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1 # Effects of NO$_x$ and SO$_2$ on the Secondary Organic Aerosol

2 # Formation from Photooxidation of α-pinene and Limonene

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12 **Abstract**

13 Anthropogenic emissions such as NO$_x$ and SO$_2$ influence the biogenic secondary organic aerosol (SOA)

14 formation, but detailed mechanisms and effects are still elusive. We studied the effects of NO$_x$ and SO$_2$ on the

15 SOA formation from photooxidation of α-pinene and limonene at ambient relevant NO$_x$ and SO$_2$ concentrations

16 (NO$_x$: < 1 ppb to 20 ppb, SO$_2$: <0.05 ppb to 15 ppb). In these experiments, monoterpene oxidation was dominated

17 by OH oxidation. We found that SO$_2$ induced nucleation and enhanced SOA mass formation. NO$_x$ strongly

18 suppressed not only new particle formation but also SOA mass yield. However, in the presence of SO$_2$ which

19 induced high number concentration of particles after oxidation to H$_2$SO$_4$, the mass yield of SOA at high NO$_x$ was

20 comparable to that at low NO$_x$. This indicates that the suppression of SOA yield by NO$_x$ was mainly due to the

21 suppressed new particle formation, leading to a lack of particle surface for the organics to condense on. By

22 compensating the suppressing effect on nucleation of NO$_x$, SO$_2$ also compensated the suppressing effect on SOA

23 yield. Aerosol mass spectrometer data show that increasing NO$_x$ enhanced nitrate formation. The majority of the

24 nitrate was organic nitrate (57%-77%), even in low NO$_x$ conditions (<~1 ppb). Organic nitrate contributed 7%-

25 26% of total organics assuming a molecular weight of 200 g/mol. SOA from α-pinene photooxidation at high

26 NO$_x$ had generally lower hydrogen to carbon ratio (H/C), compared with at low NO$_x$. The NO$_x$ dependence of the

27 chemical composition can be attributed to the NO$_x$ dependence of the branching ratio of the RO$_2$ loss reactions,

28 leading to lower fraction of organic hydroperoxide and higher fractions of organic nitrate at high NO$_x$. While

29 NO$_x$ suppressed new particle formation and SOA mass formation, SO$_2$ can compensate such effects, and the

30 combining effect of SO$_2$ and NO$_x$ may have important influence on SOA formation affected by interactions of

31 biogenic volatile organic compounds (VOC) with anthropogenic emissions.

32

33 **1 Introduction**

34 Secondary organic aerosol (SOA), as an important class of atmospheric aerosol, have important impacts on

35 air quality, human health and climate change (Hallquist et al., 2009; Kanakidou et al., 2005; Jimenez et al., 2009;

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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, O_3 and NO_3, 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, SO_2, 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 SO_2 have been shown to affect

54   SOA formation.

55   NO_x changes the fate of RO_2 radical formed in VOC oxidation and therefore can change reaction product

56   distribution and aerosol formation. At low NO_x, RO_2 mainly react with HO_2 forming organic hydroperoxide. At

57   high NO_x, RO_2 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 SO_2, the SOA yield of α-pinene photooxidation was found to increase with SO_2

69   concentration at high NO_x concentrations (SO_2: 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 H_2SO_4 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

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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 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 $HO_2\bullet$ and $RO_2\bullet$ 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

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111   analyzer (ECO PHYSICS TR480), an O_3 analyzer (ANSYCO, model O341M), and an SO_2 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 SO_2, 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 SO_2

140   levels. Four types of experiments were done: with neither NO_x nor SO_2 added (referred to as "low NO_x, low

141   SO_2"), with only NO_x added (~ 20 ppb NO, referred to as "high NO_x, low SO_2"), with only SO_2 added (~15 ppb,

142   referred to as "low NO_x, high SO_2"), and with both NO_x and SO_2 added (~20 ppb NO and ~15 ppb SO_2, referred

143   to as "high NO_x, high SO_2"). 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 SO_2 conditions, background SO_2 concentrations were below the detection limit of the SO_2 analyzer (0.05

146   ppb). In some experiments, a lower level of SO_2 (2 ppb, referred to as "moderate SO_2") was used to test the effect

147   of SO_2 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

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149 roof was opened to start photooxidation. In the experiments with SO_2, SO_2 was added and the roof was opened to

150 initialize nucleation first and then VOC was added. The particle number concentration caused by SO_2 oxidation

151 typically reached several 10^4 cm^{-3} (see Fig. 2 high SO_2 cases) and after VOC addition, no further nucleation

152 occurred. The detailed conditions of the experiments are shown in Table S1. The experiments of α-pinene and

153 limonene photooxidation were designed to keep the initial OH reactivity and thus OH loss rate constant so that

154 the OH concentrations of these experiments were more comparable. Therefore, the concentration of limonene

155 was around one-third the concentration of α-pinene due to the higher OH reactivity of limonene.

