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Daytime isoprene nitrates under changing NO_x and O_3

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Abstract. Organonitrates are important species in the atmosphere due to their impacts on NO_x , HO_x , and O_3 budgets, and their potential to contribute to secondary organic aerosol (SOA) mass. This work presents a steady-state modelling approach to assess the impacts of changes in NO_x and O_3 concentrations on the organonitrates produced from isoprene oxidation. The diverse formation pathways to isoprene organonitrates dictate the responses of different groups of organonitrates to changes in O_3 and NO_x . For example, organonitrates predominantly formed from the OH-initiated oxidation of isoprene favour formation under lower-ozone and moderate- NO_x concentrations, whereas organonitrates formed via daytime NO_3 oxidation show the highest formation under high- O_3 concentrations with little dependence on NO_x concentrations. Investigating the response of total organonitrates reveals complex and nonlinear behaviour with implications that could inform expectations of changes to organonitrate concentrations as efforts are made to reduce NO_x and O_3 concentrations, including a region of NO_x – O_3 space where total organonitrate concentration is relatively insensitive to changes in NO_x and O_3 . These conclusions are further contextualised by estimating the volatility of the isoprene organonitrates revealing the potential for high concentrations of low-volatility species under high-ozone conditions.

1 Introduction

Organonitrates are important species in the atmosphere due to their impacts on NO_x , HO_x , and O_3 budgets through gas-phase chemistry (Emmerson and Evans, 2009; Bates and Jacob, 2019; Schwantes et al., 2019, 2020; Vasquez et al., 2020). Their relatively low volatility also results in the potential to form secondary organic aerosol (SOA) via condensation onto existing particles, and some organonitrates can undergo reactive uptake to the particle phase (Hallquist et al., 2009; Schwantes et al., 2019; Palmer et al., 2022). Isoprene organonitrates have been widely studied due to the large emissions of isoprene resulting in the relevance of isoprene chemistry to a range of environments around the globe (Guenther et al., 2006; Pye et al., 2015; Reeves et al., 2021; Tsiligiannis et al., 2022).

Isoprene hydroxynitrate (IHN) is widely studied due to its formation from OH oxidation in the presence of NO resulting in high concentrations during the daytime (Fig. 1) (Xiong

et al., 2015; Wennberg et al., 2018). IHN also has formation routes from oxidation with the nitrate radical (NO_3). Other commonly studied isoprene mononitrates include isoprene carbonyl nitrate (ICN) and isoprene hydroperoxy nitrate (IPN). IPN forms through the initial NO_3 oxidation of isoprene to form an isoprene nitrooxyperoxy radical (INO_2). The reaction of INO_2 with HO_2 then forms IPN. ICN has a range of formation pathways initiated by OH and NO_3 oxidation. Isoprene dinitrate (IDN) can also form from INO_2 by its reaction with NO.

Isoprene epoxides, such as isoprene epoxydiols (IEPOX), have long been of interest due to their potential to contribute to SOA by reactive uptake to acidified particles (Paulot et al., 2009; Surratt et al., 2010). Later work outlined the similar SOA-forming properties for the nitrated epoxide, isoprene nitrooxyhydroxy epoxide (INHE), with the first proposed formation route to INHE involving the OH oxidation of IPN (Fig. 2) (Schwantes et al., 2015). Recent work aiming to improve the representation of isoprene NO_3 chemistry

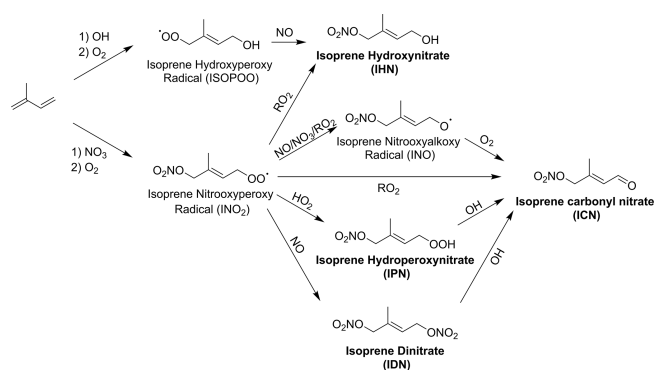


Figure 1. Formation routes to form IHN, ICN, IPN, and IDN from the OH- and NO₃-initiated oxidation of isoprene. Additional isomers and reaction pathways have been omitted for clarity.

in chemical mechanisms highlighted a previously unrepresented reaction pathway to forming nitrated epoxides from alkoxy radicals (RO) (Vereecken et al., 2021; Carlsson et al., 2023). This alkoxy-epoxidation pathway provides an alternative formation route to INHE that does not rely on a stable intermediate or the presence of OH (Fig. 3). Additionally, three more nitrated epoxides can result from this pathway: isoprene nitrooxycarbonyl epoxide (INCE), isoprene nitrooxyhydroperoxy epoxide (INPE), and isoprene dinitrooxy epoxide (IDNE).

The motivation for the work presented here is based on findings from the 2017 Atmospheric Pollution and Human Health (APHH) in a Chinese Megacity summer campaign in Beijing, showing the role of NO₃ in the formation of isoprene organonitrates and their successive particle-phase products, including the afternoon period due to the presence of high-O₃ concentrations (Hamilton et al., 2021; Newland et al., 2021). The presence of high-O₃ concentrations increased the conversion of NO to NO₂ which subsequently reduced the loss of NO₃ to reaction with NO. Geyer (2003) first highlighted this in 2003, calculating daytime NO₃ mixing ratios of up to 2–5 ppt during the afternoon during a haze period in La Porte, Texas (Geyer, 2003). Since then, daytime NO₃ has been highlighted as a potentially important chemical pathway from a range of field campaigns in various cities around the world (Brown et al., 2005; Osthoff et al., 2006; Khan et al., 2015; Xue et al., 2016; Wang et al., 2020; Foulds et al., 2021). Daytime NO₃ chemistry has also been shown to be potentially significant under forest canopies, where photolytic processes are diminished (Forkel et al., 2006; Hu et al., 2013; Mermert et al., 2021).

