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Multi-day ozone production potential of volatile organic compounds calculated with a tagging approach

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ABSTRACT

Calculation of the ozone production potential of Volatile Organic Compounds (VOC) has traditionally been performed using so-called incremental reactivity techniques, requiring multiple photochemical model runs in which the combined direct and indirect effects on ozone from slight perturbations to each VOC are investigated in turn. A new approach to this problem is presented here using an extensively tagged chemical mechanism, in which the direct effects of VOC on ozone are calculated using a single model run. The results of this approach are consistent with previous work, but deliver much more detailed information about the VOC intermediate oxidation products involved in the production of ozone. We show that different classes of VOC exhibit very different temporal evolution in their ozone production potential, with alkenes and reactive aromatic VOC producing ozone rapidly, while the ozone production potential of alkanes increases in the day after they are emitted. We suggest that this is related to the rate at which these different classes of compounds are able to produce very small oxidation fragments. This multi-day ozone production potential has implications for emission control strategies for the management of air quality in polluted regions. We also relate the ozone production potential of VOC to the OH reactivity of the VOC oxidation intermediates, and show that the early oxidation products of alkenes and reactive aromatics are more efficient at producing ozone in their subsequent reactions with OH than similarly reactive alkanes. While this study examines idealised chemical conditions in a box model, the techniques employed here could potentially be adapted to the study of a wider range of atmospheric conditions using three-dimensional air quality models.

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1. Introduction

Ozone (O_3) in the troposphere has long been recognised as a noxious pollutant (Haagen-Smit and Fox, 1956), due to its harmful effects on humans and plants, especially in "megacities" such as Los Angeles and Beijing. Many countries have had monitoring and regulation programs in place for several decades, and detailed photochemical models have been developed to study the production of ozone on urban and regional scales. Ozone is formed in the troposphere during the oxidation of VOC in the presence of NO_x (oxides of nitrogen, NO and NO_2). The formation of ozone by VOC oxidation is related to the number of transformations of NO to NO_2 by peroxy radicals occurring during the oxidation process (e.g. Kleinman et al., 1997; Sillman, 1999).

VOC can react with hydroxyl radicals (OH), and in the presence of oxygen form organic peroxy radicals (RO_2) and hydroperoxy radicals (HO_2). These peroxy radicals can then convert NO to NO_2, which can photolyse, ultimately forming O_3 (Atkinson, 2000). Due to differences in the structure and reactivity of individual VOC species, and the number of intermediate species involved in their degradation, each VOC has a different effect on NO_2, and therefore also on ozone (e.g. Atkinson, 2007). Under conditions of high NO_x, the production of ozone is limited by the availability of VOC, while under conditions of high VOC, the production of ozone is limited by the availability of NO_x (e.g. Kleinman et al., 1997; Sillman, 1999).

In many cases it can be desirable to have knowledge of the differing abilities of individual VOC to influence the production of ozone (the Ozone Production Potential, or OPP). These OPP can be used to make estimates of the potential of an airmass to produce ozone based on speciated measurements of VOC (e.g. Duan et al., 2008), for the design of reactivity-based substitution strategies for air quality control (Capps et al., 2010), and to reduce the size of

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chemical oxidation mechanisms in photochemical models by aggregating species with similar OPP (e.g. Watson et al., 2008).

Early attempts to quantify the OPP of individual VOC species involved hanging strips of vulcanised rubber in irradiated flasks containing mixtures of VOC and NO_x and measuring the total depth of cracks in the rubber thus formed (Haagen-Smit and Fox, 1956). Experiments performed in smog chambers have been used to guide emission control strategies (Dimitriades, 1977). More recently, photochemical models have been employed using incremental reactivity techniques (Carter, 1994; Derwent et al., 1998) to assess the varying impacts of different VOC on tropospheric ozone. Using these incremental reactivity techniques, several runs of a photochemical model are performed, each with a slight perturbation to the amount of a particular target VOC. The change, or increment, in the amount of ozone produced by the model in response to the change in VOC is then used to determine the ozone production potential of each VOC under consideration.

Carter (1994) investigated the maximum OPP of VOC by calculating incremental ozone reactivity scales under idealised conditions using a photochemical box model. VOC mixing ratios were averages of ambient measurements from 39 cities in the USA, and NO_x mixing ratios were systematically tuned in the model to produce the desired reactivity scale. Carter (1994) calculated two different reactivity scales: the "Maximum Incremental Reactivity" (MIR) scale; and the "Maximum Ozone Incremental Reactivity" (MOIR) scale. The MIR scale was calculated at NO_x mixing ratios such that an incremental change in each VOC produced the largest incremental change in O_3 (Carter, 1994) for a single day. The MOIR, on the other hand, was calculated at the NO_x mixing ratios yielding the largest single day O_3 mixing ratio. The MOIR was calculated at lower NO_x levels than the MIR.

Rather than calculating the maximum OPP, other studies have used similar techniques to examine ozone formation under more realistic conditions over longer timescales than a single day: Derwent et al. (1998) used an incremental reactivity technique with a photochemical trajectory model to calculate Photochemical Ozone Creation Potentials (POCP) under Western European conditions; while Martien et al. (2003) and Hakami et al. (2004) used three-dimensional air quality models to calculate the sensitivity of ozone production to emissions perturbations in California. Due to transport effects and spatial variations in NO_x emissions, the ozone productivity of VOC can vary substantially when calculated under ambient conditions, so Derwent et al. (1998), Martien et al. (2003), and Hakami et al. (2004) express their ozone reactivities relative to some reference VOC species (Derwent et al. (1998) use ethene, for example).

