



Effects of NO_x and SO₂ on the Secondary Organic Aerosol Formation from Photooxidation of α-pinene and Limonene

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Abstract

Anthropogenic emissions such as NO_x and SO₂ influence the biogenic secondary organic aerosol (SOA) formation, but detailed mechanisms and effects are still elusive. We studied the effects of NO_x and SO₂ on the SOA formation from photooxidation of α-pinene and limonene at ambient relevant NO_x and SO₂ concentrations (NO_x: < 1 ppb to 20 ppb, SO₂: < 0.05 ppb to 15 ppb). In these experiments, monoterpene oxidation was dominated by OH oxidation. We found that SO₂ induced nucleation and enhanced SOA mass formation. NO_x strongly suppressed not only new particle formation but also SOA mass yield. However, in the presence of SO₂ which induced high number concentration of particles after oxidation to H₂SO₄, the mass yield of SOA at high NO_x was comparable to that at low NO_x. This indicates that the suppression of SOA yield by NO_x was mainly due to the suppressed new particle formation, leading to a lack of particle surface for the organics to condense on. By compensating the suppressing effect on nucleation of NO_x, SO₂ also compensated the suppressing effect on SOA yield. Aerosol mass spectrometer data show that increasing NO_x enhanced nitrate formation. The majority of the nitrate was organic nitrate (57%-77%), even in low NO_x conditions (<~1 ppb). Organic nitrate contributed 7%-26% of total organics assuming a molecular weight of 200 g/mol. SOA from α-pinene photooxidation at high NO_x had generally lower hydrogen to carbon ratio (H/C), compared with at low NO_x. The NO_x dependence of the chemical composition can be attributed to the NO_x dependence of the branching ratio of the RO₂ loss reactions, leading to lower fraction of organic hydroperoxide and higher fractions of organic nitrate at high NO_x. While NO_x suppressed new particle formation and SOA mass formation, SO₂ can compensate such effects, and the combining effect of SO₂ and NO_x may have important influence on SOA formation affected by interactions of biogenic volatile organic compounds (VOC) with anthropogenic emissions.

1 Introduction

Secondary organic aerosol (SOA), as an important class of atmospheric aerosol, have important impacts on air quality, human health and climate change (Hallquist et al., 2009; Kanakidou et al., 2005; Jimenez et al., 2009;



36 Zhang et al., 2011). SOA mainly originates from biogenic volatile organic compounds (VOC) emitted by
37 terrestrial vegetation (Hallquist et al., 2009). Once emitted into the atmosphere, biogenic VOC can undergo
38 reactions with atmospheric oxidants including OH, O₃ and NO₃, and form SOA. When an air mass enriched in
39 biogenic VOC is transported over an area with substantial anthropogenic emissions or vice versa, the reaction
40 behavior of VOC and SOA formation can be altered due to the interactions of biogenic VOC with anthropogenic
41 emissions such as NO_x, SO₂, anthropogenic aerosol and anthropogenic VOC. A number of field studies have
42 highlighted the important role of the anthropogenic-biogenic interactions in SOA formation (de Gouw et al.,
43 2005; Goldstein et al., 2009; Hoyle et al., 2011; Worton et al., 2011; Glasius et al., 2011; Xu et al., 2015a;
44 Shilling et al., 2012), which can induce an “anthropogenic enhancement” effect on SOA formation.

45 Among biogenic VOC, monoterpenes are important contributors to biogenic SOA due to their high emission
46 rates, high reactivity and relative high SOA yield compared to isoprene (Guenther et al., 1995; Guenther et al.,
47 2012; Chung and Seinfeld, 2002; Pandis et al., 1991; Griffin et al., 1999; Hoffmann et al., 1997; Zhao et al.,
48 2015; Carlton et al., 2009). The anthropogenic modulation of the SOA formation from monoterpene can have
49 important impacts on regional and global biogenic SOA budget (Spracklen et al., 2011). The influence of various
50 anthropogenic pollutants on SOA formation of monoterpene have been investigated by a number of laboratory
51 studies (Sarrafzadeh et al., 2016; Zhao et al., 2016; Flores et al., 2014; Emanuelsson et al., 2013; Eddingsaas et
52 al., 2012a; Offenberg et al., 2009; Kleindienst et al., 2006; Presto et al., 2005; Ng et al., 2007; Zhang et al., 1992;
53 Pandis et al., 1991; Draper et al., 2015; Han et al., 2016). In particular, NO_x and SO₂ have been shown to affect
54 SOA formation.

55 NO_x changes the fate of RO₂ radical formed in VOC oxidation and therefore can change reaction product
56 distribution and aerosol formation. At low NO_x, RO₂ mainly react with HO₂ forming organic hydroperoxide. At
57 high NO_x, RO₂ mainly react with NO forming organic nitrate (Hallquist et al., 2009; Ziemann and Atkinson,
58 2012; Finlayson-Pitts and Pitts Jr., 1999). Some studies found that the SOA yield from α -pinene is higher at
59 lower NO_x concentration for ozonolysis (Presto et al., 2005) and photooxidation (Ng et al., 2007; Eddingsaas et
60 al., 2012a; Han et al., 2016). The decrease of SOA yield with increasing NO_x was proposed to be due to the
61 formation of more volatile products like organic nitrate under high NO_x conditions (Presto et al., 2005). In
62 contrast, a recent study found that the suppressing effect of NO_x is in large part attributed to the effect of NO_x on
63 OH concentration for the SOA from β -pinene oxidation, and after eliminating the effect of NO_x on OH
64 concentration, SOA yield only varies by 20-30% (Sarrafzadeh et al., 2016). Beside the effect of NO_x on SOA
65 yield, NO_x has been found to suppress the new particle formation from VOC directly emitted by Mediterranean
66 trees (mainly monoterpenes) (Wildt et al., 2014) and β -pinene (Sarrafzadeh et al., 2016), thereby reducing
67 condensational sink present during high NO_x experiments.

68 Regarding the effect of SO₂, the SOA yield of α -pinene photooxidation was found to increase with SO₂
69 concentration at high NO_x concentrations (SO₂: 0-252 ppb, NO_x: 242-543 ppb, α -pinene: 178-255 ppb)
70 (Kleindienst et al., 2006) and the increase is attributed to the formation of H₂SO₄ acidic aerosol. Acidity of seed
71 aerosol was also found to enhance particle yield of α -pinene at high NO_x (Offenberg et al. (2009): NO_x 100-120
72 ppb, α -pinene 69-160 ppb; Han et al. (2016): initial NO ~70 ppb, α -pinene 14-18 ppb). In constrast, Eddingsaas et
73 al. (2012a) found that particle yield increases with aerosol acidity at “high NO” condition (NO_x 800 ppb, α -
74 pinene: 20-52 ppb), but is independent of the presence of seed aerosol or aerosol acidity at both low NO_x (NO_x



75 lower than the detection limit of NO_x analyzer) and “high NO_2 ” condition (NO_x 800 ppb). Similarly, at low NO_x
76 (initial $\text{NO} < 0.3$ ppb, α -pinene ~ 20 ppb), Han et al. (2016) found that the acidity of seed has no significant effect
77 on SOA yield from α -pinene photooxidation.

