Multiday production of condensing organic aerosol mass in urban and forest outflow

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Abstract

Secondary organic aerosol (SOA) production in air masses containing either anthropogenic or biogenic (terpene-dominated) emissions is investigated using the explicit gas-phase chemical mechanism generator GECKO-A. Simulations show several-fold increases in SOA mass continuing for multiple days in the urban outflow, even as the initial air parcel is diluted into the regional atmosphere. The SOA mass increase in the forest outflow is more modest (~ 50%) and of shorter duration (1-2 days). The multiday production in the urban outflow stems from continuing oxidation of gas-phase precursors which persist in equilibrium with the particle phase, and can be attributed to multigenerational reaction products of both aromatics and alkanes, especially those with relatively low carbon numbers (C4-15). In particular we find large contributions from substituted maleic anhydrides and multi-substituted peroxide-bicyclic alkenes. The results show that the predicted production is a robust feature of our model even under changing atmospheric conditions and different vapor pressure schemes, and contradict the notion that SOA undergoes little mass production beyond a short initial formation period. The results imply that anthropogenic aerosol precursors could influence the chemical and radiative characteristics of the atmosphere over an extremely wide region, and that SOA measurements near precursor sources may routinely underestimate this influence.

1 Introduction

The contribution of anthropogenic aerosol is one of the greatest current uncertainties in the assessment of climate forcing (e.g. Forster et al., 2007). Organic aerosol (OA) comprises a significant

(20-90%) fraction of anthropogenic aerosol (Kanakidou et al., 2005; Jimenez et al., 2009; Zhang et al., 2007). OA consists, to a first approximation, of both primary organic aerosol (POA) directly emitted as particles in evaporative equilibrium with the gas phase (Robinson et al., 2007), and the much more abundant secondary organic aerosol (SOA) produced by condensation of oxidation products of gas-phase VOC (volatile organic compound) precursors (e.g. Kanakidou et al., 2005; Jimenez et al., 2009). Climate uncertainties stem from both the difficulty in characterizing the radiatively-important interactions of OA given its globally non-uniform composition (McFiggans et al., 2006), and from the difficulty in simulating its abundance and distribution (e.g. Goldstein and Galbally, 2007; Hallquist et al., 2009).

Radiative impacts of atmospheric aerosols fall into two main categories, aerosol-radiation interactions and aerosol-cloud interactions (e.g. Forster et al., 2007; Boucher et al., 2013). Aerosol-radiation interactions encompass absorption and scattering of solar radiation by aerosol particles (also known as the direct effect) and cloud evaporation due to the consequent atmospheric heating (semi-direct effects). Widely different estimates of direct radiative forcing are produced by differing estimates of global SOA mass burdens (Tsigaridis et al., 2014, after Myhre et al., 2013, and Spracklen et al., 2011). Aerosol-cloud interactions (indirect effects) encompass a range of cloud properties influenced by aerosols acting as cloud condensation nuclei (CCN). The relationship between CCN number and radiative forcing is itself complex and model parameterizations vary substantially (Boucher et al., 2013). Recent studies attribute about one-third of the total uncertainty in modeled CCN concentrations to uncertainties in SOA production (Carslaw et al., 2013), and find that CCN concentrations are sensitive to the relative proportions of POA and SOA (Trivitayanurak and Adams, 2014) and to oxidative ageing (Yu, 2011). These results show the importance of representing sources and life cycle processes that affect the mass and other climate-relevant properties of SOA in as realistic and physically-based a way as possible.

Laboratory-based descriptions of SOA formation and yields have become increasingly complex. Early calculations used precursor-specific 2-product formulations (Odum et al., 1996) which describe smog chamber OA mass yields reasonably well but produce significant underestimates of atmospheric OA in both near-source regions and in the free troposphere (e.g. Volkamer et al., 2006; Heald et al., 2011). The VBS (volatility basis set) framework (Donahue et al., 2006) uses empirical volatility distributions to describe multi-species particle-gas mixtures and their chemical transformations (ageing) over laboratory timescales (Grieshop et al., 2009; Robinson et al., 2007). This concept broadly designates SVOCs (semi-volatile organic compounds), species with significant fractions in both gas and particle phases, and IVOCs (intermediate-volatility organic compounds), gas phase species whose products are likely to condense as SOA (Donahue et al., 2009). VBS formulations have

improved SOA estimates in numerous model studies e.g. (Tsimpidi et al., 2010; Lane et al., 2008; Dzepina et al., 2011; Zhang et al., 2013). However the ageing parameterizations are often tuned to match observed OA mass distributions e.g. (Jo et al., 2013), and as such are not generalizable. In efforts to incorporate more chemical complexity and realism to representations of bulk organic aerosol properties and evolution, various two-dimensional schemes have been developed e.g. (Kroll et al., 2011; Donahue et al., 2012; Pankow and Barsanti, 2009; Barsanti et al., 2013) and implemented in regional e.g. (Murphy et al., 2012) and global e.g. (Mahmud and Barsanti, 2013) models. Other model studies have increased the number of OA precursor types represented e.g. (Pye and Pouliot, 2012), or added SOA production in cloud drops e.g. (Lin et al., 2012). These modeling advances have reduced, but not eliminated the gaps between predictions and ambient measurements of SOA.

The difficulty in reproducing observed aerosol mass distributions is partly attributable to the mismatch between the timescales accessible to laboratory studies, and the atmospheric lifetimes of OA and its precursor gases. OA lifetimes are generally considered to be of the order of about a week (Boucher et al, 2013) or more (Kristiansen et al., 2012), during which the airborne particles are continually subject to ageing processes. The dynamic nature of gas-particle condensation equilibria (Pankow, 1994b) allows for evaporation-oxidation-re-condensation cycling of OA constituents, altering the chemical composition including the relative proportions of POA and SOA. In addition, the continual chemical evolution of the associated gas phase implies product volatility changes on timescales of several days (Kroll and Seinfeld, 2008), opening the possibility of multi-day SOA formation. By contrast, practical considerations typically limit aerosol chamber studies to a few hours, although a few recent studies have achieved effective photochemical timescales of up to 3 days e.g. (Yee et al., 2012; Craven et al., 2012). Field observation of long-term aerosol evolution is also challenging owing to dilution and mixing of outflow plumes with regional air. SOA production in various plumes has been assessed by normalizing OA to ΔCO, the difference between plume and background CO values, e.g. (Kleinman et al. , 2008; DeCarlo et al., 2010) and references therein. Such observations generally extend to photochemical ages of ~1 day (DeCarlo et al., 2010). Ship-borne OA and CO observations in urban plumes with transport-based ages of up to about 4 days have clearly shown SOA production for ~2 days, with large data scatter thereafter (de Gouw et al., 2008).

Another problem of scale is inherent in the sheer number of potential chemical reactions and products leading to SOA formation (e.g. Goldstein and Galbally, 2007). Indeed, recent advances in high resolution mass spectrometry analytical techniques have enabled characterization of many hundreds of individual OA constituents (e.g. Nizkorodov et al., 2011 and references therein; Chan et al., 2013; O'Brien et al, 2013; Kourtchev et al, 2014)). Explicit modeling of hydrocarbon chemistry

involves potentially millions of intermediate species (Aumont et al., 2005). This can be simplified to only a few hundred species when considering ozone production (Szopa et al., 2005), but is far more complicated for SOA production (Camredon et al., 2007; Valorso et al., 2011; Aumont et al., 2013; Aumont et al., 2012) which is not dominated by any one species but rather results from condensation of many oxygenated intermediates and their in-particle transformations.

The atmospheric chemical processes leading to the formation of condensable vapors and ultimately to SOA may be simulated explicitly, using structure-activity relationships based on laboratory measurements of individual and fundamental chemical kinetic rates and pathways. We have previously used the explicit model GECKO-A to simulate SOA formation in the urban outflow plume from Mexico City (Lee-Taylor et al., 2011, hereinafter L-T11). That study showed OA mass production continuing for several days and yielding several times the regionally-integrated SOA mass that would be implied from concentrations near the source. In this work, we use sensitivity studies and case studies with both urban and biogenic emissions assemblages to examine whether the modeled OA mass production is a robust feature of our model, and to elucidate the chemical identities of the species responsible.

2 Approach

2.1 The GECKO-A Model

GECKO-A (Generator of Explicit Chemistry and Kinetics of Organics in the Atmosphere) is an automatic generator for atmospheric gas-phase chemical mechanisms. It is described in detail by (Aumont et al., 2005), with updates by (Camredon et al., 2007; Aumont et al., 2008; Valorso et al., 2011), and as described here. The atmospheric oxidation of aliphatic compounds is treated explicitly based directly on laboratory measurements if available, or on structure-activity relationships (SARs) where data are not available. The chemical mechanism for the oxidation of aromatic compounds is taken from the Master Chemical Mechanism, MCM v3.1 (Jenkin et al., 2003; Bloss et al., 2005a) up to the loss of the aromatic structures, and computed from GECKO-A for subsequent chemistry. Photochemistry is driven by a j-value lookup table, calculated using the TUV (Tropospheric Ultraviolet/Visible) model (Madronich and Flocke, 1998).

In this study we implement GECKO-A in a similar manner to that described by LT11, with the following modifications. We have implemented the SAR of Vereecken and Peeters (2009) for alkoxy decomposition rates as described in (Aumont et al., 2013), we modified the SAR for hydrogen abstraction from aldehydes, based on the study by (Baker et al., 2004), we added oxy radical production channels for the reactions of R-COO_2 and RO-CH_2O_2 with HO_2 (Orlando and Tyndall, 2012;

Hasson et al., 2012), and we updated the branching ratios for isoprene and methacrolein oxidation (Paulot et al., 2009; Galloway et al., 2011).

Aerosol condensation in GECKO-A is based on equilibrium partitioning (Pankow, 1994a) assuming unity activity coefficients, and using published vapor pressure (P_{vap}) parameterizations. The model focuses on the gas-particle equilibria of products of gas-phase chemistry with a simple bulk organic aerosol phase which has no aqueous or inorganic component. We prescribe a pre-existing and non-volatile bulk seed aerosol mass to act as a condensation nucleus, as detailed below. We do not consider heterogeneous or particle-phase chemistry, nor any kinetic limitations. Here we employ the vapor pressure scheme of Nannoolal et al. (2008) together with the boiling point scheme of Nannoolal et al. (2004) (together hereinafter NAN), whereas our previous work (LT11) had used the Myrdal and Yalkowsky (1997) vapor pressure scheme which included the boiling point scheme of Joback and Reid (1987) (together hereinafter JRMY). The NAN scheme has been shown to give more realistic (and typically higher) vapor pressure results for longer–chain hydrocarbons than JRMY (Barley and McFiggans, 2010), raising the possibility (examined below) that the aerosol mass production predicted by the JRMY scheme might be an artifact. In the present study we perform a sensitivity study using both methods, to assess how the selection of vapor pressure scheme affects the predicted aerosol mass production.