According to Luecken and Mebust (2008), the various relative incremental reactivity approaches tend to produce results which correlate well with each other, and also with the idealised absolute OPP scales calculated by Carter (1994). Similarity between ozone reactivity scales calculated with models using different chemical mechanisms has also been noted by Derwent et al. (2010), and attributed to the common set of experimental data which is used to construct these chemical mechanisms. Luecken and Mebust (2008) show that the MOIR scale from Carter (1994) may be more appropriate to larger areas of the USA which are subject to high rates of ozone formation than the MIR scale, which tends to exaggerate the effect on ozone of VOC with higher OPP, relative to VOC with lower OPP. Capps et al. (2010) show that reactivity-based substitution efforts to reduce ozone using the MIR can actually lead to increased ozone levels due to this exaggeration. They show that such reactivity-based emission substitution may be more effective when using the MOIR, which does not exaggerate the OPP of highly ozone-producing VOC under the most common conditions.

Derwent et al. (1998), Martien et al. (2003), and Hakami et al. (2004), despite performing model simulations for multiple day periods, do not explicitly examine the time dependence of ozone production from VOC, but rather examine the sensitivity of ozone production to continuous perturbation of VOC emissions. Using a box model to examine the time dependence of OPP, Stockwell et al. (2001) estimated the MIR and MOIR for scenarios lasting up to six days. They found that ethane and dimethoxymethane, which are normally quite unreactive in the first day of simulation, can produce more ozone as the length of the simulation is increased. Derwent et al. (2005) report some multi-day OPP from alkenes and carbonyls, two groups of species which are also highly reactive on shorter single day timescales. Neither Stockwell et al. (2001) nor Derwent et al. (2005) make systematic comparisons of the time dependence of OPP from highly reactive VOC such as alkenes with that from less reactive VOC such as alkanes.

Incremental reactivity techniques do not give any mechanistic information about the OPP of VOC (for example, which oxidation intermediates are responsible to which degree for converting NO to NO_2), and lump together two distinct effects: the incremental effects of extra VOC and their oxidation intermediates themselves (their direct effect on ozone); and the effects of these VOC increments on the ozone production from other components of the base VOC mixture through influences on the availability of radical species (their indirect effects on ozone). When different VOC have different OPP, or when different chemical oxidation mechanisms differ in their predictions of OPP for the same VOC, it can be difficult to understand exactly why this is using the incremental reactivity approach. Bowman and Seinfeld (1994) describe a technique which is capable of determining the detailed direct mechanistic effects of VOC on other species (including ozone) without using incremental techniques. Their method consists of the mathematical analysis of matrices representing the stoichiometry of the chemical mechanism in a photochemical model and the rates of production of "counter species" added to the chemical mechanism. Bowman (2005) calculated direct ozone productivities using a similar technique to Bowman and Seinfeld (1994), and found that they were generally comparable to incremental reactivities calculated similarly to those of Carter (1994). Some small differences were observed, and attributed to the different effects of VOC increments on radical concentrations (indirect effects). Neither Bowman and Seinfeld (1994) nor Bowman (2005) examine ozone production over timescales of multiple days.

In this paper, we describe an alternative method for calculating the direct OPP of VOC, without using incremental reactivity techniques, which is also able to provide a great deal of information about the mechanism of this ozone production. This technique is applied to the study of OPP of VOC over timescales of multiple days. The method is based on the principle of "tagging" the degradation sequence of each of the VOC present in the model. Tagging of chemical tracers in three-dimensional models of atmospheric chemistry has been previously used to trace the advection of airmasses from different origins (Lawrence et al., 2003), to trace the contribution of different sources of NO_x to the formation of tropospheric ozone (Lelieveld and Dentener, 2000; Grewe, 2004), to trace the composition of aerosol particles (Wang et al., 2009), and to trace isotopic composition through chemical transformations (Gromov et al., 2010). In this study tagging is used to trace the chemical evolution of VOC oxidation intermediates in order to track their direct effects on the peroxy radicals (HO_2 and RO_2) which convert NO to NO_2, thus calculating the Tagged Ozone Production Potential (TOPP) of these VOC.

Our modelling approach is described in Section 2, results are presented in Section 3, and discussion of the results and conclusions is given in Section 4.

2. Methods

A detailed description of the modelling approach and the definition of the TOPP is presented in the Supplementary material accompanying this article. A brief summary is presented here.

The photochemical box model includes a subset of the Master Chemical Mechanism (MCM) version 3.1 (Saunders et al., 2003). The primary VOC species considered are presented in Table 1, and include anthropogenic VOC and biogenic VOC (isoprene). These species were chosen based on the availability of ambient measurements in two megacities: Los Angeles (Baker et al., 2008); and Beijing (Song et al., 2007). The VOC mixtures in these two cities are quite different. Compared with Los Angeles, the total VOC loading is higher in Beijing, with ambient conditions in Beijing especially richer in aromatic species. Los Angeles has higher levels of the smaller alkanes than Beijing. The TOPP of each VOC is calculated under both of these conditions in order to examine its sensitivity to the nature of the VOC mixture in the model. In each case, VOC mixing ratios are held constant until midday of the first day of simulation, and are allowed to vary freely after that. The emissions of each VOC required to maintain the observed mixing ratios are recorded and used in calculating the TOPP.

