Organosulfate Formation from 2-Methyl-3-Buten-2-ol (MBO) as a Secondary Organic Aerosol (SOA) Tracer in the Atmosphere

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Abstract

2-methyl-3-buten-2-ol (MBO) is an important biogenic volatile organic compound (BVOC) emitted by pine trees and a potential precursor of atmospheric secondary organic aerosol (SOA) in forested regions. In the present study, hydroxyl radical (OH)-initiated oxidation of MBO was examined in smog chambers under varied initial nitric oxide (NO) and aerosol acidity levels. Results indicate measurable SOA from MBO under low-NO conditions. Moreover, increasing aerosol acidity was found to enhance MBO SOA. Chemical characterization of laboratory-generated MBO SOA reveals that an organosulfate species ($C_5H_{12}O_6S$, MW 200) formed and was substantially enhanced with elevated aerosol acidity. Ambient fine aerosol ($PM_{2.5}$) samples collected from the BEARPEX campaign during 2007 and 2009, as well as from the BEACHON-RoMBAS campaign during 2011, were also analyzed. The MBO-derived organosulfate characterized from laboratory-generated aerosol was observed in $PM_{2.5}$ collected from these campaigns, demonstrating that it is a molecular tracer for MBO-initiated SOA in the atmosphere. Furthermore, mass concentrations of the MBO-derived organosulfate are well correlated with MBO mixing ratio, temperature, and acidity in the field campaigns. Importantly, this compound accounted for an average of 0.25% and as high as 1% of the total organic aerosol mass during BEARPEX 2009. An epoxide intermediate generated under low-NO conditions is tentatively proposed to produce MBO SOA.

1. Introduction

Biogenic volatile organic compounds (BVOCs) are important precursors of secondary organic aerosol (SOA) in the atmosphere[1,2]. Current studies have focused on biogenic SOA formation from isoprene, monoterpenes, and sesquiterpenes owing to their large global emission rates[1,3,4]. 2-Methyl-3-buten-2-ol (MBO) is an oxygenated BVOC emitted by certain coniferous tree species[5,6]. Although the global emission rate of MBO is much lower than the other BVOCs[7], it can be highly abundant in certain regions such as pine forests of the western United States[5,8,9]. Due to the high volatility of MBO oxidation products, it is generally not considered as a source of SOA. However, recent studies have examined the potential of MBO for producing SOA and concluded that it can marginally contribute to SOA formation under certain atmospheric conditions[10-13].

In the troposphere, MBO can react with hydroxyl radicals (k_{OH}=5.6×10^{-11} molecule^{-1}cm^{3}s^{-1})[10], ozone (k_{O_3}=8.3×10^{-18} molecule^{-1}cm^{3}s^{-1})[10], and nitrate radicals (k_{NO_3}=1.2×10^{-14} molecule^{-1}cm^{3}s^{-1})[14]. Assuming the average tropospheric concentrations of OH (1.5×10^6 molecules cm^{-3}), O_3 (7×10^{11} molecules cm^{-3}), and NO_3 (4.8×10^8 molecules cm^{-3})[15], the estimated lifetimes of MBO reacting with these three oxidants are 3.3 h, 47.8 h, and 48.2 h, respectively. Studies have reported SOA formation from MBO initiated by these oxidants[10,11,13,16]. Chan et al.[11] and Jaoui et al.[13] investigated OH-initiated oxidation of MBO under different NO conditions. They both found that in the presence of NO, MBO does not form SOA. However, with the absence of NO, slight SOA formation was observed at SOA yields less than 1%. Jaoui et al.[13] observed 2,3-dihydroxyisopentanol (DHIP) as a MBO SOA tracer from both low-NO chamber experiments and atmospheric particulate matter (PM) samples using the GC/MS technique. In addition, MBO oxidation could produce glycolaldehyde at a high yield under both high- and low-NO

conditions[10,17,18]. Glycolaldehyde and its oxidation product, glyoxal, are both water-soluble and could produce SOA on wet aerosols and clouds[19-21].

Recent studies have proposed that organosulfates are an important class of SOA species, especially for biogenic SOA[22-28]. Isoprene- and monoterpene-derived organosulfates have been confirmed using the liquid chromatography/electrospray ionization mass spectrometry (LC/ESI-MS) technique[22-28]. These organosulfate species have been identified as important atmospheric SOA tracers representing biogenic SOA enhanced by anthropogenic emissions of NO_x and SO_2[2,29-32]. Moreover, aerosol acidity was found to enhance SOA formation from some BVOCs (e.g., isoprene, α-pinene, and β-caryophyllene) as well as the organosulfate component[22-28,33-35]. With a structure similar to isoprene, MBO may also produce organosulfates and SOA formation may be affected by aerosol acidity in a similar manner. In the present study, aerosol samples were collected from both MBO photooxidation chamber experiments and field campaigns in locations with abundant MBO emissions. Ultra performance liquid chromatography/electrospray ionization high-resolution quadrupole time-of-flight mass spectrometry (UPLC/(–)ESI-HR-Q-TOFMS) was used to analyze the filter samples and hence quantitatively investigate the organosulfate formation from MBO photooxidation in the atmosphere.

2. Experimental Section

High-NO Chamber Experiments. Two initially high-NO experiments (UNC1 and UNC2 in Table 1) with neutral versus acidified sulfate seed aerosols were conducted on the same day at the University of North Carolina 274-m^3 dual outdoor smog chamber facility (Pittsboro, NC) under natural sunlight. The detailed chamber instrumentation has been described elsewhere[36-39]. Briefly, the smog chamber is divided by a Teflon film curtain into two individual chambers with the same volume (~136 m^3). For the neutral seeded experiment, 0.06 M $(NH_4)_2SO_4$ solution was atomized into one chamber; 0.6 M

($(NH_4)_2SO_4$ + H_2SO_4) solution was used instead in the other chamber for the acidic seeded experiment. Despite the different solution concentrations, similar initial seed aerosol mass concentrations were obtained in both experiments by varying the injection time. NO was injected into the chambers from a high-pressure gas cylinder as soon as seed aerosol volume concentrations stabilized. High-purity liquid MBO (>98%, Aldrich) was then heated in a U-tube and flushed into the chamber with a N_2 flow. MBO concentration was measured using a GC/FID. Particle size distributions and the volume concentrations were measured using a scanning mobility particle sizer (SMPS) (TSI 3080) coupled with a condensation particle counter (CPC) (TSI 3022A). Aerosol filter samples (PALL Life Sciences, Quartz, 47-mm diameter, 1.0-μm pore size) were collected during the whole photochemical period at a flow rate ~ 17 L min^{-1} for each experiment.

Low-NO Chamber Experiments. A dynamic experiment with four stages (EPA1–EPA4 in Table 1) was conducted at the U.S. EPA (Research Triangle Park, NC) 14.5-m^3 Teflon chamber operated in a flow mode to produce a steady-state condition. There was no NO added to the chamber during the experiment. The photolysis of hydrogen peroxide (H_2O_2) was used as the source of OH radicals. The concentration of MBO throughout the four stages was held at a constant 15 ppmC. The concentration of H_2O_2 was maintained at ~ 9 ppm and RH was less than 5% during the whole experiment. The aerosol acidity was changed between stages by adjusting the fraction of $(NH_4)_2SO_4$ and H_2SO_4 in the seed aerosol (shown in Table 1). Particle organic carbon concentrations were measured by a semi-continuous elemental carbon-organic carbon (EC-OC) instrument (Sunset Laboratories, Tigard, OR). Aerosol samples were collected at a flow rate of 15 L min^{-1} by 47-mm Teflon filters for determination of the hydrogen ion concentration ($[H^+]_{air}$) as nmol H^+ m^{-3} using an Oakton 300 pH probe (Vernon Hills, IL) after dissolution in 10 mL of distilled deionized water. Teflon impregnated glass fiber filters (47 mm; Pall Gelman

Laboratory, Ann Arbor, MI) were used for other off-line chemical determinations. The detailed gas-phase and aerosol-phase measurements have been described elsewhere[13,34].

Field Measurements – the BEARPEX Campaigns. The BEARPEX (Biosphere Effects on Aerosols and Photochemistry Experiment) campaigns were conducted at a ponderosa pine plantation located between Sacramento and Lake Tahoe in the Sierra Nevada Mountains, California[40,41]. MBO is one of the dominant biogenic VOCs emitted by the forest at the BEARPEX site[8,42,43]. The field data used for this study were collected from September 20 – 25, 2007, and July 25 – 30, 2009. The two sampling periods were characterized by very different conditions; 2007 was cooler and wetter while 2009 was hotter and drier. A high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS, Aerodyne Research Inc., hereinafter AMS for short) was used during the BEARPEX 2007 campaign to measure non-refractory PM_1 aerosol components, from which the mass concentrations of individual components (sulfate, nitrate, ammonium, chloride, and organics) were resolved[44]. The AMS operation at BEARPEX was described by Farmer et al.[45]. In the BEARPEX 2009 campaign, the PM_1 organic mass was measured by FTIR and sulfate, nitrate, and ammonium were measured using a Metrohm ion chromatograph equipped with a Metrosep A Supp 5 column for anions and a Metrosep C 4 column for cations. The average organic mass concentrations were ~ 2.3 μg m^{-3} and ~3.7 μg m^{-3} during 2007 and 2009, respectively. Aerosol acidities (strong acidity) were estimated based on charge balance using the measured concentrations of the three inorganic components. Average acidities were estimated by averaging for each filter sampling period. MBO and isoprene were measured by two different in situ instruments; in 2007 using GC/MS operated by the National Oceanic and Atmospheric Administration (NOAA)[9,46] and in 2009 using GC/FID operated by Texas A&M University[47,48].

$PM_{2.5}$ samples were collected using high-volume samplers during the two continuous

five-day periods in 2007 and 2009, with three filters each day, to provide sufficient time resolution to examine the diurnal variation of aerosol compositions. This filter sampling approach could also separate the influence of local biogenic emissions in the morning from the anthropogenic emissions from the California Central Valley arriving in the afternoon and subsequent nighttime chemistry.

