Is Secondary Organic Aerosol Yield Governed by Kinetic Factors Rather Than Equilibrium Partitioning?

Chen Wang[1], Frank Wania[1], and Kai Uwe Goss[2,3*]

[1]Department of Physical and Environmental Sciences and Department of Chemistry, University of Toronto Scarborough, 1265 Military Trail, Toronto, ON, M1C 1A4, Canada

[2]Department of Analytical Environmental Chemistry, Centre for Environmental Research UFZ Leipzig-Halle, Permoserstraße 15, Leipzig, D-04318, Germany

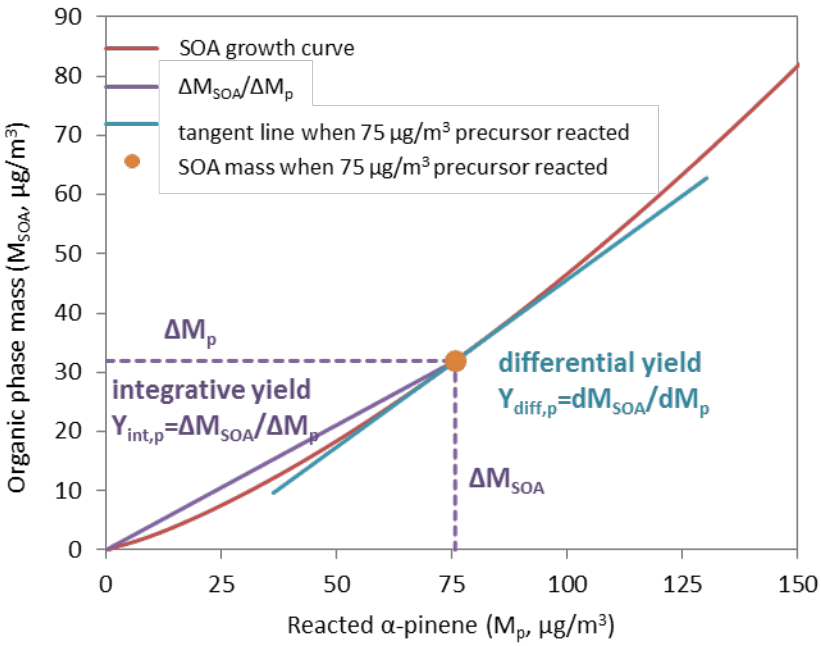
[3]Institute of Chemistry, University of Halle-Wittenberg, Kurt-Mothes-Straße 2, Halle, D-06120, Germany

[*]Corresponding author: kai-uwe.goss@ufz.de, ++49 341 235 1411

Environmental Significance

Secondary organic aerosol (SOA) comprises a major fraction of atmospheric fine particles. Predicting the formation of SOA in atmospheric models is essential for evaluating their influence on climate and human health. SOA yield as an important parameter describing the efficiency of a precursor in generating aerosol materials in chamber studies, has been proposed and used for decades, despite its limitations when applied to the ambient atmosphere. A complex and dynamic system, the atmosphere´s (gas and particle) composition is a result of competing kinetics of continuous emissions as well as chemical and physical processing. In this work, we emphasize the significance of the dynamic nature of the atmosphere and suggest the use of the differential SOA yield when describing SOA formation in realistic scenarios. We demonstrate the importance of the differential SOA yield with a model approach using the α-pinene SOA system as an example.

Graphical Abstract



Abstract

The numerical description of the formation of secondary organic aerosol (SOA) in the atmosphere relies on the use of particle yields, which are often determined in chamber experiments. What is sometimes not appreciated is that such yields (i) can be defined in different ways and (ii) depend on atmospheric conditions. Here we show with the help of hypothetical scenario simulations that the differential SOA yield upon addition of oxidation products to an atmosphere already containing such products and SOA is more relevant in the ambient atmosphere than the commonly used integrative yield from chamber studies. Furthermore, we suggest that the SOA formation scenarios that have been studied so far comprise merely a subset of possible atmospheric situations. In particular, while in the standard scenarios factors such as volatility and aerosol loading are important, scenarios can be envisaged where these factors become less important while the differential yield approaches unity for all oxidation products. Finally, we suggest aerosol growth in the atmosphere should be seen as being determined by a dynamic situation arising from many simultaneously occurring kinetic processes rather than a thermodynamic equilibrium process.

1. Introduction

As a major component of atmospheric fine particles, secondary organic aerosol (SOA) plays a significant role in atmospheric processes relevant to climate and human health. [1] One of the primary goals of SOA research is the prediction of the quantity of SOA being formed, which is a major challenge because of the complex composition and constant transformation of compounds in the atmosphere. [2] The concept of particle yield is central in this effort. Studying simplified systems using both experimental and computational methods contributes to our understanding of the amount and composition of SOA formed in the atmosphere. [3]

Laboratory studies relying on smog chambers often examine SOA formation and aging processes of individual precursors to understand their relative contributions in regional and global SOA budgets. They can be conducted in batch or continuous flow mode. [4] Precursor compounds are introduced into a chamber and oxidized at specific conditions (temperature, RH, oxidants, light, seed particles, etc.). At the end of the experiment (usually when the SOA concentration reaches a plateau because of a decrease in precursor concentration), the formed particles are characterized and a SOA yield is derived. Flow reactors have also been employed to study SOA formation. [5, 6] Such studies improve the understanding of SOA formation under relatively simple and controllable conditions, but do not completely represent realistic atmospheric conditions. Limitations of such techniques include limited residence time, insufficient levels of oxidation, and the wall loss of gas phase compounds and particles. [5, 7]

Models of SOA formation usually also rely on simplifications. [1] One common simplification is to ignore individual molecular species and instead use surrogates to represent the complex mixtures present in aerosol. These models, including the two-product model and the volatility basis set (VBS) approach, predict SOA mass based on volatility distribution of oxidation products experimentally derived in chamber studies. [8, 9] More recently models have been developed that take into consideration the molecular identity of the particle-forming compounds. [10-15] Such models predict SOA formation without relying on experimental SOA parameterizations. However, computational requirements currently limit the application of these more explicit approaches and prediction of SOA formation in most operational, large-

scale models relies on either the two-product model or VBSs. [16-19] Therefore, the models, too, may be affected by the limitations of the chamber studies that generated the parameters calibrating those approaches.

