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Research Paper

Why do organic aerosols exist? Understanding aerosol lifetimes using the two-dimensional volatility basis set

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Environmental context. Fine particles (aerosols) containing organic compounds are central players in two important environmental issues: aerosol-climate effects and human health effects (including mortality). Although organics constitute half or more of the total fine-particle mass, their chemistry is extremely complex; of critical importance is ongoing oxidation chemistry in both the gas phase and the particle phase. Here we present a method for representing that oxidation chemistry when the actual composition of the organics is not known and show that relatively slow oxidant uptake to particles plays a key role in the very existence of organic aerosols.

Abstract. Organic aerosols play a critical role in atmospheric chemistry, human health and climate. Their behaviour is complex. They consist of thousands of organic molecules in a rich, possibly highly viscous mixture that may or may not be in phase equilibrium with organic vapours. Because the aerosol is a mixture, compounds from all sources interact and thus influence each other. Finally, most ambient organic aerosols are highly oxidised, so the molecules are secondary products formed from primary emissions by oxidation chemistry and possibly non-oxidative association reactions in multiple phases, including gas-phase oxidation, aqueous oxidation, condensed (organic) phase reactions and heterogeneous interactions of all these phases. In spite of this complexity, we can make a strong existential statement about organic aerosol: They exist throughout the troposphere because heterogeneous oxidation by OH radicals is more than an order of magnitude slower than comparable gas-phase oxidation.

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Introduction

Organic aerosols are meta-stable intermediates. Most organic emissions are highly reduced,[1,2] and all organics oxidise by complex oxidation pathways in the Earth's atmosphere.[3–6] Oxidation would convert all reduced carbon in the atmosphere into CO_2, given time. Consequently, to first order, the concentration of any given constituent (C_i) will be in a pseudo-steady-state at long enough timescales; given a production rate P_i and a first-order lifetime τ_i, the pseudo steady-state concentration C_i^{ss} will be:

$$C_i^{ss} = P_i \tau_i \quad (1)$$

This means that, for a succession of molecules connected by a simple reaction sequence, $M_i \rightarrow M_j \rightarrow M_k$ with a shared production rate P_i, the steady-state concentrations of each will be directly proportional to the lifetime. More generally, the total concentration of species at a given generation number in a reaction sequence is related to the (properly weighted) average lifetime of the species in that generation. This simple equation governs organic-aerosol levels, and it shows that the atmospheric lifetime is critical.

To apply Eqn 1 we need to know the lifetimes. Unsaturated organic molecules are typically very short lived, and for the most part the double bonds will be eliminated rapidly.[7] Our main focus here is on later-generation chemistry of organic compounds, where the dominant oxidant is the OH radical. The chemical lifetime of organic vapours is governed by their rate constant for reaction with $OH^\bullet$ (k_i^{OH}), and the lifetime against oxidation by $OH^\bullet$ will be $\tau_i = 1/(k_i^{OH} C_{OH})$. For the purposes of this discussion we shall consider $C_{OH} = \sim 2 \times 10^6$ molecules cm^{-3}, which is a typical daytime average value.[8] If the chemical lifetime is shorter than the deposition timescale, oxidation will in turn dominate the overall atmospheric lifetime. The job of estimating chemical lifetimes thus reduces to estimating $OH^\bullet$ oxidation rate constants.

Rate constant estimation faces two challenges. First, the most important rate constants in this exercise involve the reaction of $OH^{\bullet}$ with oxygenated organics, especially those containing multiple functional groups. These are generally large molecules by atmospheric standards, with 5–25 carbon atoms. There are very few kinetic data to draw on.[7] Second, there are thousands, even millions of specific organic molecules involved in chemistry associated with organic aerosols.[1,9] We thus have unmeasured rate constants for unknown molecules.