156 3 Results and discussion

157 3.1 Chemical scheme: VOC oxidation pathway and RO_2 fate

158 In the photooxidation of VOC, OH and O_3 often co-exist and both contribute to VOC oxidation. In order to

159 study the mechanism, it is helpful to isolate one oxidation pathway from the other. In this study, the reaction rates

160 of OH and ozone with VOC are quantified using measured OH and O_3 concentrations multiplied by rate

161 constants. Typical OH and O_3 concentrations in an experiment were around $(1-15)\times10^6$ molecules cm^{-3} and 0-50

162 ppb, respectively, depending on the VOC and NO_x concentrations added. The relative importance of the reaction

163 of OH and O_3 with monoterpenes in a typical experiment is shown in Fig. S1. The VOC loss was dominated by

164 OH oxidation over ozonolysis. This makes the chemical scheme simple and it is easier to interpret than cases

165 when both OH oxidation and ozonolysis are important.

166 As mentioned above, RO_2 fate, i.e., the branching of RO_2 loss among different pathways has an important

167 influence on the product distribution and thus on SOA composition, physicochemical properties and yields. RO_2

168 can react with NO, HO_2, RO_2, or isomerize. The fate of RO_2 mainly depends on the concentrations of NO, HO_2

169 and RO_2. Here, the loss rates of RO_2 via different pathways were quantified using the measured HO_2, NO and

170 RO_2 and the rate constants based on MCM3.3 (Jenkin et al., 1997; Saunders et al., 2003)

171 (*http://mcm.leeds.ac.uk/MCM.*). Measured HO_2 and RO_2 concentrations in a typical experiment are shown in Fig.

172 S2 and the relative importance of different RO_2 reaction pathways is compared in Fig. 1, which is similar for both

173 α-pinene and limonene oxidation. In the low NO_x conditions of this study, RO_2+NO dominated the RO_2 loss rate

174 in the beginning of an experiment (Fig. 1a) because a trace amount of NO (up to ~0.2 ppb) was formed from the

175 photolysis of HONO produced from a photolytic process on the chamber wall (Rohrer et al., 2005). But later in

176 the experiment, RO_2+HO_2 contributed a significant fraction (up to ~40 %) to RO_2 loss because of increasing HO_2

177 concentration and decreasing NO concentration. In the high NO_x conditions, RO_2+NO overwhelmingly

178 dominated the RO_2 loss rate (Fig. 1b), and with the decrease of NO in an experiment, the total RO_2 loss rate

179 decreased substantially (Fig. 1b). Since the main products of RO_2+HO_2 are organic hydroperoxides, more organic

180 hydroperoxide relative to organic nitrate is expected in the low NO_x conditions here. The loss rate of RO_2+RO_2

181 was estimated to be ~10^{-4} s^{-1} using a reaction rate constant of 2.5×10^{-13} molecules^{-1} cm^3 s^{-1} (Ziemann and

182 Atkinson, 2012). This contribution is negligible compared to other pathways in this study, although the reaction

183 rate constants of RO_2+RO_2 are highly uncertain and may depend on specific RO_2 (Ziemann and Atkinson, 2012).

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184 **3.2 Effects of NO$_x$ and SO$_2$ on new particle formation**

185   The effects of NO$_x$ and SO$_2$ on new particle formation from α-pinene oxidation are shown in Fig. 2a. In low SO$_2$
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 RO$_2$+NO reaction, decreasing the importance of RO$_2$+RO$_2$ permutation reactions.
190   RO$_2$+RO$_2$ 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 SO$_2$ 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 H$_2$SO$_4$ alone
195   formed by SO$_2$ oxidation since the new particle formation occurred before VOC addition. The role of H$_2$SO$_4$ 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   SO$_2$ photooxidation were found for limonene oxidation (Fig. 2b).

200 **3.3 Effects of NO$_x$ and SO$_2$ 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   SO$_2$ 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 SO$_2$, 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 SO$_2$ conditions (Fig. 3b). Yet, in high SO$_2$ 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 SO$_2$ 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

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222 photooxidation of β-pinene, α-pinene and VOC emitted by Mediterranean trees (Wildt et al., 2014; Sarrafzadeh et

223 al., 2016). And on the basis of the results by Eddingsaas et al. (2012a) , the SOA yield at high NO_x (referred to as

224 "high NO" by the authors) is lower than at low NO_x in the absence of seed aerosol.

225 Our finding that SOA yield at high NO_x is comparable to that at low NO_x in high SO_2 conditions is also

226 in line with the findings of some previous studies using seed aerosols (Sarrafzadeh et al., 2016; Eddingsaas et al.,

227 2012a)). For example, Sarrafzadeh et al. (2016) found that in the presence of seed aerosol, the suppressing effect

228 of NO_x on the SOA yield from β-pinene photooxidation is substantially diminished and SOA yield only varies by

229 20-30% in the NO_x range of <1 ppb to 86 ppb at constant OH concentrations. Eddingsaas et al. (2012a) also

230 found that in presence of seed aerosol, the difference in the SOA yield between low NO_x and high NO_x is much

231 decreased. However, our finding is in contrast with the findings in other studies (Presto et al., 2005; Ng et al.,

232 2007; Han et al., 2016), who reported much lower SOA yield at high NO_x than at low NO_x in presence of seed.