2.2 Modeling Scenarios

2.2.1 Urban Precursors: Mexico City during MILAGRO

Our anthropogenic case study is based on the atmosphere in and near Mexico City during the MILAGRO (Megacity Initiative: Local and Global Research Observations) campaign of March 2006 (Molina et al., 2010). The emissions and initial conditions are defined similar to LT11, and briefly summarized here. Anthropogenic emissions are a mixture of light aromatics (21% by mass), linear alkanes to C30, (44% by mass, excluding CH4), a selection of branched alkanes to C8 (20% by mass) and alkenes to C6 (12% by mass) (see Figure 1a). Diel cycles of emission rates of chemically-similar groups with up to 10 carbons are specified following Tie et al. (2009). Emissions rates of individual species within the groups are specified according to their observed relative abundances (Apel et al., 2010). Long-chain n-alkanes are used as surrogates for all emitted semi- and intermediate-volatility organic compounds (SVOCs and IVOCs). Their emitted masses are distributed among pre-defined volatility bins as described in LT11. The NAN scheme yields vapor pressures that are progressively higher with increasing carbon number than are those given by JRMY. Hence, the emissions distribution of individual S/IVOCs required to represent the same volatility distribution differs between the two schemes, and was therefore recalculated for NAN in this study. The 9th and lowest

volatility bin in the emissions ("SVOC1", centered on C* = $1x10^{-2}$ μg m^{-3}, where C* is the effective saturation concentration) corresponds to n-alkane carbon chain lengths of 24-25 under the JRMY scheme but 32-33 for NAN. Precursors in this volatility bin have negligible influence on SOA mass production in LT11, since the ~1% of emitted S/IVOC mass they represent partitions almost exclusively, immediately and irreversibly into the particulate phase as POA. Our current NAN simulations omit emissions from bin SVOC1 to reduce computational load, and specify emissions of n-alkanes up to C30, distributed among 8 volatility bins ranging from $1x10^{-1}$ to $1x10^{6}$ μg m^{-3}. The resulting mechanism describes 10.3 million reactions involving almost 1.8 million species and predicts vapor pressures for 0.73 million non-radicals.

2.2.2 Forest Precursors: Manitou Forest during BEACHON

Our biogenic case study is based on Manitou Forest during the BEACHON-ROCS field campaign of summer 2010 (Ortega et al., 2014). The site is dominated by ponderosa pine, giving an ambient VOC mixture high in monoterpenes and low in typical anthropogenic VOCs such as aromatics, alkanes and alkenes. Emissions are represented via mixing-in of air with specified precursor concentrations based on observations (Kaser et al., 2013b). The precursor mix includes selected monoterpenes (α- and β-pinene at 0.11 ppbv each, limonene at 49 pptv, and carene at 29 pptv). Specified oxygenated C1-4 species include methyl vinyl ketone at 0.25 ppbv and methyl butenol at 0.78 ppbv. Isoprene, alkanes to C6, alkenes to C5, and aromatics are also included, in the proportions shown in Fig. 1b. Our forest case precursor mixture omits sesquiterpenes because our model has not yet been tested for their complex chemistry. Sequiterpenes would likely increase the quantity of SOA formed, however we would not expect significant changes to the timing of downwind SOA formation. Like monoterpenes, sesquiterpenes have lifetimes of the order of an hour or less (Atkinson et al., 1990; Shu and Atkinson, 1995). Changing multi-day formation rates would thus require the lifetimes and SOA yields of second or higher -generation sesquiterpene products (Ng et al., 2006) to greatly exceed those for monoterpenes since sesquiterpene source fluxes are relatively low (of the order of 10% or less of monoterpene fluxes during the BEACHON campaign, Kaser et al., 2013a).

2.3 Meteorological conditions and sensitivity studies

Our box model simulations represent photochemical evolution and aerosol condensation in an air parcel that is advected out of a source region and undergoes chemical processing during several days as part of an outflow plume. We initialize the model in the source region, in an Eulerian configuration with diurnally-varying precursor emissions, boundary layer depth, and meteorological conditions. The spin-up period in the urban scenario is driven with meteorological boundary conditions representative of average conditions in Mexico City in March 2006, as in LT11. For

biogenic simulations, spin-up meteorological conditions were based on previous regional modeling studies (Cui et al., 2014). Ambient temperatures and boundary layer behavior were similar between the urban and biogenic cases. The spin-up phase lasts for just over 1.5 days, into the early afternoon of our "day 1". The model simulation then converts into a Lagrangian or outflow period which continues for an additional 3 and 7 days in the forest and urban base cases respectively. Emissions cease and the air parcel (model box) maintains a fixed volume and meteorology and is subject to continuing photochemistry and to dilution with background air. Outflow period meteorological conditions are discussed below.

Throughout the model simulations we prescribe a chemically-inert background aerosol, to provide a seed for aerosol condensation. This seed aerosol is intended as a surrogate for regional background aerosol including that produced from local sources and from previous days' outflow, and contributes to the mass term in the partitioning equation (Pankow, 1994a). Seed aerosol concentration is 2 μg m^{-3} in the urban case after Hodzic et al. (2009) and Kleinman et al (2008) (corresponding to 6.22×10^9 molec cm^{-3} at a molar weight of 200g mol^{-1}), and 1 μg m^{-3} for the forest case. Unlike species generated by GECKO-A, the inert seed stays at a constant concentration in the outflow since outflow and background concentrations are equal, hence its relative contribution to the total aerosol mass increases with dilution.

For each scenario we perform several sensitivity studies which are initialized with the same Eulerian conditions but diverge at the beginning of the outflow period. Our "base case" simulations continue with constant temperatures of 291K and 288K in the urban and forest scenarios respectively, zero emissions, and a constant e-folding dilution rate k_{dil} of 1 day^{-1}. Outflow conditions begin at 2pm in the forest scenario. In the urban scenario temperature becomes constant and emissions cease at 3pm, and the outflow phase begins at 4pm when k_{dil} becomes fixed.

In the real world, a plume's dilution rates and air temperatures are likely to be heterogeneous, varying diurnally as well as with changing plume altitude. However the sensitivity of photochemistry and gas-particle partitioning in a detailed box model to individual environmental variables is most clearly explored by keeping these parameters constant, varying only one at a time. Warmer temperatures should shift the equilibrium towards the gas phase, potentially reducing particle-phase mass (e.g. if aerosol-forming chemical reactions are not temperature sensitive). Our simulation denoted "T+10K" explores the effect on aerosol mass of an outflow temperature increased by 10 K. Plume dilution might also be expected to lead to lower particle mass, since decreasing gas-phase concentrations shift condensation equilibria in favor of evaporation. Simulation "SLOWDIL" is constrained similarly to the base case, however with the outflow-period dilution rate reduced to 0.3 day^{-1} in the urban case and 0.46 day^{-1} in the forest case. Simulation "NODIL" uses no dilution at all.

Another variable governing the direction of condensation equilibrium is the existing particle mass itself, assuming that Raoult's law applies (Pankow, 1994a). Simulation "SEED/2" reduces seed aerosol mass by 50%, starting from the beginning of the outflow period. Most of our urban outflow simulations inadvertently employed photolysis rates ~20% lower than in LT-11. Rates of photochemical formation and transformation of condensable oxidized products scale with actinic flux, altering the particle mass formation rate. Boundary-layer aerosol pollution reduces actinic flux at the surface but enhances it aloft (Palancar et al, 2013). Simulation "HV+" tests the sensitivity of the particle mass production to increased ambient actinic flux. Effective j(O1D) in case HV+ is about twice that in our urban base case, and about one-third greater than in our forest base case. Finally, simulation "JRMY" is similar to the base case, but with the JRMY vapor pressure scheme, with the S/IVOC emissions adjusted as described above, and with outflow temperatures of 288K. This last sensitivity study was only performed for the urban case. Simulation conditions are summarized in Table 1.

3 Results

3.1 Photochemical Environment

The concentrations of key oxidants simulated within our urban scenario source region have similar profiles to those shown in Figure 3 of LT-11 for Mexico City. (Oxidants are plotted in Figure S.I.1) Peak urban source region concentrations are: [OH] = 3.2×10^6 molec cm^{-3}, [O_3] = 116 ppbv, and [NOx] = 260 ppbv. These values represent highly-polluted urban conditions, where [OH] is suppressed by high [NOx], and are within the range of observations (Dusanter et al., 2009). In the outflow, [OH] increases until stabilizing on day 5 at ~8.5×10^6molec cm^{-3}. Meanwhile, [NOx] drops rapidly to <0.8 ppbv, and O_3 also declines in response to dilution, to ~60ppbv. The forest case shows oxidant concentrations towards the high end of remote observations (e.g. Wolfe et al, 2014): In the forest outflow [OH] is fairly constant at ~ 8×10^6molec cm^{-3}, [O3] decreases from 62 to 50 ppbv and NOx falls to consistently low values (~0.2ppbv).

The reduced-dilution sensitivity runs demonstrate that net O_3 production continues in the outflow, even as its base case concentrations decrease. In case NODIL, O_3 concentrations increase, weakly in the forest scenario to ~70 ppbv on day 4, and strongly in the urban scenario to ~175 ppbv on day 5. NODIL NOx is roughly double base case values in both scenarios, which raises forest [OH] levels slightly (to 9×10^6molec cm^{-3}) but suppresses urban-outflow [OH] to daily maxima of only ~1.3×10^6molec cm^{-3}. Case SLOWDIL produces [O_3] and [NOx] levels intermediate between the base and NODIL values, and [OH] similar to NODIL in the urban scenario and similar to base values in the

forest scenario. In sensitivity case HV+, urban scenario [OH] is doubled, [O_3] is 50% higher, and afternoon [NOx] 50% lower relative to the base case, while the forest scenario has 30% higher [OH], but largely unaffected [O_3] and [NOx]. The urban scenario enhancements continue to high but not unprecedented (Rohrer et al., 2014) peak values of ~17 x10^6molec cm^{-3}, indicating that case HV+ provides a good test of the effects on particle mass formation of accelerated gas-phase photochemistry. Sensitivity studies T+10K and SEED/2 have little or no effect on oxidant outflow concentrations.

