Effects of NO\textsubscript{x} and SO\textsubscript{2} on the Secondary Organic Aerosol Formation from Photooxidation of α-pinene and Limonene

Defeng Zhao\textsuperscript{1}, Sebastian H. Schmitt\textsuperscript{1}, Mingjin Wang\textsuperscript{1,2}, Ismail-Hakki Acir\textsuperscript{1,5}, Ralf Tillmann\textsuperscript{1}, Zhaofeng Tan\textsuperscript{1,5}, Anna Novelli\textsuperscript{1}, Hendrik Fuchs\textsuperscript{1}, Iida Pullinen\textsuperscript{1, b}, Robert Wegener\textsuperscript{1}, Franz Rohrer\textsuperscript{1}, Jürgen Wildt\textsuperscript{1}, Astrid Kiendler-Scharr\textsuperscript{1}, Andreas Wahner\textsuperscript{1}, Thomas F. Mentel\textsuperscript{1}

[1] Institute of Energy and Climate Research, IEK-8: Troposphere, Forschungszentrum Jülich, Jülich, 52425, Germany
[2] College of Environmental Science and Engineering, Peking University, Beijing, 100871, China
\textsuperscript{a}Now at: Institute of Nutrition and Food Sciences, University of Bonn, Bonn, 53115, Germany; \textsuperscript{b}Now at: Department of Applied Physics, University of Eastern Finland, Kuopio, 7021, Finland.

Correspondence to: Th. F. Mentel (t.mentel@fz-juelich.de)

Abstract

Anthropogenic emissions such as NO\textsubscript{x} and SO\textsubscript{2} influence the biogenic secondary organic aerosol (SOA) formation, but detailed mechanisms and effects are still elusive. We studied the effects of NO\textsubscript{x} and SO\textsubscript{2} on the SOA formation from photooxidation of α-pinene and limonene at ambient relevant NO\textsubscript{x} and SO\textsubscript{2} concentrations (NO\textsubscript{x}: < 1 ppb to 20 ppb, SO\textsubscript{2}: <0.05 ppb to 15 ppb). In these experiments, monoterpene oxidation was dominated by OH oxidation. We found that SO\textsubscript{2} induced nucleation and enhanced SOA mass formation. NO\textsubscript{x} strongly suppressed not only new particle formation but also SOA mass yield. However, in the presence of SO\textsubscript{2} which induced high number concentration of particles after oxidation to H\textsubscript{2}SO\textsubscript{4}, the mass yield of SOA at high NO\textsubscript{x} was comparable to that at low NO\textsubscript{x}. This indicates that the suppression of SOA yield by NO\textsubscript{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\textsubscript{x}, SO\textsubscript{2} also compensated the suppressing effect on SOA yield. Aerosol mass spectrometer data show that increasing NO\textsubscript{x} enhanced nitrate formation. The majority of the nitrate was organic nitrate (57%-77%), even in low NO\textsubscript{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\textsubscript{x} had generally lower hydrogen to carbon ratio (H/C), compared with at low NO\textsubscript{x}. The NO\textsubscript{x} dependence of the chemical composition can be attributed to the NO\textsubscript{x} dependence of the branching ratio of the RO\textsubscript{2} loss reactions, leading to lower fraction of organic hydroperoxide and higher fractions of organic nitrate at high NO\textsubscript{x}. While NO\textsubscript{x} suppressed new particle formation and SOA mass formation, SO\textsubscript{2} can compensate such effects, and the combining effect of SO\textsubscript{2} and NO\textsubscript{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;
Zhang et al., 2011). SOA mainly originates from biogenic volatile organic compounds (VOC) emitted by terrestrial vegetation (Hallquist et al., 2009). Once emitted into the atmosphere, biogenic VOC can undergo reactions with atmospheric oxidants including OH, O_3 and NO_3, and form SOA. When an air mass enriched in biogenic VOC is transported over an area with substantial anthropogenic emissions or vice versa, the reaction behavior of VOC and SOA formation can be altered due to the interactions of biogenic VOC with anthropogenic emissions such as NO_x, SO_2, anthropogenic aerosol and anthropogenic VOC. A number of field studies have highlighted the important role of the anthropogenic-biogenic interactions in SOA formation (de Gouw et al., 2005; Goldstein et al., 2009; Hoyle et al., 2011; Worton et al., 2011; Glasius et al., 2011; Xu et al., 2015a; Shilling et al., 2012), which can induce an “anthropogenic enhancement” effect on SOA formation.