In previous work examining the OPP of VOC, NO_x levels have been adjusted in order to maximise ozone production (Carter, 1994); in this study the balance between radicals and NO_x was maintained by setting the emission of NO in the model at each timestep to be equal to the chemical source of radicals minus the chemical source of NO_x. The approach used here differs from previous work in that we perform this adjustment of the NO_x source online within the model, instead of running an iterated series of model simulations designed to converge on the optimal NO_x emissions, as done by Carter (1994). The online calculation of NO emissions is designed to avoid the chemical regime in which the concentration of radicals is suppressed by an excess of NO_x (e.g. Kleinman et al., 1997), while ensuring that the model remains in a chemical state in which ozone production by VOC oxidation is maximised. In reality, a major source of NO_x in urban environments is road traffic (Butler et al., 2008), which tends to peak in the mornings and evenings rather than in the middle of the day, and can lead to conditions in which the maximum potential of VOC to produce ozone is not realised. The purpose of this study is to determine the maximum potential of VOC to form ozone, and not to perform simulations which are directly applicable to the conditions at a particular place or time. Further details of our approach are given in the Supplementary material to this article.

We define the Tagged Ozone Production Potential (TOPP) of each VOC as its total effect on the chemical O_x family, which includes O_3 and NO_2, as well as a number of reservoir species which are involved in rapid cycles of production and loss with O_3 and NO_2. By virtue of the inclusion of both O_3 and NO_2, the production terms in the O_x budget represent the production of O_3 by the NO to NO_2 conversions of VOC oxidation intermediates (Section 1). By tagging all of the VOC oxidation intermediates in the chemical mechanism with the identities of the primary VOC (Table 1), we are able to determine the overall effects of these primary VOC on the O_x family (and by extension, on O_3). The O_x budget is presented in Fig. 1. The TOPP of each VOC is defined as the production of O_x attributable back to the parent VOC divided by the amount of that VOC emitted during the first day of the model run. For a more detailed description of the methods, please refer to the Supplementary material to this article.

3. Results

The results of the box model runs for the ozone production potentials of VOC mixtures typical of Los Angeles and Beijing are shown in Fig. 2. The production of O_x in Los Angeles is attributable to a different mix of VOC than the production of O_x in Beijing; alkanes contribute to O_x production in Los Angeles to a larger extent than they contribute to O_x production in Beijing, and O_x production from aromatics and alkenes is significantly more important in Beijing than in Los Angeles. Despite these differences in the mix of VOC present in these two different cities, the per-VOC TOPP derived from each model run (Fig. 2) look quite similar.

Table 1
The VOC species in the model, along with their systematic and common names, and their measurements (nmol mol^{-1}) in Los Angeles (Baker et al., 2008) and Beijing (Song et al., 2007). Mixing ratios of n-heptane and n-octane for Beijing are not reported by Song et al. (2007); reported mixing ratios for n-decane are used instead. Similarly, i-butene for Beijing is the sum of all measured butene isomers, and a 50/50 split between m-xylene and p-xylene has been assumed.

Species Code	Species Name	Los Angeles	Beijing
C2H6	ethane	6.61	3.75
C3H8	propane	6.05	3.59
NC4H10	butane (n-butane)	2.34	2.75
IC4H10	2-methyl propane (i-butane)	1.24	2.31
NC5H12	pentane (n-pentane)	1.20	1.70
IC5H12	2-methyl butane (i-pentane)	2.79	4.11
NC6H14	hexane (n-hexane)	0.39	0.65
NC7H16	heptane (n-heptane)	0.16	0.26
NC8H18	octane (n-octane)	0.08	0.26
C2H4	ethene (ethylene)	2.43	4.59
C3H6	propene (propylene)	0.49	1.16
BUT1ENE	1-butene	0.07	0.98
MEPROPENE	2-methyl propene (i-butene, butylene)	0.13	1.27
C5H8	2-methyl 1,3-butadiene (isoprene)	0.27	0.41
C2H2	ethyne (acetylene)	2.38	5.41
BENZENE	benzene	0.48	1.76
TOLUENE	methyl benzene (toluene)	1.38	3.03
MXYL	1,3-dimethyl benzene (m-xylene)	0.41	1.02
PXYL	1,3-dimethyl benzene (p-xylene)	0.21	1.02
OXYL	1,2-dimethyl benzene (o-xylene)	0.20	0.93
EBENZ	ethyl benzene	0.21	0.98

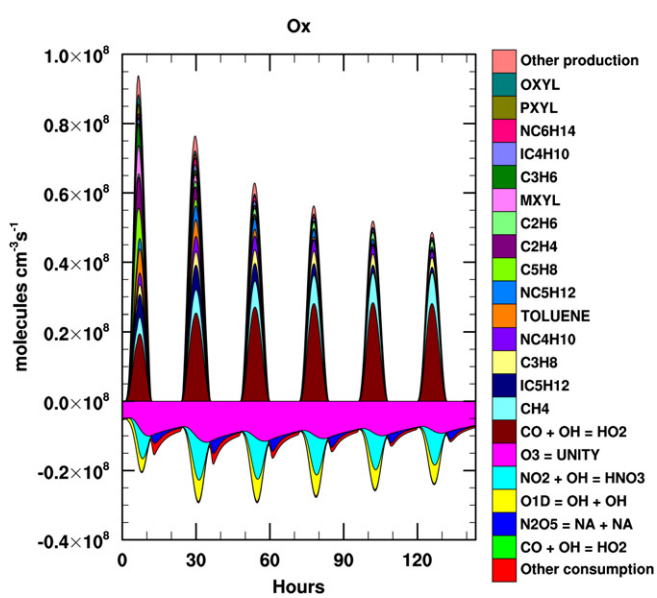

Fig. 1. The O_x budget from the Los Angeles model run with the effects of VOC oxidation intermediates attributed back to their parent VOC (names of these VOC are given in Table 1). The process "O_3 = UNITY" indicates ozone dry deposition, and "HO_2 + OH" indicates the loss of radicals by production of O_2 and H_2O, which have no further direct influence on the chemistry in the model.