Field Measurements – the BEACHON-RoMBAS Campaign. The BEACHON-RoMBAS (Bio-hydro-atmosphere interactions of Energy, Aerosols, Carbon, H_2O, Organics & Nitrogen – Rocky Mountain Biogenic Aerosol Study) campaign was conducted from July – August, 2011 at the Manitou Forest Observatory located in Pike National Forest, Colorado. Site information has been described elsewhere[49,50]. The BEACHON-RoMBAS site was chosen due to abundant BVOC emissions, in which the MBO emission is important, but with limited anthropogenic influence.

Measurements of aerosol components were performed using a high-resolution AMS[44]. The sum of MBO and isoprene was measured using two Proton-Transfer-Reaction Time-of-Flight Mass Spectrometers (PTR-TOF-MS, Ionicon Analytik GmbH, Austria and University of Innsbruck). Details about the instruments and data evaluation can be found in Jordan et al.[51], Graus et al.[52], Müller et al.[53] and Cappellin et al.[54]. Ambient air was sampled at a flow rate of ~9 SLPM through a 40m long Teflon (PFA) line (1/4" OD) mounted at 25.1 m on the canopy tower. Both instruments were sampling of the same line with a sampling period of about 10 s. The merged dataset was averaged to 6 min. The drift tube was operated at 2.3 mbar (both instruments) and a drift voltage of a drift voltage of 580 V (UIBK) and 550 V (NCAR) and a drift tube temperature of 60C (both instruments). Calibration was performed by dynamically diluting VOC standards at ppmV levels with scrubbed air. During BEACHON-RoMBAS, the average temperature (~17°C) and the organic aerosol mass (~ 1.4 μg m^{-3}) were fairly low; therefore, a 72 h-integrated aerosol

filter sampling approach with a flow rate of 1 m^3 min^{-1} was performed using a high volume sampler to collect sufficient aerosol mass on each filter. The average acidity for each filter sampling period was estimated in the same manner as the BEARPEX 2007.

Filter Sample Extractions and Chemical Analyses. Filters collected from chamber experiments and field campaigns were stored in individual pre-cleaned packets in a –20°C freezer before extraction. All filters were extracted in 15 mL of high-purity methanol (LC-MS CHROMASOLV-grade, Sigma-Aldrich) by sonication for 45 min. The methanol extracts were then blown dry under a gentle N_2 stream at ambient temperature[24]. Soot particles and quartz fibers for all filter extracts were removed using procedures outlined in[24]. Dried residues from filter extracts were reconstituted with 150 μL of 50:50 (v/v) solvent mixture of 0.1% acetic acid in methanol (LC-MS ChromaSolv-Grade, Sigma-Aldrich) and 0.1% acetic acid in water (LC-MS ChromaSolv-Grade, Sigma-Aldrich). The resultant mixtures were then shaken and sonicated for 5 min and then stored at –20 ºC before analyses. The detailed description of the UPLC/(-)ESI-HR-Q-TOFMS technique and operating conditions can be found in Zhang et al.[38]. Propyl sulfate was selected as the surrogate standard for quantifying the MBO-derived organosulfate owing to the similar solubility and retention time[35]. The detection limit is ~ 0.05 ng for this surrogate standard.

3. Results and Discussion

Effects of NO and Acidity on SOA Yields from MBO Photooxidation. Figure 1 shows the results of the initially high-NO experiments conducted at the UNC dual outdoor smog chambers on the same day. Similar gas-phase conditions were obtained for both experiments (Figure 1a) and the only variation between the two experiments was the different sulfate seed aerosol acidities. Figure 1b represents the particle volume concentrations (wall loss uncorrected) of the two MBO experiments compared to seed aerosol only experiments without MBO. Slight SOA formation (~ 7 μg m^{-3}) was observed

only in the acidic experiment and the SOA decreased rapidly after reaching the maximum. It should be noted that the SOA was not formed until after the NO concentration approached zero, when half of the initial MBO (~ 2 ppmC) remained and its peroxy radicals likely began to react with hydroperoxy radicals (RO_2+HO_2) and/or other peroxy radicals (RO_2+RO_2).

As shown in Table 1, for the low-NO experiment conducted at the EPA smog chamber, measureable SOA was formed in all the four stages with SOA yields up to 1%. In these acidity-varied experiments $[H^+]_{air}$ ranged from 125 – 1587 nmol m^{-3} and the SOA formation during each stage correlated well with increasing acidity. Figure 2 shows the relationship between the change (%) of organic carbon (OC) concentration compared to the neutral seed case and measured aerosol acidity ($[H^+]_{air}$ nmol m^{-3}) for different BVOCs. The data of isoprene, α-pinene, and β-caryophyllene are reproduced from Surratt et al.[23] and Offenberg et al.[34]. In these prior studies, SOA formation from isoprene, β-caryophyllene, and α-pinene was found to correlate with aerosol acidity as a linear relationship, however, with different slopes. From the present work, the MBO case does also follow the same trend with a slope larger than that of α-pinene and lower than those of isoprene and β-caryophyllene. It should be noted that the previous studies were performed under RH< 30%, but this study uses RH<5%, likely causing the aerosols to be more acidic and suggests the acidity effect of MBO may be weaker than this figure indicates compared to the other three BVOCs.

By combining the two sets of smog chamber experiments, SOA was found to form only when NO was not present, that is, SOA was probably formed from the RO_2+HO_2 channel and/or the RO_2+RO_2 channel. In addition, the formation of MBO SOA under low-NO conditions was likely enhanced with greater acidity, similar as the observation for the other BVOCs, such as isoprene[23], β-caryophyllene[34], and α-pinene[34].

Organosulfate Formation from MBO Photooxidation. Filter samples collected from all the chamber experiments discussed above were analyzed using UPLC/(-)ESI-HR-Q-TOFMS. The results suggest an organosulfate species was produced from all the experiments. Accurate mass data suggest that the MBO-derived organosulfate has a molecular formula of $C_5H_{12}O_6S$ (MW 200.0355). Figure 3a shows the tandem mass spectra (MS^2 spectra) of this organosulfate (*m/z* 199) from the low-NO experiments. The most abundant fragment is *m/z* 97, which indicates the presence of a sulfate ester group in this compound ($-OSO_3H$)[22]. Since this organosulfate species has the same carbon number (5) as MBO, it likely maintains the backbone of MBO. Thus, its tentative isomeric structures are proposed in Figure 3a. From a recent study by Jaoui et al.[13], another SOA tracer (DHIP, MW 120), with a similar structure to our proposed organosulfate (i.e., the sulfate ester group is substituted by a hydroxyl group), was observed by GC/MS analyses. For a similar biogenic hydrocarbon, isoprene, previous studies have found that its three major SOA tracers, the 2-methyltetrols (MW 136) and a C_5 organosulfate species (MW 216), are both derived from the same intermediate compound (i.e., isoprene epoxydiols, or IEPOX)[25,35,55]. Similarly, it is likely that both DHIP and the MBO-derived organosulfate found in the present study are formed from an epoxide intermediate, especially since reactive uptake of epoxides has been shown to be kinetically feasible in forming organosulfates and polyols under tropospheric conditions[56]. The potential mechanism is discussed further below.

Moreover, it is observed that the mass concentrations of the MBO-derived organosulfate also correlated well with acidity (R^2=0.87), as shown in Table 1 (and Figure S1). This finding is consistent with previous observations of organosulfates derived from other BVOCs[22-24]. This may suggest the formation mechanism of the MBO-derived organosulfate is similar to that of the other organosulfates. Furthermore, increased acidity tends to promote both OC and the MBO-derived organosulfate formation to a similar

extent (Figure S1), suggesting that the same mechanism may result in the organosulfate and bulk SOA formation. The $C_5H_{12}O_6S$ organosulfate is also well correlated with OC (R^2=0.96), indicating the MBO-derived organosulfate can serve as a good tracer for the OC concentrations.

Field Observations of the MBO-Derived Organosulfate. In addition to the chamber results, the MBO-derived organosulfate was also observed in ambient field samples. In the chemical analyses using UPLC/(-)ESI-HR-Q-TOFMS the same organosulfate species were observed at *m/z* 199 from BEARPEX 2007, 2009, and BEACHON-RoMBAS 2011 campaigns. The MS^2 spectra and retention times of the *m/z* 199 organosulfate from the field campaigns are identical to those from MBO chamber experiments (Figure 3b), confirming that the *m/z* 199 organosulfate observed from field campaigns was likely derived from MBO.

Figure 4a shows the averaged MBO mixing ratio and MBO-derived organosulfate mass concentration during each filter-sampling period from BEARPEX 2009. The diurnal variation of the organosulfate mass concentrations is generally consistent with that of MBO mixing ratios. Both the MBO mixing ratio and the MBO-derived organosulfate concentration consistently fell to much lower levels at night. It should be noted that sometimes the MBO mixing ratios in the morning were similar or even higher than the afternoon, but the MBO organosulfate was still higher in the afternoon. This is probably because: (1) there will be a certain time delay to form an organosulfate from MBO; (2) the OH and O_3 concentrations were highest in the afternoon which likely increased the organosulfate production rate; (3) the factors that enhance organosulfate formation such as aerosol acidity are higher in the afternoon when the relative humidity dropped to lower levels and the urban emissions arrived (See Figure 5b). Figure 4b shows the time series of isoprene mixing ratios and the IEPOX-derived organosulfate mass concentrations. The

comparison between Figures 4a and 4b suggests that both the isoprene mixing ratio and the IEPOX-derived organosulfate concentration did not follow the diurnal pattern as the MBO did at the BEARPEX site; especially for the IEPOX-derived organosulfates which accumulated to higher concentrations at the end of the week, rather than being dominated by the diurnal trend. At the BEARPEX site, MBO is locally emitted, but isoprene is emitted upwind of the site[41]. Thus, the IEPOX-derived organosulfate likely formed upwind with the urban plume before it arrived at the site. Hence, the measured IEPOX-derived organosulfate cannot be simply explained by the trends in local emissions. In some previous studies, the IEPOX-derived organosulfate was found to be the most abundant organosulfate species from ambient aerosols[29,31,32]. However, at the BEARPEX site, the MBO organosulfate has similar abundance as the IEPOX-derived organosulfate. The MBO-derived organosulfate alone can account for an average of 0.25% and as high as 1% of measured organic PM_1 at BEARPEX 2009 (Table S2). The comparison between the MBO-derived and the IEPOX-derived organosulfates further demonstrates that the two C_5 organosulfate species arose from different sources and the MBO organosulfate could be a substantial SOA component locally.

