

AEROSOL-FORMING POTENTIAL OF ATMOSPHERIC ORGANIC COMPOUNDS

John H. Seinfeld¹, Prasad Pai², and David Allen³

¹California Institute of Technology

²AER, San Ramon, CA 94583

³The University of Texas, Austin, TX 78758-4497

CONTENTS

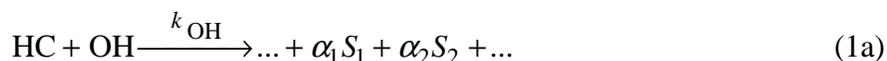
CONTENTS.....	1
INTRODUCTION.....	1
THEORY OF SECONDARY ORGANIC AEROSOL FORMATION.....	2
EXPERIMENTAL DETERMINATION OF SOA YIELDS.....	3
TREATMENT OF SECONDARY ORGANIC AEROSOLS IN CURRENT ATMOSPHERIC MODELS.....	7
INSIGHTS AVAILABLE FROM DATA ON AMBIENT ORGANIC AEROSOL.....	9
REFERENCES.....	12

INTRODUCTION

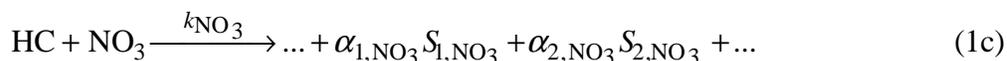
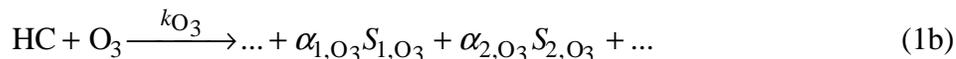
Urban fine particulate matter is comprised of a complex mixture of both primary and secondary organic and inorganic compounds and emanates from a wide variety of sources. An important component that can significantly contribute to the fine particulate burden, especially during severe urban smog episodes, is secondary organic aerosol (SOA). Like ozone, secondary organic aerosol results from the atmospheric oxidation of reactive organic gases (ROGs), but whereas the oxidation of most ROGs results in ozone formation, SOA is generally formed only from the oxidation of ROGs comprised of six or more carbon atoms. This is because oxidation products must have vapor pressures that are sufficiently low to enable them to partition into the aerosol phase.

The atmospheric chemical reaction pathways of ROG molecules sufficiently large to lead to SOA are complex, and resulting oxidation products are both numerous and difficult to quantify analytically. As a result, it is currently not possible to determine the aerosol formation potential of individual ROGs and their contribution to the secondary organic urban particulate burden strictly on the basis of atmospheric chemical reaction mechanisms.

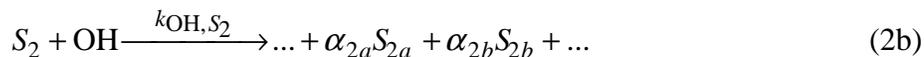
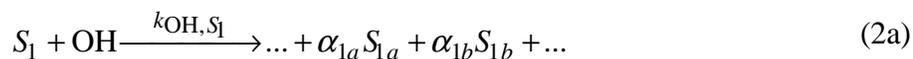
The chemical process of organic aerosol formation involves the formation of semi-volatile organic gases, S_1 , S_2 , ..., from the gas-phase reaction of a parent hydrocarbon, HC, with the OH radical,



where k_{OH} is the OH reaction rate constant, and $\alpha_1, \alpha_2, \dots$ are the stoichiometric product coefficients. Later these stoichiometric coefficients will be expressed on a mass basis, rather than the usual molar basis. If the parent hydrocarbon is an alkene, reactions with O_3 and NO_3 radicals are also possible, providing additional pathways for semi-volatile product formation,



The first-generation products, S_1, S_2, \dots may subsequently undergo gas-phase reaction themselves creating second-generation condensable products, S_{1a}, S_{1b}, \dots and S_{2a}, S_{2b}, \dots ,



where k_{OH,S_1} and k_{OH,S_2} are the OH-reaction rate constants for the products, S_1 and S_2 , respectively.

Secondary organic aerosol yields have been measured for many individual ROGs by a number of researchers over the last decade or more (Izumi and Fukuyama, 1990; Wang *et al.*, 1991ab; Pandis *et al.*, 1991; Zhang *et al.*, 1991; Odum *et al.*, 1996, 1997ab; Hoffmann *et al.*, 1997; Forstner *et al.*, 1997ab; Griffin *et al.*, 1998). Initially it was believed that each ROG should possess a unique value of its SOA yield (Grosjean and Seinfeld, 1989; Pandis *et al.*, 1992, 1993), but measured yields for an individual ROG exhibited a wide degree of variation that could not be reconciled in terms of a single, unique SOA yield for each parent ROG. Following Pankow (1994ab), Odum *et al.* (1996) formulated a framework for explaining observed SOA yield data. They suggested that secondary organic aerosol formation is best described by a gas/aerosol absorptive partitioning model. Within that framework, semi-volatile products from the atmospheric oxidation of an ROG can partition into an absorbing organic aerosol (om) phase at a concentration below their saturation concentration, analogous to the partitioning that occurs between the gas and aqueous phases of a water-soluble atmospheric constituent.