There are at least two solutions to this problem. One is to take what we do know about the kinetics and mechanisms of organic molecules and train mechanism generators to fill in the rest, connecting precursor molecules to all intermediates and ultimately to CO_2.[10] Another is to reduce the complexity by lumping the organics into groupings with similar properties. Here we choose the second approach, employing a discretised two-dimensional space consisting of volatility (saturation concentration, C^{o} in micrograms per cubic metre as the x coordinate and average carbon oxidation state ($\overline{OS}_C \equiv 2O:C–H:C \approx 3O:C-2$) as the y coordinate. This is known as the two-dimensional volatility basis set (2D-VBS),[1,11,12] and it forms the framework for this discussion.

Methods

The 2D-VBS facilitates consideration of organic oxidation and phase partitioning without requiring specific knowledge of molecular structures, even carbon numbers. The variables themselves are the fundamental quantities describing phase partitioning and oxidation chemistry. Organic aerosol levels are almost always between 1 and 100 $\mu g\,m^{-3}$, and consequently for organics to reside in the aerosol phase they must have a saturation mass concentration, $C^* < \sim 100\ \mu g\,m^{-3}$. Volatility as C^* is not the pure-component vapour pressure; at a minimum it includes activity coefficients of organics in the aerosol mixture ($C_i^* = \gamma_i\ C_i^{o}$), and more generally it includes any factors governing the equilibrium phase partitioning.[11] The relevant volatility is usually that of any product molecule in the condensed phase (i.e. ammonium oxalate or some other organic salt and not oxalic acid itself).

The equilibrium state says something about organic aerosols; however, the potential for organic aerosols to be out of equilibrium is currently under debate. It is possible that extremely low viscosity (i.e. a glassy state) may inhibit mass transfer within particles.[13–18] However, mass exchange between particles and the gas phase remains a critical topic, and particles do grow and shrink.[19] Considering uptake and condensational growth, most organic molecules that collide with particles do not stick to them. The property governing which compounds stay in the aerosol phase is volatility, and thus the x-axis of the 2D-VBS informs which phase the organic material will be in.

The y-axis of the 2D-VBS concerns oxidation. The oxidation state ($\overline{OS}_C$) monotonically increases while organics reside in the atmosphere. Gas-phase tropospheric photochemistry is almost exclusively oxidative, with the OH radical serving as the dominant oxidant.[20] Heterogeneous uptake of $OH^{\bullet}$ to aerosols is also a major cause of particle oxidation.[21,22] Ozone can oxidise organics with C=C double bonds, but although ozonolysis is extremely important, the double bonds are oxidised very rapidly and do not substantially affect the aging processes described here. Non-oxidative association reactions leading to high-molecular-weight products (oligomers) clearly occur,[23,24] but when the carbon number is followed in environments where strong oxidative aging occurs, the general tendency is for carbon number to decrease due to fragmentation.[1,25–28] The bottom line is that most organic emissions have $\overline{OS}_C < \sim -1.5$, whereas a large majority of the organics (especially organic aerosol), is highly oxidised.[29] It follows that oxidation chemistry is a crucial, inevitable, monotonic driver of organic properties in the atmosphere.

Because we use the 2D-VBS framework, in order to assess organic lifetimes we need to estimate the $OH^{\bullet}$ oxidation rate constants of organics in 2D-VBS bins. Fortunately, we do know something about composition (carbon, hydrogen and oxygen numbers, n_C, n_H, n_O, as well as the more tightly defined O : C and H : C ratios) in the 2D-VBS.[11] There is also strong evidence that the oxidised functional groups consist of approximately equal numbers of =O and –OH groups (the organic compounds appear to be, on average, either hydroxyketones or organic acids or more likely a mixture of both).[30,31] This is enough for us to begin to say something about the gas-phase $OH^{\bullet}$ reactivity in the 2D-VBS. To do this we draw upon and simplify structure–activity relations, starting along the lower edge of the 2D-VBS where the organics are simply hydrocarbons.