3.2 Organic aerosol mass production

Figure 2 shows the development of the condensed organic aerosol generated in our set of urban and pine-forest outflow simulations. Lower panels show simulated concentrations and O/C atomic ratios. The spin-up period shows a strong diurnal cycle in response to diel variations in emissions, photolysis, and ventilation. Once the outflow period begins, particle-phase concentrations first peak in response to photochemistry then generally decline in response to dilution. On day 2 (the first full day of outflow), concentrations show an additional photochemistry-induced increase superimposed on the declining baseline, however by day 3 (the second full day of outflow) chemistry-induced concentration changes are barely discernible in either case.

To quantify the regional OA mass increase in the expanding plume, which is more relevant to net direct climate effects than is local concentration, we integrate the aerosol concentrations over the entire outflow region. Following LT11, we defined M_tOA as the organic aerosol mass in a dispersed air parcel with original volume of 1 m^3, expressed in units of μg initial m^{-3}: $M_tOA = e^{t.kdil}[OA]_t$ where t is time since the start of the outflow phase. $[OA]_t$ does not include the prescribed constant seed aerosol concentration. Contrary to the progressive decreases in downwind aerosol concentrations, M_tOA increases throughout the simulation period, although the two base scenarios show very different production rate characteristics from each other. In our urban base case (Fig. 2a), M_tOA increases from 6 μg initial m^{-3} at the start of the outflow phase by 140% (to ~14 μg initial m^{-3}) in the first 24 hours of outflow, and by a factor of >4 (to 26.5 μg initial m^{-3}) over 4 days. To assess the limits of this production, we continued the simulation for a further 3 days. Particle mass increased asymptotically to a maximum of 28.4 μg initial m^{-3} after about a week. Our forest base case (Fig. 2b) also shows particle mass production, although at a far slower rate. M_tOA begins the outflow phase at 0.8 μg m^{-3} and increases by ~60% (0.5 μg initial m^{-3}) in the first 24 hours of outflow. Thereafter, however, the production rate slows substantially with M_tOA rising by only another 5% (to 1.33 μg initial m^{-3}) during the latter two days of the simulation.

Figure 2 also shows particle mass development for our sensitivity simulations. The largest differences in simulated aerosol plume mass are those produced by changing the vapor pressure scheme (performed for the urban case only). Even within the city, JRMY predicts 50% more mid-afternoon aerosol mass than NAN. Downwind, the JRMY case aerosol increases its mass excess over the NAN case, growing by more than a factor of 3 in two days before reaching an asymptote at about 30 μg initial m^{-3} at the end of day 4, slightly sooner than in the NAN case. The initial primary aerosol concentrations are very similar between the two simulations, reflecting the similar volatility distribution of the prescribed emissions. The mass differences arise during SOA production and may be explained by the large differences in estimated P_{vap} for individual species under the two different methods. For example, estimated P_{vap} values for aromatic oxidation products are generally lower by 1-3 orders of magnitude under JRMY than under NAN. This allows JRMY to condense SOA with a lesser degree of substitution and at an earlier point in the oxidation process and explains both the early relatively rapid production in the JRMY case, and its earlier slowdown as the available gas phase precursors become depleted. We discuss the chemical composition of the growing aerosol in more detail later. One should not read too much into the slightly higher ending mass of the JRMY aerosol, since this run used lower outflow temperatures. The main result here is that the predicted multiday nature of OA mass production is not unique to one particular vapor pressure scheme. The following discussion refers to simulations performed with the NAN scheme only.

The response of the aerosol production rate to environmental conditions is shown in Fig. 2. Particle mass in the outflow plume is rather insensitive to seed aerosol amount, dropping by no more than 5% when the seed aerosol is reduced by 50% (runs “SEED/2”). Raising the ambient temperature by 10°C (runs “T+10K”) lowers the condensed aerosol mass by between 8 and 25% relative to the base simulation. Increasing the available sunlight (run “HV+”) speeds up initial SOA production. The final condensed aerosol mass is unaffected in the forest scenario, but lower by 9% in the urban scenario, likely owing to increased photolytic removal of semi-volatile gases. In all these sensitivity cases, the aerosol mass reductions noted are insufficient to lead to net mass loss in either the urban or the forest scenario.

Slower dilution rates lead to higher aerosol mass concentrations, favoring condensation. In the forest scenario, dilution rate reductions (runs “SLOWDIL” and “NODIL”) give incremental increases in plume-integrated particle mass, as expected. The urban scenario gives a more complex picture. Eliminating dilution entirely (“NODIL”) speeds up initial particle mass production although at longer timescales there is little net mass difference from the base case. However, slowing dilution rates from 1 day^{-1} to 0.3 day^{-1} (run “SLOWDIL”) slows mass production throughout the simulation. This non-monotonic response must result from a combination of factors. In addition to the effect on

concentrations noted above, slower dilution leads to continued NOx-suppression of [OH] as noted above, impacting oxidation rates and SOA yields. In addition, SOA yields respond nonlinearly (e.g. Camredon et al., 2007) to [NOx] (which also varies with dilution rate, see earlier). It is likely coincidental that the combinations of conditions in the NODIL and base cases lead to similar SOA mass production. From the point of view of our sensitivity study however, the general result is that particle mass production integrated over the plume is only slightly sensitive to rather radical changes in the dilution rate. This shows that the SOA production is not an artefact of the numerical integration.

3.3 Particle phase chemical composition and properties

The O:C atomic ratio is one of the most widely-used measures of particle chemical composition and degree of oxidation. O:C ratios for the model-generated particle phase in the two base case runs are shown in the lower panels of Fig. 2. Our urban model-generated OA fraction (Fig 2a, lower) shows O:C rising from 0.17 at the start of outflow to 0.42 after 24 hours and 0.71 after 6 days, indicating a particle phase that becomes progressively more oxidized with time. Our forest model-generated OA fraction shows higher O:C ratios throughout (Fig. 2b, lower), developing from 0.84 to 0.90. The differences between the urban and forest scenarios are consistent with the forest case particle phase being already well oxidized at the beginning of the outflow phase, with delayed chemistry in the urban case outflow resulting from [OH] suppression, and with different precursor assemblages giving differently-oxidised products (e.g. Chhabra et al., 2011).

O:C values are highly sensitive to the aerosol fraction considered. Our simulations use a pre-existing seed aerosol with a mass concentration of 2 (1) $\mu g\ m^{-3}$ in the urban (forest) scenarios respectively. We assign this seed aerosol the same O:C ratio as seen at the end of our forest case (0.9), consistent with a regional background aerosol that is well oxidized and/or of largely biogenic origin (e.g. Hodzic et al. 2010). Including the seed aerosol raises calculated O:C to 0.35 (0.87) at the start of outflow in the urban (forest) cases. The seed aerosol contribution continues to influence the O:C ratio in the outflow, raising urban values to 0.55 after 24 hours and 0.71 after 2.2 days (rather than 7 days). These values are comparable to measurements in Mexico City (0.4-0.73, Aiken et al., 2008; corrected as per Canagaratna et al., 2014), although the strong sensitivity of the O:C ratio to the background aerosol means that model-measurement comparisons are of only limited utility if the background contribution is not known. Our forest scenario values are somewhat higher than measurements during the BEACHON campaign (generally 0.5 - 0.77, Palm et al., 2013), suggesting that our model forest scenario has less anthropogenic influence than does the field data.

The chemical composition of organic aerosol may also be expressed in terms of the average molecular weight per carbon (OM:OC), which includes the mass contributions of substituents such as nitrogen. Typical OM:OC values are 1.6±0.2 and 2.1±0.2 for urban and nonurban areas respectively (Turpin and Lim, 2001). OM:OC for our modeled urban outflow aerosol rises from 1.41 to 2.21 over 7 days, consistent with a progression from urban to nonurban regimes, while OM:OC in our forest outflow case rises only incrementally, from 2.25 to 2.32, in agreement with the published nonurban values.

Examining the evolution of volatility of the particle phase (Fig. 3) shows that particle composition is dynamic in both the urban and forest cases. The particles progressively lose molecules of higher volatility, and gain molecules with lower volatility. The details vary but the net result is that particle phase composition evolves, becoming less volatile with time. This is especially marked in the urban outflow scenario, where the envelope of the volatility distribution shifts to the left by two orders of magnitude.

Figure 4 investigates the molecular composition of the simulated particle phase, in terms of carbon number and extent of functionalization. Particles in the urban case (left hand panels) are initially composed mainly of condensed primary emissions ("POA", species with no functional groups, shown in grey) and SOA formed after one generation of chemistry (species with 1-2 functional groups, shown in red and orange) (Fig. 4a). Figure 4c shows the particle mass distribution after four days of urban outflow. Losses in the grey region centered on C26 show the evaporation of a significant fraction of the primary particle mass. This loss is balanced by a comparable gain in mono- and di-substituted species (red and orange, respectively) with the same carbon numbers, suggesting that the first-generation reaction products of the evaporating primary species are of sufficiently low volatility to partition strongly back to the particle phase. A similar but smaller loss is discernible in the red region around C19, showing re-evaporation also of secondary particle mass. These model results are consistent with measurements by Miracolo et al. (2010) who also found gradual conversion of evaporating POA mass to progressively more oxidized SOA, although on a much shorter time scale in a smog chamber. At lower carbon numbers, mass production occurs after multiple generations of chemistry as shown by the production in species with ≥ 3 functional groups (yellow, green or blue). Indeed, mass gains are found at progressively lower C numbers as time progresses and more highly functionalized products become more abundant. In the forest case (right hand panels) the particle phase shows a relatively high degree of functionalization from the start of the outflow period (Fig. 4b), with most of the contributing species having ≥4 functional groups. Again, the particle phase adds more highly functionalized material during the outflow period (Fig.

4d) and loses small amounts of less-functionalized material. However, the compositional differences between the early- and late-stage particle phases are much less marked than in the urban case.

The long-term particle phase production is much stronger in the urban outflow case than in the forest case, therefore we focus our attention on the urban case with the goal of identifying the compounds that are driving this production. We have already noted that O:C rises throughout the urban outflow simulation. Figure 5 divides the carbon mass in the growing particle phase into fractions based on O:C ratio. The figure shows that the long-term particle mass production is entirely due to more-highly substituted material, with O:C > 0.25. Furthermore, and consistent with Fig. 4, mass-balance considerations show that the majority of this production cannot be explained by the sequence of evaporation, oxidation (possibly including fragmentation) and re-condensation of the less-substituted fractions, since these fractions show comparatively minor losses. The production must therefore be largely due to ongoing incorporation of previously uncondensed material from the gas phase.