Here we will argue that some of the paradigms in SOA-formation-research need to be revisited. The concept of SOA yield needs to be clarified because the integrative yield that is commonly determined from chamber experiments (i.e. the mass of SOA produced per mass of reacted precursor) is different from the differential yield (i.e. the mass of SOA formed upon addition of oxidation products to an atmosphere already containing such products and SOA) and the latter is more relevant in the ambient atmosphere. Jiang [20] first introduced such a concept under the name "instantaneous SOA yield" in 2003. He defined a mathematical expression of this new concept and applied the two-product form of the equation to calculate SOA yield in chamber experiments. Here, we try to introduce this concept again using the term "differential yield" which we find more intuitive. We do not aim to calculate the differential yield using mathematical formulas as have been introduced and discussed by Jiang, [20] instead our objective is to raise awareness that the scenarios for which SOA yields have been studied experimentally so far are not necessarily those that are realistic in an atmospheric context. Most approaches to obtaining SOA mass in chamber studies do not account for the dynamic nature of SOA formation, i.e., the process of continuous emission and oxidation of precursor compounds and its effect on the gas-particle partitioning of the oxidation products and thus the formation of SOA. In a more realistic scenario, SOA precursors are continuously emitted to the atmosphere, which usually contains a considerable amount of particles, volatile organic compounds (VOCs), and semi-volatile organic compounds (SVOCs). There are potentially large uncertainties when applying SOA parameterization (based on either two-product model or VBS) from unrealistic experimental scenarios to the ambient atmosphere. In this study, we use a hypothetical experiment to study a scenario of SOA formation in which precursor is supplied and oxidized continuously. This is not necessarily more realistic than the scenarios studied in the literature already but it shows that other scenarios might be possible and that in these other scenarios SOA formation might follow other rules than those deemed important so far. In addition, with our modeling approach, we were able to investigate the differential yield for individual SOA

forming compounds with different properties and their varying behavior upon changes of the atmosphere (especially a compositional change of the absorbing phase). Finally, we argue that SOA formation can only be understood correctly if it is viewed as a result of many competing kinetic processes.

2. Method

Our approach considers a hypothetical scenario involving a parcel of the atmosphere (1 m^3, containing a fixed amount of water and ammonium sulfate) that is assumed to receive a mixture of oxidation products of α-pinene ozonolysis (of constant composition, details in Table S1 and Figure S1), yet experiences neither loss of chemicals and particles nor is being diluted with clean air. SOA is formed from the equilibrium partitioning of those products between the gas and the condensed phase, which is assumed to separate into an organic-enriched phase and an aqueous-electrolyte enriched phase. 1 µg aliquots of the mixture of oxidation products are added to the atmospheric parcel repeatedly (for a total of 200 times), and are allowed to achieve equilibrium partitioning after each addition step. The longer this model "experiment" runs, the more is SOA yield and composition expected to differ from the very beginning of the experiment. By explicitly considering the molecules involved in SOA formation we can investigate the SOA yield of individual oxidation products with different volatilities and the yield change upon addition of more oxidation products. We disregard time in this hypothetical scenario because we (i) focus on the formation of SOA as a function of the amount of added oxidation products/precursors and (ii) assume instantaneous equilibrium partitioning between gaseous and particulate phase.

The gas-particle partitioning equilibrium calculations were performed using the commercial software COSMO*therm*,[21, 22] as described previously in Wang et al..[10] The focus here is on the calculated yields, and the procedure used for quantifying gas-particle partitioning is secondary and therefore only provided in the supplementary information.

3. Results

3.1 Definition of SOA Yield

The concept of SOA yield is an important parameter in modeling the formation of SOA. SOA yield ($Y_{int,p}$) is often defined as the amount of SOA formed (ΔM_{SOA}) from certain amount of precursor reacted (ΔM_p).[8, 23] We call this an **integrative yield** based on reacted precursors ($Y_{int,p}$):

$$Y_{int,p} = \Delta M_{SOA} / \Delta M_p \quad (1)$$

Another way to define the **integrative yield** ($Y_{int,op}$) is to describe the SOA mass formed (ΔM_{SOA}) from certain amount of oxidation products (ΔM_{op}) , i.e. the fraction of oxidation products that end up making SOA mass:

$$Y_{int,op} = \Delta M_{SOA} / \Delta M_{op} \quad (2)$$

Because the reaction yield of each oxidation product of α-pinene was assumed constant in this study (Table S1) and the ratio between the mass of oxidation products formed (ΔM_{op}) and the mass of α-pinene reacted (ΔM_p) is 1.32 (calculated from reaction yield in Table S1), $Y_{int,op}$ equals 1.32 $Y_{int,p}$ for this study.