We do not know the structure of the typical organics in the 2D-VBS, so we rely on a statistical sampling of kinetic data in the (limited) regime of the 2D-VBS where kinetics are available. The kinetics are distilled by the structure–activity relationship (SAR) of Kwok and Atkinson,[32] which we sample randomly with 35 000 molecules to maintain the proper C : H : O relationships (on average) in the 2D-VBS. However, the basis for the SAR consists almost entirely of small molecules, most with either zero or one oxygenated functional group. To extrapolate this over the full range of the 2D-VBS we smooth the resulting rate-constant surface with a functional form based on three simple assumptions: (1) $OH^{\bullet}$ oxidation rate constants typically increase with increasing carbon number; (2) adding oxygenated functional groups for lightly oxygenated molecules typically increases the $OH^{\bullet}$ reactivity and (3) highly oxygenated molecules ultimately become less reactive due simply to a scarcity of abstractable hydrogens. This final assumption is supported by heterogeneous $OH^{\bullet}$ oxidation experiments on highly oxygenated aerosol surrogates, such as citric acid, which show it to be recalcitrant to oxidation.[33]

The resulting (vapour-phase) rate-constant (k^{vap}, $cm^3\ molecule^{-1}\,s^{-1}$) expression is given by Eqn 2 and plotted in the 2D-VBS in Fig. 1.

$$k^{vap} = \sim 1.2 \times 10^{-12}(n_C + 9n_O - 10\ (O:C)^2) \qquad (2)$$

The first effect (increasing k with increasing n_C) for homologous molecules is very robust.[32] The second two effects counteract each other. We express them with one term dependent on n_O alone and a second one dependent on $(O:C)^2$, which is a measure of the H-atom scarcity. Although the specifics of the functional form in Eqn 2 and the actual rate constants must be regarded as quite uncertain, overall Fig. 1 reveals rate constants that vary only modestly throughout the space. The major feature is that k_{OH} increases as C^{o} decreases, but the overall effect is less than a 1 order of magnitude increase in k over a 15 decade decrease in C^{o}. Furthermore, although we include the volatile organic carbon (VOC) region in the 2D-VBS ($C^{o} > 3 \times 10^6\ \mu g\,m^{-3}$) for completeness, no realistic simulation would actually use it for a numerical simulation in that region – VOC chemistry is represented by a standard chemical mechanism.

