies strongly influenced by urban and biomass-burning emissions and are the same data from Fig. 3a and b.

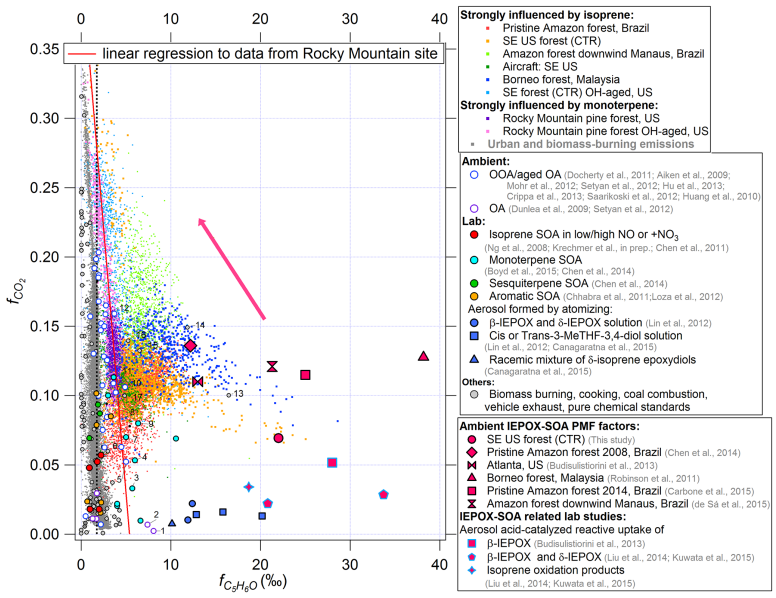

Figure 5. Scatter plot of f_{CO_2} and $f_{C_5H_6O}$ in studies strongly by isoprene and monoterpene emissions, as well as other OA sources. The grey dots represent background levels from studies strongly influenced by urban and biomass-burning emissions in Fig. 3d. f_{CO_2} and $f_{C_5H_6O}$ values from multiple sources of OA are also shown, together with IEPOX-SOA from different ambient PMF factors and chamber studies. A linear regression line of f_{CO_2} and $f_{C_5H_6O}$ calculated from Rocky Mountain pine forest is also displayed. We labeled some symbols with high $f_{C_5H_6O}$ in numbers. From number 1–12 are all OAs with biogenic influences. Number 13–17 are some pure chemical standards (acids) as discussed above. For detailed information on the meaning of the numbered symbols see Table S2.

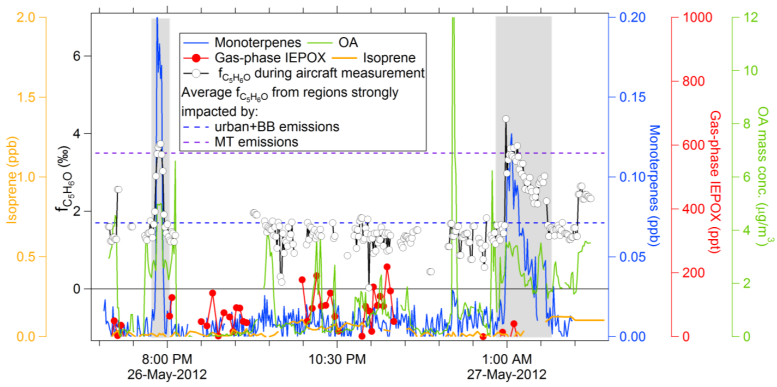

Figure 6. Time series of ambient $f_{C_5H_6O}$ in OA, gas-phase IEPOX, monoterpenes and isoprene in DC3 aircraft measurement. Average $f_{C_5H_6O}$ from regions strongly impacted by urban and biomass-burning emissions and MT emissions are also shown for reference. Two areas with grey background indicate the periods when $f_{C_5H_6O}$ increases when monoterpene concentrations increase.