Among biogenic VOC, monoterpenes are important contributors to biogenic SOA due to their high emission rates, high reactivity and relative high SOA yield compared to isoprene (Guenther et al., 1995; Guenther et al., 2012; Chung and Seinfeld, 2002; Pandis et al., 1991; Griffin et al., 1999; Hoffmann et al., 1997; Zhao et al., 2015; Carlton et al., 2009). The anthropogenic modulation of the SOA formation from monoterpenes can have important impacts on regional and global biogenic SOA budget (Spracklen et al., 2011). The influence of various anthropogenic pollutants on SOA formation of monoterpene have been investigated by a number of laboratory studies (Sarrafzadeh et al., 2016; Zhao et al., 2016; Flores et al., 2014; Emanuelsson et al., 2013; Eddingsaas et al., 2012a; Offenberg et al., 2009; Kleindienst et al., 2006; Presto et al., 2005; Ng et al., 2007; Zhang et al., 1992; Pandis et al., 1991; Draper et al., 2015; Han et al., 2016). In particular, NO_x and SO_2 have been shown to affect SOA formation.

NO_x changes the fate of RO_2 radical formed in VOC oxidation and therefore can change reaction product distribution and aerosol formation. At low NO_x, RO_2 mainly react with HO_2 forming organic hydroperoxide. At high NO_x, RO_2 mainly react with NO forming organic nitrate (Hallquist et al., 2009; Ziemann and Atkinson, 2012; Finlayson-Pitts and Pitts Jr., 1999). Some studies found that the SOA yield from α-pinene is higher at lower NO_x concentration for ozonolysis (Presto et al., 2005) and photooxidation (Ng et al., 2007; Eddingsaas et al., 2012a; Han et al., 2016). The decrease of SOA yield with increasing NO_x was proposed to be due to the formation of more volatile products like organic nitrate under high NO_x conditions (Presto et al., 2005). In contrast, a recent study found that the suppressing effect of NO_x is in large part attributed to the effect of NO_x on OH concentration for the SOA from β-pinene oxidation, and after eliminating the effect of NO_x on OH concentration, SOA yield only varies by 20-30% (Sarrafzadeh et al., 2016). Beside the effect of NO_x on SOA yield, NO_x has been found to suppress the new particle formation from VOC directly emitted by Mediterranean trees (mainly monoterpenes) (Wildt et al., 2014) and β-pinene (Sarrafzadeh et al., 2016), thereby reducing condensational sink present during high NO_x experiments.

Regarding the effect of SO_2, the SOA yield of α-pinene photooxidation was found to increase with SO_2 concentration at high NO_x concentrations (SO_2: 0-252 ppb, NO_x: 242-543 ppb, α-pinene: 178-255 ppb) (Kleindienst et al., 2006) and the increase is attributed to the formation of H_2SO_4 acidic aerosol. Acidity of seed aerosol was also found to enhance particle yield of α-pinene at high NO_x (Offenberg et al. (2009): NO_x 100-120 ppb, α-pinene 69-160 ppb; Han et al. (2016): initial NO_x ~70 ppb, α-pinene 14-18 ppb). In constrast, Eddingsaas et al. (2012a) found that particle yield increases with aerosol acidity at “high NO” condition (NO_x 800 ppb, α-pinene: 20-52 ppb), but is independent of the presence of seed aerosol or aerosol acidity at both low NO_x (NO_x
lower than the detection limit of NOx analyzer) and “high NOx” condition (NOx 800 ppb). Similarly, at low NOx (initial NO <0.3 ppb, α-pinene ~20 ppb), Han et al. (2016) found that the acidity of seed has no significant effect on SOA yield from α-pinene photooxidation.