The co-occurrence of organonitrate formation from OH and NO₃ chemistry, along with the multistage chemistry often required for their formation, results in the potential for complex dependencies on NO_x and O₃ concentrations. However, these NO_x and O₃ dependencies have not previously been investigated. This work describes efforts to investigate the sensitivity of daytime isoprene organonitrate chemistry

to changes in NO_x and O₃ concentrations through a series of steady-state models. This work also aims to identify the role of O₃ concentrations in daytime NO₃ chemistry and determine the NO_x and O₃ concentrations that facilitate this understudied reaction pathway. While the data presented here solely focus on nitrated species resulting from isoprene, similar variations in organonitrate speciation under different NO_x–O₃ regimes are likely to hold for any volatile organic compound (VOC) which can undergo oxidation by both OH and NO₃ radicals.

2 Experimental

2.1 Model description

The goal of this work is to investigate changes in NO_x and O₃ on the chemistry of isoprene nitrates in the afternoon period in Beijing. To do this, the models should demonstrate the favoured reaction pathways under different oxidant concentrations in the absence of other variables. This means that physical and photolytic processes should be held constant, i.e. the models will describe the chemistry occurring at a representative point in the day. Species must also be allowed to reach their steady-state concentrations in order to eliminate the role of the model spin-up period on resultant species concentrations. Comparison of the concentrations of species in these so-called steady-state models then allows for conclusions to be drawn as to the preferred oxidation products under various conditions.

All models described in this work were run using AtChem2, an open-source zero-dimensional box model (Sommariva et al., 2020). All models also made use of the isoprene mechanism published by Vereecken et al. (2021) (henceforth the FZJ mechanism) which aimed to improve the representation of NO₃ chemistry of isoprene by building on chemistry from the Master Chemical Mechanism (MCM) and the review of isoprene chemistry published by Wennberg et al. (2018) (Jenkin et al., 2015; Wennberg et al., 2018; Vereecken et al., 2021; Carlsson et al., 2023). In order to make the species naming consistent between the MCM portion and the added chemistry of the FZJ mechanism, ISOPCNO₃ was renamed to EISOP1N4OH as both identical species are present in the original FZJ mechanism.

The steady-state models are sets of models run at a range of fixed NO_x and O₃ mixing ratios. Models were run for NO_x mixing ratios up to 45 ppb and O₃ mixing ratios of 140 ppb, corresponding to the upper limit of measurements made in the Beijing 2017 campaign (Shi et al., 2019). In order to provide additional OH reactivity, a constant concentration of methane was added to all of the models to ensure that the modelled OH reactivity matched measured values under Beijing-like conditions; this is discussed further in the “Model Validation” section. The required mixing ratio corresponded to 82 ppm of methane in all of the models. The modelled concentration of species is taken as the final con-

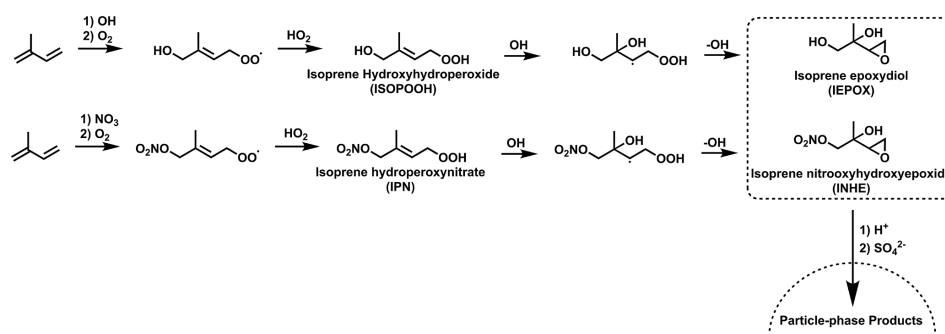


Figure 2. Established formation routes to form IEPOX and INHE via the OH oxidation of stable hydroperoxide intermediates. Additional isomers and reaction pathways have been omitted for clarity.

centration after 5 model days, after all species had been allowed to reach steady-state concentrations. Each model was run at photolysis conditions corresponding to those calculated by AtChem2 for 16:00 LT in Beijing, China. This was around the time of peak daytime NO₃ concentrations in Beijing, before concentrations rapidly increased during sunset. To ensure steady-state was reached in a reasonable time, and to provide loss routes for species without losses, species were removed from the model at a dilution rate of $2.31 \times 10^{-5} \text{ s}^{-1}$, corresponding to a dilution lifetime of 12 h. This value was selected based on a combination of the physical loss processes included in previous modelling work, and the impact of this decision is assessed in Sect. 3.1 (Mayhew et al., 2022; Edwards et al., 2014, 2013).

All models were run at a temperature of 298.15 K, a pressure of 1013 mbar, and a relative humidity of 50 %. The latitude, longitude, and date used for photolysis calculations were 39.909°, 116.398°, and 1 June 2022. NO_x was constrained by adjusting the NO and NO₂ concentrations at the beginning of each time step such that the total NO_x matched the desired concentration, but the ratio of NO and NO₂ remained constant.

Models were also run to simulate conditions in the Amazon region, with VOC concentrations adjusted to match observations of isoprene concentrations and OH reactivity in this region. These models were run at a higher-isoprene concentration of 5 ppb and methane concentrations of 100 ppm (Williams et al., 2016; Pfannerstill et al., 2021; Langford et al., 2022). The latitude and longitude values used corresponded to the city of Manaus and were -3.132 and -60.01° , respectively. The time of day was kept at 16:00 LT.