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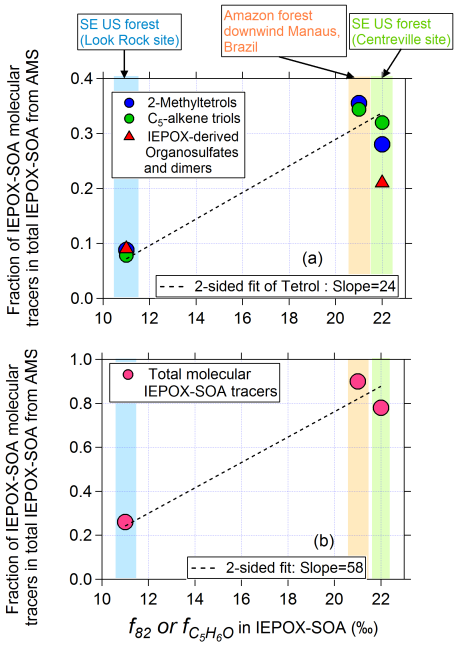

Figure 7. (a) Scatter plot between different IEPOX-SOA molecular tracers (Methyltetrol, C_5-alkene triols and IEPOX-derived organosulfates and their dimers) and f_{82} in IEPOX-SOA. **(b)** Scatter plot between total IEPOX-SOA molecular tracers (= Methyltetrol + C_5-alkene triols + IEPOX-derived organosulfates and dimers) and f_{82} in IEPOX-SOA. SOAS, the other datasets in the graph are from Budisulistiorini et al. (2015) and de Sá et al. (2015). The fraction of organosulfates and their dimers in IEPOX-SOA in Amazon forest downwind of Manaus, Brazil was assumed to be the same as that at SE US Centreville site.

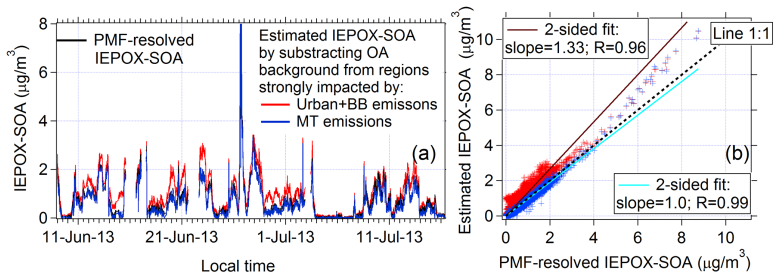

Figure 8. (a) Time series of IEPOX-SOA PMF factor and estimated IEPOX-SOA based on $C_5H_6O^+$ for the SOAS data in SE US. Two different estimates of $C_5H_6O^+$ are shown, using values from regions strongly impacted by urban and biomass-burning emissions vs. regions with strong monoterpene emissions. **(b)** Scatter plot of estimated IEPOX-SOA vs. PMF-resolved IEPOX-SOA. Note that the largest IEPOX-SOA plume on 26 June 2013 had a slightly higher $f_{C_5H_6O}$ of 24 ‰, resulting in a slight overestimation of IEPOX-SOA for those data points.

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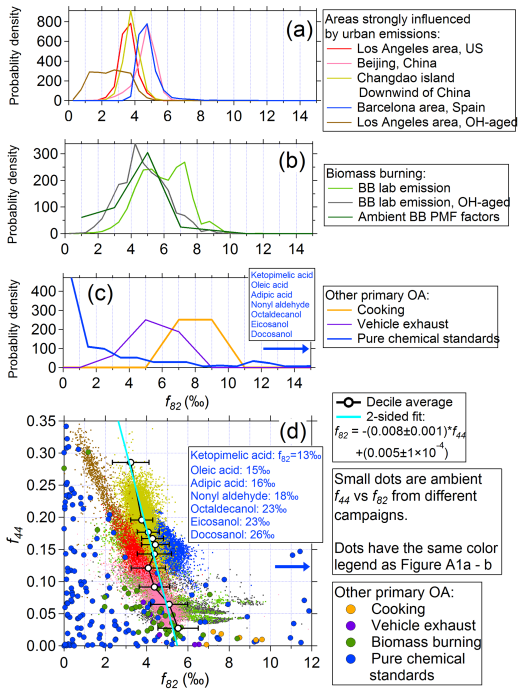

Figure A1. Probability density distributions of f_{82} in studies **(a)** strongly influenced by urban emissions; **(b)** biomass-burning emissions; **(c)** other anthropogenic primary OA sources and pure chemical standards. Several pure chemical species showing higher f_{82} between 15–30 ‰ are labeled with arrow. **(d)** Scatter plot of f_{44} ($f_{44} = m/z\ 44/\mathrm{OA}$) vs. f_{82} for all studies shown in panels **(a–c)**, using the same color scheme. Quantile averages of f_{82} across all studies sorted by f_{44} are also shown, as is a linear regression line to the quantile points.

