



Estimates of Total Molecular Polarity to Evaluate Atmospheric Evolution of Organic Aerosol

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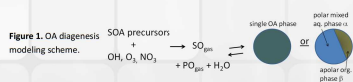
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I. ABSTRACT

The relationship between the molecular composition of organic aerosol (OA) and aerosol optical properties and activation of cloud condensation nuclei (CCN), which affect the direct and indirect forcing of Earth's climate, is poorly understood. Improving our understanding of the complex relationship requires development of model parameterizations that provide adequately detailed representations of the formation and diagenesis of OA and the evolution of OA properties that affect interactions with atmospheric water. The evolution of OA depends on the molecular composition of the gas-phase solutes and the sorbing matrix of aerosols. Gas-particle partitioning can be described by five types of intermolecular interactions that solute molecules undergo with OA: size-related interactions, polar interactions, interactions resulting from excess polarity, hydrogen bond donor, and hydrogen bond acceptor interactions, all of which are altered as OA is transformed by a series of oxidations during the atmospheric lifetime of the aerosol. Interactions of OA chemical species with water, which affect aerosol optical properties, CCN activation, and removal by precipitation, are expected to increase as the polarity/polarizability and hydrogen bond donor-acceptor (HBA) character of OA increases. However, HDA interactions with water are likely greater than interactions related to the polarity/polarizability of OA, and CCN activation is expected to increase with increasing HDA character. Pankow and Barsanti (2009; Atmos. Environ. 43, 2829-2835) proposed a representation of OA chemical species to model OA formation and diagenesis that uses carbon number and total molecular polarity (*tmp*) as dimensions. This approach is superior to approaches that employ a 2D space comprised of volatility and mean carbon oxidation state because the volatility of species with the same mean carbon oxidation state can vary by several orders of magnitude. The objective of the work presented here is to derive a measure of *tmp* from gas chromatographic retention indices of hydrocarbons with various functionalities (e.g., -OH, -CHO, C=O, -COOH, -ONO₂). A comprehensive two-dimensional gas chromatographic (GC×2GC) approach is used to determine retention indices of the organic solutes on a primary and two secondary GC columns that have stationary phases of different polarity and HBA character used as model phases for OA. Carbon number is a proxy for solute molecular size quantified using retention indices from primary column elution. Retention indices from solute elution in the two secondary columns are used to quantify molecular polarity/excess polarizability and HBA character.

II. BACKGROUND

OA diagenesis modeling scheme. Chang & Pankow (2010), hereafter CP10, presented a modeling scheme to follow organic aerosol (OA) diagenesis, where partitioning is into either a single liquid OA phase, or at higher relative humidity (RH), separate polar mixed aqueous (α) and apolar organic (β) phases (Erdakov & Pankow, 2004; Figure 1).



Use of GC×2GC to resolve, identify and quantify compounds. A GC×2GC analysis of gas- and aerosol-phase organic species can be used to identify sol (SOA) under ambient conditions. The approach involves identification and quantification of SOA precursors and products by application of the Abraham solvation parameter model (Abraham 1993) to GC×2GC-FID retention time data, with GC×2GC-ToFMS for confirmation of organic molecular identity.

Seeley et al. (2009) defined a retention index space in GC×2GC that can be extended to GC×2GC. Retention indices are parameterized relative to the isothermal retention of *n*-alkanes as the Kovats Index divided by 100 (Eq 3, Seeley et al. 2009). The primary retention index is:

$$I_p = L'_i + s'_i S'_i + a'_i A'_i + b'_i B'_i + e'_i E'_i \quad (1)$$

where prime notation represents solute parameters randomized to either constants or *i*-values, and the parameters L'_i , S'_i , A'_i , B'_i , and E'_i are solvation parameters of the solute i , and the complementary parameters l_p , s_p , a_p , b_p , e_p characterize solvation properties of the primary stationary phase. The L'_i term quantifies the contribution of dispersion interactions to sorption, the $s'_i S'_i$ term quantifies dipole-type (dipole-dipole and induced dipole-dipole) interactions, and the $a'_i A'_i$ and $b'_i B'_i$ terms quantify the contributions of solute electron acceptance (solvent electron donation) and solute electron donation (solvent electron acceptance), respectively, and the $e'_i E'_i$ term quantifies the contribution from electron lone pair interactions that occur between polarizable molecules. In the secondary dimension(s) of a retention diagram, for a secondary phase θ , ΔI is plotted here, where

$$\Delta I = I_p - I_\theta = \Delta s'_i S'_i + \Delta a'_i A'_i + \Delta b'_i B'_i + \Delta e'_i E'_i \quad (2)$$