THEORY OF SECONDARY ORGANIC AEROSOL FORMATION

Equilibrium gas-particle absorptive partitioning of a semi-volatile organic species i between the gas phase and an organic phase is described by (Bowman *et al.*, 1997)

$$p_i = x_i \zeta_i p_i^0 \quad (3)$$

where p_i (torr) is the gas-phase partial pressure of species i , x_i is the mole fraction of species i in the aerosol phase, ζ_i is the activity coefficient of species i in the aerosol-phase organic mixture, and p_i^o (torr) is the vapor pressure of species i as a pure liquid (subcooled, if necessary). The gas-phase partial pressure, p_i , can be converted to the gas-phase mass concentration, G_i ($\mu\text{g m}^{-3}$), by the relationship

$$G_i = \frac{p_i m_w}{RT} 10^6 \quad (4)$$

where m_w (g mol^{-1}) is the mean molecular weight of the absorbing organic matter, R ($=6.2 \times 10^2 \text{ torr m}^3 \text{ mol}^{-1} \text{ K}^{-1} = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) is the ideal gas constant and T (K) is temperature. The factor 10^6 accomplishes the appropriate unit conversions. For organic species with similar molecular weights, the aerosol mole fraction, x_i , is given by

$$x_i = \frac{A_i}{\sum_k A_k + M_{\text{init}}} \quad (5)$$

where A_i ($\mu\text{g m}^{-3}$) is the aerosol mass concentration of species i , $\sum A_k$ ($\mu\text{g m}^{-3}$) is the total aerosol mass concentration of all the individual semi-volatile organic species, and M_{init} represents any initially present absorbing organic mass. Equations (4) and (5) can be substituted into equation (3) and rearranged to yield

$$\frac{A_i}{G_i (\sum_k A_k + M_{\text{init}})} = \frac{RT}{m_w \zeta_i p_i^o} 10^{-6} = K_i \quad (6)$$

where K_i ($\text{m}^3 \mu\text{g}^{-1}$) is defined as the absorption partitioning coefficient of species i (Pankow, 1994a, b; Odum *et al.*, 1996). The absorption partitioning coefficient incorporates vapor pressure, activity coefficient, and molecular weight, providing a single equilibrium parameter for each compound. K_i is analogous to a Henry's law coefficient in relating gas-phase concentrations of species i to the mass fraction of species i in the aerosol phase. An important implication of Equation (6) is that, since, at a particular temperature, K_i is a constant, a greater fraction of each product must partition to the organic phase as the total organic aerosol concentration increases.

EXPERIMENTAL DETERMINATION OF SOA YIELDS

The approach that has been most successful to estimate the SOA forming capability of a ROG involves the direct measurement of secondary organic aerosol yields. The SOA yield Y is a measure of the mass of aerosol that is produced from the atmospheric oxidation of an ROG and is defined as

$$Y = \frac{\Delta M_o}{\Delta \text{ROG}} \quad (7)$$

where ΔM_o is the amount of aerosol produced ($\mu\text{g m}^{-3}$) for a given reacted amount of an ROG, ΔROG ($\mu\text{g m}^{-3}$). In the study of secondary organic aerosol formation, typically a smog chamber is initially filled with a mixture of NO_x , inorganic seed particles, and an aerosol-producing hydrocarbon. The chamber is then exposed to sunlight, or other UV sources, that initiates photooxidation. As the hydrocarbon reacts it forms semi-volatile products that condense on the seed particles. If mass transport to the available particles cannot keep up with the rate of product formation or when a seed aerosol is not initially present, the semi-volatile products accumulate in the gas phase until supersaturation is reached, and nucleation occurs (Bowman *et al.*, 1997). Studies show that the amount of aerosol produced for a given amount of reacted ROG is independent of whether a seed aerosol is present or not. Reactions are ordinarily run until the entire initial amount of ROG is consumed. Typically the volume of the initial seed aerosol is small compared to the organic aerosol volume generated, and $\sum_k A_k = \Delta M_o$

The total SOA yield from an ROG that generates N semi-volatile products is computed as follows. The total concentration of product i , C_i , is proportional to the total amount of parent organic that reacts, ΔROG ,

$$\alpha_i \Delta\text{ROG} = C_i \quad (8)$$

C_i is also equal at any time to the sum of the gas- (G_i) and aerosol - (A_i) phase concentrations of i ,

$$C_i = A_i + G_i \quad (9)$$

The yield of product i , Y_i , is $A_i/\Delta\text{ROG}$. The total SOA yield is just the sum of the individual product yields,

$$Y = \sum_{i=1}^N Y_i \quad (10)$$

Combining these relations with the definition of the gas-particle partitioning constant, K_i , gives the expression for the total yield in terms of the individual product stoichiometric coefficients α_i and partitioning coefficients, K_i , and the organic aerosol mass concentration, ΔM_o ,

$$Y = \Delta M_o \sum_{i=1}^N \frac{\alpha_i K_i}{1 + K_i \Delta M_o} \quad (11)$$

Note that in the limit of small organic aerosol mass concentration,

$$Y \sim \Delta M_o \sum_{i=1}^N \alpha_i K_i \quad (12)$$

the SOA yield is directly proportional to the amount of organic aerosol mass ΔM_o , and that in the limit of large ΔM_o ,

$$Y \sim \sum_{i=1}^N \alpha_i \quad (13)$$

where the total yield is independent of ΔM_o and is just the sum of the mass-based stoichiometric coefficients of the products.