While these studies have provided important insights into the effects of NOx and SO2 on SOA formation, a number of questions still remain elusive. For example, many studies used very high NOx and SO2 concentrations (up to several hundreds of ppb), and the effects of NOx and SO2 at concentrations relevant to ambient anthropogenic-biogenic interactions (sub ppb to several tens of ppb for NO2 and SO2) are unclear. Moreover, many previous studies on the SOA formation from monoterpene oxidation focus on ozonolysis or do not distinguish the OH oxidation and ozonolysis in photooxidation, and only few studies on OH oxidation have been conducted (Eddingsaas et al., 2012a; Zhao et al., 2015). More importantly, studies that investigated the combined effects of NOx and SO2 are scarce, although they are often co-emitted from anthropogenic sources. According to previous studies, NOx mainly has a suppressing effect on SOA formation while SO2 mainly has an enhancing effect. NOx and SO2 might have counteracting effect or a synergistic effect in SOA formation in the ambient.

In this study, we investigated the effects of NOx, SO2 and their combining effects on SOA formation from the photooxidation of α-pinene and limonene. α-pinene and limonene are two important monoterpenes with high emission rates among monoterpenes (Guenther et al., 2012). OH oxidation dominated over ozonolysis in the monoterpene oxidation in this study as determined by measured OH and O3 concentrations. The relative contributions of RO2 loss reactions at low NOx and higher NOx were also quantified using measured HO2, RO2, and NO concentrations. The effects on new particle formation, SOA yield and aerosol chemical composition were examined. We used ambient relevant NOx and SO2 concentrations so that the results can shed lights on the mechanisms of interactions of biogenic VOC with anthropogenic emissions in the real atmosphere.

2 Experimental

2.1 Experimental setup and instrumentation

The experiments were performed in the SAPHIR chamber (Simulation of Atmospheric PHotochemistry In a large Reaction chamber) at Forschungszentrum Jülich, Germany. The details of the chamber have been described before (Rohrer et al., 2005; Zhao et al., 2015). Briefly, it is a 270 m3 Teflon chamber using natural sunlight for illumination. It is equipped with a louvre system to switch between light and dark conditions. The physical parameters for chamber running such as temperature and relative humidity were recorded. The solar irradiation was characterized and the photolysis frequency was derived (Bohn et al., 2005; Bohn and Zilken, 2005).

Gas and particles phase species were characterized using various instruments. OH, HO2 and RO2 concentrations were measured using a laser induced fluorescence (LIF) system with details described by Fuchs et al. (2012). From OH concentration, OH dose, the integral of OH concentration over time, was calculated in order to better compare experiments with different OH levels. For example, experiments at high NOx in this study generally had higher OH concentrations due to the faster OH production by recycling of HO2• and RO2• to OH. The VOC were characterized using a Proton Transfer Reaction Time-of-Flight Mass Spectrometer (PTR-ToF-MS) and Gas Chromatography-Mass spectrometer (GC-MS). NOx, O3 and SO2 concentrations were characterized using a NOx...
analyzer (ECO PHYSICS TR480), an O\textsubscript{3} analyzer (ANSYCO, model O341M), and an SO\textsubscript{2} analyzer (Thermo Systems 43i), respectively. More details of these instrumentation are described before (Zhao et al., 2015).

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

In the experiments with added SO\textsubscript{2}, sulfuric acid was formed upon photooxidation. Sulfuric acid was partly neutralized by background ammonia, which was introduced into the chamber mainly due to humidification. The density of the aerosol was derived using the linear mixing of the density of organic aerosol (assuming 1.32 g cm\textsuperscript{-3} from one of our previous studies and the literature (Flores et al., 2014; Eddingsaas et al., 2012a)) and the density of ammonium sulfate/ammonium bisulfate (~1.77 g cm\textsuperscript{-3}). According to calculations based on the E-AIM model (Clegg et al., 1998; Wexler and Clegg, 2002) (http://www.aim.env.uea.ac.uk/aim/aim.php), there were no aqueous phase formed at the relative humidity in the experiments of this study (average RH 28-42% for the period of monoterpenes photooxidation).