These models are designed for comparison between one another to gain insight into the impact of changes in NO_x and O₃ on organonitrate concentration. The models show the concentrations at steady state for the provided photolysis conditions, chemistry, and dilution rate, which is in contrast to the constantly changing photolysis and dilution encountered under ambient conditions. This means that chemistry that would occur at other times (e.g. nighttime chemistry) does not contribute to the results of these models. Previous

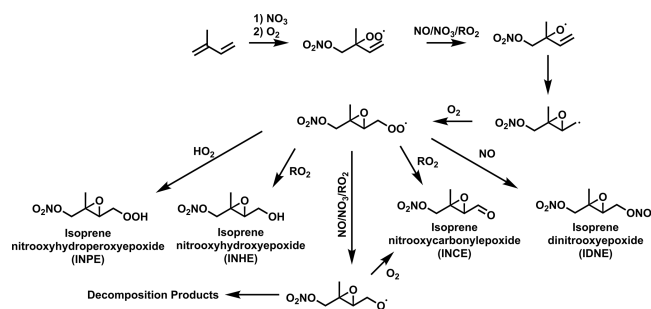


Figure 3. The alkoxy-epoxidation pathway to form a range of nitrated epoxides, as proposed by Vereecken et al. (2021). Additional isomers and reaction pathways have been omitted for clarity.

work has demonstrated not only the importance of nighttime chemistry for understanding organonitrates but also that many of the organonitrates produced overnight will decrease in concentrations over the early-morning period to reach low concentrations in the afternoon (Kenagy et al., 2020; Mayhew et al., 2022). The downstream chemistry of these nighttime organonitrates, and other nighttime species, will have some impacts on daytime chemistry that are not captured by the models presented here. However, Sect. 3.1 illustrates that the conclusions made in this paper are applicable to the Beijing afternoon conditions being investigated and that the conclusions are robust to changes in the modelling approach.

2.2 Model isopleths

Throughout this paper, the model results are investigated through the use of isopleth plots. These plots consist of the steady-state concentration of a species (or another model output such as OH reactivity) in each of the models plotted as a coloured circle at the corresponding position on a set of NO_x–O₃ axes. The colour scale is indicated by a colour bar placed alongside each set of axes and will be a different scale for each plot. A continuous colour gradient is then overlaid on the axes by interpolation over a triangular grid of the model points. Ten contour lines are also drawn over the top

of each plot to highlight the contour shape. These lines are equally spaced in the coloured dimension (e.g. species concentration), meaning close vertical lines would correspond to a strong sensitivity to changes in O₃ and close horizontal lines would correspond to a strong sensitivity to changes in NO_x.

Under real-world conditions, the O₃ concentrations will be determined by the nonlinear interactions of NO_x and VOCs, which is in contrast to the models where NO_x, O₃, and VOCs are all constrained. This means that some sections of the model isopleths will be inaccessible. For example, some amount of O₃ will form in the presence of NO_x and VOCs, so occupying the upper-left corner of the isopleths may not be possible outside of the constrained model scenario. Similarly, it may not be possible to map real-world changes to one dimension (such as a decrease in NO_x) onto the isopleth plots without accounting for a change in the other dimension (such as a change in O₃).

2.3 Volatility calculations

Section 3.6 makes use of the vapour pressure (often expressed as a log value to the base of 10) to investigate the potential contributions to SOA. The UManSysProp facility was used to do this (Topping et al., 2016); UManSysProp can estimate the vapour pressure of compounds represented as SMILES strings via a range of different group contribution methods (Barley and Mcfiggans, 2010; O'Meara et al., 2014). This work used predictions at 298 K throughout and used the “evaporation” technique, though sensitivity to all of the available prediction methods is described in Sect. 3.6.

3 Results and discussion

3.1 Model validation

As a test of the ability of the steady-state models to represent conditions present under ambient scenarios, the model results were compared to measurements collected in the summer of 2017 in Beijing (Shi et al., 2019; Hamilton et al., 2021; Whalley et al., 2021; Reeves et al., 2021; Newland et al., 2021; Mayhew et al., 2022). The NO_x mixing ratios measured in the afternoon periods in Beijing ranged between 5 and 20 ppb, and O₃ mixing ratios ranged from around 60 to 140 ppb. Isoprene mixing ratios ranged up to around 2 ppb in the afternoon period, hence a typical value of 1 ppb was chosen for the steady-state models. The concentration isopleths for inorganic species that were zoomed in to this representative range of O₃ and NO_x mixing ratios are provided in the Supplement (Sect. S1).

Measurements of OH reactivity (k_{OH}) during the afternoon period were between around 10 and 30 s⁻¹ (Whalley et al., 2021), which the models reproduced at the appropriate NO_x and O₃ mixing ratios by design due to the additional methane included in the model run for this purpose (Fig. 4a). The

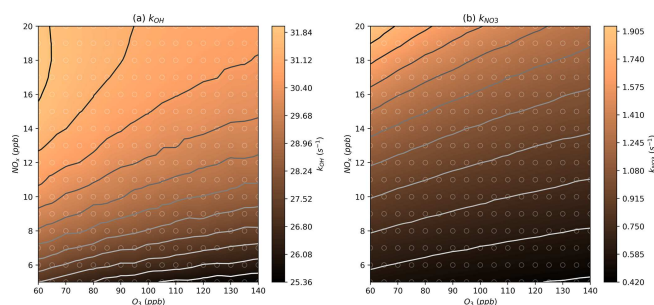


Figure 4. Modelled steady-state k_{OH} and k_{NO_3} values at different NO_x and O₃ mixing ratios. Further details on interpreting these plots are given in Sect. 2.2.

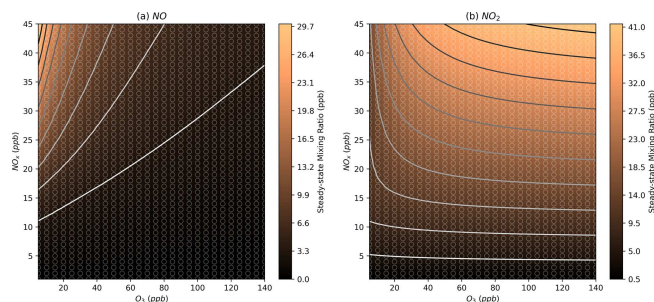


Figure 5. Modelled steady-state mixing ratios of NO and NO₂ at different NO_x and O₃ mixing ratios. Further details on interpreting these plots are given in Sect. 2.2.

modelled NO₃ reactivity (k_{NO_3}) is around 0.4–1.9 s⁻¹ compared to the estimated value of around 0.5 s⁻¹ presented in Hamilton et al. (2021) (Fig. 4b) (Hamilton et al., 2021). Values of k_{OH} and k_{NO_3} at a wider range of NO_x and O₃ mixing ratios are provided in Fig. S1.