Figures 5 a-c examine the relationship between the MBO-derived organosulfate concentrations and temperatures, aerosol acidities, and MBO mixing ratios from the BEARPEX and BEACHON-RoMBAS campaigns. Temperatures, aerosol acidities, and MBO mixing ratios were averaged for each filter-sampling period. All the BEARPEX 2009 data are much higher than the other two campaigns and have a larger dependence on sampling time during the day. Thus, the correlations analyzed at different times of day (i.e., morning, afternoon, and night) are shown separately for the BEARPEX 2009 data. The temperature during BEARPEX 2007 and BEACHON-RoMBAS are both lower than that of BEARPEX 2009 (Figure 5a). For BEARPEX 2009, the temperature during the

daytime is much higher than that during the nighttime but the temperatures in the morning and afternoon are generally similar. Similar to the temperature conditions, the aerosol acidities during BEARPEX 2007 and BEACHON-RoMBAS are also significantly lower (by an order of magnitude) than those during BEARPEX 2009. Additionally, during BEARPEX 2009 the aerosol acidity is substantially enhanced (by a factor of 3 as shown in Figure 5b) in the afternoon, likely due to the arrival of urban emissions and lower relative humidity. In general, the MBO-derived organosulfate concentration correlates well with the average aerosol acidity (represented as $[H^+]_{air}$ in nmol/m^3 in Figure 5b, R^2=0.68). As shown in Figure 5c, the MBO-derived organosulfate concentration correlates well with the average MBO mixing ratio (R^2=0.75). The MBO mixing ratios increase with increasing temperature owing to the MBO emissions being strongly sensitive to temperature[6].

Generally for the BEARPEX 2009 data, higher temperatures and MBO mixing ratios explain the increased formation of organosulfate in the morning compared to the nighttime; the higher acidity partly explains the further enhancement of organosulfate formation in the afternoon compared to the other periods in 2009. The BEACHON-RoMBAS results are similar to the BEARPEX 2007 results in terms of the lower temperatures, aerosol acidities, and MBO mixing ratios. Although the BEACHON-RoMBAS data show slightly higher MBO mixing ratios, the MBO organosulfate formation was not enhanced at the BEACHON-RoMBAS site compared to the BEARPEX 2007 results. One possible explanation might be that under low aerosol acidity, the formation of MBO organosulfate is generally low and not well correlated with MBO mixing ratio. Another possibility is that the sum of MBO and isoprene was measured from BEACHON-RoMBAS and 80% was estimated to be MBO, which might be over estimated. Overall, the field data shown in Figure 5 clearly suggest that MBO is the precursor of this organosulfate species, which is substantially enhanced as aerosol acidity increases.

Potential Mechanisms for Atmospheric MBO SOA Formation. The mechanisms by which MBO-derived organosulfate and other SOA tracers[13] form in the atmosphere are still unclear. However, there are a few potential mechanisms that may lead to MBO SOA formation. Chan et al.[11] has proposed the RO_2+RO_2 reaction could produce DHIP, which was observed from the MBO low-NO experiments by Jaoui et al.[13]. However, the formation of the *m/z* 199 organosulfate is unlikely via this pathway, since the esterification of an alcohol (i.e., DHIP) and sulfuric acid forming an organosulfate is kinetically infeasible in the particle phase under either chamber conditions or ambient conditions[57]. Consequently, alternative reactions must explain the formation of the *m/z* 199 organosulfate. As discussed above, the formation pattern of the MBO-derived organosulfate and DHIP is similar to that of the IEPOX-derived organosulfate and the 2-methyltetrols[25,35]. Similarly to the IEPOX chemistry, an epoxide is tentatively proposed to be the intermediate (oxidation) product forming MBO-derived organosulfate as shown in Scheme 1. An MBO-derived epoxide could either be produced from ozonolysis, H_2O_2 oxidation of MBO or from the further reaction of an MBO hydroxyhydroperoxide. Therefore, an MBO-derived epoxide can form organosulfates by reacting with sulfuric acid or form DHIP by hydrolysis. Epoxidation has been observed from the ozonolysis of olefins[58,59]. However, the epoxide yield from olefin ozonolysis tends to be low (<5%)[60] and this is likely a minor pathway in the atmosphere. Furthermore, an MBO-derived hydroxyhydroperoxide is unlikely to undergo further fast OH oxidation like the isoprene hydroxyhydroperoxide does because of the absence of an extra carbon-carbon double bond. Liu et al.[12] have reported MBO epoxide from acid-catalyzed oxidation of MBO with H_2O_2 (shown in Scheme 1), which is more likely an aqueous-phase process. Therefore, more work is required to characterize the formation mechanism of the MBO-derived organosulfate, as well as DHIP, in the atmosphere.

Atmospheric Implications. In the present study, MBO photooxidation is investigated in both smog chamber experiments and field campaigns where MBO emissions are important. SOA formation from MBO was observed under low-NO conditions and after NO was reacted in the high-NO chamber experiments. Under both conditions, aerosol acidity was found to promote the formation of MBO SOA. In addition, an organosulfate species ($C_5H_{12}O_6S$, MW 200) was substantially enhanced as aerosol acidity increased. From the BEARPEX and BEACHON-RoMBAS campaigns, a species with the same mass spectrometric signature was observed to correlate well with MBO mixing ratio and aerosol acidity. Moreover, the average MBO organosulfate concentration measured from the BEARPEX site is similarly abundant to the IEPOX-derived organosulfate (~ 15 ng m^{-3}); the latter has been reported to be the most abundant organosulfate tracer in a number of areas[29].

This is an important finding because MBO could be a locally abundant BVOC in certain regions, such as the western United States. Although the SOA yield reported in previous studies is low (<1%), the SOA mass concentration produced could still be appreciable with the high emission rates expected at locations like the BEARPEX site. As discussed above, the formation mechanism of MBO-derived organosulfate is likely similar to that of the IEPOX-derived organosulfate. Lin et al.[35] found that the IEPOX-derived organosulfate accounts for ~5% of total SOA from IEPOX. Assuming the same mass fraction in the MBO case, MBO SOA can accounts for as high as 0.4 μg m^{-3}, which is 10% of total organic mass on average. However, further investigation is required to provide a more accurate estimate. As a result, the inclusion of SOA formation from MBO in current air quality models may be important[61], especially for regional or local predictions of SOA. The MBO-derived organosulfate has the potential to serve as an SOA tracer for source apportionment method under further investigation. These new observations of MBO

organosulfate formation and the acidity effect are consistent with previous findings of the organosulfate formation from other BVOCs, including isoprene and monoterpenes[24,25,35]. Although additional work is warranted, it is likely that the formation mechanisms of these biogenic organosulfate species are similar.

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Table 1. Smog Chamber Experimental Conditions.

ID[a]	MBO (ppmC)	H_2O_2 (ppm)	NO (ppb)	RH (%)	$[H^+]_{air}$[c] (nmol/m^3)	seed aerosol (ug/m^3 sulfate)	Average OC (μgC/m^3)	$C_5H_{12}O_6S$[e] (ng/m^3)
UNC1	4	—	200	<30%	—	50 (AS)	—	0.95
UNC2	4	—	200	<30%	—	45 (1/2 AS + 1/2 SA)	—	1.88
EPA1	15	9	< 15[b]	<5%	125	40 (AS[d])	6.5	6.5
EPA2	15	9	< 15[b]	<5%	289	35 (2/3 AS + 1/3 SA[d])	9.6	50.4
EPA3	15	9	< 15[b]	<5%	902	35 (1/2 AS + 1/2 SA)	11.4	53.2
EPA4	15	9	< 15[b]	<5%	1587	32 (1/3 AS + 2/3 SA)	21.9	120.3

[a] Experiments UNC1 and UNC2 are the high-NO experiments conducted at the UNC dual outdoor smog chamber; experiments EPA1-EPA4 are the low-NO experiments conducted at the EPA smog chamber. [b] The NO concentrations in EPA1-4 were not obtained, but there was no NO added to the chamber during the experiments. [c] $[H^+]_{air}$ is used as an indicator of acidic levels. [d] "AS" represents ammonium sulfate; "SA" represents sulfuric acid. [e] $C_5H_{12}O_6S$ is the chemical formula of the organosulfate species discussed below.