233 The different findings in these studies from ours may be attributed to the difference in the VOC oxidation

234 pathways (OH oxidation vs. ozonolysis), VOC and NO_x concentration ranges, NO/NO_2 ratio as well as OH

235 concentrations, which all affect SOA yield. Note that even at "high NO_x" the NO_x concentration in this study was

236 much lower than in many previous studies and the NO_x concentration range here was more relevant to the

237 anthropogenic-biogenic interactions in the ambient.

3.3.2 Effect of SO_2

239 For both α-pinene and limonene, SO_2 was found to enhance the SOA mass yield, at given NO_x levels,

240 especially for the high NO_x cases (Fig. 3). The enhancing effect of SO_2 on particle mass formation can be

241 attributed to two reasons. Firstly, SO_2 oxidation induced new particle formation, which provided more surface

242 and volume for further condensation of organic vapor. Secondly, H_2SO_4 formed by photooxidation of SO_2 can

243 enhance SOA formation via acid-catalyzed heterogeneous uptake, an important SOA formation pathway initially

244 found from isoprene photooxidation (Jang et al., 2002; Lin et al., 2012; Surratt et al., 2007). For the products

245 from monoterpene oxidation, such an acid-catalyzed effect may also occur (Northcross and Jang, 2007; Wang et

246 al., 2012; Lal et al., 2012; Zhang et al., 2006; Ding et al., 2011; Iinuma et al., 2009) and in this study, the particles

247 were acidic with the molar ratio of NH_4^+ to SO_4^{2-} around 1.5-1.8. As mentioned above, inducing new particle

248 formation by SO_2 is especially important at high NO_x conditions, when nucleation was suppressed by NO_x. In

249 addition, we found that the SOA yield in limonene oxidation at a moderate SO_2 level (2 ppb) was comparable to

250 the yield at high SO_2 (15 ppb) when similar particle number concentrations in both cases were formed. Both

251 yields were significantly higher than the yield at low SO_2 (<0.05 ppb, see Fig. S3). This comparison suggests that

252 the effect in enhancing new particle formation by SO_2 seems to be more important. The role of SO_2 on new

253 particle formation is similar to adding seed aerosol on providing particle surface for organics to condense.

254 Artificially added seed aerosol has been shown to enhance SOA formation from α-pinene and β-pinene oxidation

255 (Ehn et al., 2014; Sarrafzadeh et al., 2016).

256 The finding that in presence of high SO_2, the SOA mass yield at NO_x conditions was enhanced to the

257 value comparable with that at low NO_x indicates that the suppressing effect of NO_x on SOA mass formation was

258 counterbalanced by the presence of SO_2. This has important implications for SOA formation affected by

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259 anthropogenic-biogenic interactions in the real atmosphere as discussed below when SO_2 and NO_x often co-exist

260 in relative high concentrations.

261 **3.4 Effects of NO_x and SO_2 on SOA chemical composition**

262 The effects of NO_x and SO_2 on SOA chemical composition were analyzed on the basis of AMS data. We

263 found that NO_x enhanced nitrate formation. The ratio of the mass of nitrate to organics was higher at high NO_x

264 than at low NO_x regardless of the SO_2 level, and similar trends were found for SOA from α-pinene and limonene

265 oxidation (Fig. 4a). Higher nitrate to organics ratios were observed for SOA from limonene at high NO_x, which is

266 mainly due to the lower VOC/NO_x ratio resulted from the lower concentrations of limonene (7 ppb) compared to

267 α-pinene (20 ppb) (see Table 1). Overall, the mass ratios of nitrate to organics ranged from 0.02 to 0.11

268 considering all the experiments in this study.

269 Nitrate formed can be either inorganic (such as HNO_3 from the reaction of NO_2 with OH) or organic (from

270 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

271 can be used to differentiate whether nitrate is organic or inorganic (Fry et al., 2009; Rollins et al., 2009; Farmer et

272 al., 2010; Kiendler-Scharr et al., 2016). Organic nitrate was considered to have a NO_2^+/NO^+ of ~0.1 and inorganic

273 NH_4NO_3 had a NO_2^+/NO^+ of ~0.31 with the instrument used in this study as determined from calibration

274 measurements. In this study, NO_2^+/NO^+ ratios ranged from 0.14 to 0.18, closer to the ratio of organic nitrate. The

275 organic nitrate was estimated to account for 57%-77% (molar fraction) of total nitrate considering both the low

276 NO_x and high NO_x conditions. This indicates that nitrate was mostly organic nitrate, even at low NO_x in this

277 study.