78 While these studies have provided important insights into the effects of NO_x and SO_2 on SOA formation, a
79 number of questions still remain elusive. For example, many studies used very high NO_x and SO_2 concentrations
80 (up to several hundreds of ppb), and the effects of NO_x and SO_2 at concentrations relevant to ambient
81 anthropogenic-biogenic interactions (sub ppb to several tens of ppb for NO_2 and SO_2) are unclear. Moreover,
82 many previous studies on the SOA formation from monoterpene oxidation focus on ozonolysis or do not
83 distinguish the OH oxidation and ozonolysis in photooxidation, and only few studies on OH oxidation have been
84 conducted (Eddingsaas et al., 2012a; Zhao et al., 2015). More importantly, studies that investigated the combined
85 effects of NO_x and SO_2 are scarce, although they are often co-emitted from anthropogenic sources. According to
86 previous studies, NO_x mainly has a suppressing effect on SOA formation while SO_2 mainly has an enhancing
87 effect. NO_x and SO_2 might have counteracting effect or a synergistic effect in SOA formation in the ambient.
88 In this study, we investigated the effects of NO_x , SO_2 and their combining effects on SOA formation from the
89 photooxidation of α -pinene and limonene. α -pinene and limonene are two important monoterpenes with high
90 emission rates among monoterpenes (Guenther et al., 2012). OH oxidation dominated over ozonolysis in the
91 monoterpene oxidation in this study as determined by measured OH and O_3 concentrations. The relative
92 contributions of RO_2 loss reactions at low NO_x and higher NO_x were also quantified using measured HO_2 , RO_2 ,
93 and NO concentrations. The effects on new particle formation, SOA yield and aerosol chemical composition
94 were examined. We used ambient relevant NO_x and SO_2 concentrations so that the results can shed lights on the
95 mechanisms of interactions of biogenic VOC with anthropogenic emissions in the real atmosphere.

96 2 Experimental

97 2.1 Experimental setup and instrumentation

98 The experiments were performed in the SAPHIR chamber (Simulation of Atmospheric PHotochemistry In a large
99 Reaction chamber) at Forschungszentrum Jülich, Germany. The details of the chamber have been described
100 before (Rohrer et al., 2005; Zhao et al., 2015). Briefly, it is a 270 m^3 Teflon chamber using natural sunlight for
101 illumination. It is equipped with a louvre system to switch between light and dark conditions. The physical
102 parameters for chamber running such as temperature and relative humidity were recorded. The solar irradiation
103 was characterized and the photolysis frequency was derived (Bohn et al., 2005; Bohn and Zilken, 2005).

104 Gas and particles phase species were characterized using various instruments. OH, HO_2 and RO_2 concentrations
105 were measured using a laser induced fluorescence (LIF) system with details described by Fuchs et al. (2012).
106 From OH concentration, OH dose, the integral of OH concentration over time, was calculated in order to better
107 compare experiments with different OH levels. For example, experiments at high NO_x in this study generally had
108 higher OH concentrations due to the faster OH production by recycling of $\text{HO}_2\cdot$ and $\text{RO}_2\cdot$ to OH. The VOC were
109 characterized using a Proton Transfer Reaction Time-of-Flight Mass Spectrometer (PTR-ToF-MS) and Gas
110 Chromatography-Mass spectrometer (GC-MS). NO_x , O_3 and SO_2 concentrations were characterized using a NO_x



111 analyzer (ECO PHYSICS TR480), an O₃ analyzer (ANSYCO, model O341M), and an SO₂ analyzer (Thermo
 112 Systems 43i), respectively. More details of these instrumentation are described before (Zhao et al., 2015).

113 The number and size distribution of particles were measured using a condensation particle counter (CPC,
 114 TSI, model 3786) and a scanning mobility particle sizer (SMPS, TSI, DMA 3081/CPC 3785). From particle
 115 number measurement, the nucleation rate ($J_{2.5}$) was derived from the number concentration of particles larger than
 116 2.5 nm as measured by CPC. Particle chemical composition was measured using a High-Resolution Time-of-
 117 Flight Aerosol Mass Spectrometer (HR-ToF-AMS, Aerodyne Research Inc.). From the AMS data, oxygen to
 118 carbon ratio (O/C), hydrogen to carbon ratio (H/C), and nitrogen to carbon ratio (N/C) were derived using a
 119 method derived in the literature (Aiken et al., 2007; Aiken et al., 2008). An update procedure to determine the
 120 elemental composition is reported by Canagaratna et al. (2015), showing the O/C and H/C derived from the
 121 method of Aiken et al. (2008) may be underestimated. Since only relative difference in elemental composition of
 122 SOA is studied here, different methods should not affect the relative trend in elemental composition. The
 123 fractional contribution of organics in the signals at $m/z=44$ and $m/z=43$ to total organics (f_{44} and f_{43} , respectively)
 124 were also derived. SOA yields were calculated as the ratio of organic aerosol mass formed to the amount of VOC
 125 reacted. The concentration of organic aerosol was derived using the total aerosol mass concentration measured by
 126 SMPS with a density of 1 g cm⁻³ (to better compare with previous literature) multiplied by with the mass fraction
 127 of organics in total aerosol characterized by AMS. The organic aerosol concentration was corrected for the
 128 particle wall loss and dilution loss using the method described in Zhao et al. (2015). The loss of vapor on the wall
 129 was not corrected here.

130 In the experiments with added SO₂, sulfuric acid was formed upon photooxidation. Sulfuric acid was partly
 131 neutralized by background ammonia, which was introduced into the chamber mainly due to humidification. The
 132 density of the aerosol was derived using the linear mixing of the density of organic aerosol (assuming 1.32 g cm⁻³
 133 from one of our previous studies and the literature (Flores et al., 2014; Eddingsaas et al., 2012a)) and the density
 134 of ammonium sulfate/ammonium bisulfate (~1.77 g cm⁻³). According to calculations based on the E-AIM model
 135 (Clegg et al., 1998; Wexler and Clegg, 2002) (<http://www.aim.env.uea.ac.uk/aim/aim.php>), there were no
 136 aqueous phase formed at the relative humidity in the experiments of this study (average RH 28-42% for the
 137 period of monoterpene photooxidation).