2.2 Experimental procedure

The SOA formation from α-pinene and limonene photooxidation was investigated at different NO\textsubscript{x} and SO\textsubscript{2} levels. Four types of experiments were done: with neither NO\textsubscript{x} nor SO\textsubscript{2} added (referred to as “low NO\textsubscript{x}, low SO\textsubscript{2}”), with only NO\textsubscript{x} added (~ 20 ppb NO, referred to as “high NO\textsubscript{x}, low SO\textsubscript{2}”), with only SO\textsubscript{2} added (~15 ppb, referred to as “low NO\textsubscript{x}, high SO\textsubscript{2}”), and with both NO\textsubscript{x} and SO\textsubscript{2} added (~20 ppb NO and ~15 ppb SO\textsubscript{2}, referred to as “high NO\textsubscript{x}, high SO\textsubscript{2}”). For low NO\textsubscript{x} conditions, background NO concentrations were around 0.05-0.2 ppb, and NO was mainly from the background photolytic process of Teflon chamber wall (Rohrer et al., 2005). For low SO\textsubscript{2} conditions, background SO\textsubscript{2} concentrations were below the detection limit of the SO\textsubscript{2} analyzer (0.05 ppb). In some experiments, a lower level of SO\textsubscript{2} (2 ppb, referred to as “moderate SO\textsubscript{2}”) was used to test the effect of SO\textsubscript{2} concentration. An overview of the experiments is shown in Table 1. In a typical experiment, the chamber 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 \( \text{SO}_2 \), \( \text{SO}_2 \) was added and the roof was opened to initialize nucleation first and then VOC was added. The particle number concentration caused by \( \text{SO}_2 \) oxidation typically reached several \( 10^4 \) \( \text{cm}^{-3} \) (see Fig. 2 high \( \text{SO}_2 \) cases) and after VOC addition, no further nucleation occurred. The detailed conditions of the experiments are shown in Table S1. The experiments of \( \alpha \)-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 \( \alpha \)-pinene due to the higher OH reactivity of limonene.

3 Results and discussion

3.1 Chemical scheme: VOC oxidation pathway and \( \text{RO}_2 \) fate

In the photooxidation of VOC, OH and \( \text{O}_3 \) 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 \( \text{O}_3 \) concentrations multiplied by rate constants. Typical OH and \( \text{O}_3 \) concentrations in an experiment were around \((1-15) \times 10^6 \) molecules \( \text{cm}^{-3} \) and 0-50 ppb, respectively, depending on the VOC and \( \text{NO}_x \) concentrations added. The relative importance of the reaction of OH and \( \text{O}_3 \) 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, \( \text{RO}_2 \) fate, i.e., the branching of \( \text{RO}_2 \) loss among different pathways has an important influence on the product distribution and thus on SOA composition, physicochemical properties and yields. \( \text{RO}_2 \) can react with \( \text{NO} \), \( \text{HO}_2 \), \( \text{RO}_2 \), or isomerize. The fate of \( \text{RO}_2 \) mainly depends on the concentrations of \( \text{NO} \), \( \text{HO}_2 \), and \( \text{RO}_2 \). Here, the loss rates of \( \text{RO}_2 \) via different pathways were quantified using the measured \( \text{HO}_2 \), \( \text{NO} \) and \( \text{RO}_2 \) and the rate constants based on MCM3.3 (Jenkin et al., 1997; Saunders et al., 2003) \( (http://mcm.leeds.ac.uk/MCM.) \)). Measured \( \text{HO}_2 \) and \( \text{RO}_2 \) concentrations in a typical experiment are shown in Fig. S2 and the relative importance of different \( \text{RO}_2 \) reaction pathways is compared in Fig. 1, which is similar for both \( \alpha \)-pinene and limonene oxidation. In the low \( \text{NO}_x \) conditions of this study, \( \text{RO}_2+\text{NO} \) dominated the \( \text{RO}_2 \) loss rate in the beginning of an experiment (Fig. 1a) because a trace amount of \( \text{NO} \) (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 \(~40\%\) ) to \( \text{RO}_2 \) loss because of increasing \( \text{HO}_2 \) concentration and decreasing \( \text{NO} \) concentration. In the high \( \text{NO}_x \) conditions, \( \text{RO}_2+\text{NO} \) overwhelmingly dominated the \( \text{RO}_2 \) loss rate (Fig. 1b), and with the decrease of \( \text{NO} \) in an experiment, the total \( \text{RO}_2 \) 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 \( \text{NO}_x \) conditions here. The loss rate of \( \text{RO}_2+\text{RO}_2 \) was estimated to be \(~10^{-5} \text{ s}^{-1} \) 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 \( \text{RO}_2 \) (Ziemann and Atkinson, 2012).
3.2 Effects of NOx and SO2 on new particle formation