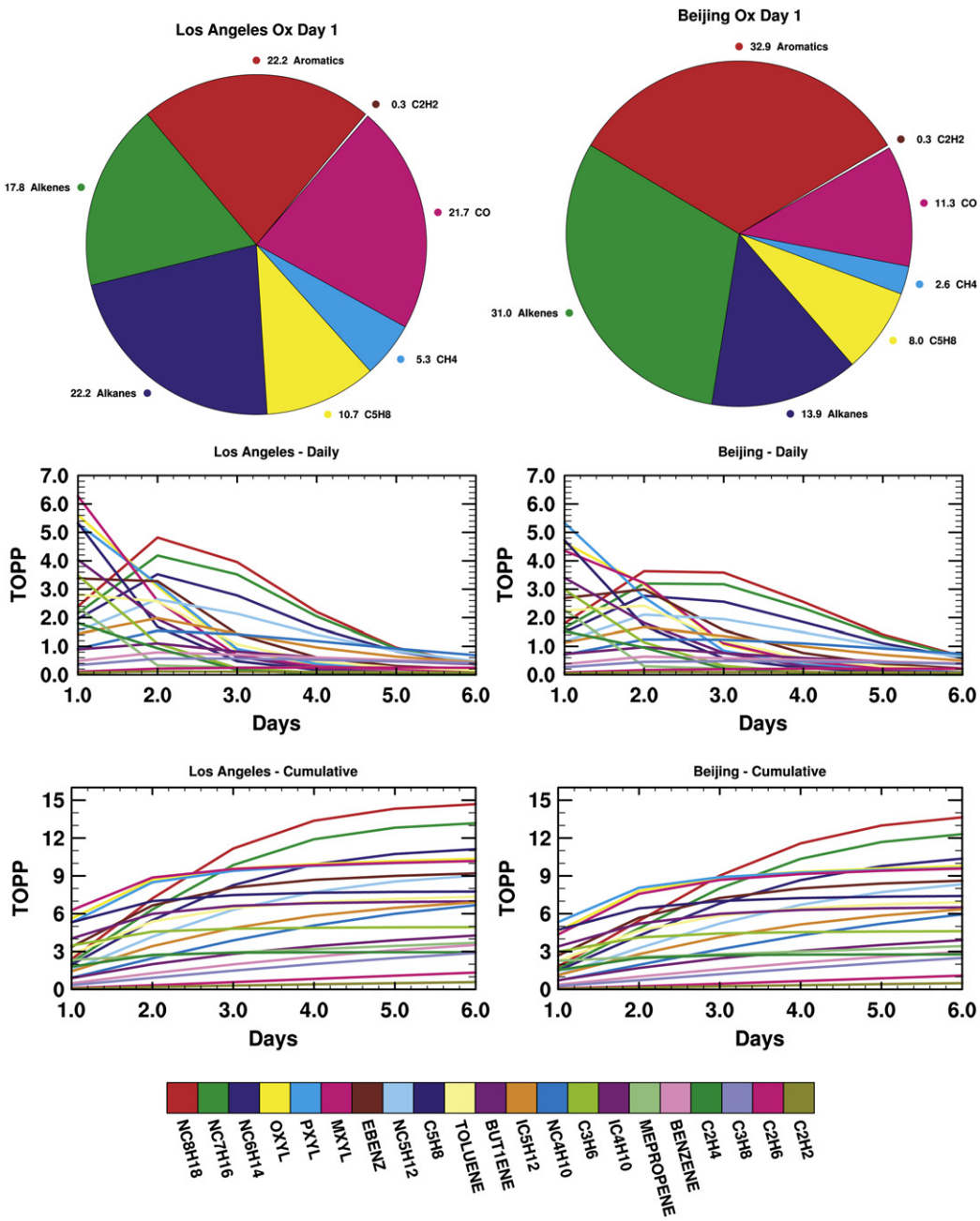

Fig. 2. O_x production in Los Angeles (left) and Beijing (right). Total aggregated production in day 1 for species classes (first row); time-dependent TOPP (molecules (O_x)/molecule(VOC), second row); and cumulative per-molecule TOPP (bottom row).

Daily averaged and cumulative values of TOPP from the model runs for Los Angeles and Beijing for six days of simulation are shown in Fig. 2. Two distinct classes of ozone-producing hydrocarbons can be identified from this figure: those whose TOPP reaches its maximum for the first day of the simulation then decreases; and those whose TOPP is maximum after the first day of simulation. Some VOC (alkenes and the more reactive aromatics such as the xylenes) attain their maximum TOPP (or very close) after the second day of simulation, while others (alkanes and less reactive aromatics such as benzene) are still converging to their maximum accumulated TOPP after six days of model simulation. The evolution of TOPP under multiple day scenarios is markedly different for different classes of VOC, with alkanes showing a much larger tendency than alkenes or aromatics to form significant amounts of ozone over longer timescales. This is explored with more mechanistic detail in Section 3.2.