Figure 6 and Table 2 illustrate the temporal development of gas-particle partitioning for the urban case. The black lines in the Figure represent the carbon mass in each C# bin at the start of the outflow period, with the lower line representing the phase partitioning at that time between particle (below the line) and gas (above the line). The colors of the sub-bars represent the partitioning after 4 outflow days. Brown shows particulate carbon, green shows gas phase carbon, and white shows the net carbon loss from each C# bin during the outflow period. Carbon is conserved in our model (numerical losses are of the order of 0.1% per model day). The lost fraction in Fig. 6 and Table 2 represents fragmentation which reduces the C# of a molecule, moving carbon to the left and eventually off the figure into species with C# <4. Some general trends are apparent. For the largest, least volatile molecules (C≥22) virtually all the carbon partitions to the particle phase, either initially or during the outflow period. Thus, further carbon mass production in this C# range is limited to small increments from evaporation-oxidation-recondensation cycling. The gas phase reservoir is also essentially depleted for the mid-sized molecules (with C# = 10 - 21). However not all the carbon has partitioned into the particle phase, with a substantial portion (up to 60%) removed by fragmentation. Some initial oxidation is usually necessary for fragmentation to occur. The competition between functionalization and fragmentation shifts in favor of increasing fragmentation for molecules with lower C# for two reasons. First, the branching ratio for CO_2 elimination from peroxy acyl radicals increases with decreasing molecular length (Arey et al., 2001; Chacon-Madrid et al., 2010), and second, longer molecules generally have lower volatility so partition earlier to the particle phase where they are protected from further gas-phase reaction (Aumont et al., 2012). For the smaller molecules (C# = 4 – 9) fragmentation is the major fate with only a few percent of the

carbon in each bin becoming condensed. However, the much greater burden of these precursors in the outflow means that their contribution to outflow SOA is comparable to that from the mid-sized molecules, and allows substantial particle mass production despite the significant losses to fragmentation. Furthermore, a gas phase carbon reservoir persists in this size range allowing the possibility of further particle mass production, if sufficient functionalization can occur.

3.4 Chemical identity of species responsible for the production

The chemical composition of the gas-particle mixture can be explored in detail uniquely with GECKO-A, because it retains the explicit molecular identity of all intermediates and products. Figure 7 shows the time evolution of production rates for different chemical types within the urban outflow particle phase. Production rates fluctuate diurnally in response to photochemistry, showing both a daytime maximum corresponding to the solar-driven cycle in OH and a secondary production peak at sunset originating from nitrate radical chemistry. Mass losses (negative production) also have photochemically-driven diurnal cycles, with aerosol constituents re-volatilizing in response to gas phase removal. The particle phase shows production far exceeding losses for the most abundant individual secondary species and for most groups of similar species.

Figure 7 and Table 3 show that a significant proportion of the production in the urban case is attributable to only a few specific chemical species in our mechanism. Of the 20 most abundant individual species (Table 3), three in particular stand out. The fastest-growing single species during daytime is hydroxy-hydroperoxy-maleic anhydride, or “MALANHYOOH”. It is a major product of the oxidation of several different precursors including toluene and α-pinene, and its production rate is roughly correlated with the increasing trend in noontime [OH]. The chemical pathway involves unsaturated γ-dicarbonyl fragmentation products which recyclize to yield maleic anhydride and then undergo addition reactions with OH and HO_2. This species accounts for about 7% of the particle phase by the simulation end. The fastest-growing species at nightfall is “MNNCATCOOH”, a post-aromatic 4^{th}-generation oxidation product of toluene. It is a peroxide-bicyclic alkene (hereafter denoted “PBA”) with five functional groups: nitrate, nitro, hydroperoxy, and two hydroxy groups. It arises from a sequence of oxidation reactions of toluene culminating in nitrate addition to nitro-di-hydroxy toluene (nitro-catechol), which breaks the aromaticity of the molecule. Its daytime analog, “MNCATECOOH”, is the nitro- hydroperoxide tri-ol, and is the second fastest-growing single species during daytime. Together these three species make up 15% of the particle phase by the end of the simulation. They are also among the most abundant aerosol species in the forest case (Table 4) despite the low abundance of aromatic precursors.

Many of the species in Table 3 arise directly from the aromatic mechanism, taken from the MCM rather than from subsequent chemistry generated by SARs from the GECKO-A code. Only the most favorable reaction channel is represented for each oxidation reaction in MCM, raising the possibility of over-representing the relative abundance of an individual product isomer. To address this, in Fig. 7a we summarize the behavior of products contained in this portion of the mechanism, *i.e.* those which retain a ring whether aromatic or otherwise. We group these species into classes with similar chemical characteristics and behaviors. Class "(M)MAL" represents the sum of MALANHYOOH and the similar methylated species MMALNHYOOH, which is the ninth-fastest contributor to particle mass production (Table 3). Class "5f-PBN" contains the five-functional PBA nitrates while class "5+4f-PB" represents their daytime analogs and includes a ~20% contribution from the four-functional PBAs. (The mechanism contains no nitrated four-functional PBAs). These two classes also include a minor contribution (<10%) from di-nitro PBAs formed via di-nitro cresols. Together, these three classes (M)MAL, 5f-PBN and5+4f-PBN account for ~30% of the aerosol mass production during the first 4 days of the urban outflow simulation, and ~40% over 7 days. Furthermore, their relative mass contributions start small (<5% of aerosol mass) but become progressively greater, reaching ~25% of aerosol mass in 4 days and ~30% in 7 days. Other ring-retaining products play little role. Class "aromatics" represents all species retaining aromaticity, including substituted cresols and catechols, which are formed on day 1 but show small net losses from the particle phase over the first 4 days of outflow (~-0.2 μg/initial m^3), mainly owing to losses of di-nitro-cresols. The final class in Fig. 7a is "others", encompassing epoxides, quinones, two- and three-functional PBAs, and substituted maleic anhydrides other than the two already described (see also Table 3). This group shows rapid particle-phase mass gains on day 1 in most types of its constituents, followed by largely compensating losses on subsequent days.

Particle phase production rates of all other species in the mechanism are plotted in Fig. 7b. POA shows daily net losses, while oxidized species show daily net production peaking around solar noon. We divide the oxidized species into four classes based on carbon number ("C>7" and "C<8") and on whether they include a nitrate or PAN moiety (designated as "N") or not ("noN"). Classes C>7N and C>7noN contribute 33% and 17% respectively to net mass production, while classes C<8N and C<8noN contribute 16% and 5% respectively. Production rates are strong for several days, mainly slowing to zero on or around day 5 with nitrated species showing more sustained production. The larger molecules (C>7), are products of oxidation reactions of aliphatic compounds. Of these, C11-C13 species have the most rapid particle-phase production rates. The smaller molecules (C<8) are products of sequential oxidation and fragmentation reactions of aromatic precursors, with C5 species contributing the most production. In terms of chemical identity, the species in these four

classes are highly diverse, usually containing at least three different functional groups. Most C<8 species with significant production contributions contain at least one PAN or carboxylic acid group, resulting from oxidative addition to a double bond. This is not the case for the major C>7 contributors, many of which contain δ-dicarbonyl, δ-hydroxy-hydroperoxy and/or δ-hydroxy-ketone groups resulting from 1,5 hydrogen migration in alkoxy radicals (Orlando et al., 2003). In addition to the daytime production, C<8N species show sustained nighttime production from nitrate and peroxy chemistry.

The chemical composition of the urban case particle phase is reflected in the shape of its volatility distribution (Fig. 3a). Figure 8 distributes by half-decade in $\log_{10}(C^*)$ the major chemical classes defined above at the end of the urban simulation. Linear and branched species (classes C>7 and C<8) give an approximately lognormal distribution with respect to $\log_{10}$ (C*). Superimposed on this base are peaks attributable entirely to products of aromatic chemistry. The largest peak, around $\log_{10}(C^*)$ = -1.5 is due to the two substituted maleic anhydrides in class (M)MAL. The secondary peak around $\log_{10}(C^*)$ = -3 results from classes 5f-PBand 5f-PBN. Class 4f-PB is more volatile, giving a small shoulder at $\log_{10}(C^*) \approx -0.5$, while the substituted aromatics produce only a tiny bump in the distribution, around $\log_{10}(C^*) = 2$.

The top 10 species in the forest particle phase are listed in Table 4. The biogenic precursors (a- and b-pinene, and to a lesser extent limonene, isoprene, and carene) give rise to a large variety of condensable oxidation products, as shown by the small mass contributions of even the most abundant species. The maximum individual contribution is only 2.4%, and the top 10 species together account for <14% of the particle mass. The forest case aerosol is highly diverse, with species having both 4- and 6- member rings as well as ring-opened species and fragmentation products. Every species listed contains at least one hydro-peroxy group, reflecting the HO2-dominant chemistry of this case study. Nitrated species account for about one-third of the mass. The multi-generational product MALANHYOOH appears as the 10th most abundant aerosol species.

4 Discussion and conclusions

Our results show that particle mass production in an outflow plume is a robust feature of our model. The production is largely insensitive to reasonable variations in the seed aerosol amount, temperature, photolysis and dilution rates; rather it appears to be a function of the identity and photo-oxidation pathways of the chemical precursors. In our forest outflow case, high O:C ratios within the plume (Fig. 2) show that the monoterpene precursors are already well oxidized by the time the outflow portion of the simulation begins. While the gas and particle phases continue to be in dynamic equilibrium and the chemical details of their composition evolve over time, there is little

change in the total particle mass in the forest case beyond the first few hours of outflow. By contrast, the initial suppression of [OH] in our urban outflow case combined with the longer oxidation lifetimes of the urban precursor mix ensures that the anthropogenic precursor mixture is only partially oxidized. Early increases in modeled urban outflow OA mass are consistent with observations (e.g. Moffett et al., 2010, who found carbon mass increases of >40% per particle over 6 hours in the Mexico City plume). The chemistry continues to mature over several days, allowing the total particle mass to grow by a factor of >4 outside the source region. The particle mass production results from multigenerational chemistry operating on gas phase precursors that persist in equilibrium with the particle phase even as the outflow plume dilutes into the surrounding region. In an equilibrium model, particle phase production rates necessarily reflect both gas phase production/loss rates and volatility. As species are depleted in the gas phase, our simulations also show their loss from the particle phase (e.g. in the case of the "other" aromatic compounds in Fig. 7). However, in both our urban and forest cases these losses are balanced by fresh condensation of other molecules and/or evaporation-oxidation-condensation processes so that the particle phase volatility distribution shifts to lower vapor pressures and becomes progressively less vulnerable to re-evaporation.