It is important to distinguish between aerosol yield, Y , and stoichiometric coefficients, α_i . Stoichiometric coefficients depend on the gas-phase chemical mechanism and are assumed constant; they represent the total amount of semi-volatile product formed, in both gas and aerosol phases, per amount of parent hydrocarbon reacted. The yield, on the other hand, which measures only the semi-volatile products that have partitioned into the aerosol phase, is not constant but will vary depending on the amount of organic mass available as an absorption medium. Stoichiometric coefficients by themselves are therefore not sufficient to predict the amount of aerosol formation (except in the limit of very large organic mass, as in equation (13)). Partitioning coefficients, stoichiometric coefficients, and organic aerosol mass are required in general to determine the SOA yield.

Ozone-forming potential of organics is determined based on atmospheric reaction mechanisms. In principle, aerosol-forming potential could be calculated based on a similar atmospheric oxidation mechanism that includes all significant semi-volatile product species. The actual amount of aerosol that would be formed under a particular set of circumstances, unlike ozone, depends on the amount of aerosol available to absorb the semi-volatile products. The relative aerosol-forming potential of a group of organics could, in principle, be determined based on their oxidation products and the thermodynamic properties of these products.

This ab initio approach represents a goal that is not yet attainable because of incomplete knowledge of the semi-volatile oxidation products of the important aerosol-forming compounds. Thus, it is necessary to rely on experimentally measured aerosol yields. Aerosol yields Y are expressed theoretically as a fraction of the available aerosol organic mass ΔM_o through Equation (11). Observed aerosol yields as a function of ΔM_o can be fit to Equation (11) by specifying the stoichiometric coefficients α_i and gas-particle partitioning coefficients K_i of each of the semi-volatile products of oxidation of the parent organic.

Over the last several years, SOA yields for over 30 aromatic and biogenic organics have been measured in the California Institute of Technology outdoor smog chamber (Table 1). In order to fit the observed yields to Equation (11), the mix of semi-volatile oxidation products for each parent compound has been represented by two empirical products, characterized by parameters α_1 , K_1 , and α_2 , K_2 . It has been determined that observed yields cannot be fit by assuming only a single product and that three products is superfluous (Odum *et al.*, 1996). Roughly speaking, one of the empirical semi-volatile products tends to represent a relatively lower vapor pressure compound and the other a relatively higher vapor pressure compound. Low-yield aromatics represent those species that fall on the lower of two curves of Y versus ΔM_o described by Odum *et al.*, (1997ab). Correspondingly, high-yield aromatics represent the species falling on the higher of the two curves.

Table 1. Aerosol Formation Parameters α_i and $K_{om,i}$ ($\text{m}^3 \mu\text{g}^{-1}$) Obtained in the Caltech Smog Chamber (Odum *et al.*, 1996, 1997a, 1997b; Hoffmann *et al.*, 1997; Griffin *et al.*, 1998)

Hydrocarbon	α_1	K_1	α_2	K_2
<u>Aromatic Compounds (17)</u>				
Low-yield aromatics	0.038	0.042	0.167	0.0014
High-yield aromatics	0.071	0.053	0.138	0.0019
Diethylbenzene	0.083	0.093	0.220	0.0010
Methylpropylbenzene	0.050	0.054	0.136	0.0023
<u>Biogenic Compounds (13)</u>				
Δ^3 -Carene	0.054	0.043	0.517	0.0042
β -Caryophyllene	1.000	0.0416	-	-
α -Humulene	1.000	0.0501	-	-
Limonene	0.239	0.055	0.363	0.0053
Linalool	0.073	0.049	0.053	0.0210
Ocimene	0.045	0.174	0.149	0.0041
α -Pinene	0.038	0.171	0.326	0.0040
β -Pinene	0.130	0.044	0.406	0.0049
Sabinene	0.067	0.258	0.399	0.0038
α -& γ -Terpinene	0.091	0.081	0.367	0.0046
Terpinene-4-ol	0.049	0.159	0.063	0.0045
Terpinolene	0.046	0.185	0.034	0.0024

It must be noted that this theory assumes that secondary products are unable to form a solution with existing inorganic seed aerosol. Accounting for the interactions between the organic compounds themselves allows it to be shown that such products can condense onto seed aerosol at concentrations lower than those predicted by saturation theory alone (Seinfeld and Pandis, 1998). In this case, the threshold amount of parent compound that must react to form secondary organic aerosol is defined as ΔROG^* . After consumption of ΔROG^* , products condense onto seed aerosol to form an initial organic layer that can then act as an absorptive medium. At this point, absorption becomes the dominant mechanism governing the partitioning of secondary products and, therefore, determining yield, as in the atmosphere.