However, in the atmosphere formation of aerosol is continuous, without an explicit beginning and end. An integrative yield cannot be a suitable parameter for describing this ongoing aerosol formation process. What is needed instead is the yield, which describes how much aerosol is formed in the system upon addition of reaction products at its actual state. Accordingly, we define the **differential yield** (Y_{diff}) as the fraction that partitions to the organic phase (dM_{SOA}) when a small amount of oxidation products (dM_{op}) is added to the system at a specific loading of the atmosphere.

$$Y_{diff,op} = dM_{SOA} / dM_{op} \quad (3)$$

The differential yield can also be calculated with respect to the reacted amount of precursor, which is the yield of SOA ($Y_{diff,p}$) after a small amount of precursor has reacted (dM_p).

$$Y_{diff,p} = dM_{SOA} / dM_p \quad (4)$$

The curves showing the growth of the SOA organic phase mass during the iterations of our hypothetical experiment (Figure 1a) illustrate the difference between integrative and differential yield. The slope of the purple line in Figure 1a represents the integrative yield. The

first derivative of the growth curve (i.e. the tangent of the red line in Figure 1a) represents the differential yield at this point of the curve, which is the slope of the blue line in Figure 1a. Figure S3 similarly displays the total mass of SOA formed against the reacted amount of precursor. The integrative and differential yields based on oxidation products and reacted precursors for our hypothetical experiment are plotted in Figure 1b. SOA yields are also plotted against total organic phase mass and compared with laboratory generated yields as chamber studies usually report SOA yields at different aerosol loadings (Figure S4 and S5). There is a general agreement between our prediction and laboratory studies, showing increasing yields with increasing SOA loading (Figure S5). Interestingly, because the SOA growth curve is convex, the differential yield is always higher than the corresponding integrative yield (see also Jiang [20]). This is because the slope of the tangent line at one point is always larger than the slope of the line from this point through the origin.

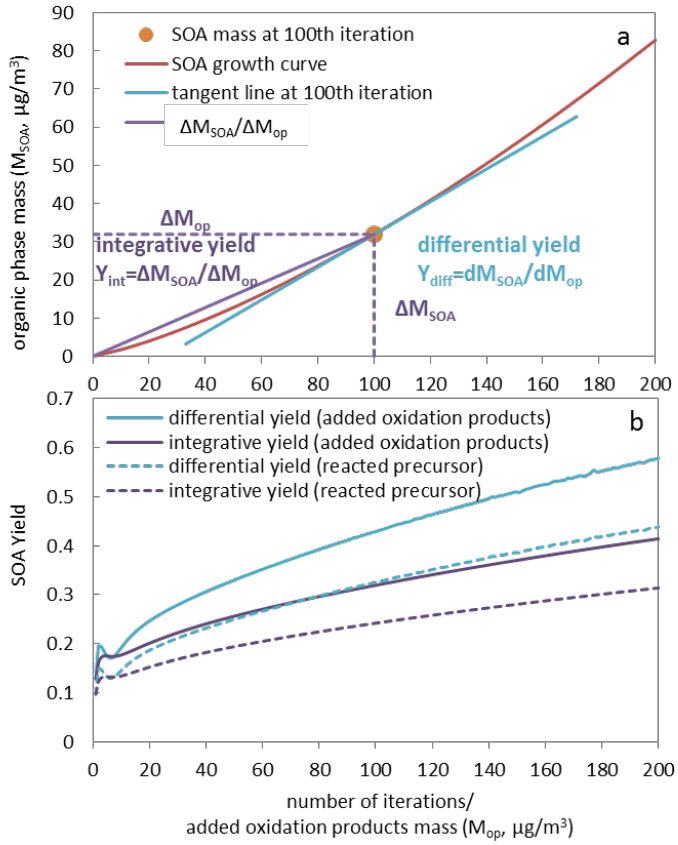


Figure 1 Organic phase mass (red curve in panel a) and SOA yields (panel b) as a function of the number of iterations. The x-axis also represents the total mass of oxidation products added to the

system (μg/m^3). In panel a, the orange dot shows the organic phase mass at the 100th iteration. The slope of the blue and purple lines shows the differential and integrative SOA yield, respectively. In panel b, both integrative yield (purple lines) and differential yield (blue lines) are calculated without including the aqueous phase. Water as a component in the organic phase is included. The dashed lines are SOA yields based on the amount of reacted precursor, which differ from the yields based on added oxidation products (solid lines) by a factor of 1.32.

The aqueous phase's contribution to the aerosol loading is quite small and becomes relatively insignificant as the mass of the organic phase increases for the α-pinene SOA system (Figure S2). In the discussion and comparison of SOA yields, the aqueous phase contribution to the overall SOA yield is therefore not included, i.e., the term SOA yield refers to the yield in the organic phase, which usually dominates overall SOA growth, especially at higher loadings. However, for other aerosol systems, the contribution of aqueous phase and multiphase chemistry can be significant, such as glyoxal SOA, for which aqueous phase chemistry, i.e. reactive uptake other than equilibrium partitioning, needs to be considered. Note that below we are using the differential yield based on oxidation products.

Similar to the definition of overall differential and integrative yields in equations (1) to (4), we can define the yield for an individual compound i based on the added amount of this oxidation product as follows:

$$Y_{diff,i} = dM_{SOA,i} / dM_{op,i} \quad (5)$$

$$Y_{int,i} = \Delta M_{SOA,i} / \Delta M_{op,i} \quad (6)$$

where $Y_{diff,i}$ is compound i's differential yield, that is the SOA formed ($dM_{SOA,i}$) from a small amount of added compound i ($dM_{op,i}$), and $Y_{int,i}$ is the integrative yield for compound i defined as the ratio of SOA formed ($\Delta M_{SOA,i}$) when $\Delta M_{op,i}$ of compound i has been added.

