

5 Supplemental Material

5.1 partitioning theory

Partitioning theory for organic aerosol was presented by Pankow,^{1-3,10} for equilibrium between the vapor and condensed phases, assuming non-dissociating condensed-phase species. We employ a modified version of this treatment, with an effective saturation concentration, C_i^* replacing the partitioning coefficient (which is the inverse of C_i^*):

$$C_i^* = \frac{C_i^{\text{vap}} C_{\text{OA}}}{C_i^{\text{aer}}} = \frac{M_i 10^6 \zeta_i' p_{L,i}^\circ}{760 R T} \quad (4)$$

C_i^{aer} ($\mu\text{g m}^{-3}$) is the mass concentration of compound i in the condensed phase, C_i^{vap} ($\mu\text{g m}^{-3}$) is the concentration in the vapor phase, C_{OA} ($\mu\text{g m}^{-3}$) is the total organic aerosol concentration, R is the gas constant, T (K) is the temperature, M_i (g mol^{-1}) molecular weight of species i , and ζ_i' is a molality-based activity coefficient, and $p_{L,i}^\circ$ (torr) is the saturation vapor pressure of pure compound i at temperature T . Equation 4 is typically developed from a version of Raoult's law based on the mole fraction χ_i of species i in the condensed phase:³

$$p_i = \chi_i \zeta_i' p_{L,i}^\circ \quad (5)$$

However, the physical basis behind Raoult's Law for vapor pressure reduction in a mixture is the physical exclusion of material from the surface – for hydrocarbons of reasonably uniform density it is thus perhaps more sensible to use molality for Raoult's law, with ϕ_i the mass fraction.

$$p_i = \phi_i \zeta_i' p_{L,i}^\circ \quad (6)$$

This modified activity coefficient is the basis for our effective saturation concentration C_i^* .

The practical effect of the modified activity coefficient is that equation 4 does away with the vexing average molar weight, M_{OA} found in most treatments of partitioning in favor of the specific molar weight M_i . C_i^* is thus an intrinsic property of compound i for an ideal solution. In each case, we tend to assume an activity coefficient ζ_i or $\zeta_i' = 1$. However, the new formulation behaves far more reasonably, especially in cases such as oligomerization. For example, assume a condensed phase containing equal portions of monomer A and monomer B, with the same molar weight and volume and unit activity coefficients. Each will experience a vapor pressure suppression of a factor of two. Now, assume that monomer B dimerizes, and that the dimer has the same density as the monomer (thus twice the molar volume). It is reasonable to assume that monomer A will still experience a factor of 2 vapor pressure suppression, as it will still occupy roughly half of the condensed-phase surface area. This result follows from equation 6.

5.2 kinetic transformation

Our approach to treating chemical evolution of semi-volatile material is to write a transformation matrix for material distributed

according to the basis set in equation 2:

$$\frac{d\vec{C}}{dt} = -\mathbf{K}_a \vec{C}_{\text{OC}} - \mathbf{K}_v \vec{C}_{\text{vap}} \quad (7)$$

where $\vec{C} = \vec{C}_{\text{OC}} + \vec{C}_{\text{vap}}$ is the total concentration of the semi-volatile organics, with \vec{C}_{OC} in the condensed phase and \vec{C}_{vap} in the vapor phase. The first-order transformation matrices \mathbf{K} have positive elements (for loss) along the diagonal and negative elements (for production) off the diagonal, representing production of different vapor-pressure material.

All processes currently receiving attention in the literature, including gas-phase oxidation (SOA formation), condensed-phase oxidation (aerosol aging) and condensed-phase oligomerization can be represented in this fashion, though reversible oligomerization requires separate bins for material that can dissociate back to more volatile monomers. In general 'extra' bins can always be added to accommodate a specific need; for example source attribution, as illustrated in Figure 1d, or in this case a reversible process like oligomerization. Extra bins are required to differentiate reversible from irreversible low-volatility mass (or in general to differentiate any processes that require separate modeling). It is likely that a reduced extra basis set $\{C_o^*\} = \{0.01, 0.1, 1\}$ could be used for reversible oligomerization, presuming that the macromolecules all have very low saturation concentrations. A separate chemical transformation matrix would need to couple $C^* \leftrightarrow C_o^*$ and, of course, the kinetics and yields would require experimental constraint.