138 2.2 Experimental procedure

139 The SOA formation from α -pinene and limonene photooxidation was investigated at different NO_x and SO₂
 140 levels. Four types of experiments were done: with neither NO_x nor SO₂ added (referred to as “low NO_x, low
 141 SO₂”), with only NO_x added (~20 ppb NO, referred to as “high NO_x, low SO₂”), with only SO₂ added (~15 ppb,
 142 referred to as “low NO_x, high SO₂”), and with both NO_x and SO₂ added (~20 ppb NO and ~15 ppb SO₂, referred
 143 to as “high NO_x, high SO₂”). For low NO_x conditions, background NO concentrations were around 0.05-0.2 ppb,
 144 and NO was mainly from the background photolytic process of Teflon chamber wall (Rohrer et al., 2005). For
 145 low SO₂ conditions, background SO₂ concentrations were below the detection limit of the SO₂ analyzer (0.05
 146 ppb). In some experiments, a lower level of SO₂ (2 ppb, referred to as “moderate SO₂”) was used to test the effect
 147 of SO₂ concentration. An overview of the experiments is shown in Table 1. In a typical experiment, the chamber
 148 was humidified to ~75% RH first, and then VOC and NO, if applicable, were added to the chamber. Then the



roof was opened to start photooxidation. In the experiments with SO_2 , SO_2 was added and the roof was opened to initialize nucleation first and then VOC was added. The particle number concentration caused by SO_2 oxidation typically reached several 10^4 cm^{-3} (see Fig. 2 high SO_2 cases) and after VOC addition, no further nucleation occurred. The detailed conditions of the experiments are shown in Table S1. The experiments of α -pinene and limonene photooxidation were designed to keep the initial OH reactivity and thus OH loss rate constant so that the OH concentrations of these experiments were more comparable. Therefore, the concentration of limonene was around one-third the concentration of α -pinene due to the higher OH reactivity of limonene.

3 Results and discussion

3.1 Chemical scheme: VOC oxidation pathway and RO_2 fate

In the photooxidation of VOC, OH and O_3 often co-exist and both contribute to VOC oxidation. In order to study the mechanism, it is helpful to isolate one oxidation pathway from the other. In this study, the reaction rates of OH and ozone with VOC are quantified using measured OH and O_3 concentrations multiplied by rate constants. Typical OH and O_3 concentrations in an experiment were around $(1\text{--}15) \times 10^6 \text{ molecules cm}^{-3}$ and 0–50 ppb, respectively, depending on the VOC and NO_x concentrations added. The relative importance of the reaction of OH and O_3 with monoterpenes in a typical experiment is shown in Fig. S1. The VOC loss was dominated by OH oxidation over ozonolysis. This makes the chemical scheme simple and it is easier to interpret than cases when both OH oxidation and ozonolysis are important.

As mentioned above, RO_2 fate, i.e., the branching of RO_2 loss among different pathways has an important influence on the product distribution and thus on SOA composition, physicochemical properties and yields. RO_2 can react with NO, HO_2 , RO_2 , or isomerize. The fate of RO_2 mainly depends on the concentrations of NO, HO_2 and RO_2 . Here, the loss rates of RO_2 via different pathways were quantified using the measured HO_2 , NO and RO_2 and the rate constants based on MCM3.3 (Jenkin et al., 1997; Saunders et al., 2003) (<http://mcm.leeds.ac.uk/MCM>). Measured HO_2 and RO_2 concentrations in a typical experiment are shown in Fig. S2 and the relative importance of different RO_2 reaction pathways is compared in Fig. 1, which is similar for both α -pinene and limonene oxidation. In the low NO_x conditions of this study, $\text{RO}_2\text{+NO}$ dominated the RO_2 loss rate in the beginning of an experiment (Fig. 1a) because a trace amount of NO (up to ~ 0.2 ppb) was formed from the photolysis of HONO produced from a photolytic process on the chamber wall (Rohrer et al., 2005). But later in the experiment, $\text{RO}_2\text{+HO}_2$ contributed a significant fraction (up to $\sim 40\%$) to RO_2 loss because of increasing HO_2 concentration and decreasing NO concentration. In the high NO_x conditions, $\text{RO}_2\text{+NO}$ overwhelmingly dominated the RO_2 loss rate (Fig. 1b), and with the decrease of NO in an experiment, the total RO_2 loss rate decreased substantially (Fig. 1b). Since the main products of $\text{RO}_2\text{+HO}_2$ are organic hydroperoxides, more organic hydroperoxide relative to organic nitrate is expected in the low NO_x conditions here. The loss rate of $\text{RO}_2\text{+RO}_2$ was estimated to be $\sim 10^{-4} \text{ s}^{-1}$ using a reaction rate constant of $2.5 \times 10^{-13} \text{ molecules}^{-1} \text{ cm}^3 \text{ s}^{-1}$ (Ziemann and Atkinson, 2012). This contribution is negligible compared to other pathways in this study, although the reaction rate constants of $\text{RO}_2\text{+RO}_2$ are highly uncertain and may depend on specific RO_2 (Ziemann and Atkinson, 2012).



184 3.2 Effects of NO_x and SO₂ on new particle formation

185 The effects of NO_x and SO₂ on new particle formation from α -pinene oxidation are shown in Fig. 2a. In low SO₂
 186 conditions, both the total particle number concentration and nucleation rate at high NO_x were lower than those at
 187 low NO_x, indicating NO_x suppressed the new particle formation. The suppressing effect of NO_x on new particle
 188 formation was in agreement with the findings of Wildt et al. (2014). This suppression is considered to be caused
 189 by the increased fraction of RO₂+NO reaction, decreasing the importance of RO₂+RO₂ permutation reactions.
 190 RO₂+RO₂ reaction products are believed to be involved in the new particle formation (Wildt et al., 2014; Kirkby
 191 et al., 2016) and initial growth of particles by forming higher molecular weight products such as highly oxidized
 192 multifunctional molecules (HOM) and their dimers and trimers (Ehn et al., 2014; Kirkby et al., 2016).

193 In high SO₂ conditions, the nucleation rate and total number concentrations were high, regardless of NO_x
 194 levels. The high concentration of particles was attributed to the new particle formation induced by H₂SO₄ alone
 195 formed by SO₂ oxidation since the new particle formation occurred before VOC addition. The role of H₂SO₄ in
 196 new particle formation has been well studied in previous studies (Berndt et al., 2005; Zhang et al., 2012; Sipila et
 197 al., 2010; Kirkby et al., 2011; Almeida et al., 2013).

198 Similar suppression of new particle formation by NO_x and enhancement of new particle formation by
 199 SO₂ photooxidation were found for limonene oxidation (Fig. 2b).

200 3.3 Effects of NO_x and SO₂ on SOA mass yield

201 3.3.1 Effect of NO_x

202 Figure 3a shows SOA yield at different NO_x for α -pinene oxidation. In order to make different
 203 experiments more comparable, the SOA yield is plotted as a function of OH dose instead of reaction time. In low
 204 SO₂ conditions, NO_x not only suppressed the new particle formation but also suppressed SOA mass yield.
 205 Because NO_x suppressed new particle formation, the suppression on SOA yield could be attributed to the absence
 206 of nucleation and thus the absence of condensational sink or to the decrease of condensable organic materials. We
 207 found that when new particle formation was already enhanced by added SO₂, the SOA yield at high NO_x was
 208 comparable to that at low NO_x and the difference in SOA yield between high NO_x and low NO_x was much
 209 smaller (Fig. 3a). This finding indicates that NO did not significantly suppress the formation of condensable
 210 organic materials, although NO obviously suppressed the formation of products for nucleation. Therefore, we
 211 conclude that the suppressing effect of NO_x on SOA yield was mainly due to suppressing nucleation, i.e., to the
 212 absence of particle surface as condensational sink.