In the NO_x–O₃ space corresponding to typical Beijing afternoon conditions, the models show NO mixing ratios of around 0.3–2.8 ppb (Figs. 5a, S2a), consistent with the low-NO observations in the afternoon period in Beijing with observed mixing ratios of around 0.25 and 3 ppb (Newland et al., 2021). The models show NO₃ mixing ratios of 0.4 to 2 ppt (Figs. 6a, S3a), which are slightly below the measured NO₃ mixing ratio in the afternoon of around 2 ppt (Hamilton et al., 2021). The modelled OH concentrations are between 2.5×10^6 and 6.5×10^6 molecules cm⁻³ (Figs. 6b, S3b), which are slightly below the measured concentrations of around 7.5×10^6 molecules cm⁻³. HO₂ is generally overpredicted with a range between 4.2×10^8 and 9.1×10^8 molecules cm⁻³, compared to measurements of around 2.5×10^8 molecules cm⁻³ (Figs. 6c, S3c) (Whalley et al., 2021). This is consistent with previous modelling studies that indicate an overprediction of HO₂ by models, particularly under the low-NO afternoon conditions being investigated here (Mayhew et al., 2022; Whalley et al., 2021). Furthermore, models that included an additional sink of HO₂ to bring it in line with mea-

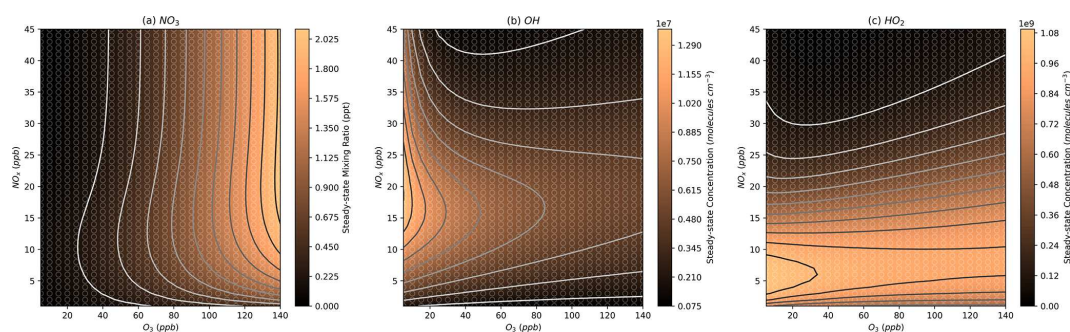


Figure 6. Modelled steady-state concentrations of NO₃, OH, and HO₂ at different NO_x and O₃ mixing ratios. Further details on interpreting these plots are given in Sect. 2.2.

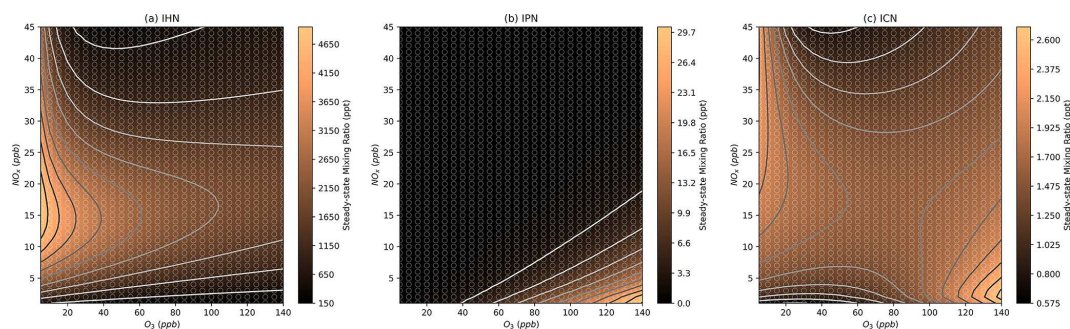


Figure 7. Modelled steady-state concentrations of isoprene hydroxynitrate (IHN), isoprene carbonylnitrate (ICN), and isoprene hydroperoxynitrate (IPN) at different NO_x and O₃ mixing ratios. Further details on interpreting these plots are given in Sect. 2.2.

measurements resulted in an underprediction of OH due to the HO_x removed from the system.

A series of sensitivity tests were carried out in order to assess the sensitivity of our conclusions to changes in model parameters. Four different parameters were adjusted: the concentration of isoprene, the concentration of methane, the dilution rate, and the time of day. These sensitivity tests were found to have little impact on the conclusions drawn in this work, and any potential impacts are discussed where required. Further details on tests are provided in the Supplement (Sect. S2).

3.2 Mononitrates

The IHN concentration isopleth (Fig. 7a) shows a strong similarity to the OH isopleth (Fig. 6b), highlighting its rapid formation from the OH oxidation of isoprene and subsequent RO₂+NO reaction to form the nitrate group (Fig. 1). This means that at high-O₃ mixing ratios, IHN shows a strong dependence on NO_x, and the dependence on O₃ becomes more significant at lower-O₃ mixing ratios.

IPN shows increasing concentrations with increasing O₃ and decreasing NO_x (Fig. 7b). This reflects the requirement for low-NO concentrations to be present for two reasons. Firstly, high-NO₃ concentrations are required to form the INO₂ radical by the reaction of isoprene with NO₃. Secondly,

the RO₂+HO₂ reaction is required to form the hydroperoxide group of IPN, and so lower-NO concentrations will reduce competition with the rapid RO₂+NO reaction. Additionally, HO₂ concentrations are highest under low-NO_x conditions (Fig. 6c), further favouring the RO₂+HO₂ reaction.

In contrast to the other nitrated species investigated here, ICN shows two peaks in concentration, one at very low O₃ and the other at very high O₃ (Fig. 7c). This is because ICN can be formed from many different routes. These routes include the abstraction of an H atom from IHN which provides a formation route under lower-O₃ conditions, when OH and IHN are both high in concentration. Alternatively, under higher-O₃ conditions, ICN can form from the reaction of OH and IPN or the decomposition of nitrated alkoxy radicals (INO). The result of these multiple peaks is that under moderate NO_x and O₃ conditions, the concentration of ICN is relatively insensitive to changes in both NO_x and O₃. It is also important to note that the absolute concentrations of ICN predicted to form in these models are very low (the peaks in concentration corresponding to mixing ratios of just over 1 ppt) due to low production rates, which is consistent with low daytime ICN mixing ratios previously identified in Beijing (Reeves et al., 2021; Mayhew et al., 2022).