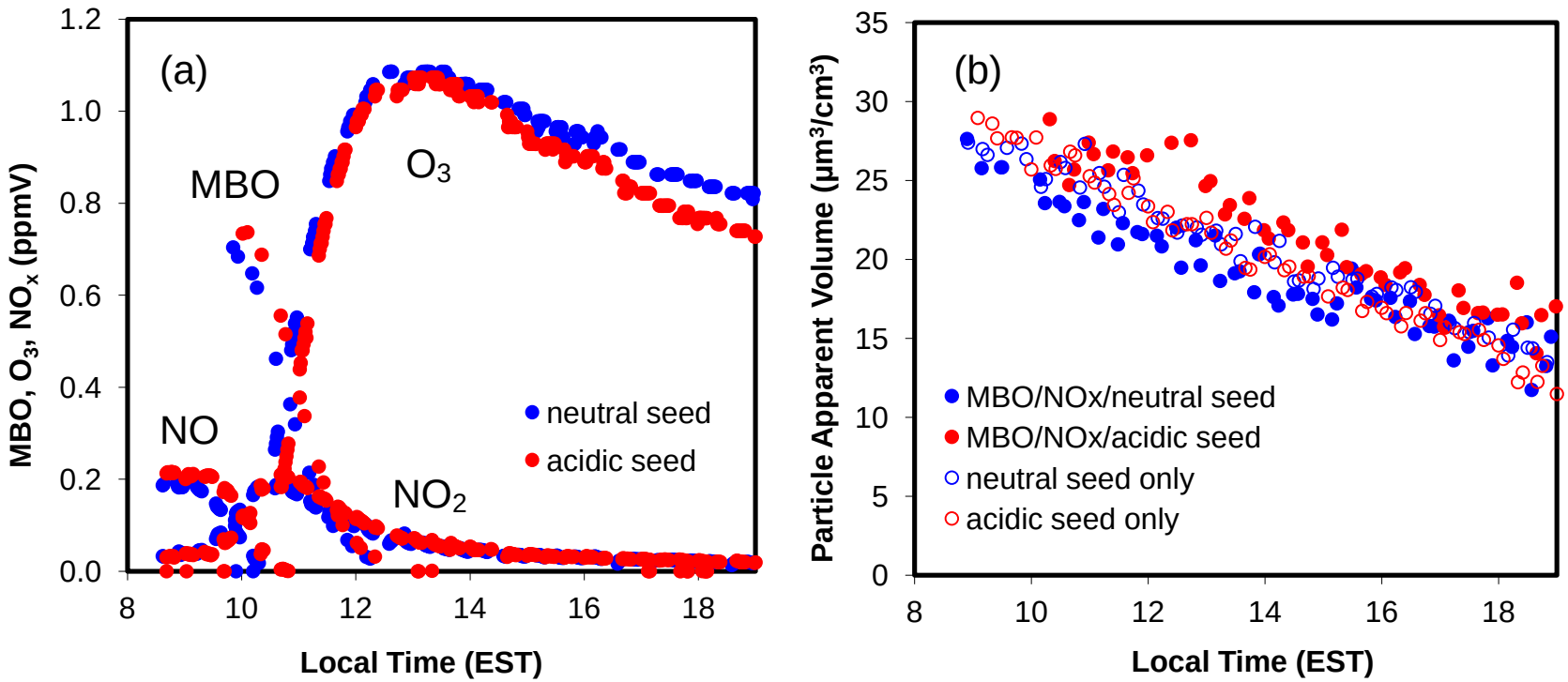


Figure 1. Online measurement results of the high-NO_x experiments (UNC1 and UNC2). (a) Time profiles of major gas-phase compounds (MBO, NO, NO_2, and O_3). (b) Wall-loss uncorrected particle apparent volume concentrations ($\mu m^3/cm^3$). Red solid circle represents the acidic seeded MBO experiment; blue solid circle represents the neutral seeded MBO experiments; the hollow circles in red and blue in (b) represent two control experiments with only acidic and neutral seeds, respectively.

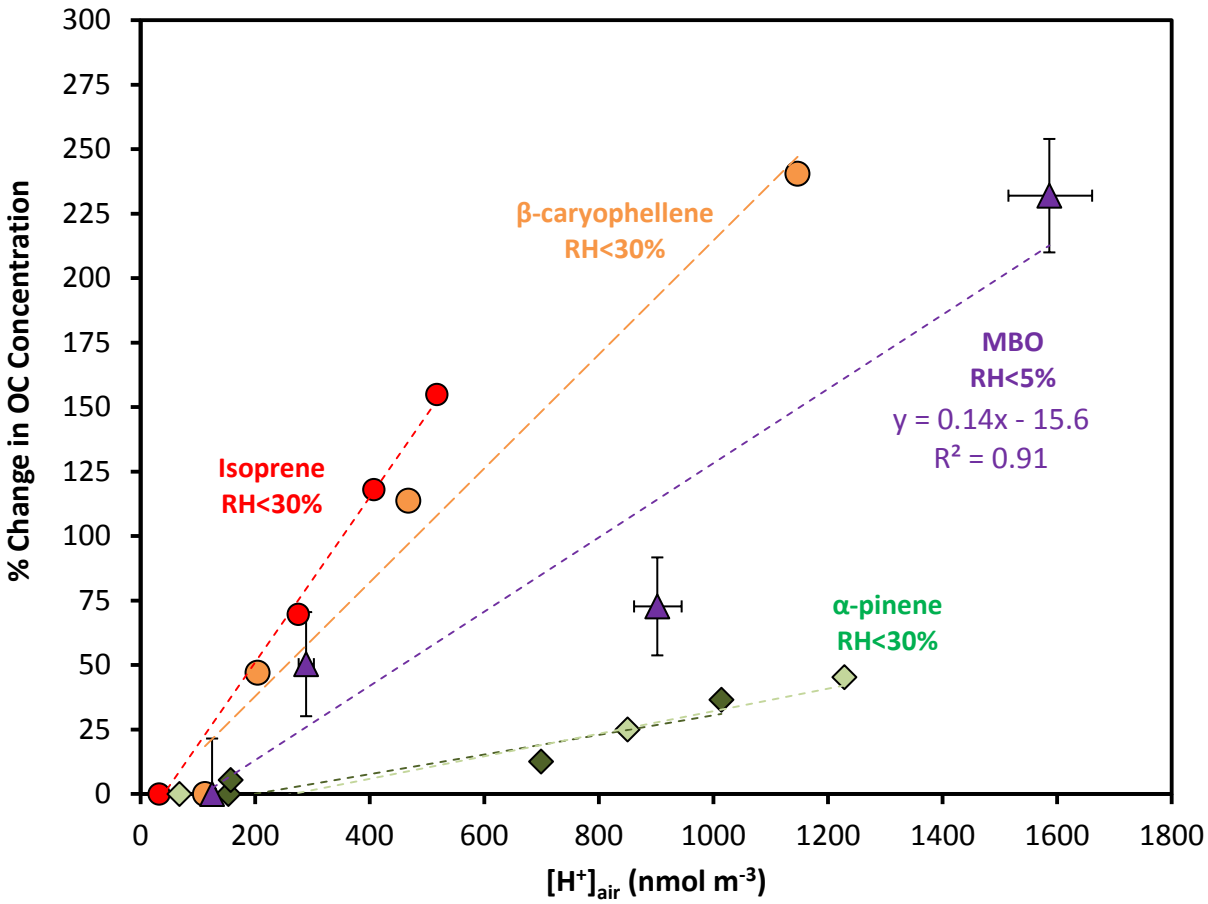


Figure 2. Relationship between the change (%) of organic carbon (OC, in μgC m^{-3}) and the measured seed aerosol acidity ($[H^+]_{air}$ nmol m^{-3}) for different BVOCs. The data of isoprene, α-pinene, and β-caryophellene are reproduced from Surratt et al.[23] and Offenberg et al.[34]. The MBO data are from the present study.

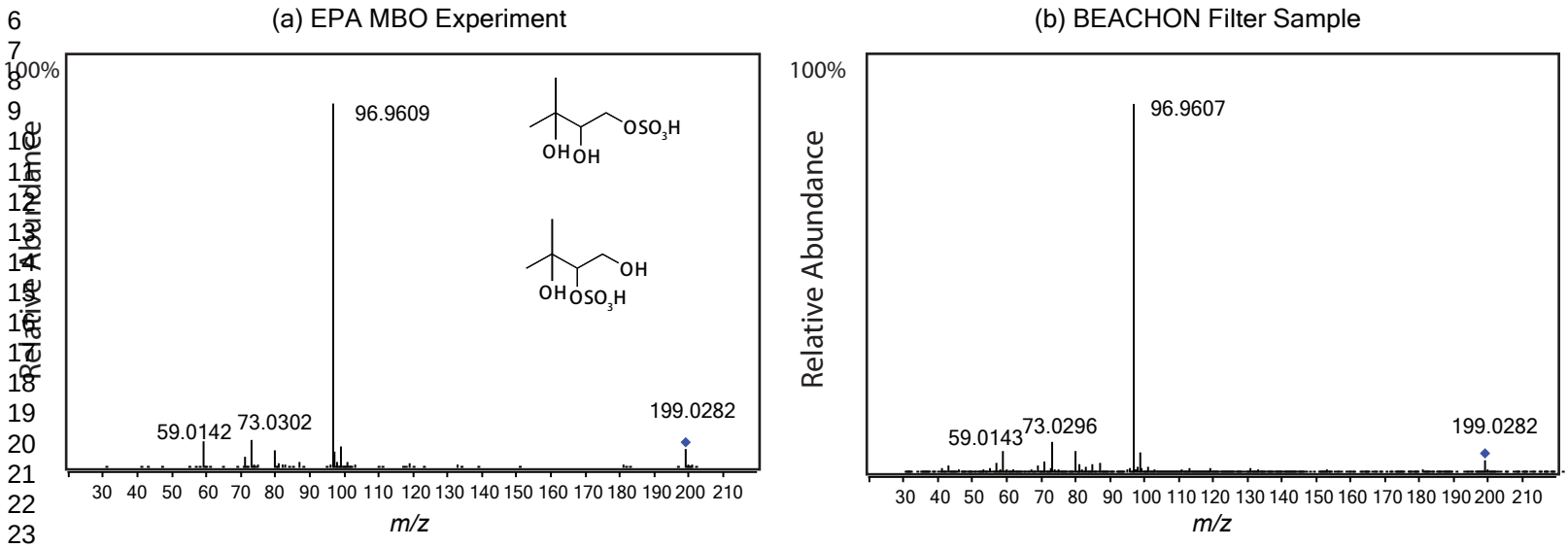


Figure 3. Tandem mass spectra (MS^2) of the MBO organosulfate (*m/z* 199) measured from (a) the EPA low-NO chamber experiment (EPA4, with sampled OC mass concentration ~ 21.9 μgC/m^3) and (b) the BEACHON aerosol samples. The proposed structural isomers of this organosulfate are shown in (a). The measured mass of the ion is within +/- 2 mDa of the calculated mass.