213 For limonene oxidation, similar results of NO_x suppressing the particle mass formation have been found
 214 in low SO₂ conditions (Fig. 3b). Yet, in high SO₂ conditions, the SOA yield from limonene oxidation at high NO_x
 215 was still significantly lower than that at low NO_x, which is different from the findings for α -pinene SOA. That
 216 might be caused by either the larger difference between the volatility of oxidation products formed under
 217 different NO_x conditions for limonene case compared to α -pinene or by the different ranges of VOC/NO_x for α -
 218 pinene (VOC/NO_x= 1 at high NO_x, see Table 1) and limonene (VOC/NO_x=0.35, at high NO_x).

219 The suppression of SOA mass formation by NO_x under low SO₂ conditions agrees with previous studies
 220 (Eddingsaas et al., 2012a; Wildt et al., 2014; Sarrafzadeh et al., 2016; Hatakeyama et al., 1991). For example, it
 221 was found that, high concentration of NO_x (tens of ppb) suppressed mass yield of SOA formed from



photooxidation of β -pinene, α -pinene and VOC emitted by Mediterranean trees (Wildt et al., 2014; Sarrafzadeh et al., 2016). And on the basis of the results by Eddingsaas et al. (2012a), the SOA yield at high NO_x (referred to as “high NO ” by the authors) is lower than at low NO_x in the absence of seed aerosol.

Our finding that SOA yield at high NO_x is comparable to that at low NO_x in high SO_2 conditions is also in line with the findings of some previous studies using seed aerosols (Sarrafzadeh et al., 2016; Eddingsaas et al., 2012a). For example, Sarrafzadeh et al. (2016) found that in the presence of seed aerosol, the suppressing effect of NO_x on the SOA yield from β -pinene photooxidation is substantially diminished and SOA yield only varies by 20-30% in the NO_x range of <1 ppb to 86 ppb at constant OH concentrations. Eddingsaas et al. (2012a) also found that in presence of seed aerosol, the difference in the SOA yield between low NO_x and high NO_x is much decreased. However, our finding is in contrast with the findings in other studies (Presto et al., 2005; Ng et al., 2007; Han et al., 2016), who reported much lower SOA yield at high NO_x than at low NO_x in presence of seed. The different findings in these studies from ours may be attributed to the difference in the VOC oxidation pathways (OH oxidation vs. ozonolysis), VOC and NO_x concentration ranges, NO/NO_2 ratio as well as OH concentrations, which all affect SOA yield. Note that even at “high NO_x ” the NO_x concentration in this study was much lower than in many previous studies and the NO_x concentration range here was more relevant to the anthropogenic-biogenic interactions in the ambient.

3.3.2 Effect of SO_2

For both α -pinene and limonene, SO_2 was found to enhance the SOA mass yield, at given NO_x levels, especially for the high NO_x cases (Fig. 3). The enhancing effect of SO_2 on particle mass formation can be attributed to two reasons. Firstly, SO_2 oxidation induced new particle formation, which provided more surface and volume for further condensation of organic vapor. Secondly, H_2SO_4 formed by photooxidation of SO_2 can enhance SOA formation via acid-catalyzed heterogeneous uptake, an important SOA formation pathway initially found from isoprene photooxidation (Jang et al., 2002; Lin et al., 2012; Surratt et al., 2007). For the products from monoterpene oxidation, such an acid-catalyzed effect may also occur (Northcross and Jang, 2007; Wang et al., 2012; Lal et al., 2012; Zhang et al., 2006; Ding et al., 2011; Iinuma et al., 2009) and in this study, the particles were acidic with the molar ratio of NH_4^+ to SO_4^{2-} around 1.5-1.8. As mentioned above, inducing new particle formation by SO_2 is especially important at high NO_x conditions, when nucleation was suppressed by NO_x . In addition, we found that the SOA yield in limonene oxidation at a moderate SO_2 level (2 ppb) was comparable to the yield at high SO_2 (15 ppb) when similar particle number concentrations in both cases were formed. Both yields were significantly higher than the yield at low SO_2 (<0.05 ppb, see Fig. S3). This comparison suggests that the effect in enhancing new particle formation by SO_2 seems to be more important. The role of SO_2 on new particle formation is similar to adding seed aerosol on providing particle surface for organics to condense. Artificially added seed aerosol has been shown to enhance SOA formation from α -pinene and β -pinene oxidation (Ehn et al., 2014; Sarrafzadeh et al., 2016).

The finding that in presence of high SO_2 , the SOA mass yield at NO_x conditions was enhanced to the value comparable with that at low NO_x indicates that the suppressing effect of NO_x on SOA mass formation was counterbalanced by the presence of SO_2 . This has important implications for SOA formation affected by



anthropogenic-biogenic interactions in the real atmosphere as discussed below when SO_2 and NO_x often co-exist in relative high concentrations.

3.4 Effects of NO_x and SO_2 on SOA chemical composition

The effects of NO_x and SO_2 on SOA chemical composition were analyzed on the basis of AMS data. We found that NO_x enhanced nitrate formation. The ratio of the mass of nitrate to organics was higher at high NO_x than at low NO_x regardless of the SO_2 level, and similar trends were found for SOA from α -pinene and limonene oxidation (Fig. 4a). Higher nitrate to organics ratios were observed for SOA from limonene at high NO_x , which is mainly due to the lower VOC/ NO_x ratio resulted from the lower concentrations of limonene (7 ppb) compared to α -pinene (20 ppb) (see Table 1). Overall, the mass ratios of nitrate to organics ranged from 0.02 to 0.11 considering all the experiments in this study.

Nitrate formed can be either inorganic (such as HNO_3 from the reaction of NO_2 with OH) or organic (from the reaction of RO_2 with NO). The ratio of NO_2^+ ($m/z=46$) to NO^+ ($m/z=30$) in the mass spectra detected by AMS can be used to differentiate whether nitrate is organic or inorganic (Fry et al., 2009; Rollins et al., 2009; Farmer et al., 2010; Kiendler-Scharr et al., 2016). Organic nitrate was considered to have a $\text{NO}_2^+/\text{NO}^+$ of ~ 0.1 and inorganic NH_4NO_3 had a $\text{NO}_2^+/\text{NO}^+$ of ~ 0.31 with the instrument used in this study as determined from calibration measurements. In this study, $\text{NO}_2^+/\text{NO}^+$ ratios ranged from 0.14 to 0.18, closer to the ratio of organic nitrate. The organic nitrate was estimated to account for 57%-77% (molar fraction) of total nitrate considering both the low NO_x and high NO_x conditions. This indicates that nitrate was mostly organic nitrate, even at low NO_x in this study.