278 In order to determine the contribution of organic nitrate to total organics, we estimated the molecular

279 weight of organic nitrates formed by α-pinene and limonene oxidation to be 200-300 g/mol, based on reaction

280 mechanisms ((Eddingsaas et al., 2012b) and MCM v3.3, via website: http://mcm.leeds.ac.uk/MCM.). We

281 assumed a molecular weight of 200 g/mol in order to make our results comparable to the field studies which used

282 similar molecular weight (Kiendler-Scharr et al., 2016). For this value, the organic nitrate compounds were

283 estimated to account for 7-26% of the total organics mass as measured by AMS in SOA. Organic nitrate fraction

284 in total organics was within the range of values found in a field observation in southeast US (5-12% in summer

285 and 9-25% in winter depending on the molecular weight of organic nitrate) using AMS (Xu et al., 2015b) and

286 particle organic nitrate content derived from the sum of speciated organic nitrates (around 1-17% considering

287 observed variability and 3% and 8% on average in the afternoon and at night, respectively) (Lee et al., 2016).

288 Note that the organic nitrate fraction was lower than the mean value (42%) for a number of European observation

289 stations when organic nitrate is mainly formed by the reaction of VOC with NO_3 (Kiendler-Scharr et al., 2016).

290 Moreover, we found that the contribution of organic nitrate to total organics (calculated using a

291 molecular weight of 200 g/mol for organic nitrate) was higher at high NO_x (Fig. 4b), although in some

292 experiments the ratios of NO_2^+ to NO^+ were too noisy to derive a reliable fraction of organic nitrate. This result is

293 consistent with the reaction scheme that at high NO_x, almost all RO_2 loss was switched to the reaction with NO,

294 which is expected to enhance the organic nitrate formation. Besides organic nitrate, the ratio of nitrogen to carbon

295 atoms (N/C) was also found to be higher at high NO_x (Fig. S4). But after considering nitrate functional group

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

297 the form of organic nitrate.

298 The chemical composition of organic components of SOA in terms of H/C and O/C ratios at different

299 NO_x and SO_2 levels was further compared. For SOA from α-pinene photooxidation, in low SO_2 conditions, no

300 significant difference in H/C and O/C was found between SOA formed at low NO_x and at high NO_x within the

301 experimental uncertainties (Fig. 5). The variability of H/C and O/C at high NO_x is large, mainly due to the low

302 particle mass and small particle size. In high SO_2 conditions, SOA formed at high NO_x had the higher O/C and

303 lower H/C, which indicates that SOA components had higher oxidation state. The higher O/C at high NO_x than at

304 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

305 still slightly higher than at low NO_x in high SO_2 conditions.

306 For the SOA formed from limonene photooxidation, no significant difference in the H/C and O/C was

307 found between different NO_x and SO_2 conditions (Fig. S5), which is partly due to the low signal resulting from

308 low particle mass and small particle size in high NO_x conditions.

309 Due to the high uncertainties for some of the H/C and O/C data, the chemical composition was further

310 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

311 high NO_x generally has lower f_{43}. Because f_{43} generally correlates with H/C in organic aerosol (Ng et al., 2011),

312 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

313 α-pinene oxidation in presence of high concentrations of SO_2 (Fig. 5). The lower f_{43} at high NO_x was evidenced

314 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}

315 are likely to be related to the reaction pathways. According to the reaction mechanism mentioned above, at low

316 NO_x a significant fraction of RO_2 reacted with HO_2 forming hydroperoxide, while at high NO_x almost all RO_2

317 reacted with NO forming organic nitrate. Compared with organic nitrate, hydroperoxide have higher H/C ratio.

318 The same mechanism also caused higher organic nitrate fraction at high NO_x, as discussed above.

319 Detailed mass spectra of SOA were compared, shown in Fig 7. For α-pinene, in high SO_2 conditions,

320 mass spectra of SOA formed at high NO_x generally had higher intensity for CHOgt1 family ions, such as CO_2^+

321 (*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

322 NO_x. In low SO_2 conditions, such difference is not apparent (Fig. 7a), partly due to the low signal from AMS for

323 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

324 high NO_x show higher intensity of CHN1 family ions. This is also consistent with the higher N/C ratio shown

325 above. For SOA from limonene oxidation, SOA formed at high NO_x had lower mass fraction at *m/z* 15 ($C_2H_3^+$),

326 28 (CO^+), 43 ($C_2H_3O^+$), 44 (CO_2^+), and higher mass fraction at *m/z* 27 (CHN^+, $C_2H_3^+$), 41 ($C_3H_5^+$), 55 ($C_4H_7^+$), 64

327 (C_4O^+) than at low NO_x (Fig. S6). It seems that overall mass spectra of the SOA from limonene formed at high

328 NO_x had higher intensity for CH family ions, but lower intensity for CHO1 family ions than at low NO_x. Note

329 that the differences in these *m/z* were based on the average spectra during the whole reaction period and may not

330 reflect the chemical composition at a certain time.

331 **4 Conclusion and implications**

332 We investigated the SOA formation from the photooxidation of α-pinene and limonene under different NO_x

333 and SO_2 conditions, when OH oxidation was the dominant oxidation pathway of monoterpenes. The fate of RO_2

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334   was regulated by varying NO_x concentrations. We confirmed that NO_x suppressed new particle formation. NO_x

335   also suppressed SOA mass yield in the absence of SO_2. The suppression of SOA yield by NO_x was mainly due to

336   the suppressed new particle formation, i.e., absence of sufficient particle surfaces for organic vapor to condense

337   on at high NO_x. NO_x did not significantly suppress the formation of condensable organics from α-pinene

338   oxidation as evidenced by the similar SOA yield at high and low NO_x in the presence of SO_2.