This delayed potential to produce ozone could have implications for emission control strategies. In the same way that reactivity-based substitution of VOC emissions must be carefully guided and evaluated in order to avoid actually increasing the ozone production (due to exaggerated OPP when using an inappropriate reactivity scale (Capps et al., 2010)), it may also be necessary in some cases to take into account the delayed potential of VOC to form ozone. It is important to note that the higher potential of alkanes to produce ozone in downwind areas may not always be reached. For example, the TOPP calculated in this study require a sufficient source of NO_x. Downwind of urban areas, such sources of NO_x may not always be available. If an urban plume from one city containing

the potential to produce ozone were to be advected over a different city, with its own sources of NO_x and VOC, then the day 2 and day 3 OPP from the first city due to alkanes could still have a large effect on the downwind city. Another consideration in this advection of OPP is the role of mixing. The model does not include any terms for the dilution of these urban plumes. This is appropriate when calculating such an idealised quantity as the OPP, the maximum potential of a VOC to produce ozone, but not when exploring particular case studies in which mixing may be important. Future work seeking to investigate these effects in more detail should include an appropriate treatment of the relevant dilution processes.

3.1. Comparison of different OPP estimates

The TOPP from the first day of the Los Angeles model run are compared with other estimates of OPP in Fig. 3. The TOPP are first compared to the Beijing model run in Fig. 3a. The TOPP calculated from the Beijing model run are slightly lower than those calculated from the Los Angeles run. This appears related to the amount of OH radical available in each model run; the larger VOC loading in the Beijing model run tends to suppress the concentrations of OH radical, leading to slower chemistry and lower per-VOC TOPP. The Beijing TOPP are uniformly lower than the Los Angeles TOPP, with the points generally close to a straight line. Despite the large differences in the amount and the mix of VOC present in Los Angeles and Beijing (Table 1), we calculate very similar TOPP for each VOC. Future work should examine TOPP calculated using VOC mixing ratios representative of other regions, examine the effects of including additional types of VOC, and investigate further the dependence on OH radical concentrations.

Comparison of the Los Angeles TOPP calculated in this study with the POCP (Photochemical Ozone Creation Potential) from Derwent et al. (1998) is shown in Fig. 3b. For the purposes of comparison we have shown the TOPP relative to ethene, as reported by Derwent et al. (1998). Despite some large differences in a small number of VOC (including ethene), these two different