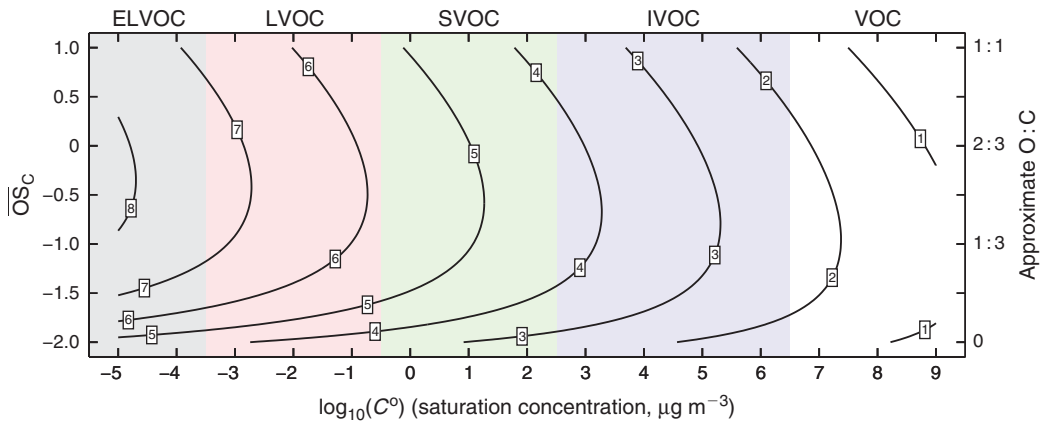

Fig. 1. Gas-phase OH• oxidation rate constants for organic species *v.* volatility and oxidation state ($\overline{OS}_C$) (contours are $k \times 10^{11}$ cm^3 molecule^{-1} s^{-1}). Rate constants are estimated based on extrapolated group contribution methods, as described in the text. The OH• oxidation rate constant increases with increasing carbon number, rapidly with increasing oxygen number, but decreases quadratically as O : C increases due to the loss of abstractable hydrogens. (ELVOC, extremely low volatility organic compounds; LVOC, low volatility organic compounds; SVOC, semivolatile organic compounds; IVOC, intermediate volatility organic compounds; VOC, volatile organic compounds.)

Results and discussion

In Fig. 2a we show the gas-phase chemical lifetime, $\tau = 1/(kC_{OH})$, in days in the 2D-VBS space, assuming $C_{OH} = \sim 2 \times 10^6$ molecules cm^{-3}. The semi-volatile range is $0.3 \leq C^o \leq 300$ μg m^{-3}, organics with lower C^o values will be almost completely in the condensed phase under typical conditions. The critical point is that organic species over the entire range of volatilities representative of aerosols have a gas-phase lifetime of less than 0.2 days. Thus, aerosol species would evolve through upwards of five generations of chemistry in 24 h, if they were in the gas phase. Because the probability of fragmentation and consequent sharp increases in volatility rises rapidly with increasing oxidation state,[25–27] this unrestrained oxidation would sweep the system clean of organic aerosols within a day or two. For example, a C_{10} backbone, with on average 1.5 oxygen atoms added per generation, will have a simple fragmentation probability $(O:C)^{1/4}$ of 0, 0.62, 0.74, 0.82, 0.88 and 0.93 for generations 0–5.

Organic species, however, do not reside solely in the gas phase. The less volatile ones condense to form organic aerosol, and in the condensed phase they are protected from gas-phase OH• by the diffusion rate of OH• to the particles. For the purposes of this work, the heterogeneous uptake of OH• to particles can be converted into an effective gas-phase rate constant, which depends on particle size.[34,35] Here we assume that OH• will react with unit efficiency with the first organic species it encounters in a particle, and thus the effective rate constant will be independent of composition.[36] For 500-nm diameter particles, the effective rate constant will be $k^{eff} = 1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, resulting in an oxidation lifetime of 5.8 days, whereas organics in 200-nm diameter particles would have a lifetime of ~3 days. This will apply regardless of the condensed-phase composition, provided that the pseudo-ideal solution theory relevant to C^o holds and that the near-surface particle composition is approximately the same as the bulk organic phase composition. This will be true if the particle viscosity is not so high as to significantly limit condensed-phase mass transfer to the particle surface; the timescale for diffusion within the particles must be faster than the timescale for heterogeneous oxidation (6 days in this example).[36,37] Evidence from relative rate experiments of mixtures made by coating primary organic particles with laboratory secondary organic aerosol (SOA) supports this assumption.[38]

The condensed-phase lifetime of 6 days is thus much longer than the ~0.1-day gas-phase lifetime of the organic molecules in the low-volatility range. However, it is still comparable to the residence time of particles in the atmosphere, so heterogeneous oxidation *will* play a role even for organics that are more or less homogeneously distributed in the condensed phase. The overall average lifetime of semi-volatile organics will depend on their fraction (ξ_i) in the condensed phase:

$$\xi_i = (1 + C_i^*/C_{OA})^{-1} \quad (3)$$

which gives an overall rate constant (k_i^{tot}) based on the effective heterogeneous rate constant (k^{eff}) and the gas-phase rate constant (k_i^{vap}) from Eqn 2.

$$k_i^{tot} = \xi_i k_i^{eff} + (1 - \xi_i) k_i^{vap} \tau_i = 1/(k^{tot} C_{OH}) \quad (4)$$

The overall lifetimes including the gas-phase diffusion limitations for heterogeneous oxidation are shown in Fig. 2b for a case with concentration of organic aerosol $C_{OA} = 1$ μg m^{-3}. Based on Eqn 1, the steady-state concentration of species sequestered in particles will thus be ~30 times higher than it would otherwise be if they were oxidised at the rate given by pure gas-phase oxidation shown in Fig. 2a.