In order to determine the contribution of organic nitrate to total organics, we estimated the molecular weight of organic nitrates formed by α -pinene and limonene oxidation to be 200-300 g/mol, based on reaction mechanisms ((Eddingsaas et al., 2012b) and MCM v3.3, via website: <http://mcm.leeds.ac.uk/MCM>). We assumed a molecular weight of 200 g/mol in order to make our results comparable to the field studies which used similar molecular weight (Kiendler-Scharr et al., 2016). For this value, the organic nitrate compounds were estimated to account for 7-26% of the total organics mass as measured by AMS in SOA. Organic nitrate fraction in total organics was within the range of values found in a field observation in southeast US (5-12% in summer and 9-25% in winter depending on the molecular weight of organic nitrate) using AMS (Xu et al., 2015b) and particle organic nitrate content derived from the sum of speciated organic nitrates (around 1-17% considering observed variability and 3% and 8% on average in the afternoon and at night, respectively) (Lee et al., 2016). Note that the organic nitrate fraction was lower than the mean value (42%) for a number of European observation stations when organic nitrate is mainly formed by the reaction of VOC with NO_3 (Kiendler-Scharr et al., 2016).

Moreover, we found that the contribution of organic nitrate to total organics (calculated using a molecular weight of 200 g/mol for organic nitrate) was higher at high NO_x (Fig. 4b), although in some experiments the ratios of NO_2^+ to NO^+ were too noisy to derive a reliable fraction of organic nitrate. This result is consistent with the reaction scheme that at high NO_x , almost all RO_2 loss was switched to the reaction with NO, which is expected to enhance the organic nitrate formation. Besides organic nitrate, the ratio of nitrogen to carbon atoms (N/C) was also found to be higher at high NO_x (Fig. S4). But after considering nitrate functional group



separately, N/C ratio was very low, generally <0.01 , which indicates majority of the organic nitrogen existed in the form of organic nitrate.

The chemical composition of organic components of SOA in terms of H/C and O/C ratios at different NO_x and SO_2 levels was further compared. For SOA from α -pinene photooxidation, in low SO_2 conditions, no significant difference in H/C and O/C was found between SOA formed at low NO_x and at high NO_x within the experimental uncertainties (Fig. 5). The variability of H/C and O/C at high NO_x is large, mainly due to the low particle mass and small particle size. In high SO_2 conditions, SOA formed at high NO_x had the higher O/C and lower H/C, which indicates that SOA components had higher oxidation state. The higher O/C at high NO_x than at low NO_x is partly due to the higher OH dose at high NO_x , although even at same OH dose O/C at high NO_x was still slightly higher than at low NO_x in high SO_2 conditions.

For the SOA formed from limonene photooxidation, no significant difference in the H/C and O/C was found between different NO_x and SO_2 conditions (Fig. S5), which is partly due to the low signal resulting from low particle mass and small particle size in high NO_x conditions.

Due to the high uncertainties for some of the H/C and O/C data, the chemical composition was further analyzed using f_{44} and f_{43} since f_{44} and f_{43} are less noisy (Fig. 6). For both α -pinene and limonene, SOA formed at high NO_x generally has lower f_{43} . Because f_{43} generally correlates with H/C in organic aerosol (Ng et al., 2011), lower f_{43} is indicative of lower H/C, which is consistent with the lower H/C at high NO_x observed for SOA from α -pinene oxidation in presence of high concentrations of SO_2 (Fig. 5). The lower f_{43} at high NO_x was evidenced in the oxidation of α -pinene based on the data in a previous study (Chhabra et al., 2011). The lower H/C and f_{43} are likely to be related to the reaction pathways. According to the reaction mechanism mentioned above, at low NO_x a significant fraction of RO_2 reacted with HO_2 forming hydroperoxide, while at high NO_x almost all RO_2 reacted with NO forming organic nitrate. Compared with organic nitrate, hydroperoxide have higher H/C ratio. The same mechanism also caused higher organic nitrate fraction at high NO_x , as discussed above.

Detailed mass spectra of SOA were compared, shown in Fig 7. For α -pinene, in high SO_2 conditions, mass spectra of SOA formed at high NO_x generally had higher intensity for CHOgt1 family ions, such as CO_2^+ (m/z 44), but lower intensity for CH family ions, such as C_2H_3^+ (m/z 15), C_3H_3^+ (m/z 39) (Fig. 7b) than at low NO_x . In low SO_2 conditions, such difference is not apparent (Fig. 7a), partly due to the low signal from AMS for SOA formed at high NO_x as discussed above. For both the high SO_2 and low SO_2 cases, mass spectra of SOA at high NO_x show higher intensity of CHN1 family ions. This is also consistent with the higher N/C ratio shown above. For SOA from limonene oxidation, SOA formed at high NO_x had lower mass fraction at m/z 15 (C_2H_3^+), 28 (CO^+), 43 ($\text{C}_2\text{H}_3\text{O}^+$), 44 (CO_2^+), and higher mass fraction at m/z 27 (CHN^+ , C_2H_3^+), 41 (C_3H_5^+), 55 (C_4H_7^+), 64 (C_4O^+) than at low NO_x (Fig. S6). It seems that overall mass spectra of the SOA from limonene formed at high NO_x had higher intensity for CH family ions, but lower intensity for CHO1 family ions than at low NO_x . Note that the differences in these m/z were based on the average spectra during the whole reaction period and may not reflect the chemical composition at a certain time.

4 Conclusion and implications

We investigated the SOA formation from the photooxidation of α -pinene and limonene under different NO_x and SO_2 conditions, when OH oxidation was the dominant oxidation pathway of monoterpenes. The fate of RO_2



was regulated by varying NO_x concentrations. We confirmed that NO_x suppressed new particle formation. NO_x also suppressed SOA mass yield in the absence of SO_2 . The suppression of SOA yield by NO_x was mainly due to the suppressed new particle formation, i.e., absence of sufficient particle surfaces for organic vapor to condense on at high NO_x . NO_x did not significantly suppress the formation of condensable organics from α -pinene oxidation as evidenced by the similar SOA yield at high and low NO_x in the presence of SO_2 .

SO_2 enhanced SOA yield from α -pinene and limonene photooxidation. SO_2 oxidation produced high number concentration of particles and compensated for the suppression of SOA yield by NO_x . The enhancement of SOA yield by SO_2 is likely to be mainly caused by facilitating nucleation by H_2SO_4 , although the contribution of acid-catalyzed heterogeneous uptake cannot be excluded.