The stoichiometric and partitioning parameters allow direct evaluation of the aerosol-forming potential of the parent organics. The SOA yield Y is the mass of aerosol produced per unit mass of parent organic reacted, and Y depends on the amount of organic aerosol mass available to absorb the semi-volatile oxidation products. SOA potentials are given by Odum *et al.* (1997ab) for 17 aromatic precursors and by Griffin *et al.* (1998) for 14 biogenic precursors.

Odum *et al.* (1997ab) showed, moreover, that aerosol yields for the photooxidation of a mixture of parent hydrocarbons can be predicted simply as the sum of the SOA yields for the individual parent compounds. This suggests that, at least for the case of a pure organic absorbing phase, oxidation products of different parent hydrocarbons are as soluble in a mixed organic product phase as in an organic phase consisting exclusively of their own oxidation products.

The experimentally determined SOA yields reported by Odum *et al.* (1997ab) and Griffin *et al.* (1998) have been measured at relative humidity (RH) less than 5%. At this level of RH the seed aerosol, $(\text{NH}_4)_2\text{SO}_4$, is dry and the resulting organic aerosol is water-free. Experiments are presently underway at Caltech to measure SOA yields as a function of RH over realistic ambient RH ranges. Because organic products will likely be most soluble in their own liquids, SOA yields measured at essentially 0% RH can be expected to represent an upper limit to the aerosol partitioning that will result. While many SOA products are water soluble (Saxena and Hildemann, 1996), they are not expected to be more soluble in an aqueous mixture than in a pure organic phase.

TREATMENT OF SECONDARY ORGANIC AEROSOLS IN CURRENT ATMOSPHERIC MODELS

Because of the difficulties in characterizing SOA on a molecular basis and considering the significant uncertainties associated with model input data - for example emissions of VOC that are SOA precursors - the treatment of SOA in current air quality models is limited. Seigneur *et al.* (1998) recently reviewed the treatment of SOA formation in current regulatory and research-grade air quality models. Table 2, adapted from Seigneur *et al.* (1998), compares the SOA treatment in eight current air quality models. Details on the individual air quality models can be obtained from the original references provided in Table 2.

Of the eight models that treat SOA formation, six (DAQM, RPM, SAQM-AERO, UAM-AERO, UAM-AIM and VISHWA) use the lumped SOA yield approach of Pandis *et al.* (1992), which makes use of the VOC-specific fractional aerosol coefficients of Grosjean and Seinfeld (1989). In this approach, each class of VOC in the gas-phase chemical kinetic mechanism is assumed to lead to a fixed fraction of SOA product through its oxidation reactions. This results from the basic assumption that a fixed fraction of the products of the VOC oxidation is condensable. The amount of the condensable organics that exceeds the corresponding saturation vapor pressure is converted to the particulate phase. The saturation vapor pressure in most models is typically set to zero or a small value (1ppt). The six air quality models that employ the lumped SOA yield approach of Pandis *et al.* (1992) use different gas-phase mechanisms. These

Table 2. Treatment of SOA Formation in Current Air Quality Models

Air Quality Model	Secondary Organic Aerosol Treatment		Reference
	Gas Phase Chemical Mechanism	SOA Formation	
CIT	Extended LCC	Absorption mechanism with mass transfer	Meng <i>et al.</i> (1998)
DAQM	RADM2	Lumped aerosol yields of Pandis <i>et al.</i> (1992)	Moucheron and Milford (1996)
GATOR	GATOR	Solubility in water	Jacobson (1997)
REMSAD	Condensed CBM-IV chemistry	VOC emission fraction	Guthrie <i>et al.</i> (1995)
RPM	RADM2	Lumped aerosol yields of Pandis <i>et al.</i> (1992)	Binkowski and Shankar (1995)
SAQM-AERO	CBM-IV and SAPRC	Lumped aerosol yields of Pandis <i>et al.</i> (1992)	Dabdub <i>et al.</i> (1998)
UAM-AERO	CBM-IV and SAPRC	Lumped aerosol yields of Pandis <i>et al.</i> (1992)	Lurmann <i>et al.</i> (1997)
UAM-AIM	CBM-IV and SAPRC	Lumped aerosol yields of Pandis <i>et al.</i> (1992)	Sun and Wexler (1998)
UAM-LC	Parameterized chemistry	None	Lurmann and Kumar (1996)
VISHWA	Condensed chemistry (7 reactions and 7 species)	2-component approach with aromatic and terpene lumped aerosol yields of Pandis <i>et al.</i> (1992) adjusted downward to match ambient observations	Venkatram <i>et al.</i> (1997)

gas-phase mechanisms include the Carbon Bond Mechanism (CBM-IV), RADM2, GATOR, SAPRC, and extended LCC mechanisms, which are described by Gery *et al.* (1989), Stockwell *et al.* (1990), Jacobson (1994), Carter (1990, 1995), and Harley *et al.* (1993), respectively. In five of the six air quality models listed in Table 2, the lumped SOA yields of Pandis *et al.* have been used without any modifications. In the VISHWA model, the lumped SOA yields of Pandis *et al.* for the two lumped SOA precursors used, i.e., aromatics and terpenes, have been adjusted downward by a factor of about eight, reportedly to match experimental observations. UAM-LC does not currently treat SOA formation and REMSAD uses fixed yields for VOC emissions, i.e., it does not have kinetic treatment of SOA formation.