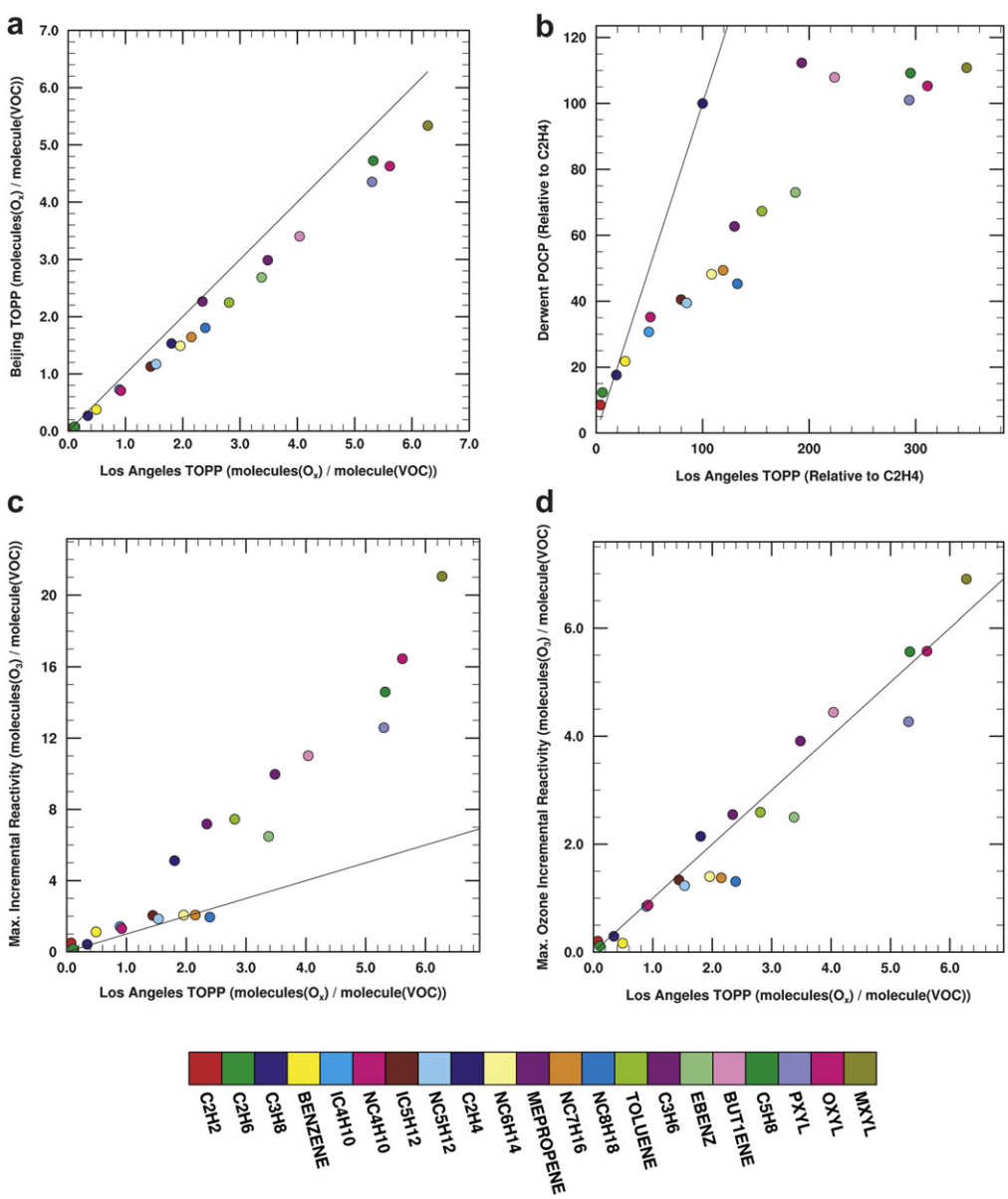

Fig. 3. Comparisons of (a) Los Angeles and Beijing TOPP, (b) Los Angeles TOPP with the POCP of Derwent et al. (1998), (c) the MIR of Carter (1994), and (d) the MOIR of Carter (1994).

metrics of ozone production potential are clearly well correlated with each other. The study of Derwent et al. (1998) has some similarities with this study; both studies use a photochemical box model employing the Master Chemical Mechanism (Saunders et al., 2003). The study of Derwent et al. (1998) differs from this study, however, in that it attempts to explicitly simulate conditions relevant to a Lagrangian trajectory through western Europe over a five day period. This includes mixing processes between the boundary layer and the free troposphere, which may explain why the POCP of alkanes compares well with the TOPP from day 1 of the simulation (Fig. 3b). The potential to produce ozone after the first day of emission appears to be diminished due to dilution by the mixing of boundary layer air with the free troposphere.

The day 1 Los Angeles TOPP is compared with the Maximum Incremental Reactivity (MIR) and Maximum Ozone Incremental Reactivity (MOIR) scales of Carter (1994), calculated with the SAPRC-07 chemical mechanism (Carter, 2010), in Fig. 3c and d. We have converted the MIR and MOIR scales from units of g(O_3)/g(VOC) to units of molecules (O_3)/molecule (VOC) for better comparison with these results. There is good agreement between the TOPP and the MIR scales for alkanes, although the agreement breaks down for the more reactive alkenes and aromatic species. The MOIR, on the other hand, correlates very well with the entire range of calculated TOPP values. The tendency of the MIR scale to overestimate the OPP of highly reactive VOC relative to the MOIR scale has been noted earlier (Section 1). The lower NO_x conditions under which the MOIR scale is calculated are directly comparable with the tuning of the NO_x source in the model to balance the model-calculated source of radicals (Section 2). It is shown in the Supplementary material to this article that this produces a maximum in O_3, and that at higher NO_x, the increased production of O_x in the model does not translate into increased production of O_3.

3.2. Analysis of VOC oxidation intermediates

The approach of tagging the chemical mechanism allows the analysis of the production of O_x from each VOC in greater mechanistic detail than is possible when using incremental reactivity techniques (such as used to calculate the MOIR (Carter, 1994)). Using the reaction rates of the tagged intermediates, it is possible to quantify exactly which reactions contribute to O_x production (and therefore the TOPP) for each parent VOC. This information is shown for m-xylene and n-octane in Fig. 4. The difference in the time evolution of TOPP from these two species was shown in Fig. 2. As seen in Fig. 4, a major difference in the mechanism of O_x production between these two species is the timing of O_x production from smaller fragments such as CH_3CO_3, CH_3O_2 and CH_3O radicals. These