and $\Delta s'_i = s'_i - s'_\theta$, $\Delta a'_i = a'_i - a'_\theta$, $\Delta b'_i = b'_i - b'_\theta$, and $\Delta e'_i = e'_i - e'_\theta$. GC×2GC provides two secondary θ -dimensions also designated α and β here. Placing the primary dimension on the z-axis and the θ -dimensions on the x- and y-axes, respectively, a three-dimensional retention diagram is generated using GC×2GC. For the x-y plane:

$$\Delta I = I_p - I_\theta = \Delta s'_i S'_i + \Delta a'_i A'_i + \Delta b'_i B'_i + \Delta e'_i E'_i \quad (3)$$

where $\Delta s'_i = s'_i - s'_\theta$, $\Delta a'_i = a'_i - a'_\theta$, $\Delta b'_i = b'_i - b'_\theta$, and $\Delta e'_i = e'_i - e'_\theta$.

n_c vs. *tmp* grid. Pankow & Barsanti (2009) presented means to manage organic molecular data for input to the SOA component of chemical transport models. Organic compound data is divided into bins of number of carbon atoms, n_c , and an estimate of total molecular polarity, *tmp*. Here, we quantify *tmp* by summing the polar interaction terms of the Abraham solvation model for gas-particle partitioning. For a given sample containing gaseous organics, g , and a single or two liquid phases, *tmp* values can be computed for a given bin as

$$tmp = a_g \sum S_g + a_l \sum A_l + b_l \sum B_l + e_l \sum E_l + a_w \sum S_w + a_m \sum A_m + b_m \sum B_m \quad (4)$$

where s_p , a_p , and b_p are assumed equal to one, and values for liquid liquid and the mixed aqueous phase are assumed to equal those of the Duedorf fall sample from Arp et al. (2008; $s_{p1}=1.19$, $a_{p1}=3.37$, $b_{p1}=0.03$) and those of water in Eq. 5-22 of the textbook by Schwarzenbach et al. (2003; $s_w=5.78$, $a_w=8.71$, $b_w=11.1$), respectively, and k represents a *tmp* bin ranging from 1 to 25.

III. OBJECTIVE AND APPROACH

Objective

Compare and evaluate, using the surrogate PCA, precursor SOA, and SOA compound identity and concentration dataset of CP10, two approaches to characterize molecular organic compound composition for input to SOA modules of chemical transport models:

- 1) n_c vs. *tmp* grid;
- 2) GC×2GC analytic technique.

Approach 1: In each characterization approach, starting surrogate SOA precursor (Fig. 2a) and POA composition POA (Fig. 3; assumed to be untransformed) is compared with surrogate SOA (Fig. 2b) and POA composition.

Approach 2: $pX = -\log(\text{mole fraction})$ or X is plotted vs. n_c and *tmp* computed according to Eq 4. Mole fractions are estimated from data presented in the CP10 paper and using Henry's law constants from the SPARC Program (Hilal et al. 2004).

Approach 2: Theoretical retention diagrams are generated based on Eqs 1-3 to simulate organic compound retention in phases having known values of solvation parameters (Poole & Poole, in press) in GC×2GC. Compound solvation parameters were obtained using Absolv software (ACD/LABS, 1994).

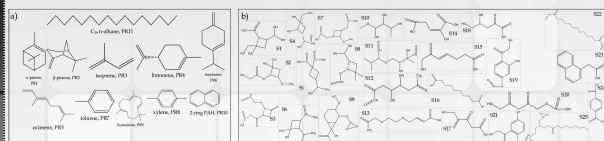


Figure 2. a) Surrogate SOA precursors and b) SOAs included in the study of Chang & Pankow (2010).

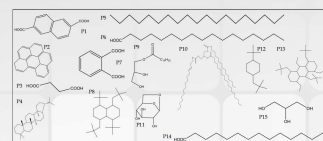


Figure 3. Surrogate POAs included in the study of Chang & Pankow (2010).

IV. RESULTS

Figure 4. pX or X vs. *tmp* and n_c for a) the simulated initial whole sample, b) the whole air sample following reaction and partitioning, and c) the liquid phases of oxidized and partitioned sample for (c1) RH=5%, $\theta = \alpha$; (c2) RH=5%, $\theta = \beta$; (c3) RH=80%, $\theta = \alpha$; and (c4) RH=80%, $\theta = \beta$.