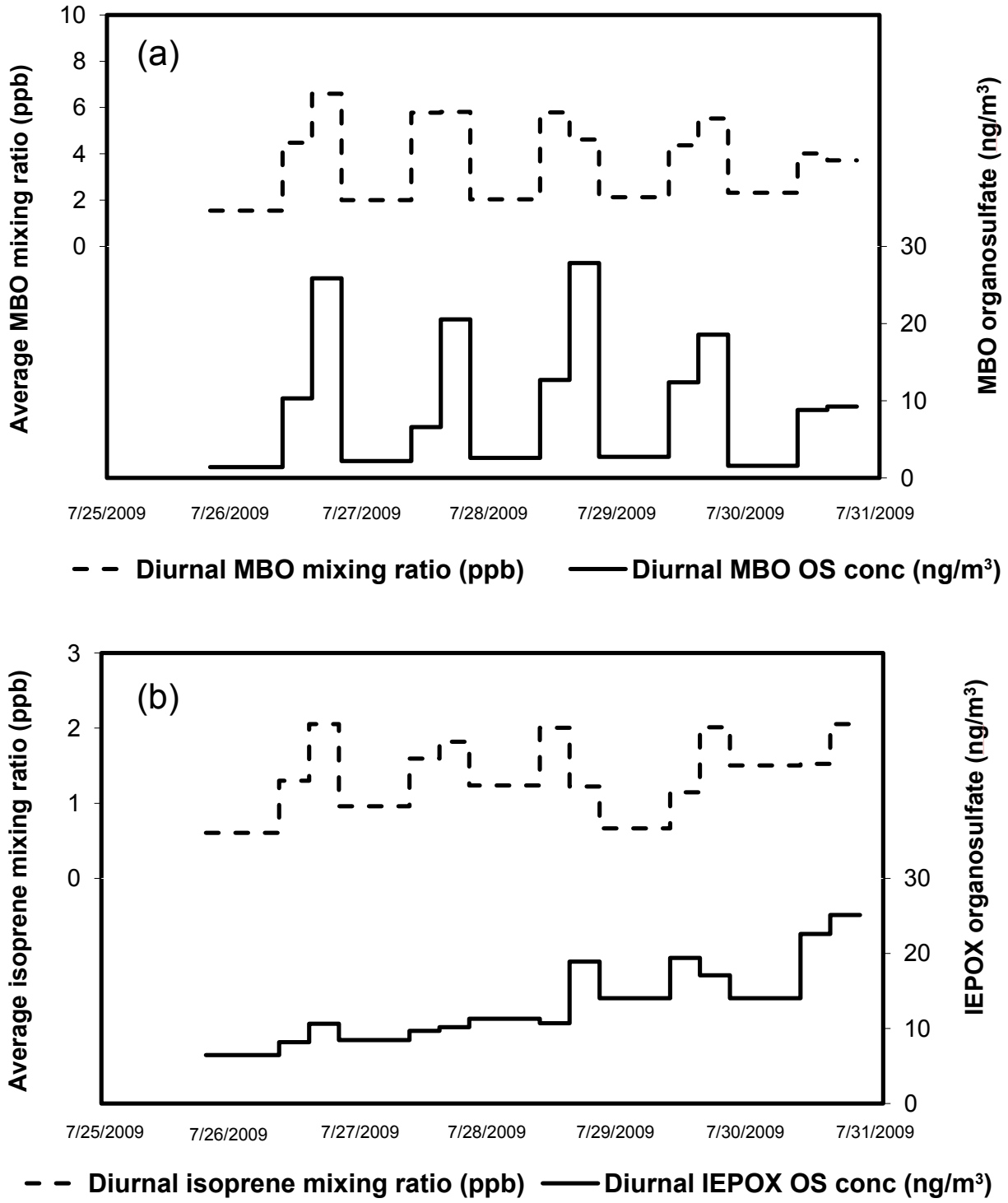


Figure 4. Comparison of diurnal variation of organosulfates and their precursors during the 2009 BEARPEX campaign. (a) Average MBO mixing ratio and the MBO organosulfate; (b) Average isoprene mixing ratio and the IEPOX-derived organosulfate. The BVOC mixing ratios are in ppb; the organosulfate mass concentrations are in ng/m^3.

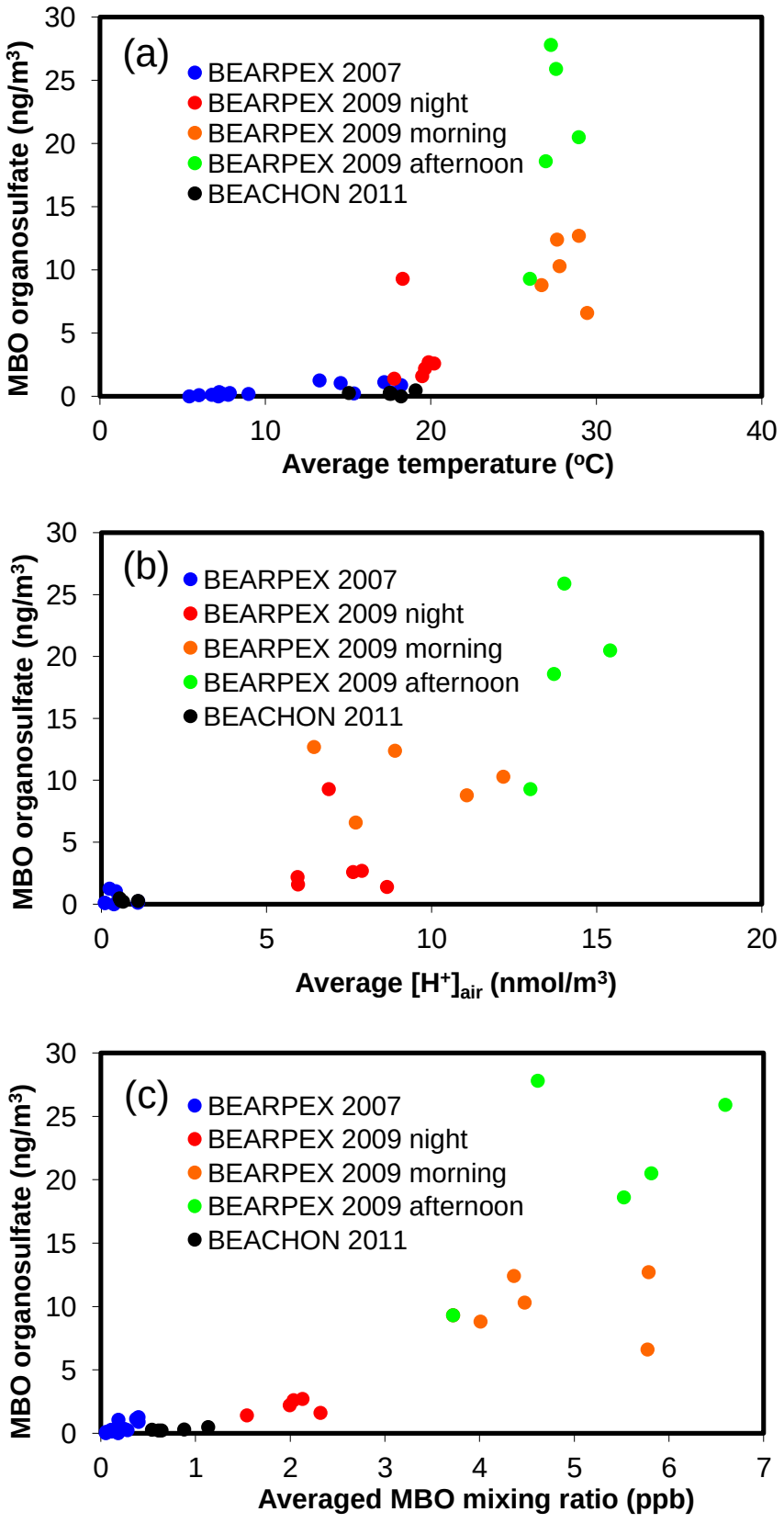
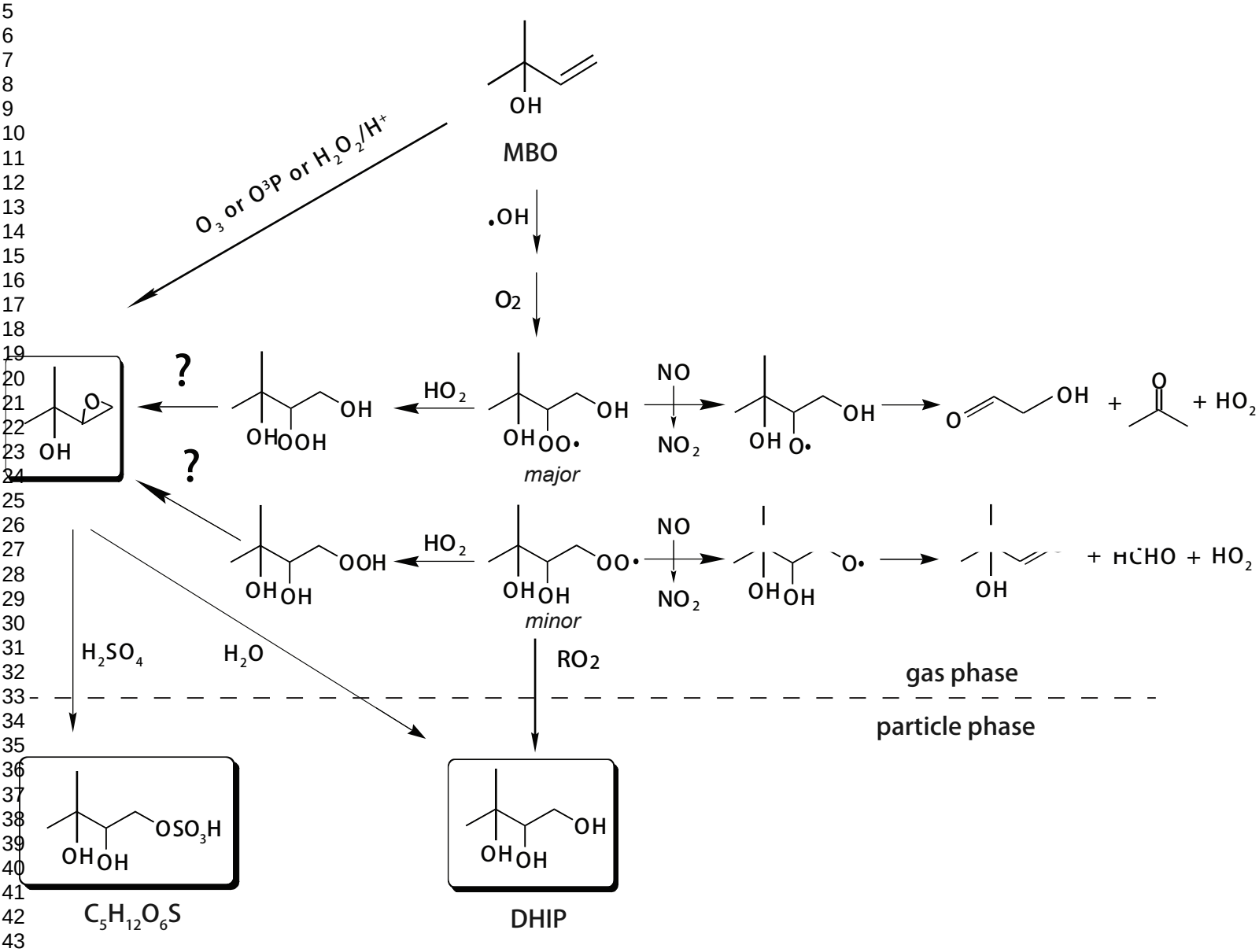