339   SO$_2$ enhanced SOA yield from α-pinene and limonene photooxidation. SO_2 oxidation produced high number

340   concentration of particles and compensated for the suppression of SOA yield by NO_x. The enhancement of SOA

341   yield by SO_2 is likely to be mainly caused by facilitating nucleation by H_2SO_4, although the contribution of acid-

342   catalyzed heterogeneous uptake cannot be excluded.

343   NO_x promoted nitrate formation. The majority (57-77%) of nitrate was organic nitrate at both low NO_x and

344   high NO_x, based on the estimate using the NO_2^+/NO^+ ratios from AMS data. The significant contribution of

345   organic nitrate to nitrate may have important implications for deriving the hygroscopicity from chemical

346   composition. For example, a number of studies derived the hygroscopicity parameter by linear combination of the

347   hygroscopicity parameters of various components such as sulfate, nitrate and organics, assuming all nitrates are

348   inorganic nitrate (Wu et al., 2013; Cubison et al., 2008; Yeung et al., 2014; Bhattu and Tripathi, 2015; Jaatinen et

349   al., 2014; Moore et al., 2012; Gysel et al., 2007). Because the hygroscopicity parameter of organic nitrate may be

350   much lower than inorganic nitrate (Suda et al., 2014), such derivation may overestimate hygroscopicity.

351   Organic nitrate compounds are estimated to contribute 7-26% of the total organics using an average

352   molecular weight of 200 g/mol for organic nitrate compounds and a higher contribution of organic nitrate was

353   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

354   higher contribution of organic nitrate to total organics and lower H/C at high NO_x than at low NO_x is attributed to

355   the reaction of RO_2 with NO, which produced more organic nitrate relative to organic hydroperoxide formed via

356   the reaction of RO_2 with HO_2. The different chemical composition of SOA between high and low NO_x conditions

357   may affect the physicochemical properties of SOA such as volatility, hygroscopicity, and optical properties and

358   thus change the impact of SOA on environment and climate.

359   The different effects of NO_x and SO_2 on new particle formation and SOA mass yields have important

360   implications for SOA formation affected by anthropogenic-biogenic interactions in the ambient. When an air

361   mass of anthropogenic origin is transported to an area enriched in biogenic VOC emissions or vice versa,

362   anthropogenic-biogenic interactions occur. Such scenarios are common in the ambient in many areas. For

363   example, Kiendler-Scharr et al. (2016) shows that the organic nitrate concentrations are high in all the rural sites

364   all over Europe, indicating the important influence of anthropogenic emissions in rural areas which are often

365   enriched in biogenic emissions. [14]C analysis in several studies show that modern source carbon, from biogenic

366   emission or biomass burning, account for large fractions of organic aerosol even in urban areas (Szidat et al.,

367   2009; Weber et al., 2007; Sun et al., 2012), indicating the potential interactions of biogenic emissions with

368   anthropogenic emissions in urban areas. In such cases, anthropogenic NO_x alone may suppress the new particle

369   formation and SOA mass from biogenic VOC oxidation, as we found in this study. However, due to the co-

370   existence of NO_x with SO_2, H_2SO_4 formed by SO_2 oxidation can counteract such suppression of particle mass

371   because regardless of NO_x levels, H_2SO_4 can induce new particle formation especially in the presence of water,

372   ammonia or amine (Berndt et al., 2005; Zhang et al., 2012; Sipila et al., 2010; Almeida et al., 2013; Kirkby et al.,

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373   2011; Chen et al., 2012). The overall effects on SOA mass depend on specific NO_x, SO_2 and VOC concentrations

374   and VOC types as well as anthropogenic aerosol concentrations and can be a net suppressing, neutral or

375   enhancing effect. Such scheme is depicted in Fig. 8. Other anthropogenic emissions, such as primary

376   anthropogenic aerosol and precursors of anthropogenic secondary aerosol, can have similar roles as SO_2. By

377   affecting the concentrations of SO_2, NO_x and anthropogenic aerosol, anthropogenic emissions may have

378   important mediating impacts on biogenic SOA formation. Considering the effects of these factors in isolation

379   may cause bias in predicting biogenic SOA concentrations. The combined impacts of SO_2, NO_x and

380   anthropogenic aerosol are also important to the estimate on how much organic aerosol concentrations will change

381   with the ongoing and future reduction of anthropogenic emissions (Carlton et al., 2010).