3.2 Hypothetical SOA Formation Experiment

In the ambient atmosphere SOA is formed constantly with no clearly defined start or end. Oxidation products are continuously formed in an atmosphere that already contains particles of various loadings, compositions and sizes (which are quite different from seed particles used in chamber experiments) and at the same time particles are subject to constant removal by wet or

193 dry deposition, evaporation or condensation due to temperature change, or dilution or
194 concentration by mixing processes. Thus realistic atmospheric conditions are quite different
195 from the scenarios that have typically been studied in the lab. The scenario we describe here, in
196 which oxidation products are constantly added to an atmosphere, is not a realistic scenario
197 either, because, for example, it ignores particle deposition and disregards the element of time.
198 Nevertheless, it helps to explore the range of possible scenarios in aerosol formation and how
199 they may differ from scenarios that have been studied so far.

200 In order to do this, 15 α-pinene oxidation products, which are continuously added to an
201 atmosphere as described in the Methods section, partition into aerosol particle phase to form
202 SOA. At equilibrium the mass of compound i (i= 1 to 15) in the organic phase ($M_{SOA,i}$) can be
203 described by the following equations when partitioning into an aqueous phase is ignored:

204 $$M_{SOA,i} = M_{op,i} / (1 + 1/(K_{org/gas,i} \cdot M_{SOA}/\rho)) \quad (7)$$

205 $$M_{SOA} = \sum(M_{SOA,i}) \quad (8)$$

206 where $M_{SOA,i}$ is the amount of compound i in the organic phase (µg/m^3), $M_{op,i}$ is the amount of
207 oxidation product i in both gas and condensed phase (determined by the reaction yield and the
208 precursor concentration), $K_{org/gas,i}$ is the organic-gas phase partition coefficient of compound i
209 (in unit of m^3 air /m^3 organic phase), M_{SOA} is total organic phase mass in µg/m^3 and ρ is the
210 density of the organic phase (µg/m^3). By calculating the SOA mass formed cumulatively from
211 the total amount of products added, the integrative SOA can be derived. These equations show
212 that the SOA yield depends on the partition properties of the reaction products and the
213 sorptive affinity of the organic phase which both enter into the partition coefficient. In addition,
214 the yield also depends on the amount of the existing organic mass (M_{SOA}), which initially is the
215 organic seed and later is the sum of all compounds that have partitioned to the organic phase.
216 For the purpose of our hypothetical experiment, we had to apply equations 7 and 8 iteratively
217 in small steps because $K_{org/gas}$ changes in the process due to aerosol composition change and
218 M_{SOA} depends on the aerosol composition itself. Note, that while the differential yield is given
219 by the first derivative of equation 7, we cannot evaluate this derivative of M_{SOA} to M_{op}, because
220 $K_{org/gas}$ and M_{SOA} are complex functions of the actual scenario under consideration. Jiang [20]

221 derived an equation to calculate the instantaneous yield mathematically on the basis of the
222 Odum two product model without considering the complexity of SOA formation scenarios in
223 the ambient atmosphere. Knipping et al. [24] commented on the limitation of the equation and
224 instead recommended a direct partitioning based approach. We agree with Knipping et al. [24]
225 that neither can a realistic yield be directly calculated from an analytical expression nor can
226 aerosol formation in an air quality model be simply represented using parameterizations from
227 unrealistic experimental studies. Instead we have used a direct partitioning based SOA
228 algorithm as also favored by Knipping et al.. [24] Although SOA yield may not be a necessary
229 parameter in realistic atmosphere and in explicit models, the concept of a differential yield is
230 useful to analyze and compare various scenarios and oxidation products in their efficiency to
231 produce secondary aerosols.

232 To study the contribution of an individual oxidation product to the growth of SOA and the
233 influencing factors, the growth curve of individual compounds, the SOA composition and the
234 individual SOA yield are plotted in Figure 2. Generally, both the differential and integrative SOA
235 yields increase with increasing number of iterations (Figure 2c and 2d). The differential yield for
236 each component is always higher than the integrative yield, except for C20H30O18, and the
237 difference is larger for more volatile compounds (See Figure S6). There are some fluctuations in
238 the first few iterations, which are due to the initially rapid compositional change (as shown in
239 Figure 2b). During the first few iterations the change of phase composition depends on the
240 composition and mass of the organic seed assumed to be present initially (see SI). However,
241 these initial conditions quickly lose their influence on the partitioning properties when the SOA
242 mass increases.