In this work we are considering heterogeneous oxidation by OH radical uptake only. Especially at higher relative humidity (and certainly in droplets), aqueous-phase reactions will also contribute to oxidation; it is unclear whether the net effect of these processes will augment or deplete the total organic-aerosol mass, although oxidation of soluble volatile species can clearly contribute to SOA.[39,40] For example, levoglucosan can be oxidised in most particles and droplets with lifetimes in the order of days.[41] However, with a saturation concentration of the order of 7 μg m^{-3},[42] levoglucosan will reside principally in the gas phase under many circumstances.[12] As Eqn 4 and experimental data show,[43] the majority of oxidation is likely to

be by gas-phase OH• reactions. This will apply to other organics even well into the low volatility organic compound region (LVOC) region.

The lifetime contours in Fig. 2b show something profound. The sharp increase in lifetimes with decreasing volatility and thus decreasing gas-phase fractions is the most dramatic feature of the figure (note that the influence of gas-phase oxidation extends to quite low C^o). However, just as notable is the broad area of minimum lifetime for semi-volatile organic compounds (SVOC range in green) and intermediate volatility organic compounds (IVOC range in blue). Until recently, many atmospheric models treating SVOCs contained semi-volatile lumped species whose properties (C^* and molar yields) were based on empirical fits to smog-chamber data. Often these species were effectively immortal in the model, or at most suffered from deposition to the surface. In fact, these SVOCs have a minimum lifetime and thus will have a minimum steady-state concentration of all molecules in a given reaction sequence. Atmospheric chemistry will thus tend to sweep out the SVOC range with progressive aging downwind of a source region, forming either much lower volatility functionalised products or more volatile fragmentation products and thus producing very low volatility, highly oxidised aerosol in the remote atmosphere. This is exactly what is observed.[29,44]

The lifetime of individual organic molecules is not the same as the lifetime of the aerosol mass itself. So, in order to test our assertion that without condensed-phase sequestration the atmosphere would be rapidly swept clear of organic aerosol, we simulated the evolution of a SOA plume in a simple box model. The model is initiated by SOA formation by ozonolysis of α-pinene, assuming 30 ppb of ozone and 20 μg m^{-3} of α-pinene (~2 ppbv). The initial fresh SOA formation and subsequent aging chemistry follow the yields and chemistry described previously,[29,45,46] and the model (including slow heterogeneous oxidation) matches observed aging behaviour well.[47] Briefly, OH• reacts with semi-volatile vapours with the rate constants described above. The resulting reaction products are distributed according to two oxidation 'kernels', with a 'functionalisation' fraction distributed exclusively to lower C^* values and a 'fragmentation' fraction dispersed widely in volatility space. The probability of fragmentation is assumed to vary as $(O:C)^{1/4}$, so as organics become highly oxidised they will inevitably fragment towards CO_2, which is required by thermodynamics.

The results of our box-model simulation are shown in Fig. 3. The α-pinene was allowed to react with ozone in the dark for 12 h, forming ~1 μg m^{-3} of 'fresh' SOA with a mass yield of ~5 %. At $t = 0$ the OH• concentration was suddenly increased