382   **Acknowledgements**

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688   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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691   (a)   (b)
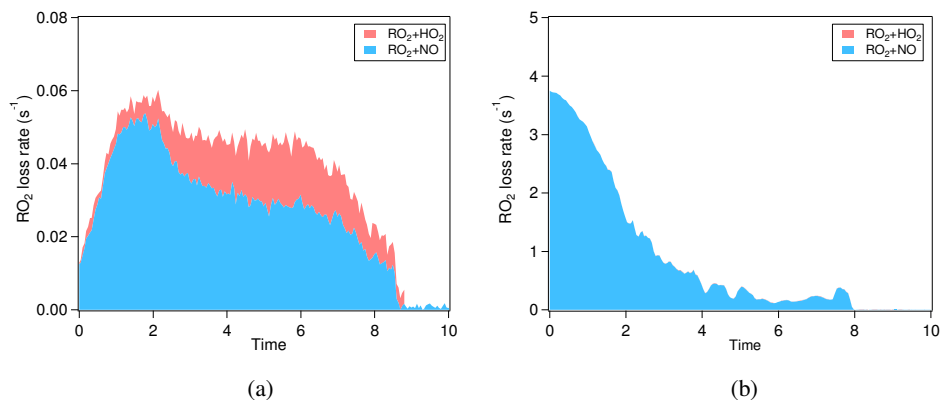
692   Figure 1. Typical loss rate of RO_2 by RO_2+NO and RO_2+HO_2 in the low NO_x (a) and the high NO_x (b) conditions

693   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

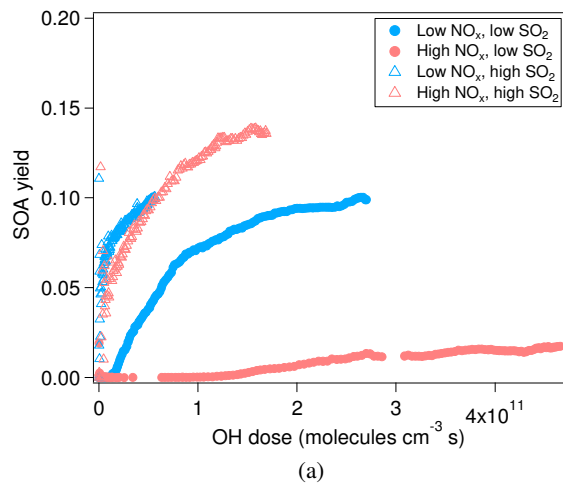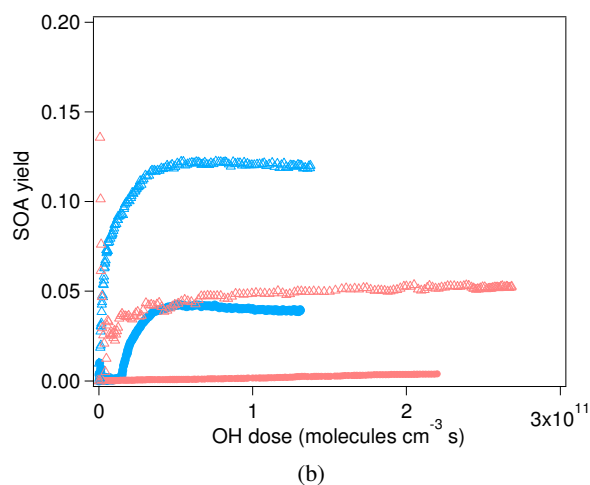694   panel a and b. In panel b, the contribution of RO_2+HO_2 is very low and barely noticeable.
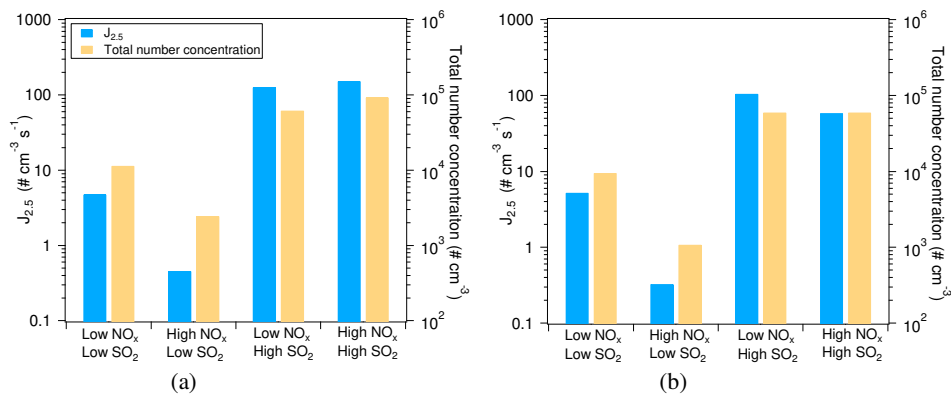
Figure 2. Nucleation rates ($J_{2.5}$) and maximum total particle number concentrations under different NO_x and SO_2 conditions for the SOA from α-pinene oxidation (a) and from limonene oxidation (b).
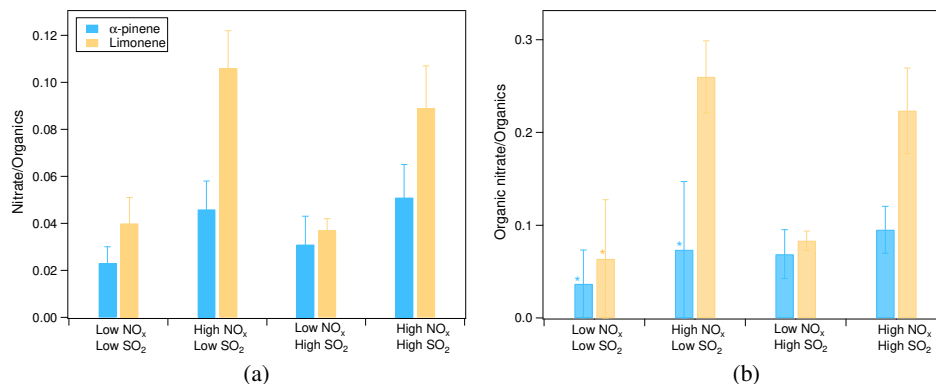
699