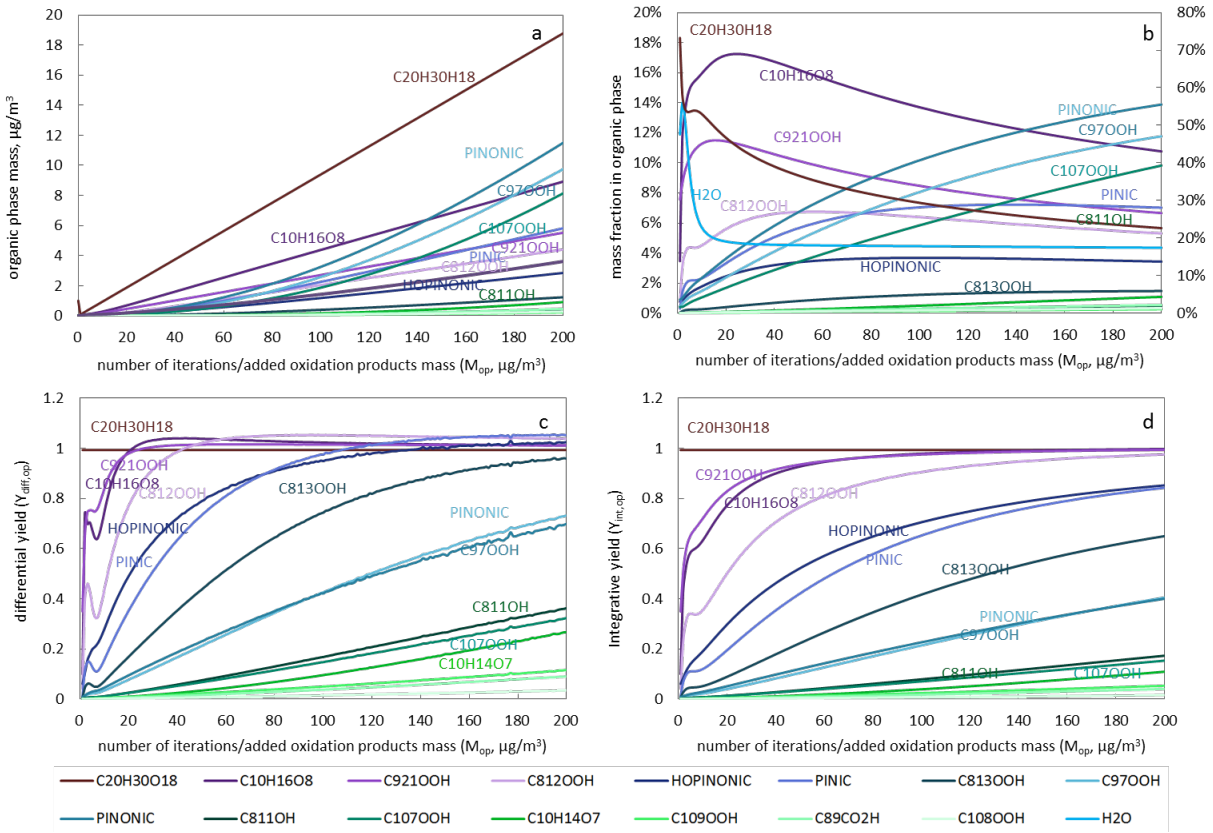


Figure 2 Organic phase mass (panel a), composition (panel b), differential and integrative yields (panel c and d) as a function of the added oxidation products (same as number of iterations). In panel b, the mass fraction of C20H30O18 is shown on the right y-axis. Major contributors to the particles are labeled with their names.

C20H30O18, an extremely low volatile compound (ELVOC), has a differential yield of 1 at different SOA loadings (the dark red line in Figure 2c). Similarly, the integrative yield is also 1 (Figure 2d). This is reasonable because as long as it is formed it will prefer the condensed phase due to its extremely low volatility. The partitioning behaviour of such ELVOCs is largely independent of vapor pressures or partitioning coefficients and existing particle mass and composition. Thus, the difference between their differential and integrative yield is small. Even though C20H30O18 has a very low reaction yield (molar yield in Table S1), it is still the dominant component in the organic phase due to its high $K_{org/gas}$ (Figure S7). Its contribution is decreasing as more SVOC compounds with lower $K_{org/gas}$ start to partition into the condensed phase at higher organic phase loadings (Figure 2b). These SVOC such as C107OOH, PINONIC and

C97OOH have relatively high reaction yields (molar yield of 0.2385, 0.140 and 0.115 in Table S1). The mass fraction of these three compounds in the particulate phase is increasing from the first to the last iteration (Figure 2b).

Some compounds, such as C10H16O8, C921OOH, C812OOH, and after the 100th iteration also HOPINONIC and PINIC, have differential yields exceeding 1, i.e., the amount of a compound that partitions to the organic phase is higher than the amount added in that iteration. The "excess" amount is compound from previous iterations that had been stored in the gas phase but that now partitions into the particle phase in addition to the amount just added. Reasons for differential yields above 1 are the increasing loading of the organic phase and a changing organic phase composition that becomes more favorable for some of the compounds. For instance, there is an increase in $K_{org/gas}$ (and a decrease in activity coefficient) for C10H16O8, C812OOH and PINIC with more iterations (Figure S7 and S8), indicating that the particle phase composition becomes more favourable for their solvation. Obviously, the differential yield of any compound that transitorily exceeds unity has to drop back to unity eventually at higher loadings. The integrative yield can never exceed 1 (Figure 2d).

Once a compound starts to build up higher and higher gas phase concentrations, more of any additionally added amount of this compound will sorb to the condensed phase no matter its volatility. The volatility of a compound only determines when it reaches a differential yield of 1, with less volatile compound reaching that threshold earlier. For example, in Figure 2c the ELVOC C20H30H18 reaches a differential yield of 1 immediately after it starts to form particles and the differential yield for other relatively low volatility compounds such as C10H16O8, C921OOH, C812OOH (with log $K_{org/gas}$ higher than 11 in Figure S7) increases quickly to 1 and above. Eventually, when enough gas phase species have accumulated and when the SOA loading is high, even relatively volatile compounds will approach a very high differential yield. While this may seem counter-intuitive at first, it becomes clearer if one realizes that any single compound continuously added to a finite gas phase will eventually approach its saturation vapor pressure and from that point onwards any additionally added amount would condense into its own liquid pure phase i.e. have a differential yield of unity, no matter how volatile it is