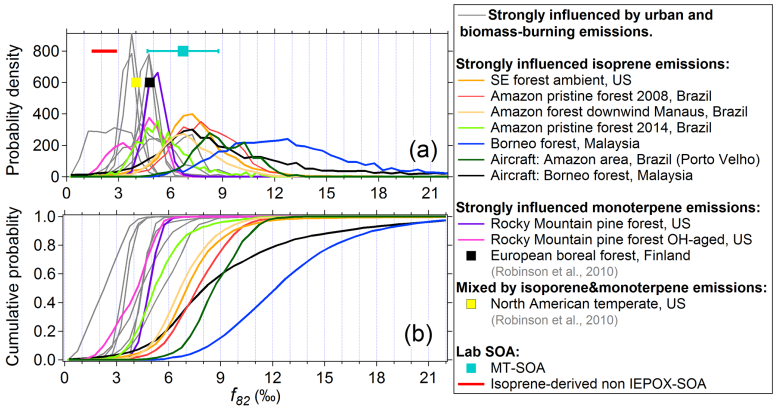

Figure A2. (a) Probability density and **(b)** cumulative probability distributions of f_{82} in studies strongly influenced by isoprene and/or monoterpene emissions. The ranges of f_{82} from other non IEPOX-derived isoprene-SOA and MT-SOA are also shown. The background grey lines are from studies strongly influenced by urban and biomass-burning emissions and are the same data from Fig. A1a and b.

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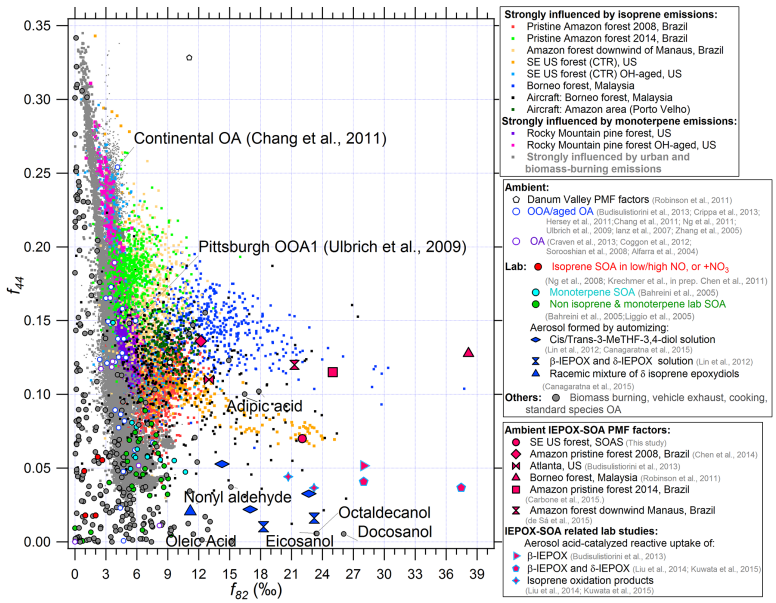

Figure A3. Scatter plot of f_{44} and f_{82} in studies strongly by isoprene and monoterpene emissions, as well as other OA sources. The grey dots represent background levels from studies strongly influenced by urban and biomass-burning emissions in Fig. A1d. f_{44} and f_{82} values from multiple sources of OA (Jimenez-Group, 2015) are also shown, together with IEPOX-SOA from different ambient PMF factors and chamber studies.

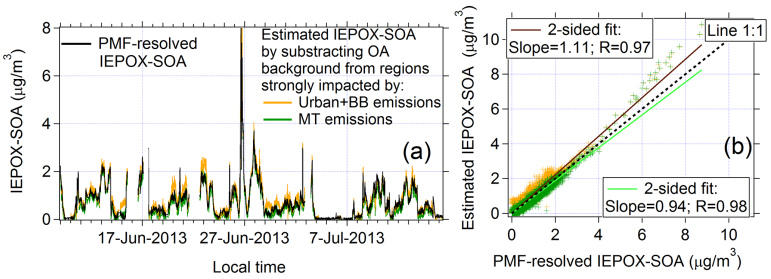

Figure A4. (a) Time series of IEPOX-SOA PMF factor and estimated IEPOX-SOA based on m/z 82 for the SOAS-CTR data in SE US forest. Two different estimates of $C_5H_6O^+$ are shown, using values from regions strongly impacted by urban and biomass-burning emissions vs. regions with strong monoterpene emissions. **(b)** Scatter plot of estimated IEPOX-SOA vs. PMF-resolved IEPOX-SOA. Note that the largest IEPOX-SOA plume (> 4 μg m^{-3}) on 26 June 2013 had a slightly higher $f_{C_5H_6O}$ of 24 ‰, resulting in a slight overestimation of IEPOX-SOA for those data points.

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