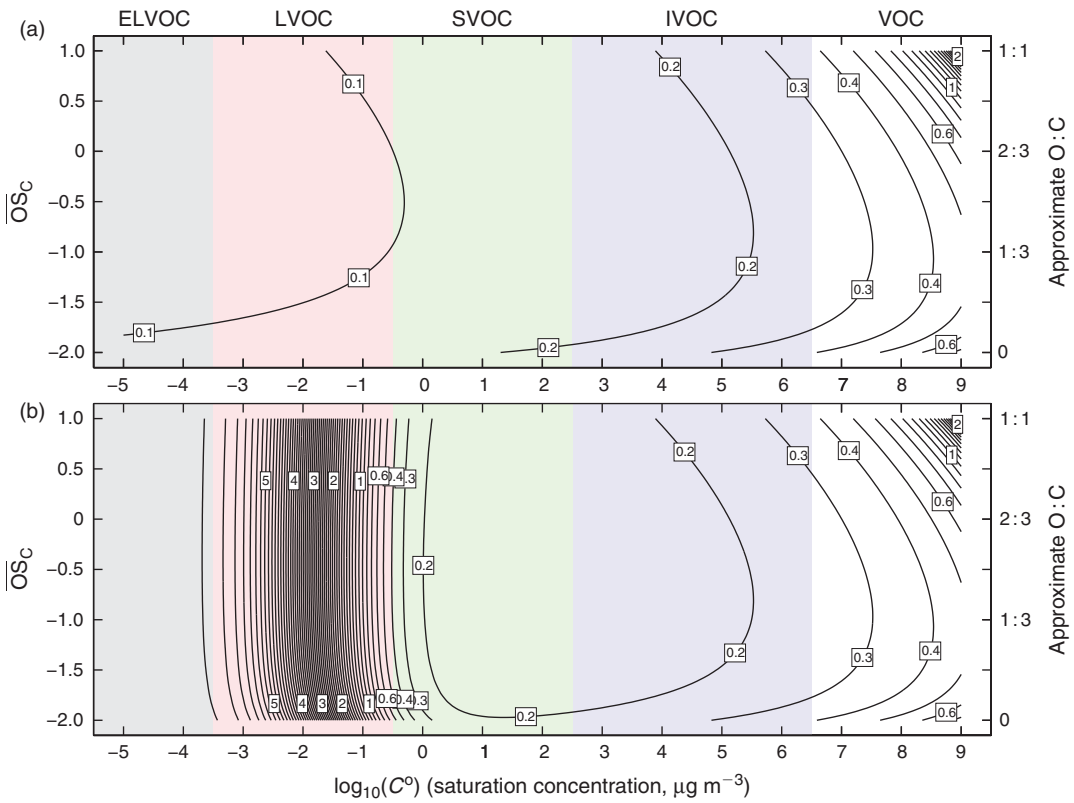

Fig. 2. OH• oxidation lifetimes in days of organic compounds in the two-dimensional volatility basis set. Contour intervals are 0.1 day. (a) Gas-phase lifetimes based on the rate constants in Fig. 1 and an assumed OH radical concentration of 2×10^6 molecules cm^{-3}. In the semi-volatile range of C^o values relevant to organic aerosols (green and blue shading), the gas-phase lifetimes of organic vapours will be less than 0.2 days. (b) Lifetimes including the effect of phase partitioning, where heterogeneous oxidation by OH• uptake to particles is limited by gas-phase diffusion and the heterogeneous oxidation lifetime is 5.6 days (for 500-nm diameter particles). Consequently, semi-volatile organics are the shortest lived species, with a lifetime of ~0.2 days. (ELVOC, extremely low volatility organic compounds; LVOC, low volatility organic compound region; SVOC, semivolatile organic compounds; IVOC, intermediate volatility organic compounds; VOC, volatile organic compounds; $\overline{OS}_C$, oxidation state.)

to 2×10^6 molecules cm^{-3}. In the base-case simulation the $OH^{\bullet}$ oxidation rate constants are given by Eqn 4. We assume that the mechanism (the product distribution) is not affected by whether the $OH^{\bullet}$ reaction occurs homogeneously in the gas phase or heterogeneously near the particle surface. This is almost certainly an over simplification, but there are insufficient data to describe the chemistry in more detail. The solid curve in Fig. 3 shows the organic aerosol evolution as this aging chemistry progresses. With most of the first-generation ozonolysis products in the vapour phase, the aging causes a dramatic, almost 10-fold, increase in aerosol concentrations over the first half day, but the subsequent aging chemistry is slow because of the slow heterogeneous oxidation. This is broadly consistent with published smog-chamber experiments on SOA aging, although the magnitude of the fractional mass increase is large because of the very low (for a chamber experiment) initial SOA mass loading.[47]