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

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

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

3.3 Effects of NOx and SO2 on SOA mass yield

3.3.1 Effect of NOx

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

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

The suppression of SOA mass formation by NOx under low SO2 conditions agrees with previous studies (Eddingsaas et al., 2012a; Wildt et al., 2014; Sarrafzadeh et al., 2016; Hatakeyama et al., 1991). For example, it was found that, high concentration of NOx (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 NOx (referred to as “high NO” by the authors) is lower than at low NOx in the absence of seed aerosol.

Our finding that SOA yield at high NOx is comparable to that at low NOx in high SO2 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 NOx on the SOA yield from β-pinene photooxidation is substantially diminished and SOA yield only varies by 20-30% in the NOx 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 NOx and high NOx 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 NOx than at low NOx 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 NOx concentration ranges, NO/NO2 ratio as well as OH concentrations, which all affect SOA yield. Note that even at “high NOx,” the NOx concentration in this study was much lower than in many previous studies and the NOx concentration range here was more relevant to the anthropogenic-biogenic interactions in the ambient.

3.3.2 Effect of SO2

For both α-pinene and limonene, SO2 was found to enhance the SOA mass yield, at given NOx levels, especially for the high NOx cases (Fig. 3). The enhancing effect of SO2 on particle mass formation can be attributed to two reasons. Firstly, SO2 oxidation induced new particle formation, which provided more surface and volume for further condensation of organic vapor. Secondly, H2SO4 formed by photooxidation of SO2 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; Inumna et al., 2009) and in this study, the particles were acidic with the molar ratio of NH4+ to SO42- around 1.5-1.8. As mentioned above, inducing new particle formation by SO2 is especially important at high NOx conditions, when nucleation was suppressed by NOx. In addition, we found that the SOA yield in limonene oxidation at a moderate SO2 level (2 ppb) was comparable to the yield at high SO2 (15 ppb) when similar particle number concentrations in both cases were formed. Both yields were significantly higher than the yield at low SO2 (<0.05 ppb, see Fig. S3). This comparison suggests that the effect in enhancing new particle formation by SO2 seems to be more important. The role of SO2 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 SO2, the SOA mass yield at NOx conditions was enhanced to the value comparable with that at low NOx indicates that the suppressing effect of NOx on SOA mass formation was counterbalanced by the presence of SO2. 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 NO$_2^+$/NO$^+$ of ~0.1 and inorganic NH$_4$NO$_3$ had a NO$_2^+$/NO$^+$ of ~0.31 with the instrument used in this study as determined from calibration measurements. In this study, NO$_2^+$/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$_x$ (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
NOx and SO2 levels was further compared. For SOA from α-pinene photooxidation, in low SO2 conditions, no
significant difference in H/C and O/C was found between SOA formed at low NOx and at high NOx within the
experimental uncertainties (Fig. 5). The variability of H/C and O/C at high NOx is large, mainly due to the low
particle mass and small particle size. In high SO2 conditions, SOA formed at high NOx had the higher O/C and
lower H/C, which indicates that SOA components had higher oxidation state. The higher O/C at high NOx than at
low NOx is partly due to the higher OH dose at high NOx, although even at same OH dose O/C at high NOx was
still slightly higher than at low NOx in high SO2 conditions.