Particle-phase mass production in our urban simulation is attributable in roughly equal proportion to oxidation products of light aromatic and long-chain n-alkane precursors. Dodecane has been shown in laboratory photo-oxidation experiments to produce SOA with fourth and higher generation products under low-NOx conditions (Yee et al., 2012; Craven et al., 2012). These experiments were performed over relatively long timescales (up to 36 hours) and yielded cumulative OH exposures up to about $1x10^8$ molec cm^{-3} hr, similar to the 3-day OH exposure experienced by our base case urban aerosol (~$1.5x10^8$ molec cm^{-3} hr). The production in aerosol mass we predict from 4- and 5-functional products of C11-C13 n-alkanes during the first half of our simulation is, therefore, consistent with laboratory results. We use long-chain n-alkanes in this study as surrogates for the wealth of different alkane species emitted in anthropogenic situations (Isaacman et al., 2012; Fraser et al., 1997; Chan et al., 2013). This seems a reasonable approximation since n-alkanes have been shown in several laboratory studies (Lim and Ziemann, 2009a; Yee et al., 2013; Loza et al., 2014) to give SOA yields intermediate between those of branched and of cyclic alkanes, owing to differing OH reaction rates and to the increased (decreased) propensity of branched (cyclic) alkanes to undergo fragmentation. Our model reproduces this behavior (Aumont et al., 2013). Using a more diverse anthropogenic precursor mix from that assumed here could alter the modeled particle-phase production rates and resulting mass, in either direction, but is unlikely to eliminate the production. Therefore these

qualifications do not detract from our central result that the particle phase continues to grow for several days downwind of the urban source.

We have identified two specific classes of oxidation products of light aromatics, the substituted maleic anhydrides and 5-functional peroxide-bicyclic alkenes (including those with and without nitrate), as major contributors to the SOA production especially in the later days of the simulation. Their delayed influence in the evolving urban outflow is consistent with greater SOA yields from aromatic species under low-NOx conditions as observed by Chan et al. (2009) and Ng et al. (2007). In the present urban outflow study, these multi-generational products together contribute roughly 30% of the particle phase production. Admittedly, our calculations use the NAN vapor pressure scheme far beyond the list of species for which it was validated. However, even if their vapor pressures are underestimated by 1-2 orders of magnitude, these products should be sufficiently involatile to partition strongly to the particle phase (see Fig. 7). We suggest that the substituted maleic anhydrides and 5-functional peroxide-bicyclic alkenes might be useful targets for observational studies seeking to validate our prediction of multiday anthropogenic aerosol production. The fact that only a few species classes contribute such a large proportion of our predicted particle mass production also affects the volatility distribution of the developing aerosol, so that it deviates from a simple lognormal shape. If it can be shown that these species types are indeed important contributors to regional anthropogenic-origin SOA, it will be important to parameterize their volatility distributions for inclusion in regional and global models of aerosol development.

Parameterizing SOA formation for routine modeling use is a complex task, and beyond the scope of this paper. Our results can, however, offer some insight. First, and as might be expected, our results illustrate that biogenic, aliphatic anthropogenic, and light-aromatic anthropogenic SOA precursors may be regarded as three distinct classes based on the timescales of resulting SOA mass development and the shapes of the product vapor pressure distributions. Within each of these broad groupings, there is considerable variability of product volatility and chemical characteristics, and GECKO-A has already been used to parameterize correlations for use in 3D models, e.g., between effective Henry's Law constant and volatility (Hodzic et al., 2013 and 2014), between volatility and mean oxidation state (Aumont et al., 2012) and between carbon number and polarity (Chung et al., 2012). The specific insights given by these studies should contribute to mechanism parameterization efforts.

In this study we do not address loss processes that could affect the particle mass in a plume. Explicit chemistry simulations have found dry deposition to be more important than wet deposition (Hodzic et al., 2014). Dry deposition reduces anthropogenic –origin SOA by 15% -40% and biogenic –origin

SOA by 40-60% over regionally-relevant timescales, and depending on model conditions and assumed boundary layer depth (Hodzic et al., 2013, Hodzic et al, 2014). Other possible conversion processes include in-particle accretion reactions (Barsanti and Pankow, 2004), heterogeneous oxidation (George and Abbatt, 2010a; Smith et al., 2009; Molina et al., 2004), photolysis (Nizkorodov et al., 2004), and multiphase chemistry (Pun and Seigneur, 2007; Ervens and Volkamer, 2010; Lim and Ziemann, 2009b). These processes which become increasingly important at longer timescales could either increase or decrease particle mass, affect particle hygroscopicity (e.g. George and Abbatt 2010b), and will also likely increase the SOA O:C ratio (e.g. Heald et al, 2010).

If our results are generalizable to outflow from anthropogenic sources worldwide, the multiday particle mass production we predict from explicit chemical considerations represents a large but diluting secondary source which is not easily discerned in concentration data. This has implications for the radiative forcing (RF) of climate by anthropogenic organic aerosols. For example, Smith and Bond (2014) recently attributed most RF by organic particles to human-caused biomass burning, with current annual emissions of 17.4 Tg C yr^{-1}. Their assessment relies on the assumption that these OA are purely scattering in the shortwave spectrum, with RF per unit mass comparable to that of sulfate aerosols. Our results, on the other hand, suggest a much larger regional contribution from SOA of urban origin, specifically from the use of fossil fuels comprised in large part of aromatics and long-chain alkanes. The remarkable production shown in Fig. 2(a) would lead to a much larger anthropogenic contribution to the regional - and possibly global - burden of SOA, and their associated RF.

A crude estimate shows that large increases in anthropogenic SOA are plausible when viewed together with long-term anthropogenically-driven increases in tropospheric ozone. Northern Hemisphere tropospheric background ozone has increased from pre-industrial values around 10 ppb (Volz and Kley, 1988) to 30-40 ppb (Oltmans et al., 2013). While their precise precursors and formation/removal pathways differ, both tropospheric O_3 and SOA are byproducts of the NOx-catalyzed photo-oxidation of hydrocarbons, and are indeed highly correlated in urban observations. Examples of correlation slopes vary from30 $\mu g\ m^{-3}\ ppm^{-1}$ in Houston to 160 $\mu g\ m^{-3}\ ppm^{-1}$ in Mexico City (e.g. Wood et al., 2010), and application of these slopes to the NH industrial-era increase in background O_3 would correspond to background SOA concentration increases of 0.6-3.2 $\mu g\ m^{-3}$. A simple extrapolation over the entire NH in a 1 km PBL implies a hemispheric burden of 0.15-0.8 Tg, and, assuming a 10 day lifetime e.g. (Kristiansen et al., 2012), an annual production rate of 5-30 Tg $year^{-1}$. Thus it is evident that regional SOA of urban origin have a large potential to modify RF on much larger scales. Unfortunately the optical properties of these SOA particles remain largely unknown; empirical evidence is mounting for strong absorption in the near UV (Kanakidou et al.,

2005; Barnard et al., 2008; Lambe et al., 2013) and possibly visible wavelengths as particles age (Updyke et al., 2012), consistent with the presence of complex chromophores such as conjugated carbonyls formed by particle-phase oligomerization (which is not currently represented in our model). The combined uncertainties from the regional production and optical properties of anthropogenic SOA cast some doubt on their current representation in global models.

We note also that, in contrast to the anthropogenic SOA, biogenic SOA does not seem to show strong multiday regional production. Given that biogenics represent over 90% of global VOC emissions, even moderate production would have had a large impact on the total SOA budget and would likely yield unrealistically high global SOA concentrations. Anthropogenic VOCs, on the other hand, are shown by our study to have a potentially much larger sphere of influence than previously suspected. Of course we acknowledge many assumptions and approximations inherent in our study, and so we put forward our conclusions tentatively and semi-quantitatively, but with hopefully a clear message that further study is urgently needed to resolve these issues and increase confidence in our understanding of how humans are affecting Earth's climate.

Author contributions

J. Lee-Taylor, S. Madronich and A. Hodzic designed the study. J. Lee-Taylor and A. Hodzic performed the simulations. All co-authors contributed to model development. J. Lee-Taylor prepared the manuscript with contributions from all co-authors.

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1 Table 1. List of sensitivity simulations

Name	Conditions: urban (forest)
Base case	T = 291 K (288 K), dilution rate = 1 day^{-1}, seed aerosol = 2 μg m^{-3} (1 μg m^{-3}), NAN vapor pressures, no dry deposition
T+10K	Outflow temperature = 301 K (298 K)
SLOWDIL	Dilution rate in outflow = 0.3 day^{-1} (0.46 day^{-1})
NODIL	Dilution rate in outflow = 0 day^{-1} (both scenarios)
SEED/2	Seed aerosol = 1 μg m^{-3} (0.5 μg m^{-3}) during outflow
HV+	Increased photolysis : j(O1D) ~100% (~35%) higher
JRMY	Uses JRMY vapor pressures (urban case only), outflow T = 288K

2

Table 2. Carbon partitioning budget timeseries for the urban outflow simulation. Values are assessed at midnight on the days indicated. Losses are assessed relative to 4pm on day 1. Values < 100 are rounded to either two significant figures or two decimal places.

day	Particle phase carbon (mgC initial m^{-3})				Gas phase carbon (mgC initial m^{-3})				Net carbon loss (mgC initial m^{-3})			
	C4-C9	C10-C15	C16-C21	C22-C30	C4-C9	C10-C15	C16-C21	C22-C30	C4-C9	C10-C15	C16-C21	C22-C30
1	0.88	0.61	1.9	1.8	171	7.3	2.1	0.29	4.0	0.12	0.04	0.01
2	1.9	1.6	2.7	2.0	146	5.5	1.0	0.14	27	1.0	0.25	0.01
3	2.4	2.5	3.1	2.0	122	3.5	0.48	0.07	52	2.1	0.47	0.02
4	3.3	3.2	3.2	2.1	92	1.4	0.17	0.03	80	3.4	0.67	0.03
5	4.0	3.5	3.1	2.1	65	0.44	0.07	0.02	107	4.2	0.81	0.04
6	4.3	3.4	3.1	2.1	47	0.19	0.05	0.01	125	4.5	0.90	0.05
7	4.5	3.3	3.0	2.1	36	0.11	0.04	0.01	136	4.6	0.96	0.06

Table 3. The top 20 contributors to modeled particle-phase production over the first 4 days[1] of the urban outflow simulation.