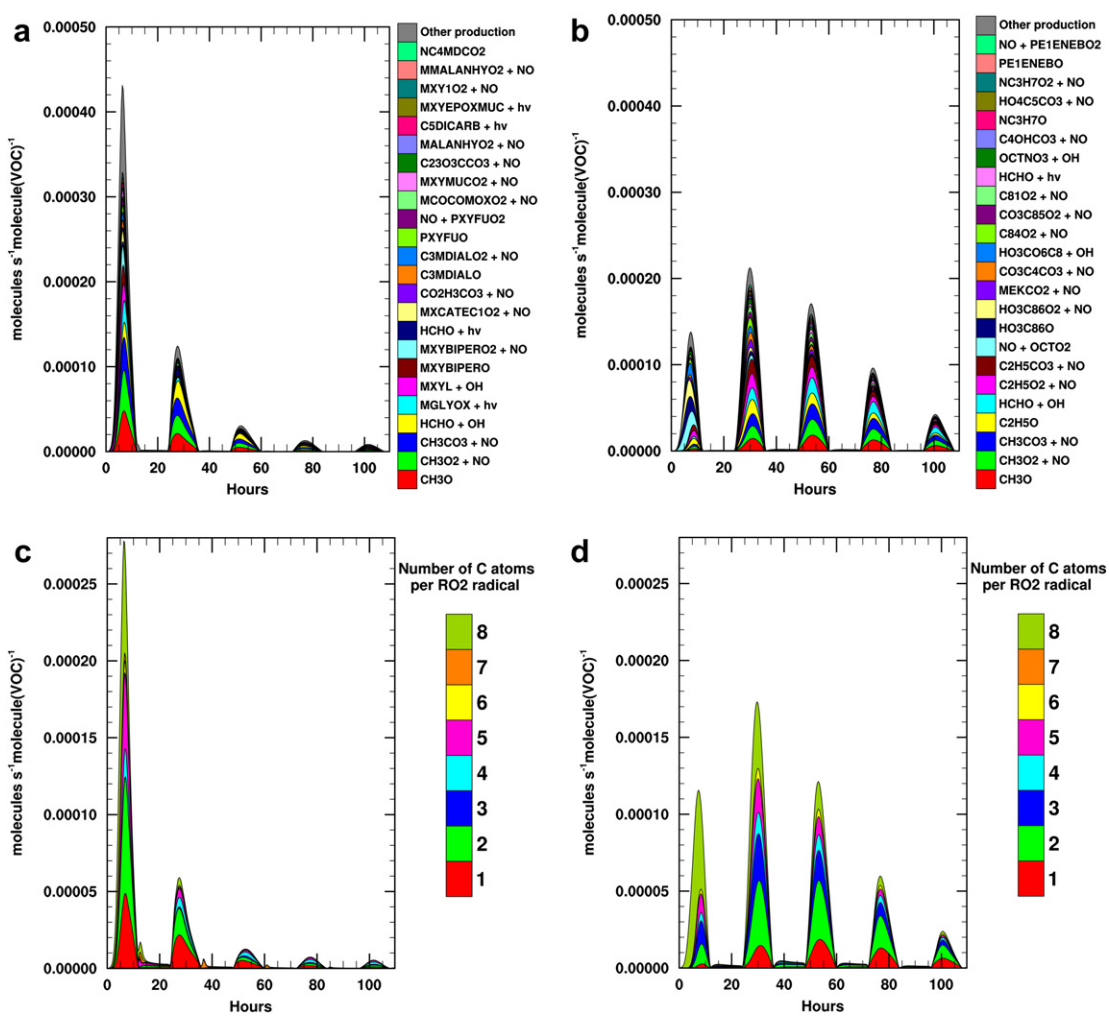

Fig. 4. Production of O_x broken down by process for (a) m-xylene and (b) n-octane. Yield of RO_2 radicals by number of carbon atoms for (c) m-xylene and (d) n-octane. Units are molecules or radicals produced per second per molecule of parent VOC emitted during the model run.

three radicals in fact form a direct degradation chain from each other. Under the conditions in the model, the rate constant for initial attack by the OH radical is approximately double for m-xylene compared with n-octane, but it appears from Fig. 4 that the difference in TOPP between these two VOC has more to do with the rate at which they break into smaller fragments than the rate of initial reaction with OH. The organic peroxy radicals produced from m-xylene during the first day of simulation consist to a very large degree of radicals with one or two carbon atoms, while eight-carbon radicals are the most numerous of the first-day RO_2 from n-octane oxidation.

It is well recognised that VOC oxidation is a multi-step process involving many intermediate peroxy radicals and multiple NO to NO_2 conversions (Atkinson, 2000). Many of these steps involve reactions with the OH radical, and thus contribute to the OH reactivity (the inverse of the OH lifetime). OH reactivity of VOC has been linked with ozone production several times in the literature (e.g. Kirchner et al., 2001; Kleinman, 2005). It has also been assumed that each reaction of a VOC with an OH radical produces two peroxy radicals (an RO_2 and an HO_2, Sadanaga et al. (2005)), so one might expect to see a close relationship between the OH reactivity attributable to a VOC (including the OH reactivity of all of its oxidation intermediates) and its TOPP. The dependence of TOPP on the attributed, integrated, and normalised OH reactivity is shown in Fig. 5. OH reactivity is attributed to each parent VOC based on the rates of reaction of tagged reaction intermediates with the OH radical, is integrated over time, and normalised by the emissions of each parent VOC during the first day of the model simulation. This calculation is described in more detail in the Supplementary material. Units of this attributed, integrated and normalised OH reactivity are [cm^3 molecule(VOC)$^{-1}$]. Fig. 5a shows the relationship between this quantity and TOPP for the first day of the Los Angeles model simulation, and 5b shows the cumulative values after six days.

After six days, when most of the VOC in the model simulation have exhausted their potential to produce ozone (Fig. 2), there is indeed a close relationship between the attributed, integrated, and normalised OH reactivity of each VOC and its TOPP, indicating broad similarities among the VOC in their yields of peroxy radicals through reaction with OH radicals. For the first day of simulation (Fig. 5a), however, there are differences between different types of VOC; alkanes and alkenes with similar attributed OH reactivity do not show the same TOPP. Isobutane (IC4H10) and methyl propene (MEPROPENE), for instance have very similar attributed OH reactivity, but methyl propene has a TOPP about 60% higher. Similarly, n-octane (NC8H18) and 1-butene (BUT1ENE) have similar attributed OH reactivity and very different TOPP, with the alkene producing more ozone per unit of OH reactivity than the alkane.

From Fig. 5a it appears that larger alkanes and their larger oxidation fragments tend to yield fewer peroxy radicals from their reactions with OH radicals than the oxidation intermediates of alkenes (and aromatics). This is consistent with the increasing importance of the radical-terminating formation of alkyl nitrates from reaction of RO_2 with NO as the size of the RO_2 radical increases (Atkinson, 2007). Another effect is that the yield of HO_2 from decomposition of the alkoxy radicals, which result from reaction of RO_2 with NO, decreases as the number of carbon atoms in these alkoxy radicals increases above four. This is due to the isomerisation (1,5-H-shift) reactions which these alkoxy radicals can undergo, which are competitive with decomposition reactions (Atkinson, 2007). These isomerisation reactions lead to the production of a δ-hydroxy-R'O_2 radical instead of an HO_2 radical.