Recent work has highlighted species with the formula C₄H₇NO₅ as potentially major oxidation products of iso-

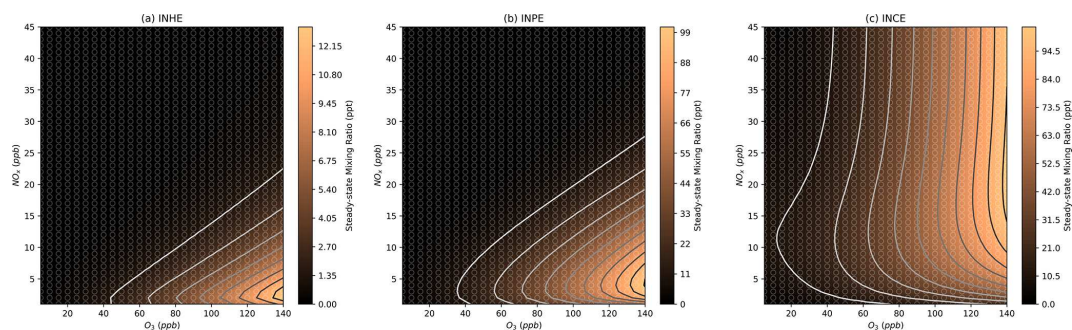


Figure 8. Modelled steady-state concentrations of isoprene hydroxynitrooxyepoxide (INHE), isoprene carbonylnitrooxyepoxide (INCE), and isoprene hydroperoxynitrooxyepoxide (INPE) at different NO_x and O_3 mixing ratios. Further details on interpreting these plots are given in Sect. 2.2.

prene (Tsiligiannis et al., 2022). Consistent with previous modelling studies (Mayhew et al., 2022), these models largely form $\text{C}_4\text{H}_7\text{NO}_5$ from OH-initiated oxidation, meaning the concentration isopleth is similar to that of OH and IHN.

3.3 Nitrated epoxides

Both INHE and INPE show a similar pattern as IPN in the NO_x – O_3 isopleths (Fig. 8a, b), with the highest concentrations occurring at low NO_x and very high O_3 . INPE is reliant on high NO_3 and HO_2 in a similar manner to IPN as the $\text{RO}_2 + \text{HO}_2$ step is still required to form INPE. While HO_2 is not required to form INHE via the alkoxy-epoxidation pathway, the formation of INHE from IPN is the major formation route under lower- NO_x conditions. Additionally, the alkoxy-epoxidation pathway to the formation of INHE relies on an RO_2 – RO_2 cross reaction. This cross reaction will be favoured under low- NO_x –high- O_3 conditions, where NO concentrations will be the lowest, meaning that the competition with the rapid RO_2 – NO reaction is minimal. This requirement for very high O_3 and low NO_x means that we should expect very low concentrations of daytime INHE and INPE under typical urban conditions. This is consistent with modelling of Beijing which showed that while INHE may comprise a large fraction of nighttime $\text{C}_5\text{H}_9\text{NO}_5$ compounds, the daytime contribution is very small (Mayhew et al., 2022).

In contrast, INCE shows reasonably high concentrations under high- O_3 mixing ratios at a range of NO_x mixing ratios. The profile of these concentrations is very similar to the NO_3 isopleth (Fig. 6a) and stems from the main formation route to INCE requiring the NO_3 oxidation of isoprene followed by an $\text{RO}_2 + \text{NO}$ reaction step. This formation route shares similarities with the dinitrates discussed in Sect. 3.4.

3.4 Dinitrates

As previously noted for INCE, Fig. 9 shows that the steady-state concentrations of isoprene dinitrate (IDN) and isoprene

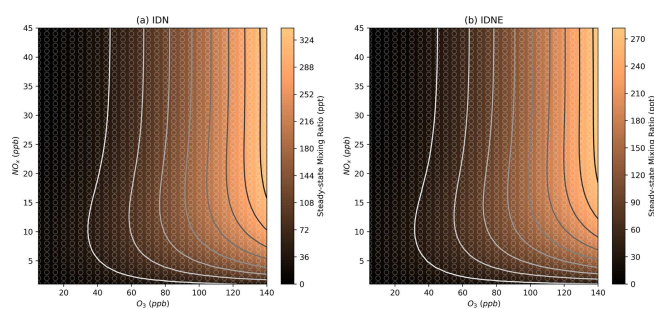


Figure 9. Modelled steady-state concentrations of isoprene dinitrate (IDN) and isoprene dinitrooxyepoxide (IDNE) at different NO_x and O_3 mixing ratios. Further details on interpreting these plots are given in Sect. 2.2.

dinitrooxyepoxide (IDNE) are very similar to the NO_3 concentration isopleth (Fig. 6a). This is indicative of the formation route of IDN and IDNE, where an initial NO_3 oxidation is followed by the reaction of the resulting RO_2 with NO to form the second nitrate group (Figs. 1 and 3). At any daytime concentration of NO_x where sufficient NO_3 is present to perform the initial oxidation step, there will also be sufficient NO present to rapidly react with the resulting RO_2 . Although the high- O_3 mixing ratios observed in Beijing result in low- NO concentrations compared to typical daytime concentrations in a polluted megacity, there is still ample NO present to react with peroxy radicals produced by the initial NO_3 oxidation. Figure 9 shows that at each O_3 , there is a critical NO_x concentration above which the concentration of IDN, IDNE, and INCE is almost exclusively controlled by O_3 concentrations. This critical NO_x mixing ratio is reasonably low compared to typical urban NO_x mixing ratios, indicating that the concentration of dinitrates in urban environments may be largely controlled by the O_3 mixing ratios present.