GATOR does not use the lumped SOA yield approach but instead describes gas-particle partitioning of about ten condensable and soluble organic species that, however, are not directly representative of ambient condensable reaction products. In CIT, SOA is modeled by mass transport between gas and particulate phases, which is governed by the same formulation as that for inorganic volatile compounds. The surface vapor concentrations of semi-volatile organic compounds G_i^{eq} are calculated according to Equation (6),

$$G_i^{eq} = \frac{A_i}{K_i OM} \quad (14)$$

where A_i ($\mu\text{g m}^{-3}$) is the concentration of organic species i in the aerosol phase, K_i ($\text{m}^3 \mu\text{g}^{-3}$) is the absorption partitioning coefficient, and OM ($\mu\text{g m}^{-3}$) is the absorbing organic mass concentration. Recent work by Strader *et al.* (1998) combines the organic-phase absorption approach of Odum *et al.* (1996, 1997ab) with recent experimental data on saturation vapor pressures of organic compounds. Strader *et al.* (1998) used a model with six condensable products (6 partition parameters): one from alkane precursors (also for benzaldehyde phenol, cresol, and nitrophenol), three from aromatic precursors, one from alkene precursors, and two from monoterpenes. Each precursor forms one or two condensable products, resulting in 14 yield parameters determined on the basis of data from the Caltech chamber. This approach has been incorporated in the revised version of the UAM-AERO air quality model.

The key differences between Odum *et al.* and the Strader *et al.* approaches lie in the determination of the absorption partitioning coefficient K_i ($\text{m}^3 \mu\text{g}^{-3}$) and in the precursor/product species that are modeled. As noted earlier, Odum *et al.* (1997ab) assumed two condensable products for each aerosol precursor, with the absorption model fitted to data obtained in smog chamber experiments to determine empirically the yield and partition parameters. Strader *et al.*, (1998) invoked solution theory in their determination of the partition coefficients. Raoult's law describes the equilibrium partition of an ideal gas-ideal solution system,

$$y_i p = x_i p_i^{sat} \quad (15)$$

where $y_i p$ is the partial pressure of compound i in the gas phase, x_i is the mole fraction of i in the liquid phase, and p_i^{sat} is the saturation vapor pressure of i at the system temperature. Converting the units from pressure to mass concentration in the gas phase,

$$c_i^{gas} = x_i c_i^{gas.sat} \quad (16)$$

Instead of the equilibrium constant K_i , the partitioning of compound i is calculated via the saturation concentration, $c_i^{gas.sat}$, of i in the gas phase. Since the identities of the condensing SOA compounds are frequently unknown, $c_i^{gas.sat}$ is chosen based on smog chamber results and laboratory experiments for the temperature dependence of the saturation concentrations. The methodology of Strader *et al.* (1998) provides the framework for incorporating mechanistic information of the condensing species when it becomes available. At present, however, both methods rely on empirical data to determine the partition parameters.

INSIGHTS AVAILABLE FROM DATA ON AMBIENT ORGANIC AEROSOL

In the interest of space, we do not endeavor to survey here data on ambient levels of secondary organic aerosol in different areas of the United States. We refer the reader to the recent review of Turpin *et al.* (1999) and references therein. The most extensive data base on secondary organic aerosol is available for the California South Coast Air Basin, where levels can

reach 50% or more of the organic PM_{2.5} mass during photochemical pollution episodes. The extent of importance in other areas of the country will need to be evaluated through a combination of ambient measurements and atmospheric modeling.

Data on the composition of ambient organic aerosol can provide some insights into the magnitude of secondary organic aerosol formation and the chemical pathways and precursors that are responsible for the aerosol formation. Three types of data on ambient aerosol can be used in these assessments:

- Data on organic and elemental carbon in ambient aerosol can be used to estimate the overall magnitude of secondary aerosol formation;
- Data on organic compound classes, such as carbonyl groups and organonitrate groups, can be used to assess the magnitude of secondary organic aerosol formation and the approximate composition of the secondary aerosol;
- Concentrations of molecular tracers can be used to assess the role of individual hydrocarbon precursors in secondary organic aerosol formation.

Each of these approaches is discussed briefly below.