and no matter how much particulate phase is available. Because SOA formation involves organic mixtures, eventually not a pure phase of a single chemical is formed but an azeotropic mixture. The "saturated" gas phase concentrations at which every newly formed product immediately and completely "condenses" into the azeotrope are typically much smaller than the saturation vapor concentrations of all the single components themselves. Compounds with $K_{org/gas}$ (or vapor pressures) differing by orders of magnitude will eventually have similar differential yields if the particulate phase comes close to an azeotropic mixture. For example, C20H30H18, C10H16O8, C921OOH, C812OOH, HOPINONIC, PINIC and C813OOH all have differential yields around 1 at the 200th iteration, even though their $K_{org/gas}$ varies from 10^{10} to 10^{19} (Figure S7). If we had continued our calculations in Figure 2 much further then eventually all oxidation products, even the most volatile ones, would have reached a differential yield of unity and the particulate phase would have become an azeotrope mixture whose composition would not change any more when more oxidation products (of constant composition) were added. In this situation the growth of the particle phase would be identical to the addition of oxidation products so that compounds with highest reaction yields would also dominate aerosol formation. This agrees with the statement from Seinfeld and Pankow [25] that "the SOA yield approaches a constant value as the amount of particulate organic into which the gaseous products absorb reaches large values, and this asymptotic amount is determined purely by reaction stoichiometry". Apart from the widely known aerosol loading effect as proposed by Seinfeld and Pankow, [25] we were also able to demonstrate the effect of changing composition (i.e. the activity of organic products in the condensed phase) and gas phase accumulation on SOA formation.

4. Discussion

A realistic scenario of SOA formation has to consider that usually different levels of oxidation products have accumulated in the gas phase, precursors are emitted constantly and new oxidation products are formed continuously. Figure 2 illustrates that neither the yield nor the composition of gas and particle phase at higher loadings can be easily extrapolated from those measured at lower loadings or vice versa. The formed SOA mass will be higher than traditionally

calculated based on chamber experiment fits (either using the two product model or the VBS approach) by using the differential yield, when considering the continuous emission of precursors and their oxidation products in the atmosphere.

Conventional chamber experiments aid in understanding reaction pathways and kinetics but they are not providing the SOA formation parameters most relevant to the situation in the real atmosphere. That situation is dynamic, i.e., varies temporally and spatially with different loadings of particles and gas phase compounds. When oxidized compounds are formed in a clean atmosphere without many pre-existing particles, low volatility compounds will partition to the condensed phase first and the formed particles consist of compounds with low volatility. Relatively volatile products will remain in the gas phase. In this situation the differential SOA yield for individual products depends strongly on their partition coefficient and the concentration of already available sorbing particles. The total yield (i.e. integrated over all reaction products) depends on the individual yields weighted by the mole fraction that they contribute to the sum of all reaction products. Thus, quite different total yields are to be expected for different types and amounts of seed particles but also for different reaction pathways that may lead to various species and amounts of oxidation products.

While the particle grows, more volatile compounds start to partition and contribute to SOA and thus the SOA yield for individual compounds increases (Figure 2c). This is similar to oxidation products being emitted to an atmosphere with some pre-existing particles. For example, partitioning of the compounds to the particles at the 80th iteration is very different from partitioning into the initial particle, because of the different mass (24 µg vs. 0.5 µg) and composition (Figure 2a and 2b) of the organic phase. In the extreme, the scenario eventually converges towards a situation where all oxidation products have a differential yield of unity independent of their volatility and independent of the amount of available sorbing phase. In this final state the composition of the particle approaches that of an azeotrope mixture and the products with the highest reaction yields govern particle growth.

In general, we can conclude that close to the source of precursors and with a stable atmosphere (limited mixing and removal), e.g. a smog situation, the atmosphere is likely to

build up substantial gas phase concentrations of partitioning species and thus achieve rather high yields. The type and amount of existing SOA then has diminished influence on the yield and even the volatility of the reaction products will become less important. If the atmosphere is rather clean, well mixed and further away from the emission of precursors, the SOA formation might be closer to that in the chamber experiments. In summary we conclude that there might exist scenarios in the atmosphere in which the differential SOA yield is not as dependent on compound volatility and existing particle mass as has been indicated by chamber experiments and theoretical investigations previously.

5. Looking forward

Figure 2 illustrates how much the equilibrium partitioning of oxidation products between gas and particle phase can change if more and more oxidation products are added. The curves in Figure 2 change somewhat for different temperatures, relative humidity and/or with different precursors/oxidation products. However, all of these curves still do not resemble the situation in the real atmosphere, because the dimension of time is ignored in our “experiment”. The concentration of gaseous organic compounds depends on their emission or formation rate in the air compared to the removal rate by sorption, mixing, reaction or deposition. Similarly, while particles are formed and grow, they are - at the same time - removed from an air parcel by gravitational settling or washing out or they are exchanged with neighboring air parcels by turbulent mixing. A realistic treatment cannot separate these processes from the formation of particles because the amount of existing particles has an immediate feedback on the formation of new particles. In order to understand aerosol formation in the atmosphere in qualitative and quantitative terms, it will therefore be necessary to consider the kinetics of many relevant processes even if one finds that the partition process itself is so quick that it can still be treated as an instantaneous equilibrium. If an air parcel can be considered stable for a while, a steady-state situation may arise for which a differential yield could then be calculated. It might be quite challenging though to establish where this steady-state is located, because it requires knowledge of the emission rate of precursor gases and primary particles, the reaction rate constants for all relevant reactions of the precursors, as well as the rate constants for

370 atmospheric mixing, dry and wet deposition, and particle coagulation. Such an analysis will have
371 to consider the simultaneous existence of particles of differing size and composition, which also
372 differ in their growth and elimination.