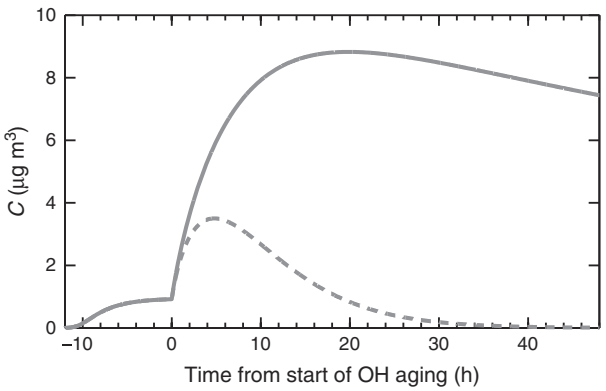

Fig. 3. Evolution of organic aerosol concentrations (C) in an idealised box model. Secondary organic aerosol is formed by oxidation of α-pinene by ozone over 12 h ($t < 0$). For $t \geq 0$, $[OH^{\bullet}] = 2 \times 10^6$ molecules cm^{-3}. The solid curve is the best model estimate of evolving organic aerosol mass concentrations, with a substantial increase caused by gas-phase oxidation and very little influence from (diffusion limited) OH radical uptake to particles. In the simulation shown with a dashed curve all organics are oxidised with their equivalent gas-phase rate constants. The oxidation chemistry rapidly fragments the organics, causing the aerosol to evaporate.

In the second, dashed curve in Fig. 3, the heterogeneous aging k^{eff} is artificially made equal to the gas-phase $OH^{\bullet}$ oxidation rate constant, so the oxidation proceeds unimpeded by diffusion limitations. In this case the organic aerosol rapidly dissipates, vanishing in ~1 day. This dramatic difference in behaviour shows that the simple steady-state analysis described by Eqn 1 gives a valid picture for bulk organic-aerosol concentrations as well. A typical average age of aerosols in even an urban setting such as Pittsburgh is greater than 2 days,[48] and the ratio in modelled organic aerosol concentrations for $0 \leq t \leq 48$ h in Fig. 3 is more than a factor of five.

The calculations presented so far have been for 'typical' ambient conditions, but in certain times and places the atmosphere can be far more oxidising. One example is the eastern Mediterranean. During the MINOS campaign at the Finokalia research station in Crete in August 2001, ambient $OH^{\bullet}$ levels reached 2×10^7 molecules cm^{-3}.[49] Under these extreme conditions, the gas-phase lifetimes of SVOC within the 2D-VBS are less than 1 h, and even the heterogeneous oxidation timescale is just over 12 h, as shown in Fig. 4 – we show lifetimes for the diurnal maximum $OH^{\bullet}$ levels because under these conditions the oxidation timescales are so fast that the diurnal average is barely meaningful. We thus expect organic aerosols to become completely oxidised very quickly, unless some compounds are able to 'hide' in the particles because they are so viscous that they cannot reach the surface to be oxidised.[14,36]

Organic-aerosol observations using a unit mass resolution aerosol mass spectrometer (Q-AMS, Aerodyne Inc., Billerica, MA, USA) during the EUCAARI campaigns in May 2008 and February 2009 show that in the late spring organic aerosols arriving at Finokalia were completely oxidised, with no evidence of *any* primary organic aerosol,[50] whereas Q-AMS observations at the same site in winter 2009 showed significant levels of primary organic aerosol.[44] The highly oxidised aerosols during late spring 2008 were observed even when air-mass back trajectories showed that the sampled air had been in the boundary layer over Athens less than 2 days earlier. The very short lifetimes shown in Fig. 4 confirm this, and the almost complete absence of unoxidised peaks in the mass spectra (even for air recently over Athens) shows that diffusion limitations do not protect extremely