NO_x promoted nitrate formation. The majority (57-77%) of nitrate was organic nitrate at both low NO_x and high NO_x , based on the estimate using the $\text{NO}_2^+/\text{NO}^+$ ratios from AMS data. The significant contribution of organic nitrate to nitrate may have important implications for deriving the hygroscopicity from chemical composition. For example, a number of studies derived the hygroscopicity parameter by linear combination of the hygroscopicity parameters of various components such as sulfate, nitrate and organics, assuming all nitrates are inorganic nitrate (Wu et al., 2013; Cubison et al., 2008; Yeung et al., 2014; Bhattu and Tripathi, 2015; Jaatinen et al., 2014; Moore et al., 2012; Gysel et al., 2007). Because the hygroscopicity parameter of organic nitrate may be much lower than inorganic nitrate (Suda et al., 2014), such derivation may overestimate hygroscopicity.

Organic nitrate compounds are estimated to contribute 7-26% of the total organics using an average molecular weight of 200 g/mol for organic nitrate compounds and a higher contribution of organic nitrate was found at high NO_x . Generally, SOA formed at high NO_x has a lower H/C compared to that at low NO_x . The higher contribution of organic nitrate to total organics and lower H/C at high NO_x than at low NO_x is attributed to the reaction of RO_2 with NO , which produced more organic nitrate relative to organic hydroperoxide formed via the reaction of RO_2 with HO_2 . The different chemical composition of SOA between high and low NO_x conditions may affect the physicochemical properties of SOA such as volatility, hygroscopicity, and optical properties and thus change the impact of SOA on environment and climate.

The different effects of NO_x and SO_2 on new particle formation and SOA mass yields have important implications for SOA formation affected by anthropogenic-biogenic interactions in the ambient. When an air mass of anthropogenic origin is transported to an area enriched in biogenic VOC emissions or vice versa, anthropogenic-biogenic interactions occur. Such scenarios are common in the ambient in many areas. For example, Kiendler-Scharr et al. (2016) shows that the organic nitrate concentrations are high in all the rural sites all over Europe, indicating the important influence of anthropogenic emissions in rural areas which are often enriched in biogenic emissions. ^{14}C analysis in several studies show that modern source carbon, from biogenic emission or biomass burning, account for large fractions of organic aerosol even in urban areas (Szidat et al., 2009; Weber et al., 2007; Sun et al., 2012), indicating the potential interactions of biogenic emissions with anthropogenic emissions in urban areas. In such cases, anthropogenic NO_x alone may suppress the new particle formation and SOA mass from biogenic VOC oxidation, as we found in this study. However, due to the co-existence of NO_x with SO_2 , H_2SO_4 formed by SO_2 oxidation can counteract such suppression of particle mass because regardless of NO_x levels, H_2SO_4 can induce new particle formation especially in the presence of water, ammonia or amine (Berndt et al., 2005; Zhang et al., 2012; Sipila et al., 2010; Almeida et al., 2013; Kirkby et al.,



2011; Chen et al., 2012). The overall effects on SOA mass depend on specific NO_x , SO_2 and VOC concentrations and VOC types as well as anthropogenic aerosol concentrations and can be a net suppressing, neutral or enhancing effect. Such scheme is depicted in Fig. 8. Other anthropogenic emissions, such as primary anthropogenic aerosol and precursors of anthropogenic secondary aerosol, can have similar roles as SO_2 . By affecting the concentrations of SO_2 , NO_x and anthropogenic aerosol, anthropogenic emissions may have important mediating impacts on biogenic SOA formation. Considering the effects of these factors in isolation may cause bias in predicting biogenic SOA concentrations. The combined impacts of SO_2 , NO_x and anthropogenic aerosol are also important to the estimate on how much organic aerosol concentrations will change with the ongoing and future reduction of anthropogenic emissions (Carlton et al., 2010).

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Table 1 Overview of the experiments in this study

Precursor	SO ₂	NO _x	NO (ppb)	SO ₂ (ppb)
α-pinene	Low SO ₂	Low NO _x	0.05-0.2	<0.05
		High NO _x	~20	<0.05
(~20 ppb)	High SO ₂	Low NO _x	0.05-0.2	~15
		High NO _x	~20	~15
Limonene	Low SO ₂	Low NO _x	0.05-0.2	<0.05
		High NO _x	~20	<0.05
(~7 ppb)	High SO ₂	Low NO _x	0.05-0.2	~15
		High NO _x	~20	~15
	Moderate SO ₂	High NO _x	~20	~2

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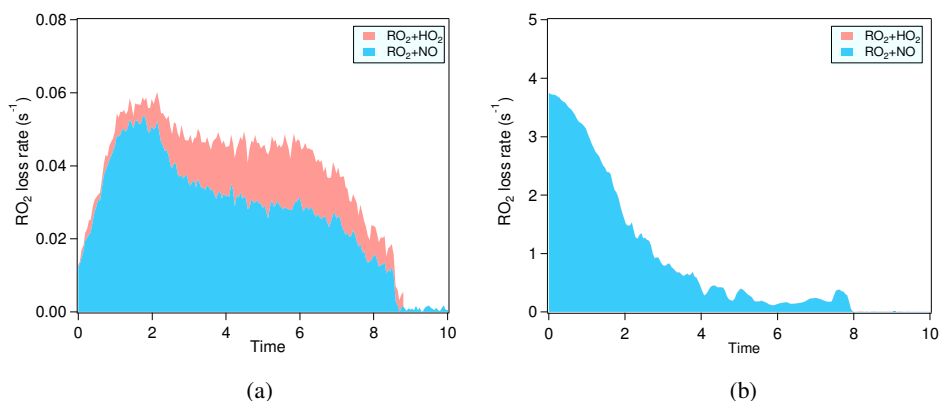


Figure 1. Typical loss rate of RO_2 by RO_2+NO and RO_2+HO_2 in the low NO_x (a) and the high NO_x (b) conditions of this study. The RO_2+HO_2 rate is stacked on the RO_2+NO rate. Note the different scales for RO_2 loss rate in panel a and b. In panel b, the contribution of RO_2+HO_2 is very low and barely noticeable.

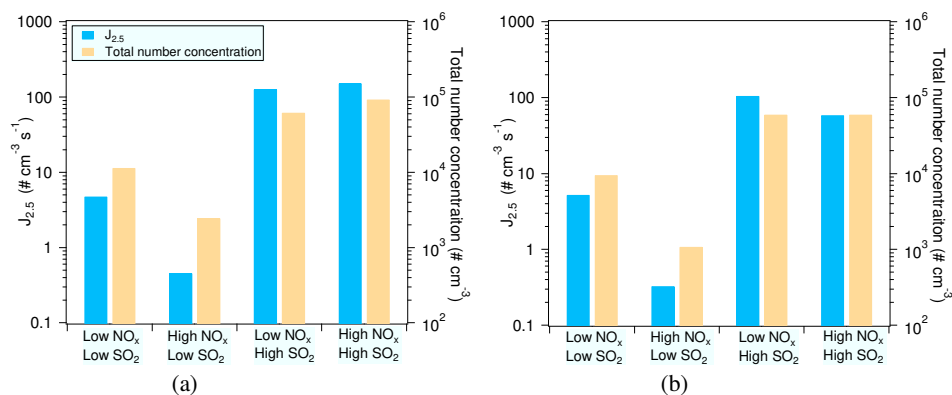


Figure 2. Nucleation rates ($J_{2.5}$) and maximum total particle number concentrations under different NO_x and SO_2 conditions for the SOA from α -pinene oxidation (a) and from limonene oxidation (b).