Often, the only data available on the carbonaceous fraction of organic aerosol are measurements of “organic” and “elemental” carbon. Elemental carbon is roughly defined as the material that will not thermally desorb from a filter sample and is generally attributed to graphitic, soot-like structures. Elemental carbon is assumed to be exclusively due to primary emissions. Organic carbon is roughly defined as material that will thermally desorb from a filter sample and may be associated with either primary or secondary aerosol. The most common approach for using ambient data on organic and elemental carbon to estimate the magnitude of secondary organic aerosol formation involves using the ratios of elemental to organic carbon. (Turpin and Huntzicker, 1991; Turpin *et al.*, 1991; McMurry, 1989; McMurry and Zhang, 1989; Gray *et al.*, 1986) By assuming that all of the elemental carbon is primary and that the primary organic aerosol has a characteristic ratio of organic to elemental carbon, it is possible to estimate the fraction of organic aerosol that is primary. The remainder of the organic aerosol is assumed to be secondary. The accuracy of these estimates of secondary organic aerosol formation is highly dependent on having accurate values for the ratio of organic to elemental carbon in the primary aerosol - a quantity that is not known with certainty. Thus, estimates of secondary aerosol formation based on organic and elemental carbon measurements may be subject to inaccuracies. Nevertheless, because organic and elemental carbon measurements are often the only data available on the carbonaceous component of atmospheric aerosol, these methods will remain in common use.

Functional group measurements are an alternative to using organic and elemental carbon to estimate secondary organic aerosol concentrations. A large fraction of organic aerosol can be characterized using compound class or functional group measurements based on infrared spectroscopy (Pickle *et al.*, 1990; Mylonas *et al.*, 1991; Allen *et al.*, 1994). In these functional group measurements, the organic fraction of an ambient sample is typically assumed to consist of aliphatic carbon, aromatic carbon, carbonyl, organonitrate, nitroaromatic, and a few other

functional groups. Some of these functional groups, such as ketones, aldehydes and organonitrates, are due almost exclusively to secondary organics. Other functional groups, such as aliphatic and aromatic carbons could be either primary or secondary. Thus, the concentrations of groups like ketones, aldehydes and organonitrates can provide a lower bound on secondary aerosol formation and assumptions about average structures of the compounds that make up secondary organic aerosol can be used to estimate total secondary organic concentrations. Again, this method of estimating secondary organic aerosol has uncertainties associated with it. The method does provide, however, measurements that are complementary to the usual measurements of elemental and organic carbon, and the functional group measurements begin to provide some insight into the chemical structures making up the secondary organic aerosol.

Neither organic carbon/elemental carbon measurements nor functional group measurements identify which gas phase precursors led to the secondary aerosol. In order to attribute secondary organic aerosol to specific hydrocarbon precursors, it is necessary to perform molecular level characterizations of ambient organic aerosol. A number of recent studies (see, for example, Hildemann, *et al.*, 1994) have been used individual compounds as tracers for aerosol sources. This molecular tracer approach has been quite successful in identifying the major sources of primary carbonaceous aerosol, but to date, the method has not been applied to secondary aerosol because the yields and stabilities of the molecular products of gas-phase photooxidation reactions are relatively unknown. A literature on molecular tracers for secondary organic aerosol is beginning to emerge, however, and this approach to understanding the precursors for secondary aerosol is likely to become increasingly important.

To summarize, ambient data on aerosol composition provides some information on the magnitude and structure of secondary organic aerosol, but this information is incomplete and requires that significant assumptions be made in interpreting the ambient data. Our understanding of the chemical nature and sources of secondary organics would be significantly improved by the identification of suitable molecular tracers of organic aerosol formation pathways.

Atmospheric chemical reaction mechanisms currently included in urban-and regional-scale models were designed for accurate prediction of ozone formation chemistry. Generally, these mechanisms do not account for the chemistry of organics in sufficient detail to predict the generation of semi-volatile products. Many of the higher molecular weight organics that are not important in ozone formation, but are sources of secondary organic aerosol, are not represented in current mechanisms. To predict SOA formation, chemical reaction mechanisms need to be expanded to include all important SOA-forming organics and to include, to the extent known, a representation of the semi-volatile products formed from each parent compound. Evaluation of the organics that need to be included will be based on available chamber data, on estimated atmospheric oxidation mechanisms, and on the estimated vapor pressures of the oxidation products. While this expansion may not lead to substantially improved ozone prediction, it is essential to prediction of SOA formation.