Figure 5. Correlation of the MBO organosulfate mass concentrations to (a) average temperature; (b) average acidity; (c) average MBO mixing ratio from the BEARPEX and BEACHON campaigns. The data from different times of day are shown separately for the BEARPEX 2009 results.



Scheme 1. Proposed mechanism of MBO photooxidation forming SOA. Some structual isomers are not shown.

Supporting Information

Organosulfate Formation from 2-Methyl-3-Buten-2-ol (MBO) as a Secondary Organic Aerosol (SOA) Tracer in the Atmosphere

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Table S1. Supporting data from BEARPEX 2007 campaign.

Start Time	average temperature (°C)	average RH (%)	average O_3 (ppb)	average organics (μg/m^3)	average [H^+] [a](nmol/m^3)	average MBO (ppb)	MBO OS[b] (ng/m^3)	average isoprene (ppb)	IEPOX OS[b] (ng/m^3)	Fraction of MBO OS in total organics
9/20/07 18:45	7.4	89.5	29.8	3.98	0.00	0.10	0.19	0.18	1.63	0.00%
9/21/07 7:45	17.6	42.7	41.2	1.93	0.00	0.25	0.33	0.12	1.87	0.02%
9/21/07 13:15	13.3	62.7	49.8	3.10	0.24	0.40	1.26	0.28	1.23	0.04%
9/21/07 18:45	7.8	82.5	40.9	3.56	NA	0.11	0.27	0.08	0.42	0.01%
9/22/07 7:45	7.2	97.2	NA	2.62	NA	0.18	0.34	NA	1.93	0.01%
9/22/07 13:15	7.2	98.5	34.4	1.46	0.00	0.18	0.00	0.03	0.54	0.00%
9/22/07 18:45	5.4	99.2	29.1	1.53	0.37	0.05	0.00	0.02	0.60	0.00%
9/23/07 7:45	6.8	99.1	37.4	1.24	0.10	0.08	0.13	0.02	0.92	0.01%
9/23/07 13:15	9.0	88.0	34.0	1.71	0.00	0.18	0.19	0.10	1.76	0.01%
9/23/07 18:45	6.0	80.1	27.7	1.38	0.10	0.05	0.10	0.07	1.26	0.01%
9/24/07 7:45	14.5	37.0	37.8	1.39	0.43	0.18	1.05	0.04	1.10	0.08%
9/24/07 13:15	15.3	44.8	48.5	2.92	1.11	0.28	0.24	0.10	1.64	0.01%
9/24/07 18:45	7.7	68.3	41.1	2.46	1.10	0.11	0.13	0.19	2.40	0.01%
9/25/07 7:45	17.2	39.1	NA	NA	NA	0.37	1.13	NA	3.18	NA
9/25/07 13:15	18.2	37.7	NA	3.43	NA	0.40	0.89	NA	3.11	0.03%

[a] [H^+] is calculated from charge balance based on the AMS data of [SO_4^{2-}], [NO_3^-], and [NH_4^+].
[b] "OS" represents organosulfate.

Table S2. Supporting data from BEARPEX 2009 campaign.

Start Time	average temperature (°C)	average RH (%)	average O_3 (ppb)	average organics (μg/m^3)	average $[H^+]$[a] (nmol/m^3)	average MBO (ppb)	MBO OS[b] (ng/m^3)	average isoprene (ppb)	IEPOX OS[b] (ng/m^3)	Fraction of MBO OS in total organics
7/25/09 19:15	17.8	50.3	45.1	2.42	8.64	1.54	1.39	0.61	6.44	0.06%
7/26/09 8:45	27.8	28.5	49.4	2.26	12.17	4.47	10.31	1.30	8.16	0.46%
7/26/09 14:15	27.6	30.8	64.5	3.04	14.02	6.59	25.86	2.05	10.63	0.85%
7/26/09 19:45	19.6	37.7	51.3	2.16	5.93	1.99	2.18	0.96	8.44	0.10%
7/27/09 8:45	29.4	24.5	54.3	1.95	7.70	5.77	6.59	1.59	9.66	0.34%
7/27/09 14:15	28.9	26.3	70.1	3.18	15.40	5.81	20.55	1.82	10.15	0.65%
7/27/09 19:45	20.2	45.1	50.5	3.08	7.62	2.03	2.60	1.24	11.28	0.08%
7/28/09 8:45	28.9	33.7	53.3	3.36	6.43	5.78	12.69	2.01	10.70	0.38%
7/28/09 14:15	27.2	36.3	68.7	5.19	NA	4.61	27.85	1.22	18.91	0.54%
7/28/09 19:45	19.9	51.9	60.9	4.61	7.88	2.13	2.72	0.67	14.02	0.06%
7/29/09 8:45	27.6	35.3	NA	3.58	8.89	4.36	12.37	1.14	19.40	0.35%
7/29/09 14:15	26.9	41.7	NA	8.37	13.70	5.52	18.56	2.01	17.09	0.22%
7/29/09 19:45	19.5	61.8	NA	5.28	5.95	2.32	1.56	1.51	14.02	0.03%
7/30/09 8:45	26.7	39.8	NA	9.80	11.06	4.01	8.81	1.52	22.57	0.09%
7/30/09 14:15	26.0	42.1	NA	4.63	12.99	3.72	9.26	2.06	25.11	0.20%
7/30/09 19:45	18.3	NA	NA	3.70	6.88	NA	1.83	NA	13.38	0.05%

[a] $[H^+]$ is calculated from charge balance based on the IC measurements of $[SO_4^{2-}]$, $[NO_3^-]$, and $[NH_4^+]$.
[b] "OS" represents organosulfate.

Table S3. Supporting data from BEACHON 2011 campaign.

Start Time[a]	average temperature (°C)	average RH (%)	average O_3 (ppb)	average organics (μg/m^3)	average $[H^+]$[b] (nmol/m^3)	average MBO (ppb)	MBO OS[c] (ng/m^3)	DHIP[d] (ng/m^3)	IEPOX OS[c] (ng/m^3)	Isoprene tetrols[e]& triols[f] (ng/m^3)	Fraction of MBO OS in total organics
7/23/11 18:40	19.1	48.8	57.6	1.10	0.55	1.13	0.48	0.11	1.61	0.35	0.04%
8/1/11 17:10	15.0	73.5	42.5	1.26	1.10	0.54	0.27	0.08	1.06	0.52	0.02%
8/4/11 18:25	17.6	49.4	43.8	1.16	0.00	0.61	0.21	0.06	1.97	0.48	0.02%
8/7/11 19:45	17.5	39.3	45.9	1.52	0.58	0.88	0.29	0.03	1.05	0.36	0.02%
8/10/11 17:05	17.5	50.2	46.8	1.83	0.65	0.64	0.21	0.02	1.14	0.32	0.01%
8/16/11 18:15	18.2	47.1	39.3	1.30	0.58	0.84	0.00	0.11	0.09	0.48	0.00%

[a] The total sampling time for each sample is ~ 3 days (72 hrs); The total sampling volume for each sample is ~ 4320 m^3.
[b] $[H^+]$ is calculated from charge balance based on the AMS data of $[SO_4^{2-}]$, $[NO_3^-]$, and $[NH_4^+]$.
[c] "OS" represents organosulfate. Propyl sulfate was used as a surrogate standard for quantification.
[d] "DHIP" represents the 2,3-dihydroxyisopentanol measured from GC/EI-MS. *meso*-erythritol was used as a surrogate standard for quantification.
[e] "isoprene tetrols" represent the 2-methyltetrols measured from GC/EI-MS. *meso*-erythritol was used as a surrogate standard for quantification.
[f] "isoprene triols" represent the C5-alkenetriols measured from GC/EI-MS. *meso*-erythritol was used as a surrogate standard for quantification.

GC/EI-MS chemical analysis to measure DHIP:

Dried residues were trimethylsilylated by the addition of 100 μL of BSTFA + trimethylchlorosilane (99:1 (v/v), Supleco) and 50 μL of pyridine (Sigma-Aldrich, 98%, anhydrous), and the resultant mixture was then heated for 1 h at 70 ºC. SOA compounds that contain carboxyl and hydroxyl moieties are converted into volatile trimethylsilyl (TMS) derivatives that can be detected by GC/MS (Surratt et al., 2006). The details of the GC/MS technique and the operation procedures can be found in Zhang et al. (2011).