As discussed in Sect. S2, increasing the total VOC in the model leads to a broadening in the NO_x axis of the transition between sensitive regimes of NO_x and O_3 for NO_3 ; the same also applies to IDN, IDNE, and INCE. For a fixed ozone con-

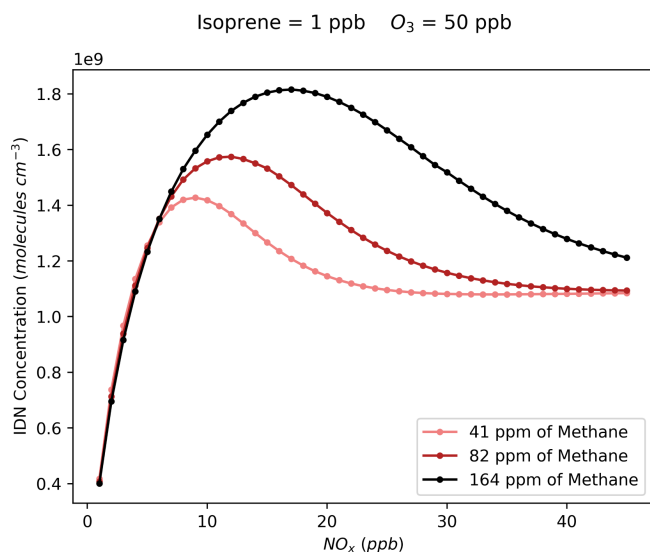


Figure 10. Modelled steady-state concentrations of IDN with changing NO_x in models runs with 50 ppb of O₃ and different mixing ratios of NO_x and additional methane.

centration, increasing the NO_x from 0 will increase IDN, IDNE, or INCE concentrations due to the increased NO₃ resulting from the increased availability of NO₂ (Fig. 10). Then, once the threshold NO_x concentration is reached and NO₃ concentrations are not limited by the availability of NO_x, the concentration becomes controlled by O₃ and HO₂ (Sect. S2), creating the “hump” in concentration which then stabilises as HO₂ concentrations begin to decrease at high NO_x and the NO₂/NO ratio becomes increasingly controlled by the fixed O₃ concentration. This means that with high-VOC concentrations, at a given O₃ concentration, reductions in NO_x will result in increased IDN, IDNE, or ICNE concentrations sooner than under lower-VOC conditions.

3.5 Total organonitrates

By summing the model concentrations for all organonitrates present in the mechanism, an isopleth of total organonitrates was obtained (Fig. 11). This shows a band of high-organonitrate concentrations at moderate NO_x. At high O₃, further changes to O₃ have little effect on the total organonitrate concentration. Total organonitrates also become less sensitive to changes in NO_x in this high-O₃ region. This band is the result of organonitrates produced by OH and NO₃ oxidation of isoprene. At low-O₃ mixing ratios, the total organonitrates are dominated by OH-initiated species such as IHN (Fig. 7a). Conversely, at high-O₃ mixing ratios, NO₃-initiated species such as IDN comprise a larger fraction of total organonitrates (Fig. 9a). This is illustrated in the pie charts in Fig. 11 which show the organonitrate composition under different NO_x–O₃ regimes.

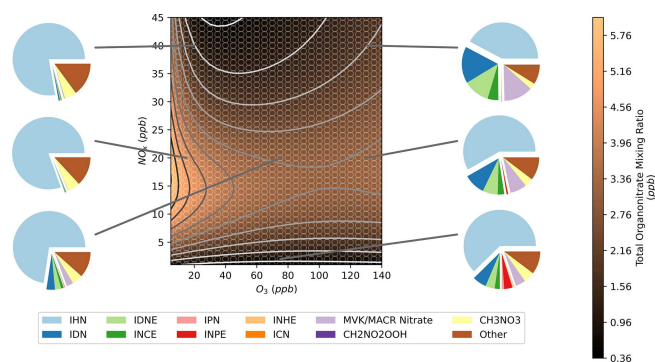


Figure 11. Modelled steady-state concentrations of the total organonitrates at different NO_x and O₃ mixing ratios along with the composition of the total organonitrates at selected NO_x and O₃ mixing ratios. Further details on interpreting these plots are given in Sect. 2.2.

The composition breakdown also reveals that total isoprene organonitrates are dominated by IHN under most conditions, but this fraction decreases as ozone mixing ratios increase. At higher O₃, a large fraction of the composition comes from IDN, IDNE, and INCE due to their higher concentrations under high-O₃ conditions (Sect. 3.3 and 3.4). CH₃NO₃ comprises a substantial fraction of total organonitrates in these models. CH₃NO₃ can be formed by the OH oxidation of methane via the methylperoxy radical, and so its concentrations in these models are exaggerated due to the large amounts of methane added to the model. Formation from the OH oxidation of methane comprises the majority of all of the methylperoxy formation in all of the models, excluding formation from the reversible decomposition of methane peroxyxynitrate (CH₃O₂NO₂) which is balanced by the opposing formation reaction. CH₂NO₂OOH is also listed in Fig. 11. CH₂NO₂OOH is formed from the products of isoprene ozonolysis, explaining the higher concentrations under high-O₃ conditions. There are no chemical losses in the mechanism for CH₂NO₂OOH, which likely explains the high contribution to total organonitrates. The remaining portion of “other” organonitrates corresponds to a wide range of species, none of which contribute more than 6% to the total organonitrate sum in any models.

As noted in Sect. S2, changing the VOC concentration affects the position in NO_x–O₃ space where the maximum organonitrate concentrations are observed. In the case of total organonitrates, decreasing the total VOC concentration results in the band of high concentrations moving to lower NO_x. Figures S7 and S8 show that with lower-methane concentrations in the model, the peak organonitrate concentrations occur at around 12 ppb of NO_x whereas this increases to around 25 ppb of NO_x in the high-methane case. The peak organonitrate concentrations at each of these NO_x concentrations are similar in each of these sets of model runs.

3.6 Volatility assessment

One of the major motivations for studying isoprene nitrates is their potential to contribute to secondary organic aerosol (SOA) by condensation or reactive uptake to existing particles. While the highest concentration species such as IHN and IDN may be most significant when considering the role of isoprene nitrates as NO_x reservoirs, low-concentration species can be much more important for SOA formation if they are of a sufficiently low volatility. As an estimation of the impact of changing NO_x and O₃ on particle-phase processes, the log of the vapour pressure was estimated for each organonitrate in the mechanism based on the species' structure using UManSysProp (Topping et al., 2016). As a measure of a compound's volatility, a lower vapour pressure value corresponds to a less volatile compound which will more readily partition into existing particles. This volatility-based approach does not account for potential reactive uptake, which is likely to be important for the epoxide species previously discussed. Furthermore, the hydrolysis of organonitrates, particularly tertiary nitrates, may reduce particle-phase concentrations (Vasquez et al., 2020). This particle-phase hydrolysis may then have knock-on effects for the gas-phase organonitrates, particularly where the tertiary nitrate isomer comprises a large fraction of the composition, such as for IHN.