REFERENCES

- Allen, D. T., Palen, E. J., Haimov, M. I., Hering, S. V., and Young, J. R. (1994) Fourier transform infrared spectroscopy of aerosol collected in a low pressure impactor: Method development and field calibration, *Aerosol Science and Technology*, **21**, 325-342.
- Binkowski, F. S. and Shankar, U. (1995) The regional particulate matter model, 1: model description and preliminary results, *J. Geophys. Res.*, 100, 26,191-26,209.
- Bowman, F.M., Odum, J. R., Pandis, S. N., and Seinfeld, J. H. (1997), Mathematical model for gas/particle partitioning of secondary organic aerosols, *Atmos. Environ.*, **31**, 3921-3931.
- Carter, W. P. L. (1990) A detailed mechanism for the gas phase atmospheric reactions of organic compounds, *Atmos. Environ.*, **24A**, 481-518.
- Dabdub, D., Dehaan, L. L., Kumar, N., Lurmann, F., and Seinfeld, J. H. (1998) Computationally efficient acid deposition model for California, Draft Report, ARB Contract #92-304, California Resources Board, Sacramento, California.
- Forstner, H. J. L., Flagan, R. C., and Seinfeld, J. H. (1997a) Secondary organic aerosol formation from the photooxidation of aromatic hydrocarbons: molecular composition. *Environ. Sci. Technol.*, **31**, 1345-1358.
- Forstner, H. J. L., Seinfeld, J. H., and Flagan, R. C. (1997b), Molecular speciation of secondary organic aerosol from the higher alkenes: 1-octene and 1-decene, *Atmos. Environ.*, **31**, 1953-1964 (1997).
- Gery, M. W., Whitten, G. Z., Killus, J. P., and Dodge, M. C. (1989) A photochemical kinetics mechanism for urban and regional scale computer modeling, *J. Geophys. Res.*, **94**.
- Gray, H. A., Cass, G. R., Huntzicker, J. J., Heyerdal, E. K., and Rau, J. A. (1986) Characteristics of atmospheric organic and elemental carbon particle concentrations in Los Angeles, *Environ. Sci. Technol.*, **20**, 580-589.
- Griffin, R. J., Cocker, D. R., Flagan, R. C., and Seinfeld, J. H. (1998) Organic aerosol formation from the oxidation of biogenic hydrocarbons, *J. Geophys. Res.*, in press.
- Grosjean, D. and Seinfeld, J. H. (1989) Parameterization of the formation potential of secondary organic aerosols. *Atmos. Environ.*, **23**, 1733-1747.
- Guthrie, P. D., et al. (1995) Development and preliminary testing of the regulatory modeling system for aerosols and deposition (REMSAD), technical memorandum SYSAPP-96111, Systems Applications International, San Rafael, California.

- Harley, R. A., Russell, A. G., and Cass, G. R. (1993) Mathematical modeling of the concentrations of volatile organic compounds: Model performance using a lumped chemical mechanism, *Environ. Sci. Technol.* **27**, 1638-1649.
- Hildemann, L., Klinedinst, D. B., Klouda, G. A., Currie, L. A., and Cass, G. R. (1994) Sources of urban contemporary carbon aerosol, *Environ. Sci. Technol.*, **28**, 1565-1575.
- Hoffmann, T., Odum, J. R., Bowman, F., Collins, D., Klockow, D., Flagan, R. C., and Seinfeld, J. H., (1997) Formation of organic aerosols from the oxidation of biogenic hydrocarbons, *J. Atmos. Chem.*, **26**, 189-222.
- Izumi, K. and Fukuyama, T. (1990) Photochemical aerosol formation from aromatic hydrocarbons in the presence of NO_x. *Atmos. Environ.*, **24**, 1433-1441.
- Jacobson, M. Z. (1994) Developing, coupling, and applying a gas, aerosol, transport, and radiation model to study urban and regional air pollution, Ph.D. thesis, Department of Atmospheric Sciences, University of California, Los Angeles, California.
- Jacobson, M. Z. (1997) Development and application of a new air pollution modeling system. Part II: Aerosol module structure and design, *Atmos. Environ.*, **31**, 131-144.
- Lurmann, F. W. and Kumar, N. (1996) Development of chemical transformation algorithms for annual PM10 dispersion models, draft report STI-95410-1602-DFR, South Coast Air Quality Management District, Diamond Bar, California.
- Lurmann, F. W., Wexler, A. S., Pandis, S. N., Musarra, S., Kumar, N., and Seinfeld, J. H. (1997) Modeling urban and regional aerosols: II. Application to California's South Coast Air Basin, *Atmos. Environ.*, **31**, 2695-2715.
- McMurray, P. H. (1989) Organic and elemental carbon size distributions of Los Angeles aerosols measured during SCAQS, Report to the Coordinating Research Council and the California Air Resources Board (CARB Contract A732-075: 1989).
- McMurray, P. H., and Zhang, X. Q. (1989) Size distributions of ambient organic and elemental carbon, *Aerosol Science and Technology*, **10**, 430-437.
- Meng, Z., Dabdub, D., and Seinfeld, J. H. (1998) Size- and chemically-resolved model of atmospheric aerosol dynamics, *J. Geophys. Res.*, **103**, 3419-3435.
- Moucheron, M. C. and Milford, J. (1996) Development and testing of a process model for secondary organic aerosols, Air & Waste Management Association Annual Meeting, Paper 96-FA1308.03, Nashville, Tennessee.
- Mylonas, D. T., Allen, D. T., Ehrman, S. H., and Pratsinis, S. E. (1991) The sources and size distributions of organonitrates in Los Angeles aerosol, *Atmos. Environ.*, **5**, 2855-2861.