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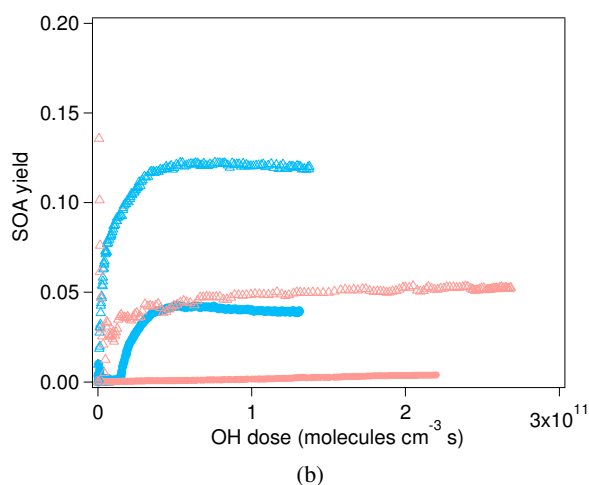
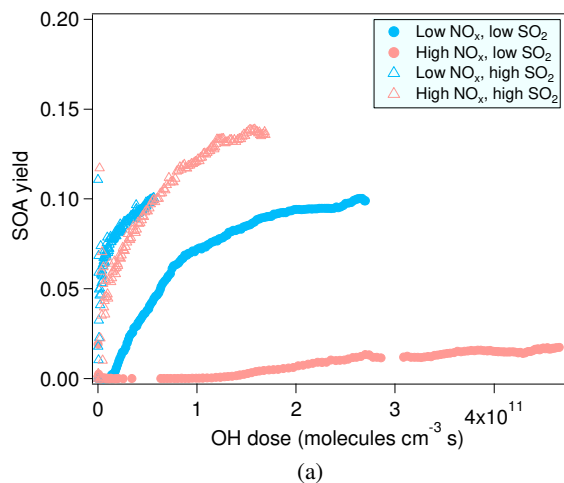
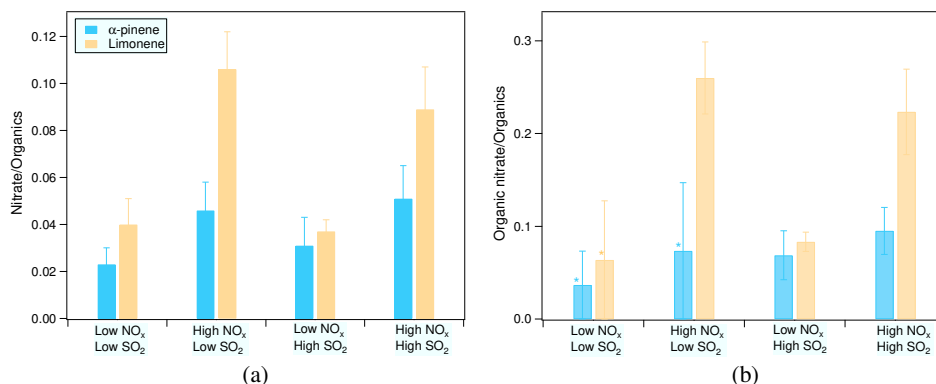


Figure 3. SOA yield of the photooxidation of α -pinene (a) and limonene (b) in different NO_x and SO_2 conditions.



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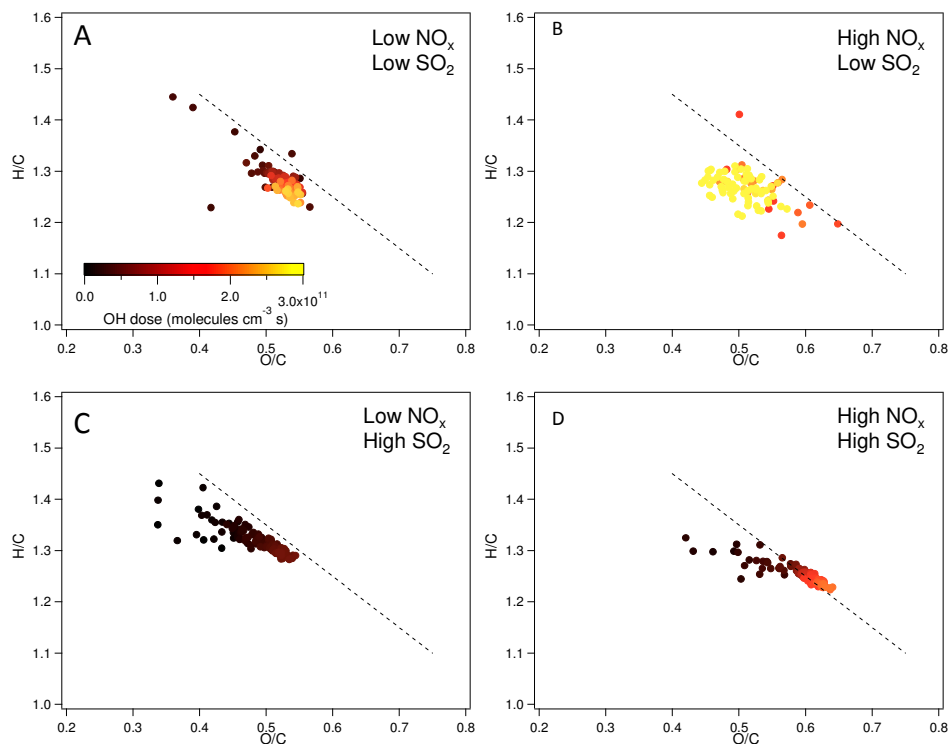
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Figure 4. (a) The ratio of nitrate mass concentration to organics mass in different NO_x and SO_2 conditions; (b) the fraction of organic nitrate to total organics in different NO_x and SO_2 conditions calculated using a molecular weight of 200 g/mol for organic nitrate. In panel b, * indicate the experiments where the ratios of NO_2^+ to NO^+ were too noisy to derive a reliable fraction of organic nitrate. For these experiments, 50% of total nitrate was assumed to be organic nitrate and the error bars show the range when 0 to 100% of nitrate are assumed to be organic nitrate.