Efforts to link measurements of the bulk VOC–OH reactivity of airmasses with their ozone production characteristics (e.g. Kirchner et al., 2001; Sadanaga et al., 2005) may be influenced by the nature of the particular VOC mixture being measured; airmasses with

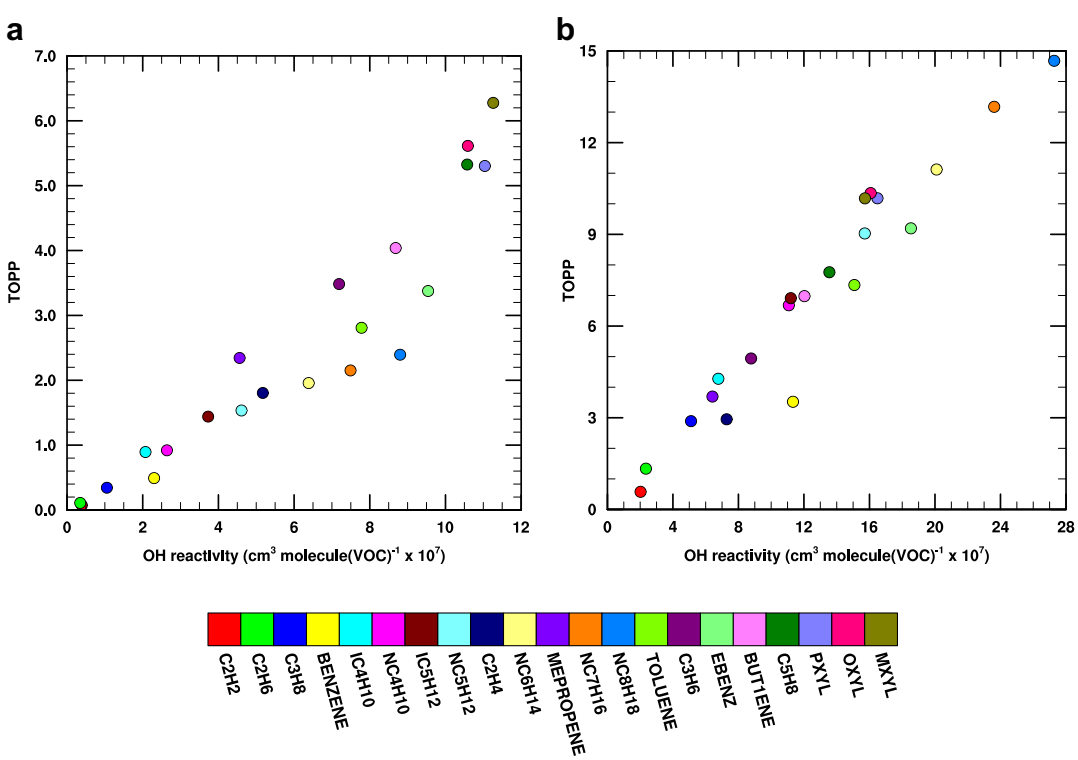

Fig. 5. Per-VOC TOPP vs. attributed, integrated, and normalised OH reactivity [cm^3 molecule(VOC)$^{-1}$] for (a) the first day of the model simulation, (b) six days of model simulation.

a high degree of freshly emitted alkanes will have a different relationship between OH reactivity and TOPP than aged or aromatic-dominated airmasses (Fig. 5). Future work should examine these differences between VOC in more detail, preferably in conjunction with multiple chemical mechanisms and chamber experiments.

4. Discussion and conclusions

Ozone production potentials for volatile organic compounds are idealised, yet useful quantities. We have shown in this study that a tagging approach can be used to produce a measure of the ozone production potential of VOC (our TOPP). Our method calculates only the direct effects of VOC on ozone production, in contrast with incremental reactivity techniques which calculate the combination of direct and indirect effects. We have shown here that under conditions of maximum ozone production, these two different approaches produce comparable results. Our TOPP appear broadly applicable to ozone production in very different regions and VOC mix characteristics, although they also appear to be sensitive to the ambient OH concentrations calculated by the photochemical model.

Calculation of the TOPP yields highly detailed mechanistic information about the ozone formation pathways involved during VOC oxidation. We have shown that alkanes in particular can have higher TOPP in the two days subsequent to their emission than more highly reactive VOC such as alkenes and substituted aromatic compounds (which reach their maximum TOPP much earlier in their oxidation chains), and we have linked this with the rate at which these different classes of VOC are able to yield smaller peroxy radical oxidation fragments. This has important implications for ozone production downwind of major VOC emission sources, or airmasses which are stagnant or recirculating, and for the design of reactivity-based substitution strategies for reducing ozone production. The integrated OH reactivity of a VOC and its oxidation intermediates is a good indicator of its TOPP; however, larger alkanes are less efficient at producing ozone for a given degree of OH reactivity than alkenes and aromatic hydrocarbons during the early stages of their oxidation due to production of alkyl nitrates from their large organic peroxy radicals.

Our TOPP, like other measures of ozone production potential previously presented in the literature, represents the maximum potential of VOC to form ozone. Similarly to previous work, we have tuned the source of NO_x in the model in order to maximise the production of ozone. This has been achieved by setting the source of NO in the model to be equal to the model-calculated source of radicals at every model timestep. This maximum ozone production potential will not always be reached under actual atmospheric conditions. Future work could extend our technique to attribute ozone production to VOC under more realistic conditions, where the NO_x source is not optimised to produce the maximum amount of ozone. Given sufficient computing resources, this tagging approach could also be employed in three-dimensional photochemical models to attribute spatial patterns of ozone formation to localised VOC emission sources.

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Appendix. Supplementary material

Supplementary data related to this article can be found online at doi:10.1016/j.atmosenv.2011.03.040.

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