- Odum, J. R., Hoffmann, T., Bowman, F., Collins, D., Flagan, R. C., and Seinfeld, J. H. (1996) Gas/particle partitioning and secondary organic aerosol yields. *Environ. Sci. Technol.*, **30**, 2580-2585.
- Odum, J. R., Jungkamp, T. P. W., Griffin, R. J., Forstner, H. J. L., Flagan, R. C., and Seinfeld, J. H. (1997a), Aromatics, reformulated gasoline, and atmospheric organic aerosol formation, *Environ. Sci. Technol.*, **31**, 1890-1897 (1997).
- Odum, J. R., Jungkamp, T. P. W., Griffin, R. J., Flagan, R. C., and Seinfeld, J. H. (1997b) The atmospheric aerosol-forming potential of whole gasoline vapor. *Science*, **276**, 96-99.
- Pandis, S. N., Paulson, S. E., Seinfeld, J. H., and Flagan, R. C. (1991) Aerosol formation in the photooxidation of isoprene and beta-pinene. *Atmos. Environ.*, **25**, 997-1008.
- Pandis, S. N., Harley, R. A., Cass, G. R., and Seinfeld, J. H. (1992) Secondary organic aerosol formation and transport. *Atmos. Environ.*, **26**, 2269-2282.
- Pandis, S. N., Wexler, A. S., and Seinfeld, J. H. (1993) Secondary organic aerosol formation and transport —II. Predicting the ambient secondary organic aerosol size distribution. *Atmos. Environ.*, **27**, 2403-2416.
- Pankow, J. F. (1994a) An absorption model of gas/particle partitioning of organic compounds in the atmosphere. *Atmos. Environ.*, **28**, 185-188.
- Pankow, J. F. (1994b) An absorption model of gas/aerosol partitioning involved in the formation of secondary organic aerosol. *Atmos. Environ.*, **28**, 189-193.
- Pickle, T., Allen, D. T., and Pratsinis, S. E. (1990) The sources and size distributions of aliphatic and carbonyl carbon in Los Angeles aerosol, *Atmos. Environ.*, **24A**, 2221-2228.
- Saxena, P. and Hildemann, L. M. (1996) Water-soluble organics in atmospheric particles: a critical review of the literature and application of thermodynamics to identify candidate compounds, *J. Atmos. Chem.*, **57**, 57-109.
- Seigneur, C., Pai, P., Louis, J. F., Hopke, P., and Grosjean, D. (1998) Review of three-dimensional air quality models for particulate matter, Report No. 4669, American Petroleum Institute, Washington, D.C.
- Seinfeld, J. H. and Pandis, S. N. (1998) *Atmospheric Chemistry and Physics*, John Wiley, New York.

- Stockwell, W. R., Middleton, P., Chang, J. S., and Tang, X. (1990) The second-generation regional acid deposition model chemical mechanism for regional air quality modeling, *J. Geophys. Res.*, **95D**, 16,343-16,367.
- Strader, R., Gurciullo, C., Pandis, S., Kumar, N., and Lurmann, F. W. (1998) Development of gas-phase chemistry, secondary organic aerosol, and aqueous-phase chemistry modules for PM modeling, 1998. Draft Final Report STI-99510-1822-DFR, Coordinating Research Council, Atlanta, Georgia.
- Sun, Q. and Wexler, A. S. (1998) Modeling urban and regional aerosols near acid neutrality-application to the June 24-25 SCAQS Episodes, *Atmos. Environ.*, submitted.
- Turpin, B. J., Huntzicker, J. J., Larson, S. M., and Cass, G. M. (1991) Los Angeles summer midday particular carbon: Primary and secondary aerosol, *Environ. Sci. Technol.*, **25**, 1788-1793.
- Turpin, B. J. and Huntzicker, J. J. (1991) Secondary formation of organic aerosol in the Los Angeles basin: A descriptive analysis of organic and elemental carbon concentrations, *Atmos. Environ.*, **25A**, 207-213.
- Turpin, B. J., Saxena, P., and Andrews, E. (1999) Measuring and simulating particulate organics in the atmosphere: Problems and prospects, *Atmos. Environ.*, in press.
- Venkatram, A., Karamchandani, P., Pai, P., Sloane, C., Saxena, P., and Goldstein, R. (1997) The development of a model to examine source-receptor relationships for visibility on the Colorado Plateau, *J. Air Waste Manage. Assoc.*, **47**, 286-301.
- Wang, S. C., Paulson, S. E., Grosjean, D., Flagan, R. C., and Seinfeld, J. H. (1991a) Aerosol formation and growth in atmospheric organic/NO_x systems—I. Outdoor smog chamber studies of C₇- and C₈-hydrocarbons. *Atmos. Environ.*, **26**, 403-420.
- Wang, S. C., Flagan, R. C., and Seinfeld, J. H. (1991b) Aerosol formation and growth in atmospheric organic/NO_x systems—II. Aerosol dynamics. *Atmos. Environ.*, **26**, 421-434.
- Yu, J., Flagan, R. C., and Seinfeld, J. H., Identification of products containing -COOH, -OH, and -C=O in atmospheric oxidation of hydrocarbons, *Environ. Sci. Technol.*, **32**, 2357-2370.
- Zhang, S. H., Shaw, M., Seinfeld, J. H., and Flagan, R. C., Photochemical aerosol formation from α - and β -Pinene, *Geophys. Res.*, **97**, 20717-20730 .