700
701

(a)

702
703   (b)
704   Figure 3. SOA yield of the photooxidation of α-pinene (a) and limonene (b) in different NO_x and SO_2 conditions.

705

706
707   (a)   (b)

708 Figure 4. (a) The ratio of nitrate mass concentration to organics mass in different NO_x and SO_2 conditions; (b) the

709 fraction of organic nitrate to total organics in different NO_x and SO_2 conditions calculated using a molecular

710 weight of 200 g/mol for organic nitrate. In panel b, * indicate the experiments where the ratios of NO_2^+ to NO^+

711 were too noisy to derive a reliable fraction of organic nitrate. For these experiments, 50% of total nitrate was

712 assumed to be organic nitrate and the error bars show the range when 0 to 100% of nitrate are assumed to be
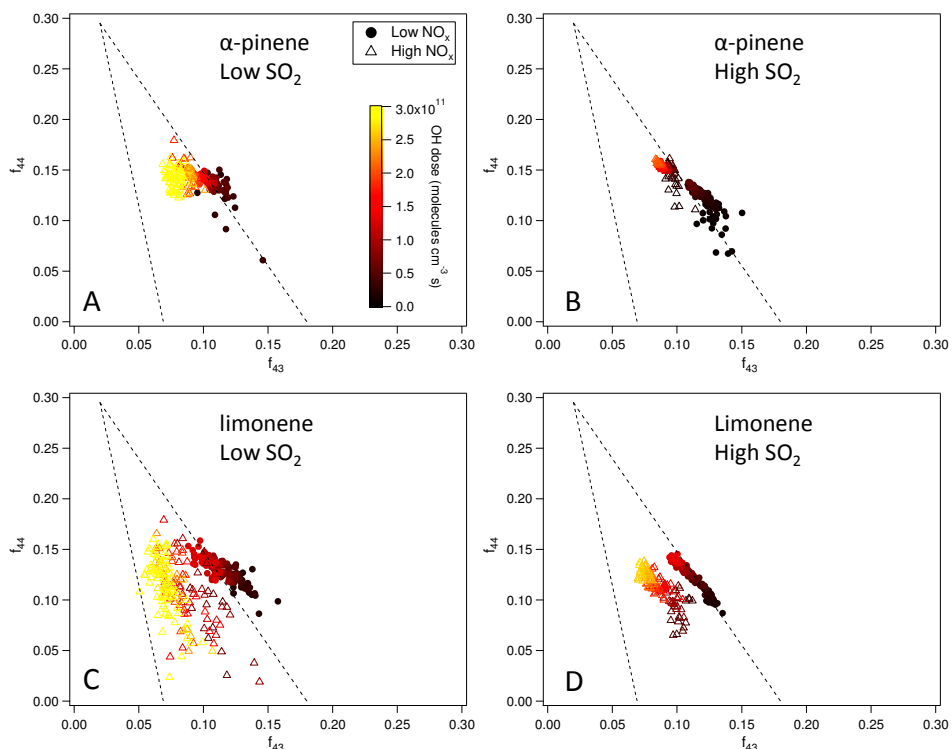
713 organic nitrate.