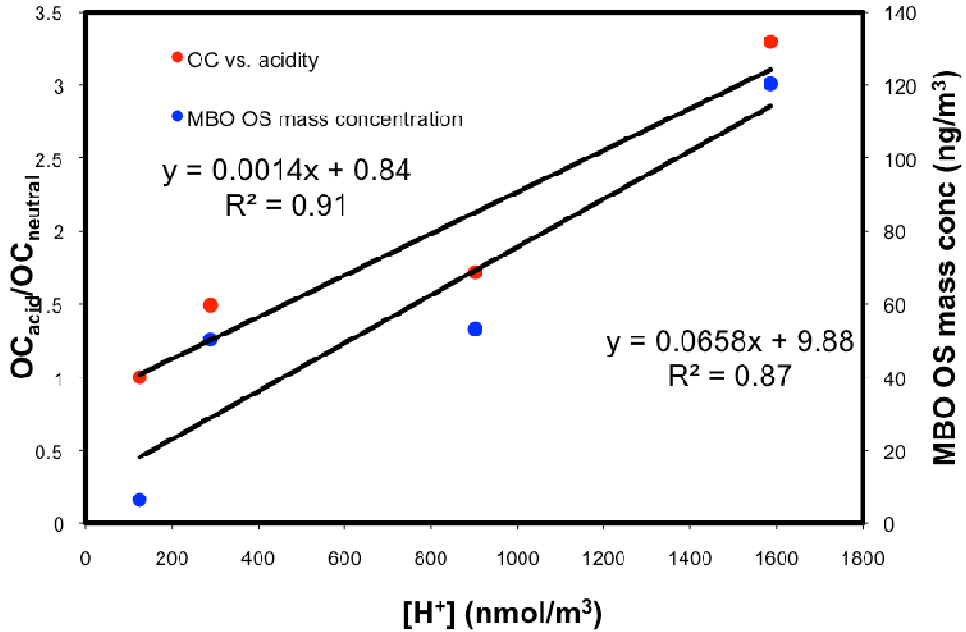

Figure S1. Correlation of the ratio of organic carbon (OC) concentration at elevated acidity relative to the neutral seed case and measured MBO organosulfate to measured aerosol acidity ($[H^+]_{air}$ nmol m^{-3}).

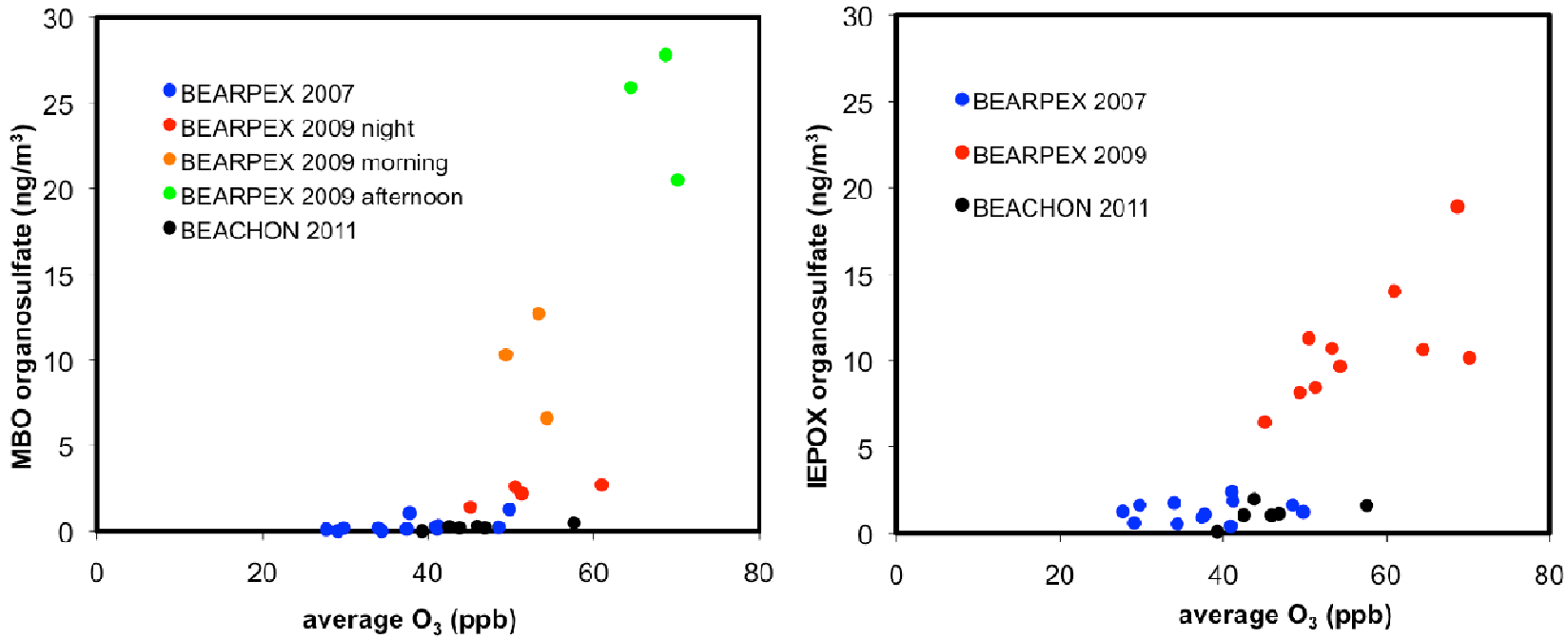

Figure S2. Correlations of MBO organosulfate (a) and IEPOX-derived organosulfate (b) mass concentrations to averaged O_3 from field measurements. The correlations suggest both ozone and organosulfates are secondary pollutants.

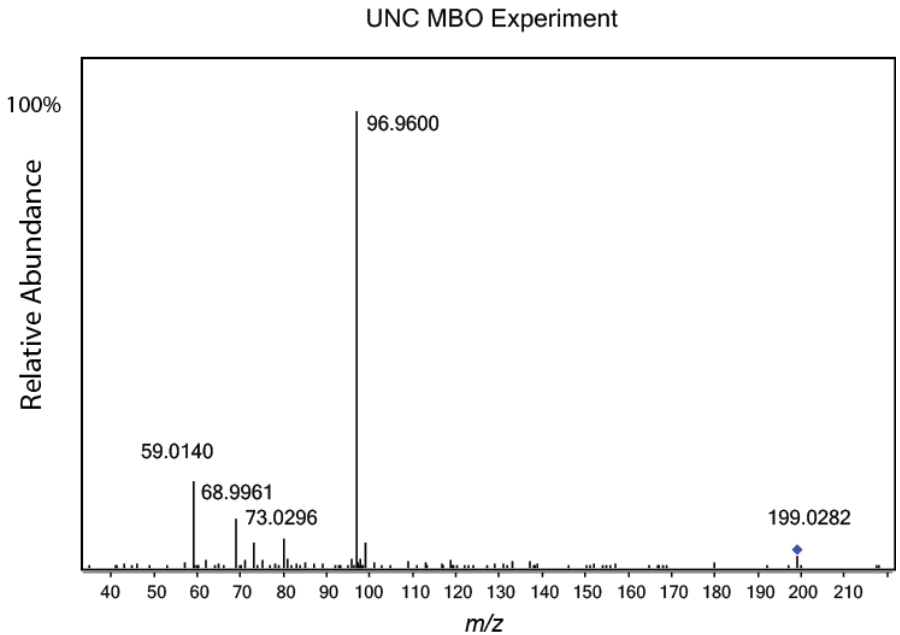

Figure S3. Tandem mass spectra (MS^2) of the MBO organosulfate (*m/z* 199) measured from the UNC high-NO chamber experiments.

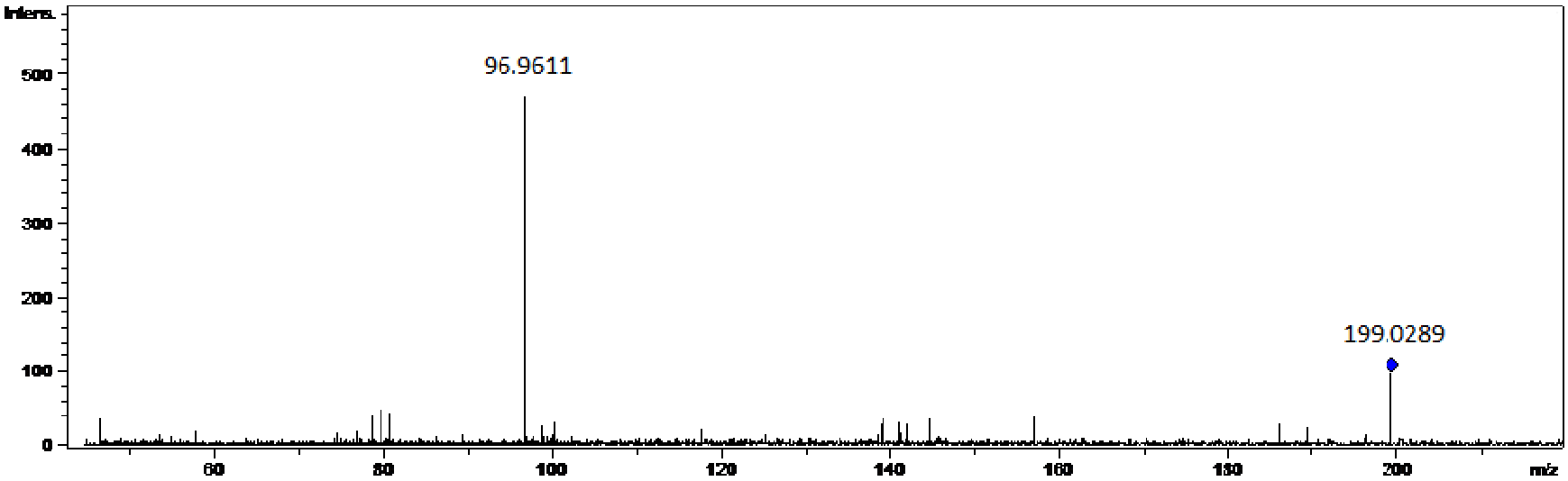

Figure S4. Tandem mass spectra (MS^2) of the MBO organosulfate (*m/z* 199) measured from the BEARPEX campaigns.