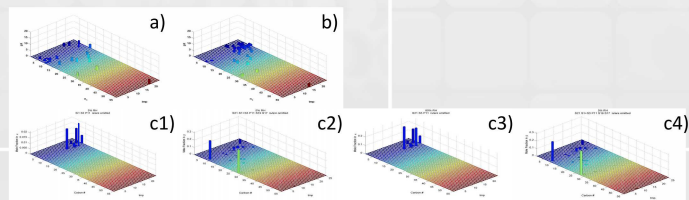
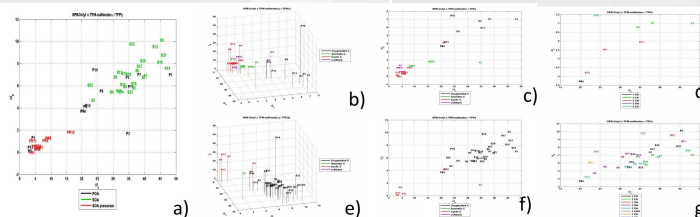


Figure 5. a) all-compound secondary dimensions plot; b) 3D retention diagram of initial whole air sample (surrogate precursor SOAs + POAs); secondary dimensions of c) initial whole air sample, and d) oxygenated compounds in initial whole air sample only; e) retention diagram of final whole air sample (surrogate SOAs + POAs); secondary dimensions of f) final whole air sample, and g) oxygenated compounds in final whole air sample only.



V. DISCUSSION

Although the binning demonstrated in the n_c vs. *tmp* grids in Figure 4 provides significantly improved resolution over the commonly-used two-product model (Odum et al. 1996), binning provides coarser resolution than is obtained using the GC×2GC analytic approach simulated in Figure 5. When OA is lumped by *tmp*, specific oxidation products may not be quantified. In addition, when gas and aerosol phases are lumped by *tmp*, it may not be possible to follow early generations of oxidation that produce gas-phase oxygenated products. This is demonstrated through comparison of the subplots in Figure 4. The lumped *tmp* of the evolved whole air sample in Figure 4b does not allow determination of gas-phase composition, which may contain gas-phase oxidation products that if subsequently oxidized can yield SOAs.

The organic molecular approach demonstrated in Figure 5 is superior because the volatile, semi-volatile, and nonvolatile oxidation products can be determined, with no loss in resolution of polarity through binning. Figure 5a demonstrates resolution of the surrogate SOA precursors and SOA compounds. Figure 5b and 5e demonstrate separation according to n_c in the primary dimension, and according to polarity in the second dimensions. Even oxygenated organic compounds that contain multi- and polyfunctionality can be resolved, as demonstrated in Figures 5d and 5g.

VI. CONCLUSION

The n_c vs. *tmp* grid is useful for visualizing trends in atmospheric organic character, however the organic molecular approach has greater potential to quantify organic molecular character in chemical transport modules. With RH, temperature, and levels of gas-phase oxidants, the GC×2GC analysis of the gas- and aerosol-phase organic species can be used as input to an SOA model.

VII. REFERENCES

- Abraham MH. 1993. Scales of solute hydrogen-bonding: their construction and application to physicochemical and biochemical processes. *Chem. Soc. Rev.* 22:73-83
- ACD/LABS. 1994. ACD/ADME Suite. Toronto, CA
- Arp HPH, Schwarzenbach RP, Goss KU. 2008. Ambient gas/particle partitioning. 2: The influence of particle source and temperature on sorption to dry terrestrial aerosols. *Environ. Sci. Technol.* 42:5951-7
- Chang EJ, Pankow JF. 2010. Organic particulate matter formation at varying relative humidity using surrogate secondary and primary organic compounds with activity corrections in the condensed phase obtained using a method based on the Wilson equation. *Atmos. Chem. Phys.* 10:5475-90
- Erdakov GB, Pankow JF. 2004. Gas/particle partitioning of neutral and ionizing compounds to single- and multi-phase aerosol particles. 2. Phase separation in liquid particulate matter containing polar and low-polarity organic compounds. *Atmos. Environ.* 38:1005-13
- Hilal SH, Carreira LA, Karickhoff SW. 2004. Prediction of the solubility, activity coefficient, gas/liquid and liquid/liquid distribution coefficients of organic compounds. *QSAR & Combinatorial Science* 23:709, SPARC Website URL: <http://ibimic2.chem.uga.edu/sparc/>, accessed 3-25-11
- Odum JR, Hoffman T, Bowman F, Collins D, Flagan RC, Seinfeld JH. 1996. Gas/particle partitioning and secondary organic aerosol yields. *Environ. Sci. Technol.* 30:2580-5
- Pankow JF, Barsanti KC. 2009. The carbon number-polarity grid: a means to manage the complexity of the mix of organic compounds when modeling atmospheric organic particulate matter. *Atmos. Environ.* 43:2829-35
- Poole CF, Poole SK. 2011. Ionic liquid stationary phases for gas chromatography. *J. Sep. Sci.* 34:in press
- Schwarzenbach RP, Gschwend PM, Imboden DM. 2003. *Environmental Organic Chemistry*. New York: Wiley Interscience. 681 pp.
- Seeley JV, Libby EM, Edwards KAH, Seeley SK. 2009. Solvation parameter model of comprehensive two-dimensional gas chromatography separations. *J. Chromatogr. A*. 1216:1650-7

VIII. ACKNOWLEDGEMENTS

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