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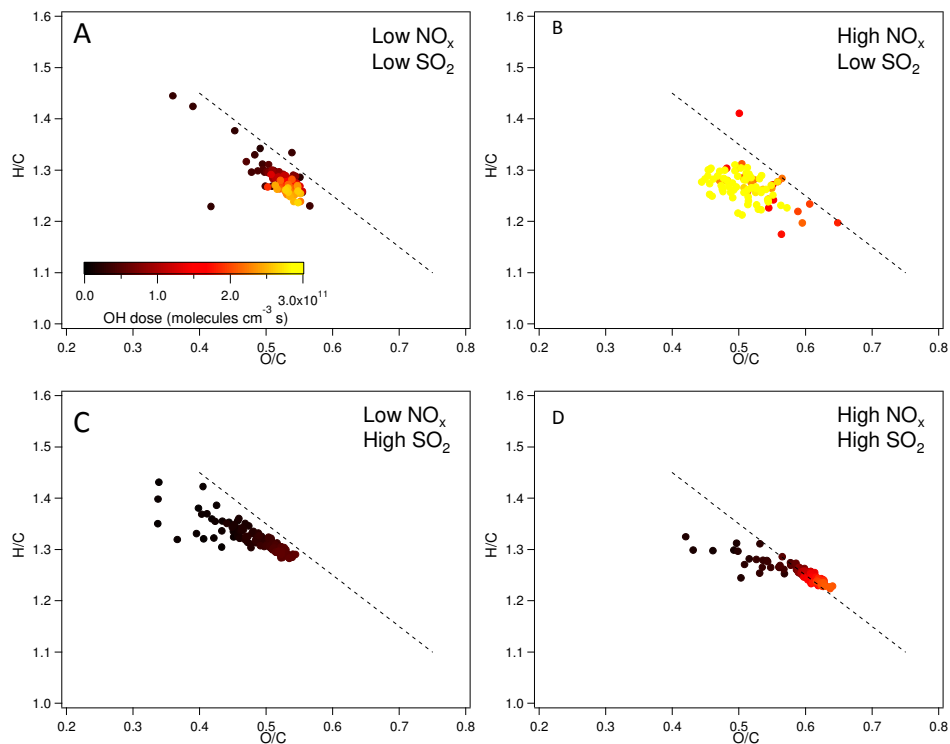
Figure 5. H/C and O/C ratio of SOA from photooxidation of α-pinene in different NO_x and SO_2 conditions. A: low NO_x, low SO_2, B: high NO_x, low SO_2, C: low NO_x, high SO_2, D: high NO_x, high SO_2. The black dashed line corresponds to the slope of -1.

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Discussions

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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.
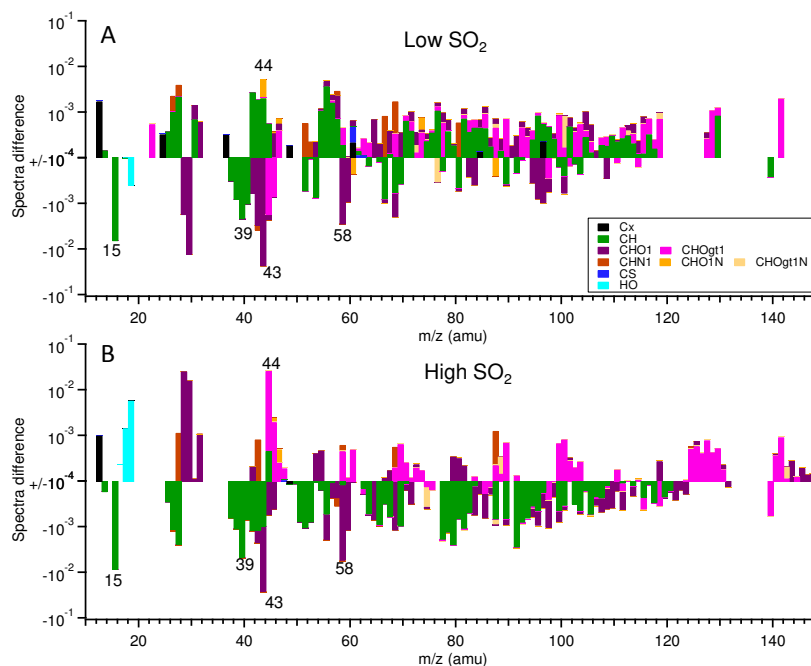
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Figure 7. The difference in the mass spectra of organics of SOA from α-pinene photooxidation between high NO_x

726   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

727   chemical family of high resolution mass peaks are stacked at each unit mass *m/z* ("gt1" means greater than 1).

728   The mass spectra were normalized to the total organic signals. Note the log scale of y-axis and only the data with

729   absolute values large than 10^{-4} are shown.
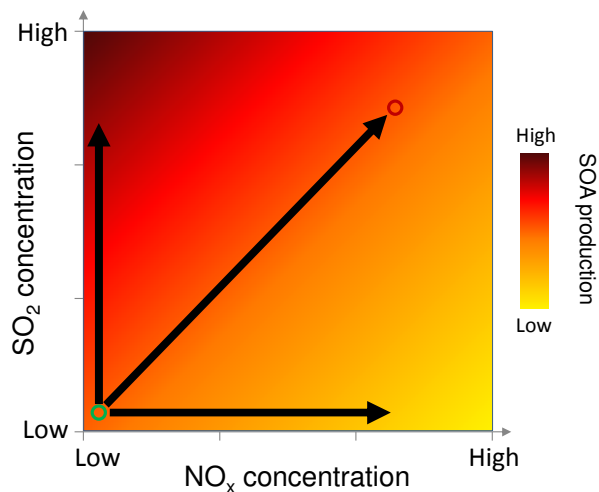
731
732 Figure 8. Conceptual schematic showing how NO_x and SO_2 concentrations affect biogenic SOA mass production.
733 The darker colors indicate higher SOA production. The circle on the bottom left corner indicates biogenic cases
734 and the circle on the right top corner indicates the anthropogenic 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.