Rank	Formula	Unique SMILES[2] name	Class[3]	Notes/ MCM name[4]	Precursor	p_{vap} (atm)	Contribution to production Day 1	Day 4	4 days
1	$C_4H_4O_6$	OOC1C(O)C(=O)OC1=O	MMAL	MALANHYOOH	aromatics	$6.1E^{-12}$	2.2%	23.0%	9.6%
2	$C_7H_8O_{11}N_2$	CC12OOC(C1O[N](=O)=O)C(=C(O)C2(O)OO)[N](=O)=O	5f-PBN	MNNCATCOOH	toluene	$1.3E^{-13}$	0.9%	15.1%	5.9%
3	$C_7H_9O_9N$	CC12OOC(C1O)C(=C(O)C2(O)OO)[N](=O)=O	5f-PB	MNCATECOOH	toluene	$2.6E^{-13}$	0.2%	8.5%	3.1%
4	$C_5H_8O_6$	CC(=O)C(O)C(OO)C(O)=O	C<8	fragment[5]	aromatics	$2.5E^{-11}$	0.8%	0.2%	1.2%
5	$C_5H_7O_9N$	OOCC(=O)C(O)C(O)C(=O)OO[N](=O)=O	C<8,N	fragment	aromatics	$2.7E^{-12}$	0.5%	1.3%	1.2%
6	$C_8H_{10}O_{11}N_2$	CC12OOC(C)(C1O[N](=O)=O)C(O)(OO)C(=C2[N](=O)=O)O	5f-PBN	MXNNCATOOH	m-xylene	$1.0E^{-13}$	0.4%	1.1%	1.1%
7	$C_5H_8O_6$	CC(=O)C(OO)C(O)C(O)=O	C<8	fragment	aromatics	$2.5E^{-11}$	0.8%	-	1.1%
8	$C_8H_{10}O_{11}N_2$	CC1=C(O)C(O)(OO)C2(OOC1(C)C2O[N](=O)=O)[N](=O)=O	5f-PBN	OXNNCATOOH	o-xylene	$9.5E^{-14}$	0.2%	1.8%	1.1%
9	$C_5H_6O_6$	CC1(OO)OCOC(=O)C1O	MMAL	MMALNHYOOH	aromatics	$5.9E^{-12}$	-	4.1%	1.0%
10	$C_8H_{11}O_8N$	CC1=CC(O)(OO)C2(OOC1(C)C2O)[N](=O)=O	4f-PB	TM124NOOH	1,2,4 TMB	$2.9E^{-11}$	-	2.8%	0.9%
11	$C_7H_7O_{12}N_3$	CC12OOC(C=C([N](=O)=O)C1(O)OO)(C2O[N](=O)=O)[N](=O)=O	5f-PBN	NDNCRESOOH	toluene	$3.0E^{-14}$	1.4%	0.9%	0.9%
12	$C_5H_5O_{13}N_3$	OOCC(C(O[N](=O)=O)C(=O)OO[N](=O)=O)C(=O)OO[N](=O)=O	C<8,N	fragment	aromatics	$2.2E^{-11}$	1.1%	-	0.9%
13	$C_5H_7O_8N$	CC(=O)C(O[N](=O)=O)C(OO)C(O)=O	C<8,N	fragment	aromatics	$1.9E^{-11}$	1.5%	0.2%	0.8%
14	$C_8H_{10}O_{11}N_2$	CC1=C(O)C(O)(OO)C2(C)OOC1(C2O[N](=O)=O)[N](=O)=O	5f-PBN	PXNNCATOOH	p-xylene	$9.5E^{-14}$	0.2%	1.1%	0.7%
15	$C_{11}H_{21}O_7N$	CCC(CCC(O)CC(=O)CCCOO)O[N](=O)=O	C>7,N	isomers[6]	undecane	$6.8E^{-13}$	0.2%	0.9%	0.7%
16	$C_8H_{10}O_{11}N_2$	CCC12OOC(C1O[N](=O)=O)C(=C(O)C2(O)OO)[N](=O)=O	5f-PBN	ENNCATCOOH	e-benzene	$3.4E^{-14}$	-	1.4%	0.6%
17	$C_8H_9O_{12}N_3$	CC1=C([N](=O)=O)C2(OOC(C)(C2O[N](=O)=O)C1(O)OO)[N](=O)=O	5f-PBN	NDNMXYLOOH	m-xylene	$1.9E^{-14}$	-	0.5%	0.6%
18	$C_6H_9O_8N$	CC(=O)C(C)(OO)C(O[N](=O)=O)C(O)=O	C<8,N	fragment	aromatics	$1.3E^{-11}$	0.8%	0.3%	0.5%
19	$C_7H_9O_8N$	CC12OOC(C1O)C(O)(OO)C(=C2)[N](=O)=O	4f-PB	TL4ONO2OOH	p-xylene	$2.2E^{-11}$	-	1.6%	0.5%
20	$C_{12}H_{23}O_7N$	CCCC(CCC(O)CC(=O)CCCOO)O[N](=O)=O	C>7,N	isomers	dodecane	$2.0E^{-13}$	0.1%	0.6%	0.5%
				Total[7] contribution to production			11.3%	65.4%	32.7%

Notes: [1]Days as used in this table are 24-hour periods beginning at 4pm. [2]Unique SMILES notation is based on the original definition of Weininger (1988) and referenced online at http://cactus.nci.nih.gov/translate/, February 2014. [3]Class names are defined in the text. [4]MCM names follow the notation of Jenkin et al. (2003); Bloss et al. (2005b), as referenced online at http://mcm.leeds.ac.uk/MCM, February2014. [5]Fragmentation products shown here all have

several different aromatic precursors. [6]Isomer lumping protocol is described by Valorso et al. (2011) and Aumont et al. (2008); [7]The remainder consists of species whose individual contributions are not in the top 20.

Table 4. The top 10 contributors to modeled particle mass at the end of the forest outflow simulation

Rank	Formula	Unique SMILES[1] name	Notes	Precursor	p_{vap} (atm)	Contribution to mass
1	$C_{10}H_{18}O_5$	CC1(C)C(CCO)C(OO)C1C(=O)CO	6-member ring opened	β-pinene	$7.7E^{-12}$	2.4%
2	$C_5H_{12}O_6$	CC(OO)C(O)C(CO)OO	Fragment	terpenes	$2.7E^{-12}$	2.0%
3	$C_{10}H_{18}O_6$	CC(C)(C(CCO)OO)C(C=O)C(=O)CO	fully opened	β-pinene	$1.8E^{-13}$	1.5%
4	$C_{10}H_{17}O_7N$	C(C)(OO)C1CC(=O)CCC1(CO)O[N](=O)=O	4-member ring opened	β-pinene	$5.8E^{-12}$	1.3%
5	$C_5H_{12}O_6$	CC(CO)(OO)C(O)COO	Fragment	limonene, isoprene	$2.7E^{-12}$	1.2%
6	$C_{10}H_{17}O_8N$	CC1(C)C2(O)CC(O[N](=O)=O)C(C)(OO)C1(C2)OO	2 rings, 4 substituents	α-, β-pinene	$8.3E^{-14}$	1.2%
7	$C_{10}H_{17}O_8N$	CC(C)(OO)C(CCC(=O)CO)CC(=O)OO[N](=O)=O	fully opened	β-pinene, limonene	$5.1E^{-12}$	1.1%
8	$C_{10}H_{17}O_7N$	CC(C)(C(CCO)O[N](=O)=O)C(C=O)C(=O)CO	fully opened	β-pinene	$3.4E^{-12}$	1.1%
9	$C_{10}H_{16}O_9N_2$	CC1(C)C2(O)CC1(CC(O[N](=O)=O)C2(C)O[N](=O)=O)OO	2 rings, 4 substituents	α-pinene	$1.7E^{-12}$	1.0%
10	$C_4H_4O_6$	OOC1C(O)C(=O)OC1=O	MALANHYOOH[2]	aromatics	$6.1E^{-12}$	0.9%
				Total contribution to mass		13.6%

Notes: [1]Unique SMILES notation, see Table 2. [2]MCM name, as in Table 2.