373 Due to the non-linear nature of many of the involved processes, rather small changes in the
374 boundary conditions may lead to different, stable steady-state situations. Note that SOA
375 parameterization based on single or a few chamber experiments (i.e. using the volatility
376 distribution obtained from chamber experiments in the treatment of SOA formation in most
377 current atmospheric models, e.g. the two-product or VBS approach) may not describe SOA
378 growth in such a kinetically controlled system in a meaningful way. Such kinetically controlled
379 systems are far from the thermodynamic considerations that dominate the discussion of
380 aerosol formation in the literature. We believe research on SOA formation needs to focus on
381 these kinetic questions and problems. It will be an interesting but also highly demanding task to
382 unravel the factors that dominate aerosol formation in the real atmosphere. For example,
383 recent studies have investigated the sensitivity of SOA evolution to different processes and
384 parameterizations, including emissions, removal processes (such as dry deposition, photolysis
385 and heterogeneous chemistry) and particle-phase transformation of SOA to low volatility, which
386 demonstrate that SOA is a far more dynamic system and a subset of complex and uncertain
387 processes are governing the lifecycle of SOA. [26-28] The ultimate goal is to identify mechanisms
388 and processes that could be most influential in affecting evolution of SOA and to understand
389 how different parameters contribute to the overall uncertainty.

390 It is unrealistic to assume the composition and volatility distribution of the oxidation products
391 in the chamber experiments is the same as in the ambient atmosphere for a specific precursor.
392 Instead, a direct and explicit prediction of SOA formation is required [24]. Nevertheless, there is
393 still a use for the SOA yield as a quantitative measure in comparing the efficiency of aerosol
394 formation under different scenarios for different precursors. In this context it is certainly
395 important to acknowledge that the differential yield is preferable over the integrative yield.

Acknowledgement

We acknowledge financial support from the Natural Sciences and Engineering Research Council of Canada, an Ontario Graduate Scholarship and a Special Opportunity Travel Fellowship from Department of Chemistry at University of Toronto. We thank Arthur Chan and Jon Abbatt for comments on our manuscript. C.W. is grateful for Stephen Wood's help with coding.

Electronic Supplementary Information

Additional information on the description of method, information for the organic compounds, aqueous phase composition, comparison with laboratory studies, contribution of water in the organic phase, comparison with previous studies, and additional tables and figures referenced in the text is provided in Electronic Supplementary Information.

References

1. M. Hallquist, J. C. Wenger, U. Baltensperger, Y. Rudich, D. Simpson, M. Claeys, J. Dommen, N. M. Donahue, C. George, A. H. Goldstein, J. F. Hamilton, H. Herrmann, T. Hoffmann, Y. Iinuma, M. Jang, M. E. Jenkin, J. L. Jimenez, A. Kiendler-Scharr, W. Maenhaut, G. McFiggans, T. F. Mentel, A. Monod, A. S. H. Prevot, J. H. Seinfeld, J. D. Surratt, R. Szmigielski and J. Wildt, *Atmospheric Chemistry and Physics*, 2009, **9**, 5155-5236.
2. M. Glasius and A. H. Goldstein, *Environmental Science & Technology*, 2016, **50**, 2754-2764.
3. E. A. Bruns, I. El Haddad, A. Keller, F. Klein, N. K. Kumar, S. M. Pieber, J. C. Corbin, J. G. Slowik, W. H. Brune, U. Baltensperger and A. S. H. Prévôt, *Atmos. Meas. Tech.*, 2015, **8**, 2315-2332.
4. J. E. Shilling, Q. Chen, S. M. King, T. Rosenoern, J. H. Kroll, D. R. Worsnop, K. A. McKinney and S. T. Martin, *Atmos. Chem. Phys.*, 2008, **8**, 2073-2088.
5. A. T. Lambe, P. S. Chhabra, T. B. Onasch, W. H. Brune, J. F. Hunter, J. H. Kroll, M. J. Cummings, J. F. Brogan, Y. Parmar, D. R. Worsnop, C. E. Kolb and P. Davidovits, *Atmos. Chem. Phys.*, 2015, **15**, 3063-3075.
6. A. T. Lambe, A. T. Ahern, L. R. Williams, J. G. Slowik, J. P. S. Wong, J. P. D. Abbatt, W. H. Brune, N. L. Ng, J. P. Wright, D. R. Croasdale, D. R. Worsnop, P. Davidovits and T. B. Onasch, *Atmos. Meas. Tech.*, 2011, **4**, 445-461.
7. X. Zhang, C. D. Cappa, S. H. Jathar, R. C. McVay, J. J. Ensberg, M. J. Kleeman and J. H. Seinfeld, *Proceedings of the National Academy of Sciences of the United States of America*, 2014, **111**, 5802-5807.
8. J. R. Odum, T. Hoffmann, F. Bowman, D. Collins, R. C. Flagan and J. H. Seinfeld, *Environ. Sci. Technol.*, 1996, **30**, 2580-2585.
9. N. M. Donahue, A. L. Robinson, C. O. Stanier and S. N. Pandis, *Environmental Science & Technology*, 2006, **40**, 2635-2643.
10. C. Wang, K.-U. Goss, Y. D. Lei, J. P. D. Abbatt and F. Wania, *Environmental Science & Technology*, 2015, **49**, 8585-8594.
11. A. Zuend and J. H. Seinfeld, *Atmospheric Chemistry and Physics*, 2012, **12**, 3857-3882.