MBO intercalibration at BEARPEX

Measurements of MBO were made at 6.4m (NOAA, 2007) and 17.8m (TAMU, 2009). PTRMS measurements of the sum of MBO plus isoprene were made at five heights (1.5, 6.1, 9.3, 14.3 and 17.8m) through the canopy in both campaigns by the University of California, Berkeley (UCB). The diurnal profiles of MBO and isoprene were very different because MBO is locally emitted and isoprene is advected in from several hours upwind (Figure A). MBO concentrations are dominant over isoprene in the early morning (Figure A) when light and temperature driven emissions accumulate in the shallow boundary layer and transport from upwind is minimal. Figure A shows the comparison of MBO+isoprene (PTRMS) and MBO+isoprene (GC/MS or GC/FID) for the early morning (06:30 – 08:30, 2007; 07:00 – 10:00, 2009) and 2009 (TAMU) when MBO is dominant over isoprene. The comparable slopes of NOAA and TAMU versus UCB show that the MBO calibration scales are similar and that differences in the absolute observed concentrations are due to real variations driven by meteorological conditions between the two campaigns. The MBO+isoprene signal shows a strong vertical gradient through the canopy (Figure B). This gradient is entirely driven by MBO and not isoprene as it is the local emitted species and this is supported by the absence of a gradient in the sum of methyl vinyl ketone and methacrolein (MVK+macr), the first generation oxidation products of isoprene (Figure B). Due to the strong gradient concentrations at 6.1m are 17.8m (Figure B), this difference has not be taken into account in the concentrations reported here but would make the concentrations in 2009 approximately 1.5 times higher.

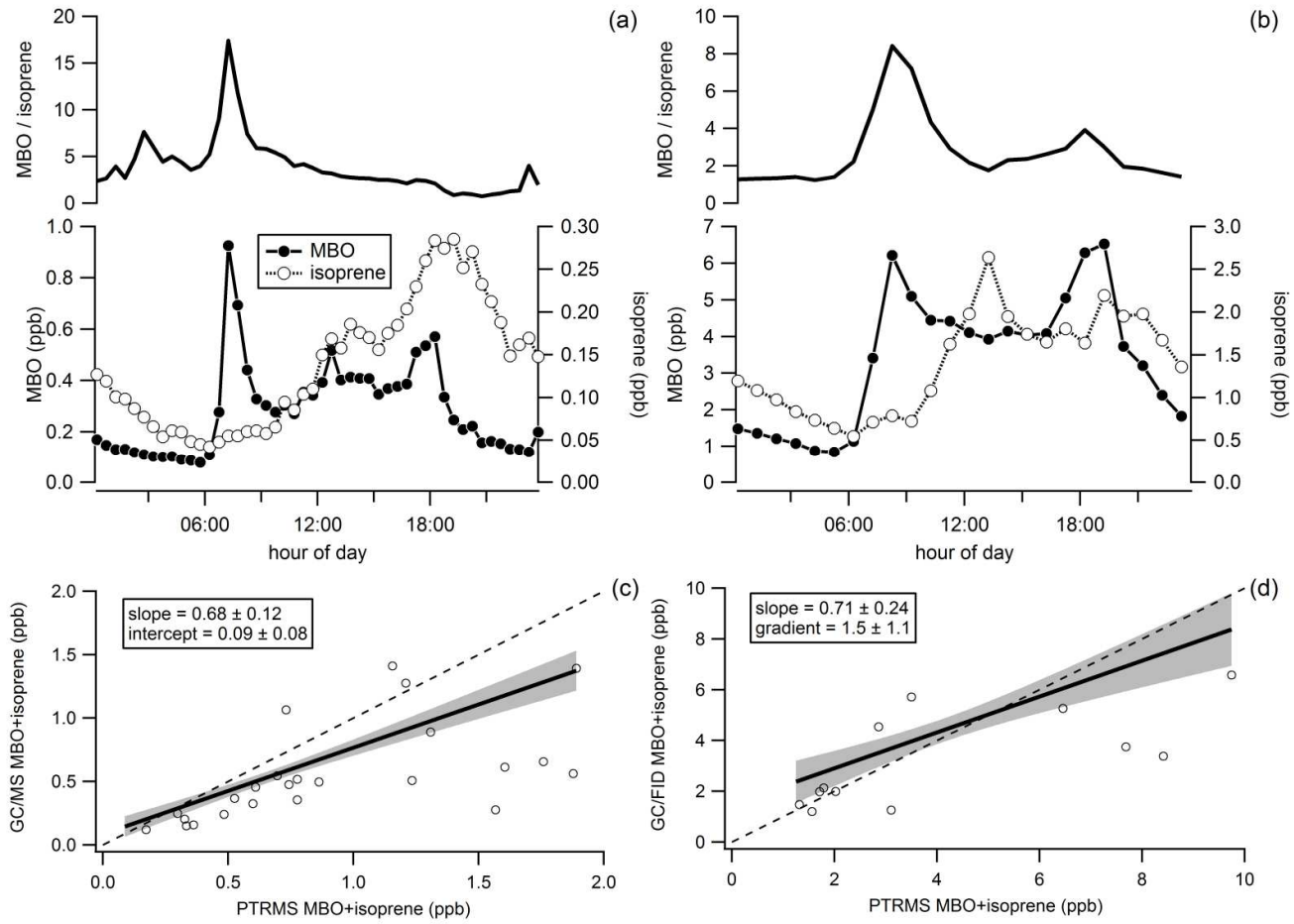

Figure S5. Diurnal variation of MBO, isoprene and the ratio of MBO to isoprene during (a) 2007 and (b) 2009. Comparison of the sum of MBO+isoprene in the early morning only measured by GC and PTRMS during (c) 2007 and (d) 2009.

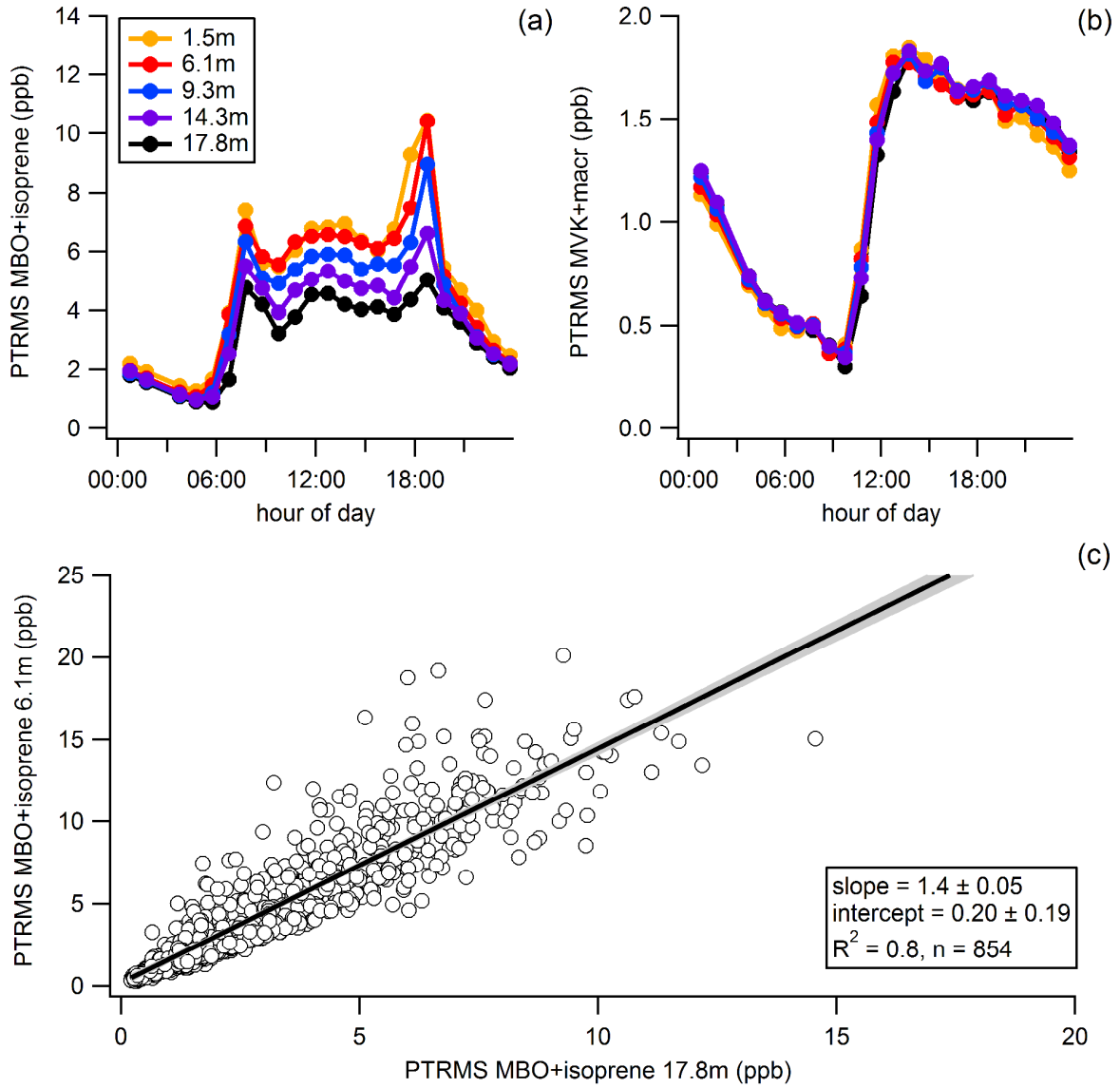

Figure S6. PTRMS gradient measurements at 5 heights (1.5, 6.1, 9.3, 14.3 and 17.8m) in 2009 for (a) MBO+isoprene and (b) methyl vinyl ketone+methacrolien (MVK+macr). Comparison of MBO+isoprene concentrations at 17.8 and 6.1m heights in 2009.