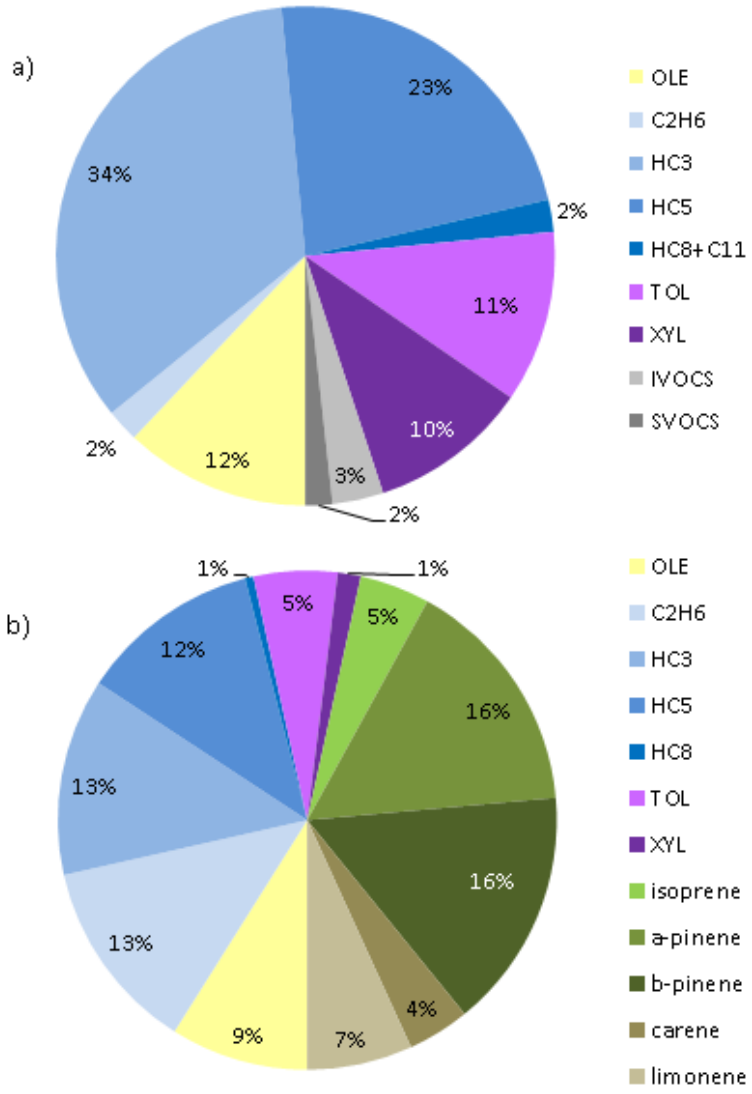


Figure 1. Precursor NMHC mass distributions for the outflow simulation runs. a) Urban case emissions by mass. Total emissions are 2.6 g m^{-2} day^{-1}. Species classes correspond loosely to those of the RACM mechanism (Stockwell et al., 1997), and the volatility-based nomenclature of Donahue et al. (2009). "OLE", olefins; "C2H6", ethane; "HC3", propane and similar species ; "HC5", n-pentane and similar species; "HC8+C11", n-alkanes with 8 to 11 carbons, and cyclohexane; "TOL", toluene, benzene, and ethyl benzene; "XYL", xylenes, trimethyl benzenes, and ethyl toluene; "IVOCS", n-alkanes with 12 to 17 carbons; 'SVOCS", n-alkanes with 18 to 30 carbons. Branched alkanes constitute 16% and 66% of the mass in classes "HC3" and "HC5" respectively. b) Forest case precursor inputs. Species classes are as in a). Inputs shown total 0.23 g m^{-2} day^{-1}. Inputs of oxygenated C1-4 species are omitted for clarity, and comprise an additional 0.7 g m^{-2} day^{-1} including 0.2 g m^{-2} day^{-1} from methyl vinyl ketone and methyl butenol.

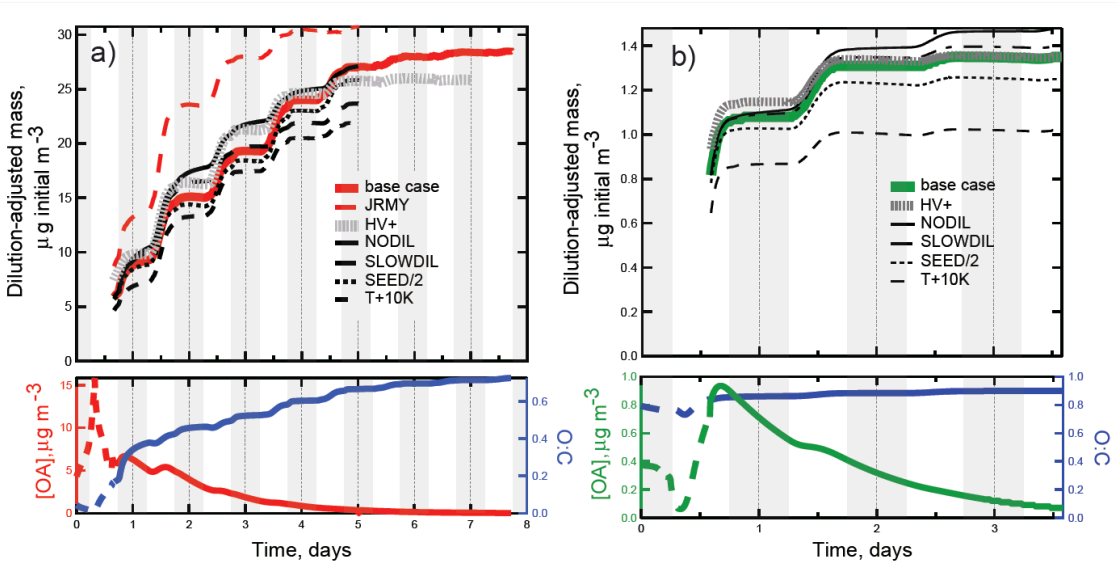


Figure 2. Simulated aerosol development for the a) urban and b) forest cases. Upper panels show plume-integrated mass during the outflow phase, lower panels show concentrations and O:C ratios for the model-generated aerosol fraction in the source regions and outflow phases. Grey shading indicates approximate night-time periods.

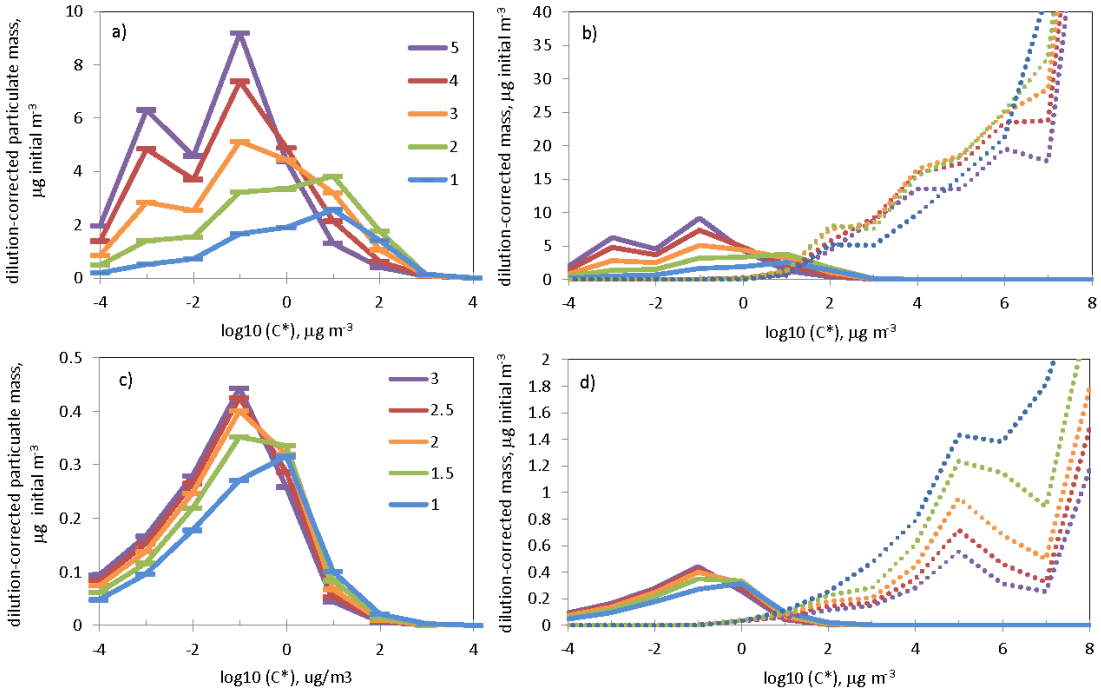


Figure 3. Time evolution of volatility distributions. a) and b) urban case; c) and d) forest case. Solid lines, particle phase; dotted lines, gas phases. Colors represent different times (see key): whole numbers are midnight values (e.g. “1” = midnight between days 1 and 2), and half-day numbers are noon values (e.g. “1.5” = noon on day 2). The volatility continuums have been binned in decadal increments for ease of comparison with so-called Volatility Basis Set (VBS) parameterizations.

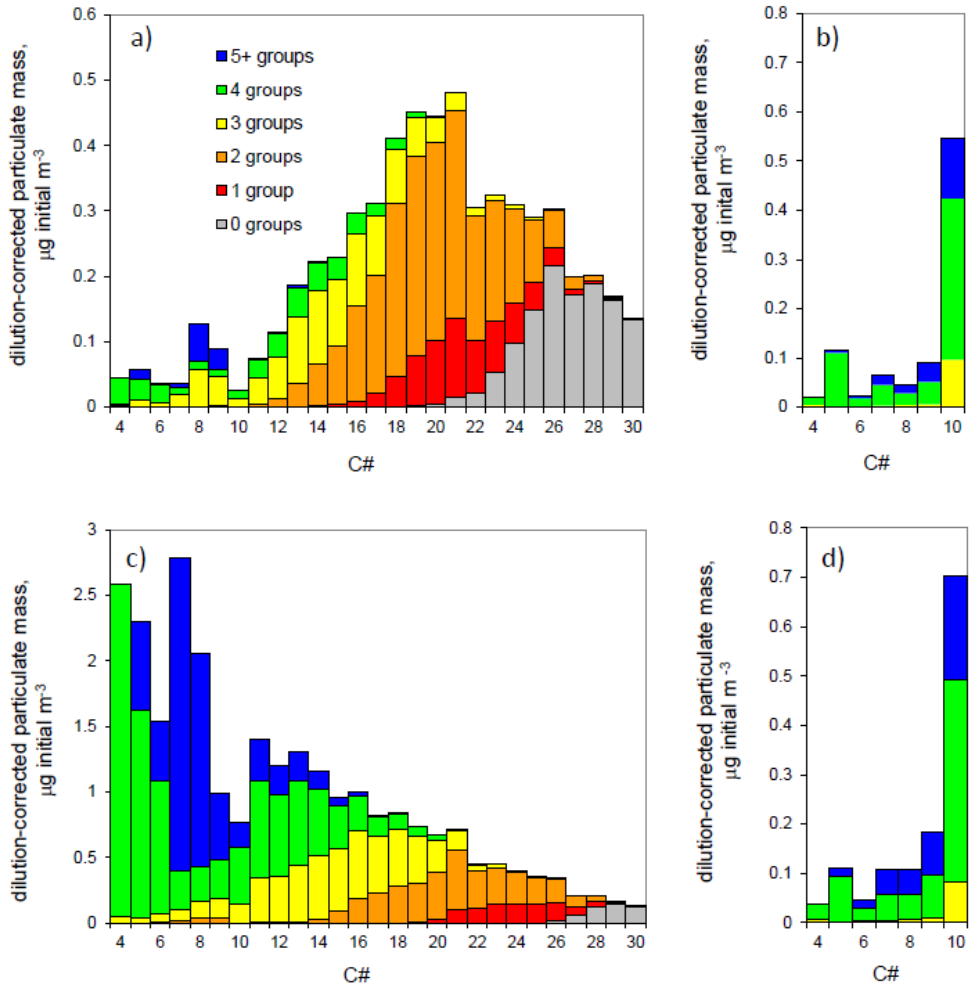
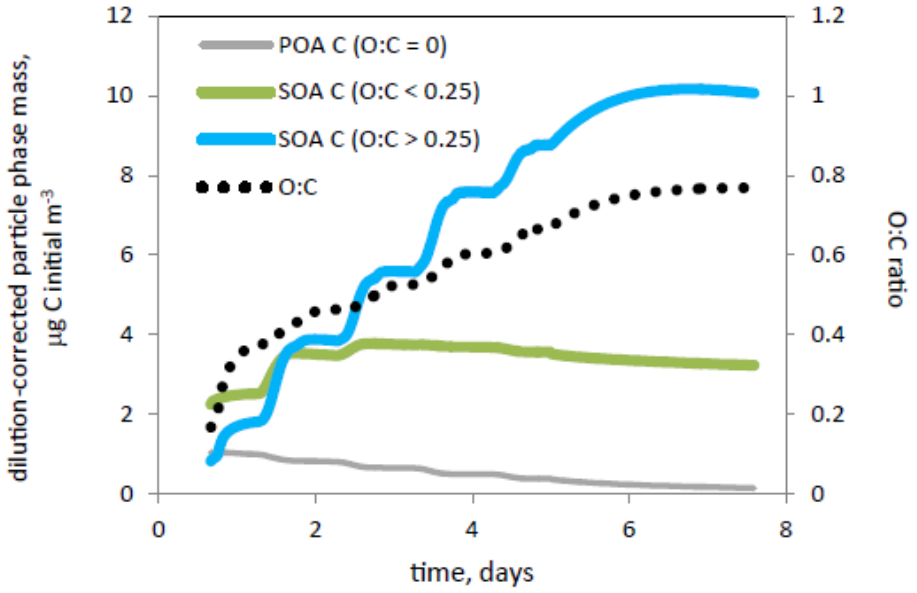