For the SOA formed from limonene photooxidation, no significant difference in the H/C and O/C was
found between different NOx and SO2 conditions (Fig. S5), which is partly due to the low signal resulting from
low particle mass and small particle size in high NOx conditions.

Due to the high uncertainties for some of the H/C and O/C data, the chemical composition was further
analyzed using f44 and f43 since f44 and f43 are less noisy (Fig. 6). For both α-pinene and limonene, SOA formed at
high NOx generally has lower f43. Because f43 generally correlates with H/C in organic aerosol (Ng et al., 2011),
lower f43 is indicative of lower H/C, which is consistent with the lower H/C at high NOx observed for SOA from
α-pinene oxidation in presence of high concentrations of SO2 (Fig. 5). The lower f43 at high NOx 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 f43
are likely to be related to the reaction pathways. According to the reaction mechanism mentioned above, at low
NOx, a significant fraction of RO2 reacted with HO2 forming hydroperoxide, while at high NOx almost all RO2
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 NOx, as discussed above.

Detailed mass spectra of SOA were compared, shown in Fig 7. For α-pinene, in high SO2 conditions,
mass spectra of SOA formed at high NOx generally had higher intensity for CHOgt1 family ions, such as CO2+
(m/z 44), but lower intensity for CH family ions, such as C5H11+ (m/z 15), C3H7+ (m/z 39) (Fig. 7b) than at low
NOx. In low SO2 conditions, such difference is not apparent (Fig. 7a), partly due to the low signal from AMS for
SOA formed at high NOx as discussed above. For both the high SO2 and low SO2 cases, mass spectra of SOA at
high NOx 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 NOx had lower mass fraction at m/z 15 (C5H11+),
28 (CO+), 43 (C2H5O+), 44 (CO2+), and higher mass fraction at m/z 27 (CHN+), C2H7+, 41 (C6H13+), 55 (C7H15+), 64
(C8O+) than at low NOx (Fig. S6). It seems that overall mass spectra of the SOA from limonene formed at high
NOx had higher intensity for CH family ions, but lower intensity for CHO1 family ions than at low NOx. 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 NOx
and SO2 conditions, when OH oxidation was the dominant oxidation pathway of monoterpenes. The fate of RO2,
was regulated by varying NO\textsubscript{x} concentrations. We confirmed that NO\textsubscript{x} suppressed new particle formation. NO\textsubscript{x} also suppressed SOA mass yield in the absence of SO\textsubscript{2}. The suppression of SOA yield by NO\textsubscript{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\textsubscript{x}. NO\textsubscript{x} did not significantly suppress the formation of condensable organics from \(\alpha\)-pinene oxidation as evidenced by the similar SOA yield at high and low NO\textsubscript{x} in the presence of SO\textsubscript{2}.

SO\textsubscript{2} enhanced SOA yield from \(\alpha\)-pinene and limonene photooxidation. SO\textsubscript{2} oxidation produced high number concentration of particles and compensated for the suppression of SOA yield by NO\textsubscript{x}. The enhancement of SOA yield by SO\textsubscript{2} is likely to be mainly caused by facilitating nucleation by H\textsubscript{2}SO\textsubscript{4}, although the contribution of acid-catalyzed heterogeneous uptake cannot be excluded.