In the simplified example presented in this work we use a single transformation matrix $\mathbf{K} = k(\mathbf{A} - \mathbf{I})$ for both phases as an illustrative simplification. The matrix \mathbf{A} describes the redistribution of material upon reaction, using a slightly more expansive basis set than we use for the other examples in the paper ($\{C^*\} = \{1 \text{ ng} \rightarrow 1 \text{ g}\} \text{ m}^{-3}$).

$$\mathbf{A} = \begin{bmatrix} 0.4 & 0.4 & 0.4 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0.5 & 0.4 & 0.4 & 0.4 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0.1 & 0 & 0.4 & 0.4 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0.1 & 0 & 0.4 & 0.4 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0.1 & 0 & 0.4 & 0.4 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0.1 & 0 & 0.4 & 0.4 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0.1 & 0 & 0.4 & 0.4 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0.1 & 0 & 0.4 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0.1 & 0 & 0 \\ 0.1 & 0.1 & 0.1 & 0.1 & 0.1 & 0.1 & 0.1 & 0.1 & 0.2 & 0 \end{bmatrix}$$

For example, the first column means that 40% of the reactions in bin 1 (the least volatile bin) move material to bin 1 (they do nothing), 50% move material to the slightly more volatile bin 2, and 10% move material to the essentially completely volatile bin 10. Aside from the three least volatile bins, which mostly redistribute material among each other while bleeding off 10% to the volatile end (ultimately everything will be oxidized to CO_2), the characteristic pattern is that for each bin, 40% of the reactions move material down 2 bins, 40% of the reactions move material down 1 bin, 10% move material up one bin, and 10% evolve a volatile

product. This is on a mass basis, not a molar basis; this is an unfortunate consequence of the ubiquity of mass measurements in aerosol science. In our transformation matrix we have chosen to conserve mass, with one notable exception – the volatile bin, bin 10, also decays away completely upon reaction (the rough model is $\text{CH}_2\text{O} \rightarrow \text{CO}_2$). This is to let us track the loss of ‘condensable’ mass. This coupling matrix is needlessly complex, but it does have a few characteristics that arguably make it typical of reality. The lower 3 bins muck around mostly to prevent an ugly accumulation in the least volatile bin, which just looks bad in the plots.

We do not simulate deposition here, as we are interested only in understanding how chemistry that has up till now been neglected in aerosol models may influence the average aerosol loading. Furthermore, deposition (at least wet deposition) is a stochastic process best left to regional models.

5.2.1 forms of chemistry

The framework based on equations 1, 2 and 7 can easily accommodate the forms of chemistry likely to affect the organic aerosol mass.

First is the gas-phase oxidation of numerous unidentified intermediate volatility compounds (IVOC). Again, these are not the commonly identified SOA precursors but rather the enormous number of larger, partially oxidized compounds implicitly presumed by aerosol partitioning models to exist in the vapor phase in equilibrium over the condensed phase. As we have seen above, oxidation of these compounds could quite easily double the aerosol volume in a short time.

Second is the condensed-phase oxidation of the equally numerous condensed-phase compounds. The only reason for separating the phases is if either the oxidation rate or the oxidation products differ in the two phases. Of course, this is likely; condensed phase aging may be somewhat slower than gas-phase oxidation, and products could well differ – as an example, it is quite possible that the RO_2 cross reactions in the condensed phase could lead to cross-linked peroxides (ROOR),^{37,41} while in the gas phase they lead to bimolecular reaction products. This cross linking could well be an important, irreversible, component of oligomer formation in organic aerosols.

Third, oligomer formation in general is easily accommodated. The effect of oligomerization is merely to move material from a highly volatile bin to a lower volatility bin. If it is reversible, separate bins would have to be added to a simulation, but to do so is trivial. To the extent that highly volatile organics like glyoxal are important contributors to oligomerization,³⁸ the basis set would either need to be extended to include the small fraction of these species in the condensed phase at equilibrium (which would then be processed rapidly to oligomers in the condensed phase chemistry module), or such an important process could be treated explicitly.