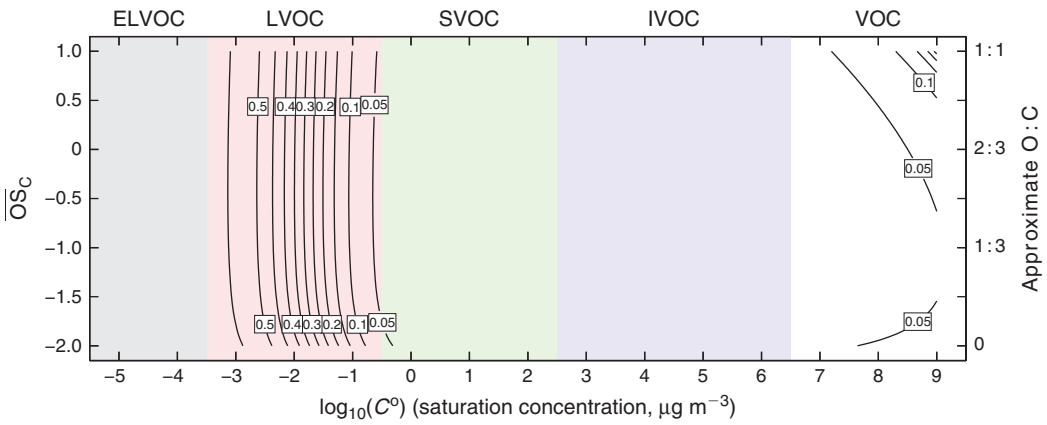

Fig. 4. $OH^{\bullet}$ oxidation lifetimes in days of organic compounds in the two-dimensional volatility basis set for conditions observed in the summertime eastern Mediterranean with an assumed OH radical concentration of 2×10^7 molecules cm^{-3}. Contour intervals are 0.05 day. Extreme oxidation conditions will oxidise gas-phase species in less than 1 h; even heterogeneous oxidation will occur during daylight t of a single day. (ELVOC, extremely low volatility organic compounds; LVOC, low volatility organic compound region; SVOC, semivolatile organic compounds; IVOC, intermediate volatility organic compounds; VOC, volatile organic compounds; $\overline{OS}_C$, oxidation state.)

low volatility primary compounds within the particles under ambient conditions. Given that the heterogeneous oxidation timescale in Fig. 4 is ~12 h, this suggests that the diffusional timescales for organics within the aerosols sampled during FAME-08 were faster than this. That in turn suggests a diffusion constant $D \geq 10^{-14}$ cm ^{2} s^{-1}, or a dynamic viscosity $\eta \leq 3 \times 10^5$ Pa s,[15] even for quite highly oxidised organic aerosol.

Environmental implications

Oxidation of organic compounds, carried to completion, will form CO_2, and consequently oxidation is fundamentally destructive to organic aerosol. However, as Fig. 3 shows, oxidation clearly is a source of organic aerosol as well. Consequently, organic aerosols can only be viewed as metastable intermediates.[1] Its concentrations are thus controlled by its lifetime, and as we show the fundamental governor of this lifetime is the delay caused by diffusion of OH radicals to aerosols. Without this, organic aerosol levels would be many times lower than they are, rendering organics virtually irrelevant to aerosol concentrations and properties.

Conversely, although organic compounds can run, they cannot hide. Sequestration into the condensed phase delays oxidation because of diffusion limitations in the gas phase, but heterogeneous oxidation is still important. The near complete oxidation observed in situations where transport occurs within ~1 day from intense sources indicates that the diffusion timescale for organics within particles is (in at least some cases relevant to the atmosphere) less than 1 day.

Acknowledgements

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