Figure 12 shows the total organonitrate plot normalised to the vapour pressure value for each compound, which gives an estimation of the contribution of organonitrate uptake to SOA at each NO_x and O₃ mixing ratio. Since the predicted vapour pressures range over 10 orders of magnitude, lower-volatility species can have a large effect on SOA formation despite their much lower concentration. The lowest vapour pressures predicted here are for the two MCM species NC524NO₃ and NC524OOH. These two compounds comprise almost 100 % of the normalised concentration in Fig. 12 under all NO_x and O₃ conditions, and their individual concentration profiles can be seen in Fig. 13. The concentration isopleths for the 15 lowest volatility compounds are shown in Fig. S17. Many of these species show profiles similar to that of NC524OOH, with the highest concentrations occurring at low urban NO_x concentrations.

According to Fig. 12, reductions in NO_x from typical urban conditions would result in higher normalised concentrations of organonitrates, meaning the contribution of isoprene nitrates to SOA may increase with decreasing NO_x until very low urban NO_x conditions are met. However, it is important to note the difficulty in representing the lowest-volatility species in the isoprene oxidation mechanism. Many of these species are the product of multiple oxidation steps with large uncertainties surrounding their rates of formation. Additionally, many of the lowest-volatility species do not contain any chemical losses in the mechanism due to a lack of information on their reactions.

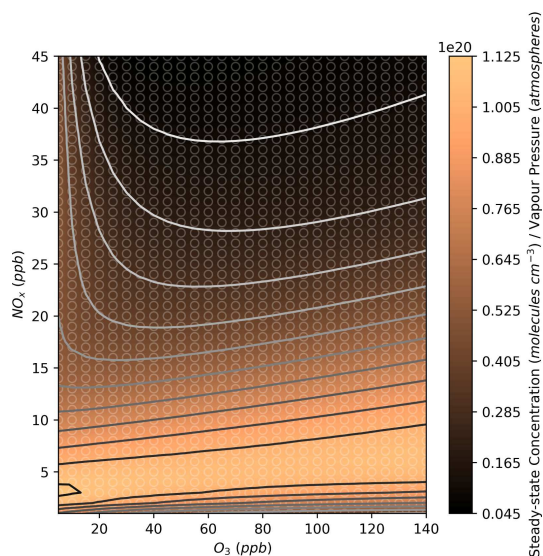


Figure 12. Modelled steady-state concentrations of the total organonitrates normalised to each compound's estimated vapour pressure at different NO_x and O₃ mixing ratios. Further details on interpreting these plots are given in Sect. 2.2.

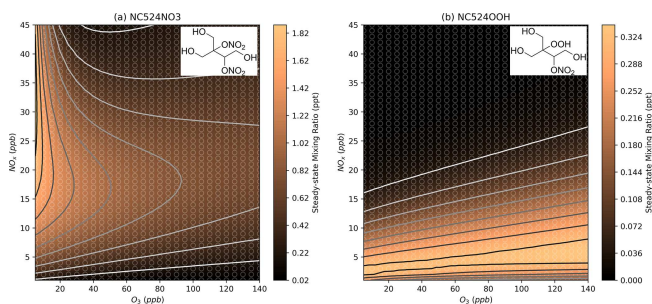


Figure 13. Modelled steady-state concentrations of the MCM species NC524NO₃ and NC524OOH at different NO_x and O₃ mixing ratios. Further details on interpreting these plots are given in Sect. 2.2.

The low predicted volatilities of NC524NO₃ and NC524OOH are the result of the many functional groups present in the molecules. Similarly, oxidised species could be described as highly oxidised molecules (HOMs) (Bianchi et al., 2019). The chemistry of HOMs is not currently well represented in many mechanisms due to their varied autoxidation formation pathways. For example, the profile of NC524OOH concentrations in Fig. 13b results from the requirement of HO₂ to form the hydroperoxide group, hence the profile is similar to that of HO₂. If an RO₂ H-shift formation pathway to NC524OOH, or similar HOMs, were included in the mechanism, then this might alter the profile in Fig. 12 (Vereecken and Nozière, 2020). It should be expected that the formation of HOMs would be sensitive to changes in ozone as the lower-NO concentrations at higher ozone will reduce the competition of the RO₂+NO path-

way with the RO₂ autoxidation reactions that form HOMs. Inclusion of improved autoxidation chemistry in the mechanisms would also increase the number of low-volatility compounds produced from the oxidation of isoprene. There is also the potential for the oxidation products of nighttime species to be low-volatility compounds that would contribute to SOA but would not be captured by these models which represent the steady-state concentration of organonitrates at 16:00 LT, without the contribution of chemistry occurring at other times of the day.

Figure S16 shows that the results presented here are reasonably insensitive to the choice of vapour pressure and boiling point prediction methods selected within UManSysProp. Section S3 also outlines the results using an alternative volatility estimation method, making use of only the molecular formula of each compound.

3.7 Application to less polluted environments

In order to test the investigation of less polluted environments, a series of models were run at a range of lower-NO_x and lower-O₃ mixing ratios. Measurements collected in the Amazon rainforest were taken as an example of an unpolluted environment, and the model was adjusted to match typical isoprene mixing ratios and OH reactivity observed in this environment. The results from these models are presented in the supplementary information (Sect. S5).

The reduced NO_x and O₃ mixing ratios used in these models mean that, despite the changes to isoprene and methane concentrations, they correspond well to higher-resolution models of the low-NO_x and low-O₃ portions of the Beijing models. Figure S19 shows that the total organonitrates in the Amazon models are sensitive to changes in NO_x, with increasing ozone slightly reducing total organonitrates.