NO\textsubscript{x} promoted nitrate formation. The majority (57-77\%) of nitrate was organic nitrate at both low NO\textsubscript{x} and high NO\textsubscript{x}, based on the estimate using the NO\textsubscript{2}\textsuperscript{-}/NO\textsuperscript{+} 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\textsubscript{x}. Generally, SOA formed at high NO\textsubscript{x} has a lower H/C compared to that at low NO\textsubscript{x}. The higher contribution of organic nitrate to total organics and lower H/C at high NO\textsubscript{x} than at low NO\textsubscript{x} is attributed to the reaction of RO\textsubscript{2} with NO, which produced more organic nitrate relative to organic hydroperoxide formed via the reaction of RO\textsubscript{2} with HO\textsubscript{2}. The different chemical composition of SOA between high and low NO\textsubscript{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\textsubscript{x} and SO\textsubscript{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\textsubscript{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\textsubscript{x} with SO\textsubscript{2}, H\textsubscript{2}SO\textsubscript{4} formed by SO\textsubscript{2} oxidation can counteract such suppression of particle mass because regardless of NO\textsubscript{x} levels, H\textsubscript{2}SO\textsubscript{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., 2014).
2011; Chen et al., 2012). The overall effects on SOA mass depend on specific NO\textsubscript{x}, SO\textsubscript{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\textsubscript{2}. By affecting the concentrations of SO\textsubscript{2}, NO\textsubscript{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\textsubscript{2}, NO\textsubscript{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      | Low NO$_x$   | 0.05-0.2 | <0.05        |
| (~20 ppb)   | High     | High NO$_x$  | ~20      | <0.05        |
| Limonene    | Low      | Low NO$_x$   | 0.05-0.2 | <0.05        |
| (~7 ppb)    | High     | High NO$_x$  | ~20      | ~15          |
| Moderate    | High     | High NO$_x$  | ~20      | ~15          |

Limonene
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 $\alpha$-pinene oxidation (a) and from limonene oxidation (b).
Figure 3. SOA yield of the photooxidation of $\alpha$-pinene (a) and limonene (b) in different NO$_x$ and SO$_2$ conditions.
Figure 4. (a) The ratio of nitrate mass concentration to organics mass in different NO\textsubscript{x} and SO\textsubscript{2} conditions; (b) the fraction of organic nitrate to total organics in different NO\textsubscript{x} and SO\textsubscript{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\textsubscript{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.
Figure 5. H/C and O/C ratio of SOA from photooxidation of α-pinene in different NO\textsubscript{x} and SO\textsubscript{2} conditions. A: low NO\textsubscript{x}, low SO\textsubscript{2}, B: high NO\textsubscript{x}, low SO\textsubscript{2}, C: low NO\textsubscript{x}, high SO\textsubscript{2}, D: high NO\textsubscript{x}, high SO\textsubscript{2}. The black dashed line corresponds to the slope of -1.
Figure 6. $f_{44}$ and $f_{43}$ of SOA from the photooxidation of α-pinene and limonene in different NO$_x$ and SO$_2$ conditions. A: α-pinene, low SO$_2$, B: α-pinene, high SO$_2$, C: limonene, low SO$_2$, D: limonene, high SO$_2$. Note that in the low SO$_2$, high NO$_x$ condition (panel C), the AMS signal of SOA from limonene oxidation was too low to derive reliable information due to the low particle mass concentration and small particle size. Therefore, the 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\textsubscript{x} and low NO\textsubscript{x} conditions (high NO\textsubscript{x}-low NO\textsubscript{x}). SOA was formed at low SO\textsubscript{2} (a) and high SO\textsubscript{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.
Figure 8. Conceptual schematic showing how NO\textsubscript{x} and SO\textsubscript{2} concentrations affect biogenic SOA mass production. The darker colors indicate higher SOA production. The circle on the bottom left corner indicates biogenic cases and the circle on the right top corner indicates the anthropogenic cases. And the horizontal and vertical arrows indicate the effect of NO\textsubscript{x} and SO\textsubscript{2} alone. The overall effects on SOA production depend on specific NO\textsubscript{x}, SO\textsubscript{2} concentrations and VOC concentrations and speciation.