12. J. Li, M. Cleveland, L. D. Ziemba, R. J. Griffin, K. C. Barsanti, J. F. Pankow and Q. Ying, *Atmospheric Environment*, 2015, **102**, 52-61.
13. J. F. Pankow, M. C. Marks, K. C. Barsanti, A. Mahmud, W. E. Asher, J. Li, Q. Ying, S. H. Jathar and M. J. Kleeman, *Atmospheric Environment*, 2015, **122**, 400-408.
14. B. Aumont, R. Valorso, C. Mouchel-Vallon, M. Camredon, J. Lee-Taylor and S. Madronich, *Atmos. Chem. Phys.*, 2012, **12**, 7577-7589.
15. J. Lee-Taylor, S. Madronich, B. Aumont, A. Baker, M. Camredon, A. Hodzic, G. S. Tyndall, E. Apel and R. A. Zaveri, *Atmos. Chem. Phys.*, 2011, **11**, 13219-13241.
16. A. G. Carlton, P. V. Bhave, S. L. Napelenok, E. O. Edney, G. Sarwar, R. W. Pinder, G. A. Pouliot and M. Houyoux, *Environmental Science & Technology*, 2010, **44**, 8553-8560.
17. H. O. T. Pye, A. W. H. Chan, M. P. Barkley and J. H. Seinfeld, *Atmos. Chem. Phys.*, 2010, **10**, 11261-11276.
18. S. C. Farina, P. J. Adams and S. N. Pandis, *Journal of Geophysical Research-Atmospheres*, 2010, **115**.
19. K. Tsigaridis, N. Daskalakis, M. Kanakidou, P. J. Adams, P. Artaxo, R. Bahadur, Y. Balkanski, S. E. Bauer, N. Bellouin, A. Benedetti, T. Bergman, T. K. Berntsen, J. P. Beukes, H. Bian, K. S. Carslaw, M. Chin, G. Curci, T. Diehl, R. C. Easter, S. J. Ghan, S. L. Gong, A. Hodzic, C. R. Hoyle, T. Iversen, S. Jathar, J. L. Jimenez, J. W. Kaiser, A. Kirkevåg, D. Koch, H. Kokkola, Y. H. Lee, G. Lin, X. Liu, G. Luo, X. Ma, G. W. Mann, N. Mihalopoulos, J. J. Morcrette, J. F. Müller, G. Myhre, S. Myriokefalitakis, N. L. Ng, D. O'Donnell, J. E. Penner, L. Pozzoli, K. J. Pringle, L. M. Russell, M. Schulz, J. Sciare, Ø. Seland, D. T. Shindell, S. Sillman, R. B. Skeie, D. Spracklen, T. Stavrakou, S. D. Steenrod, T. Takemura, P. Tiitta, S. Tilmes, H. Tost, T. van Noije, P. G. van Zyl, K. von Salzen, F. Yu, Z. Wang, R. A. Zaveri, H. Zhang, K. Zhang, Q. Zhang and X. Zhang, *Atmos. Chem. Phys.*, 2014, **14**, 10845-10895.
20. W. Jiang, *Atmospheric Environment*, 2003, **37**, 5439-5444.
21. A. Klamt and F. Eckert, *Fluid Phase Equilibria*, 2000, **172**, 43-72.
22. A. Klamt, *From Quantum Chemistry to Fluid Phase Thermodynamics and Drug Design*, Elsevier, Amsterdam, 2005.
23. J. F. Pankow, *Atmospheric Environment*, 1994, **28**, 189-193.
24. E. M. Knipping, R. J. Griffin, F. M. Bowman, B. Pun, C. Seigneur, D. Dabdub and J. H. Seinfeld, *Atmospheric Environment*, 2004, **38**, 2759-2761.
25. J. H. Seinfeld and J. F. Pankow, *Annual Review of Physical Chemistry*, 2003, **54**, 121-140.
26. M. Shrivastava, C. Zhao, R. C. Easter, Y. Qian, A. Zelenyuk, J. D. Fast, Y. Liu, Q. Zhang and A. Guenther, *Journal of Advances in Modeling Earth Systems*, 2016, **8**, 499-519.
27. A. Hodzic, P. S. Kasibhatla, D. S. Jo, C. D. Cappa, J. L. Jimenez, S. Madronich and R. J. Park, *Atmos. Chem. Phys.*, 2016, **16**, 7917-7941.
28. K. Tsigaridis, N. Daskalakis, M. Kanakidou, P. J. Adams, P. Artaxo, R. Bahadur, Y. Balkanski, S. E. Bauer, N. Bellouin, A. Benedetti, T. Bergman, T. K. Berntsen, J. P. Beukes, H. Bian, K. S. Carslaw, M. Chin, G. Curci, T. Diehl, R. C. Easter, S. J. Ghan, S. L. Gong, A. Hodzic, C. R. Hoyle, T. Iversen, S. Jathar, J. L. Jimenez, J. W. Kaiser, A. Kirkevåg, D. Koch, H. Kokkola, Y. H. Lee, G. Lin, X. Liu, G. Luo, X. Ma, G. W. Mann, N. Mihalopoulos, J. J. Morcrette, J. F. Müller, G. Myhre, S. Myriokefalitakis, N. L. Ng, D. O'Donnell, J. E. Penner, L. Pozzoli, K. J. Pringle, L. M. Russell, M. Schulz, J. Sciare, Ø. Seland, D. T. Shindell, S. Sillman, R. B. Skeie, D. Spracklen, T. Stavrakou, S. D. Steenrod, T. Takemura, P. Tiitta, S. Tilmes, H. Tost, T. van Noije, P. G. van Zyl, K. von Salzen, F. Yu, Z. Wang, R. A. Zaveri, H. Zhang, K. Zhang, Q. Zhang and X. Zhang, *Atmospheric Chemistry and Physics*, 2014, **14**, 10845-10895.