Figure 4. Particle mass composition binned by carbon number and number of functional groups per constituent molecule. a) urban case at start of outflow phase; b) forest case at start of outflow phase; c) urban case after 4 days; d) forest case after 3 days.



1

2 Figure 5. Evolution of the O:C ratio in the particle phase, for the urban case. Left axis and solid lines:
3 plume-integrated carbon mass of particle phase fractions, segregated by O:C ratio. Right axis and
4 black dotted line: O:C ratio of the entire particle phase.

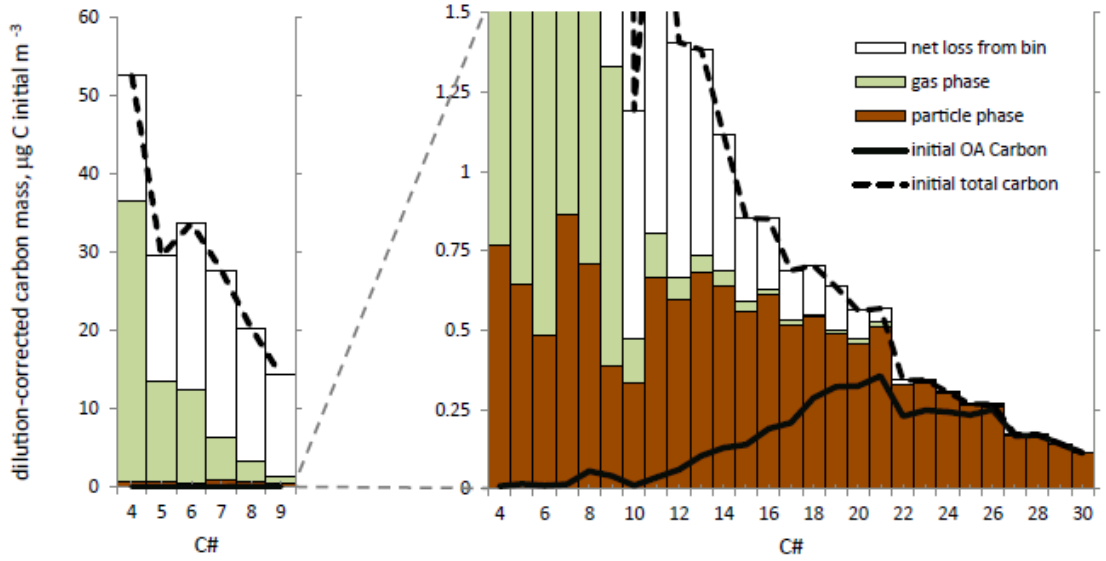


Figure 6. Carbon partitioning budget during the urban outflow simulation. Black lines show the gas (dashed line) and particle (solid line) phases at the start of outflow. Stacked bars show partitioning after 4 days: brown, particle phase; light green, persisting gas phase; white, net loss to fragmentation. Carbon numbers 4 to 9 are plotted twice, on different scales, to allow the details of the partitioning to be seen more clearly.

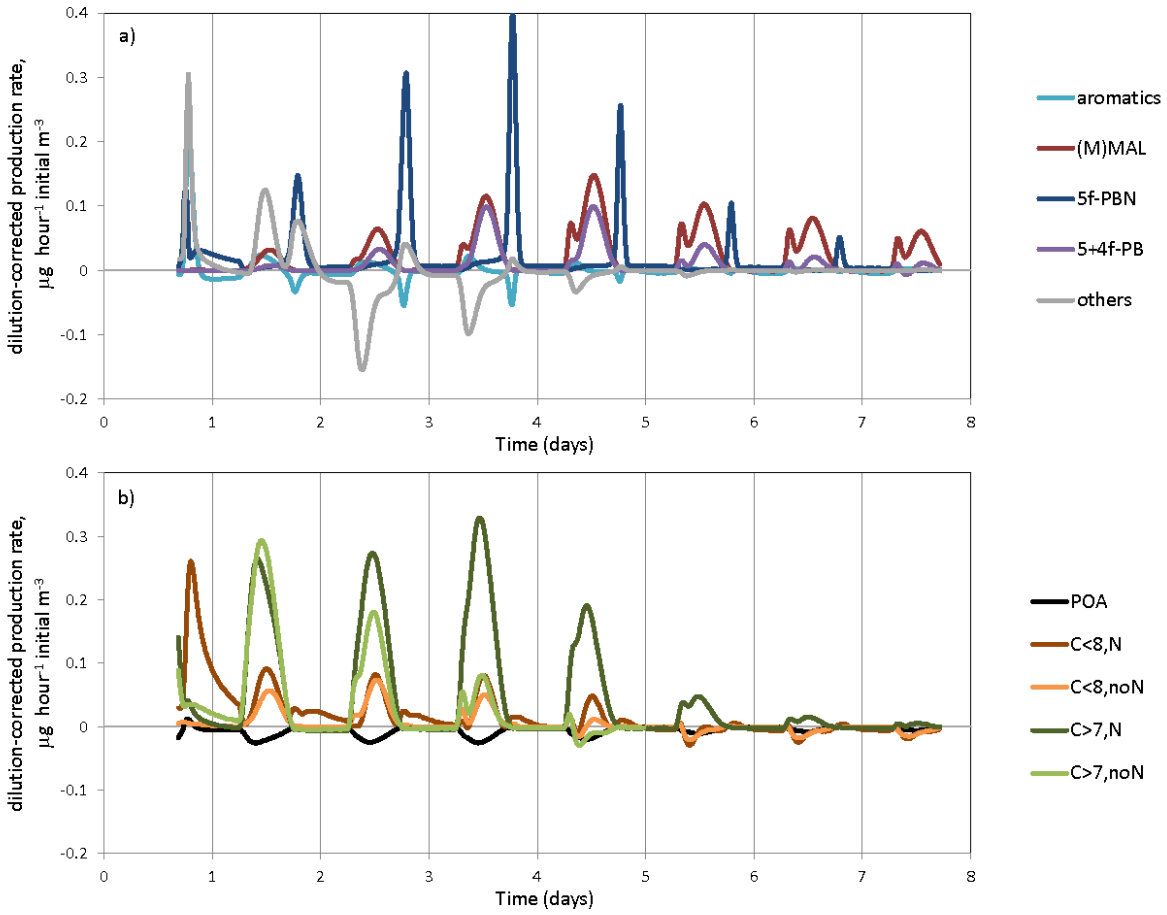


Figure 7. Hourly production rates of all species in the urban case particle phase, aggregated by broad chemical characteristics. a) Cyclic products of aromatic precursors; b) all other species. Colors show species groupings. See text for details.

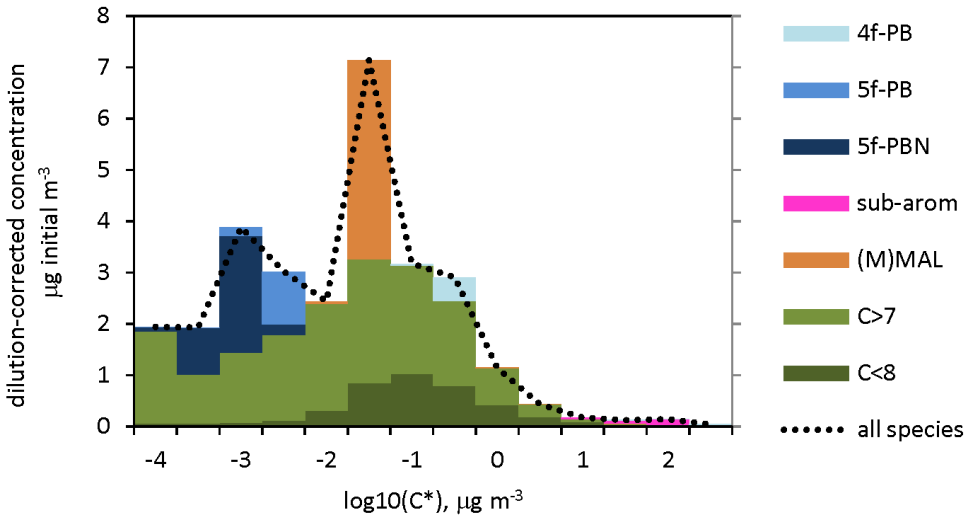


Figure 8. Chemical composition of the particle phase at the end of the urban outflow simulation, distributed by volatility. Colors show species groupings as discussed in the text: "C<8" and "C>7", linear/branched molecules separated by carbon number (no distinction for nitrate is made here); "(M)MAL", substituted maleic anhydrides; "sub-arom", substituted rings that retain aromaticity; "5f-PBN", PBAs with 5 functional groups including nitrate; "5f-PB", as 5f-PBN without nitrate; "4f-PB", PBAs with 4 functional groups. Dotted line shows total particle phase mass. The leftmost bin also includes the mass from species with $\log_{10}(C^*)$ <-4.