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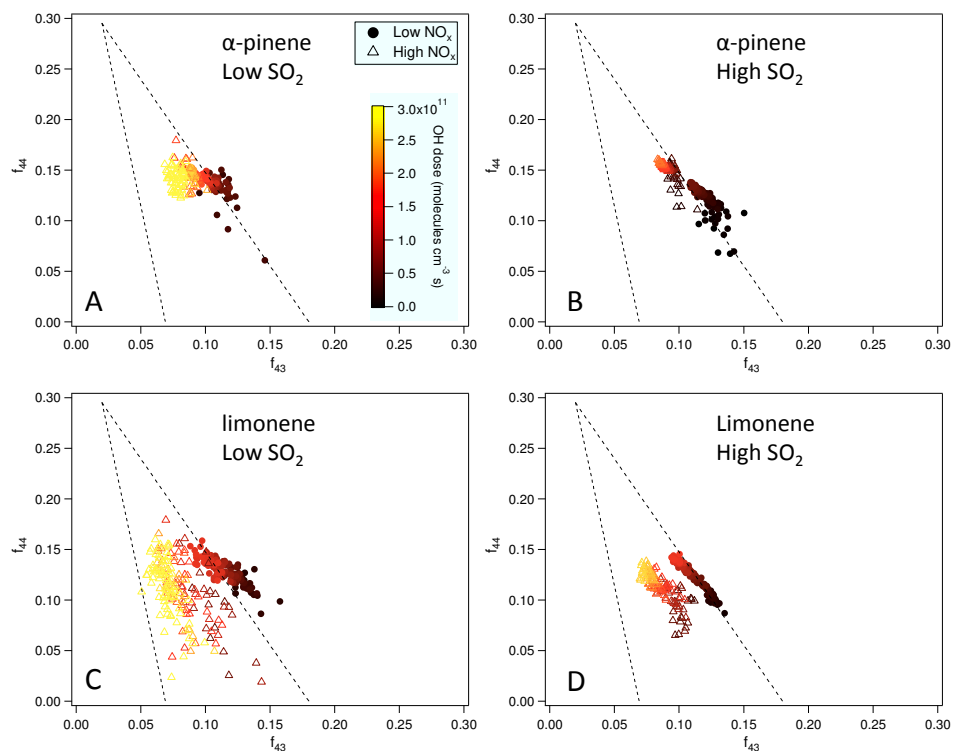


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716 Figure 5. H/C and O/C ratio of SOA from photooxidation of α -pinene in different NO_x and SO₂ conditions. A:

717 low NO_x, low SO₂, B: high NO_x, low SO₂, C: low NO_x, high SO₂, D: high NO_x, high SO₂. The black dashed line

718 corresponds to the slope of -1.



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 720 Figure 6. f_{44} and f_{43} of SOA from the photooxidation of α -pinene and limonene in different NO_x and SO_2
 721 conditions. A: α -pinene, low SO_2 , B: α -pinene, high SO_2 , C: limonene, low SO_2 , D: limonene, high SO_2 . Note
 722 that in the low SO_2 , high NO_x condition (panel C), the AMS signal of SOA from limonene oxidation was too low
 723 to derive reliable information due to the low particle mass concentration and small particle size. Therefore, the
 724 data for high NO_x in panel C show an experiment with moderate SO_2 (2 ppb) and high NO_x instead.

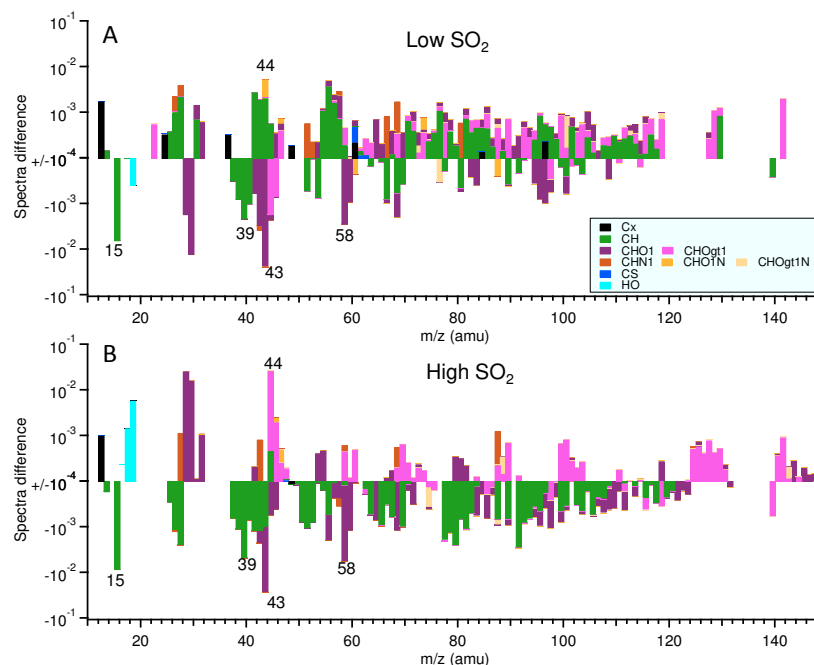
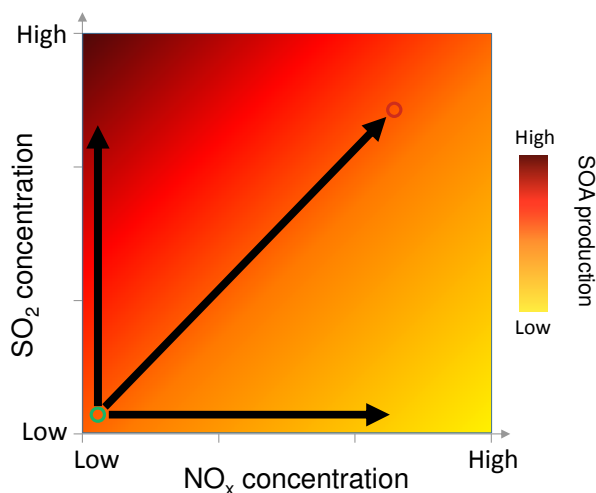


Figure 7. The difference in the mass spectra of organics of SOA from α -pinene photooxidation between high NO_x and low NO_x conditions (high NO_x -low NO_x). SOA was formed at low SO_2 (a) and high SO_2 (b). The different chemical family of high resolution mass peaks are stacked at each unit mass m/z (“gt1” means greater than 1). The mass spectra were normalized to the total organic signals. Note the log scale of y-axis and only the data with absolute values large than 10^{-4} are shown.



731
 732 Figure 8. Conceptual schematic showing how NO_x and SO_2 concentrations affect biogenic SOA mass production.
 733 The darker colors indicate higher SOA production. The circle on the bottom left corner indicates biogenic cases
 734 and the circle on the right top corner indicates the anthropogenic cases. And the horizontal and vertical arrows
 735 indicate the effect of NO_x and SO_2 alone. The overall effects on SOA production depend on specific NO_x , SO_2
 736 concentrations and VOC concentrations and speciation.