As discussed in the introduction, IEPOX is one of the major precursors of isoprene SOA, particularly under low-NO_x conditions where the IEPOX precursor, ISOPOOH, can form from oxidation by OH and further reaction with HO₂. This dependence on HO₂ means that the Amazon models predict increasing concentrations of IEPOX as NO_x is increased from close to 0, regardless of the O₃ concentration (Fig. 14b). This is in agreement with findings from Shrivastava et al. who found increases in isoprene SOA resulting from increases in NO_x and O₃ from an urban plume (Shrivastava et al., 2019). The increased SOA could be further explained by the increases in nitrated epoxides and dinitrated species predicted on increasing both NO_x and O₃ (Fig. S19).

Methyl vinyl ketone (MVK) and methacrolein (MACR) are also often of interest in isoprene oxidation, particularly in pristine environments such as the Amazon where the production of MVK and MACR relies on the presence of NO (Langford et al., 2022). This is illustrated in Fig. 14d, whereas Fig. 14c illustrates that the abundance of NO under typical urban conditions means that the MVK + MACR concentra-

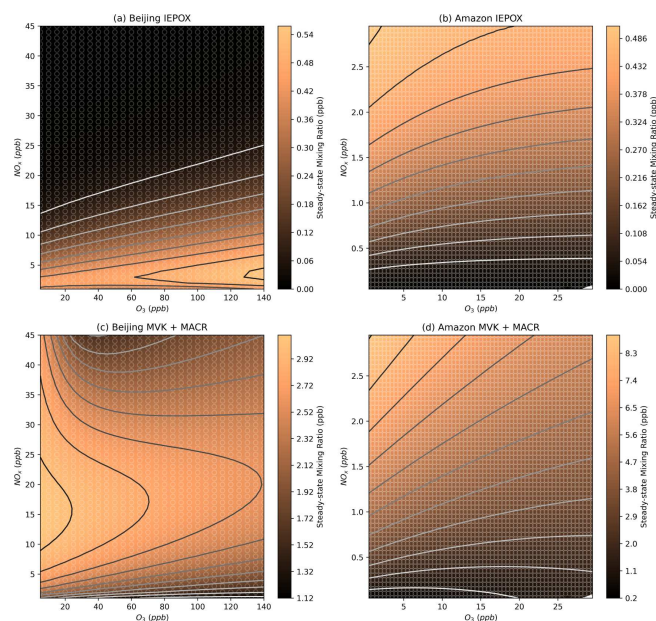


Figure 14. Modelled steady-state IEPOX and MVK + MACR concentrations for the Beijing (a, c) and Amazon (b, d) models.

tions in the Beijing models are dependent on OH concentrations.

4 Conclusions

The work presented here illustrates that each isoprene nitrate species will have a different NO_x–O₃ regime in which maximum concentrations will be produced during the afternoon period. For example, the facile formation of IHN from OH oxidation means that daytime concentrations are largely dictated by the concentration of OH. Alternatively, the concentrations of species such as IDN, IDNE, and ICN are largely dictated by the available daytime NO₃ as the reaction of RO₂ with NO is very rapid, even under low urban NO_x conditions. Finally, IPN, INHE, and INPE only show the highest concentrations under low-NO_x–high-O₃ conditions due to their increased formation under high-NO₃ concentrations and their requirement for low NO_x to avoid competition with the RO₂+NO reaction pathway.

The fact that the concentrations of different organonitrates will respond differently to changes in NO_x and O₃ will have implications for those considering pathways to reducing the concentrations of organonitrates in the atmosphere. The work presented here indicates that reductions in NO_x may not reduce total organonitrate concentrations until low urban NO_x conditions are met and that, for many of the species resulting from the daytime NO₃ oxidation of isoprene, organonitrate concentrations may be much more sensitive to changes in O₃ than in NO_x. Additionally, accounting for the volatility of the organonitrates can have very large impacts, and the models presented here are dominated by a small num-

ber of low-volatility compounds. An improved representation of late-stage oxidation and autoxidation is likely to improve the ability to predict the effect of changing O₃ and NO_x on SOA formation. It is important to note that the simplified models presented here represent the formation of daytime isoprene organonitrates at 16:00 LT and will not capture the effect of organonitrates produced during the nighttime or those produced from the oxidation of nighttime products or other VOCs.

As efforts are made to reduce NO_x, VOC, and O₃ concentrations around the world, care should be taken to ensure that the nonlinearity of responses to changes does not result in unintended increases in important SOA precursors. For example, previous work has indicated that Beijing occupies a VOC-limited regime with respect to O₃ formation and that decreasing NO_x concentrations without a concurrent decrease in VOC concentrations would result in increased O₃ (Wei et al., 2019; Ren et al., 2021). Figure 12 suggests that many of the lowest-volatility daytime isoprene organonitrates may form in higher concentrations under higher O₃ and lower NO_x. Furthermore, INHE, IDNE, INPE, and INCE all favour formation under high-O₃ conditions and may be subject to reactive uptake to the particle phase. This may be further compounded or mitigated with changing VOC concentrations due to the impact on the organonitrate isopleths as well as the nonlinear behaviour of O₃ with changing NO_x and VOC.

Future chamber and field studies could validate the findings from this work by making more comprehensive observations of total and speciated organonitrates under different NO_x, O₃, and VOC concentrations. The comparative nature of these isopleth plots mean that the organonitrate measurement would not necessarily need to be calibrated, provided that the instrument response to specific organonitrates can be assumed to be constant. This makes long-term measurements made with chemical ionisation mass spectrometry (CIMS) a promising dataset as various CIMS techniques using a range of reagent ions (including I⁻, Br⁻, and CF₃O⁻) have been shown to be very sensitive to these multifunctional compounds, but calibration is often difficult (Mayhew et al., 2022; Lee et al., 2014; Schwantes et al., 2019; Carlsson et al., 2023).

Code availability. The AtChem2 software used for modeling is open source and freely available via <https://github.com/AtChem> (AtChem, 2023; <https://doi.org/10.5194/gmd-13-169-2020>, Sommariva et al., 2020).

Data availability. No data sets were used in this article.

Supplement. The supplement related to this article is available online at: <https://doi.org/10.5194/acp-23-8473-2023-supplement>.

Author contributions. AWM performed the model simulations and prepared the paper. PME and JFH provided supervision and advice throughout the project.

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