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Discussion

Comment on "Instantaneous secondary organic aerosol yields and their comparison with overall aerosol yields for aromatic and biogenic hydrocarbons" by Weimin Jiang

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In the introduction to the Technical Note, "Instantaneous secondary organic aerosol yields and their comparison with overall aerosol yields for aromatic and biogenic hydrocarbons", Jiang (2003) states that "[t]o model the formation of secondary organic aerosol, SOA, a concept called aerosol yield (or SOA yield), loosely defined as the SOA mass formed per unit mass of reactive organic gas (ROG) reacted, has been widely used." He goes on to suggest an expanded concept called instantaneous aerosol yield (IAY), applied to the case of pre-existing organic aerosol. While this IAY method may at first seem reasonable, there is a major assumption in its derivation that limits its use for atmospheric models. Additionally, aerosol yield approaches in general are inappropriate for describing the reversible partitioning process that occurs in the atmosphere.

An aerosol-yield-based approach estimates the extent or increment of SOA formation based on the equation

$$\Delta\mathrm{SOA} = \mathrm{AY} \times \Delta\mathrm{ROG}, \tag{1}$$

where ΔSOA is an incremental increase in SOA mass (later defined as ΔM_o), AY is an aerosol yield, and ΔROG is the amount of ROG, the parent hydrocarbon, that has undergone an oxidation reaction leading to the formation of semi-volatile or low-volatility products that can partition to the particle phase.

Experimental studies (Odum et al., 1996) and gas/particle partitioning theory (Pankow, 1994) have demonstrated that the aerosol yield can be expressed as a function of several parameters and the organic aerosol mass concentration, M_o. In this expression, M_o includes both previously existing mass as well as that formed from the oxidation of the parent hydrocarbon. This function, referred to as "Odum's equation" in the Technical Note, is correctly defined as describing the overall aerosol yield (OAY). Experiments have shown that Odum's equation can represent adequately the formation of SOA mass assuming the formation of two condensable species during the oxidation reaction. The two-product form of Odum's equation is

$$\mathrm{OAY} = \frac{\Delta M_o}{\Delta\mathrm{ROG}} = M_o\left(\frac{\alpha_1 K_{om,1}}{1 + K_{om,1} M_o} + \frac{\alpha_2 K_{om,2}}{1 + K_{om,2} M_o}\right), \tag{2}$$

where α_i and $K_{om,i}$ are the mass-based stoichiometric coefficient and the partitioning coefficient of the ith condensable species, respectively. These parameters are determined empirically by fitting to experimental data the pseudo-physical approximation given by the two-product form of Odum's equation. In brief, every *final* data point ($\Delta\mathrm{ROG}, \Delta M_o$) of the series of experiments for a single parent hydrocarbon must satisfy (within experimental error and fitting tolerances) the OAY function described by Odum's equation with $M_o = \Delta M_o$.

In an attempt to improve SOA algorithms, Jiang suggests that a more mathematically rigorous form of the AY term used in Eq. (1), particularly for conditions where pre-existing organic aerosol mass is present,

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would require an IAY. The equation for the IAY is defined as the derivative of M_o with respect to ΔROG and was derived by Jiang to be

$$\mathrm{IAY} = \frac{\mathrm{d}M_o}{\mathrm{d}\Delta\mathrm{ROG}} = \frac{\left(\sum_i \alpha_i K_{om,i}/(1 + K_{om,i}M_o)\right)^2}{\sum_i \alpha_i K_{om,i}^2/(1 + K_{om,i}M_o)^2} \quad (3)$$

which can also be expressed in a compact manner for two products. The IAY is then computed for specific values of M_o with knowledge of the parameters α_i and $K_{om,i}$ obtained appropriately from Odum's equation.

While on the surface this IAY approach apparently leads to a more suitable yield expression for use in Eq. (1) to simulate SOA formation in three-dimensional models, a significant limitation is included in the derivation of Eq. (3). Jiang assumes in his derivation that ΔM_o in Eq. (2) can be replaced simply by M_o, as is valid *only* in smog chamber scenarios with no initial aerosol mass. This is not the case in the ambient atmosphere.

In its most general form, Eq. (2) can be expressed as

$$\frac{\Delta M_o}{\Delta\mathrm{ROG}} = (\Delta M_o + P)\left(\frac{\alpha_1 K_{om,1}}{1 + K_{om,1}(\Delta M_o + P)} + \frac{\alpha_2 K_{om,2}}{1 + K_{om,2}(\Delta M_o + P)}\right), \quad (4)$$

where P is the mass concentration of any previously existing organic aerosol and M_o is written as the sum of ΔM_o and P. In this form, it is clear that the assumed instantaneous equilibrium of gas and aerosol phases leads to inclusion of ΔM_o in M_o. Taking the derivative of ΔM_o with respect to ΔROG yields the IAY. For the general case of Eq. (4) the resulting IAY expression will be a function of both ΔM_o and P. Because ΔM_o would be implicit, this expression cannot be used to calculate an IAY for use in Eq. (1), whose purpose is to determine ΔM_o. Unlike the expression of Jiang, the limiting behavior of the derivative as calculated using Eq. (4) agrees with the limiting behavior of the expression from which it was derived, the Odum Equation. As M_o $(\Delta M_o + P)$ approaches zero, the value becomes zero. As M_o approaches infinity, the derivative of Eq. (4) approaches a limiting value of $\alpha_1 + \alpha_2$, as expected.

The IAY equation presented by Jiang is only valid for cases where $P = 0$. However, it must be stressed that only for chamber experiments, where there is no existing absorbing mass, is $\Delta M_o = M_o$ (that is, in chamber experiments the total amount of organic aerosol mass is that generated by the oxidation of the parent hydrocarbon). This specific case is not representative of the atmosphere where organic aerosol from a variety of sources preexist.

Furthermore, this is not the assumption that has been used in air quality models that do employ a yield-based approach. During the development of the Environmental Protection Agency's (EPA) Community Multiscale Air Quality (CMAQ) model, the two-product form of Odum's Equation representation of SOA production (Binkowski and Roselle, 2003) was employed using an aerosol-yield-based approach for calculating increments in SOA mass. Such an approach was also used to model SOA formation in Europe (Andersson-Skold and Simpson, 2001; Schell et al., 2001). These models assume that the incremental addition of organic aerosol mass from a given ROG during a time step is relatively small, such that $M_o \approx P$. For this case, where $\Delta M_o = 0$ and P is independent of ΔROG, IAY is the same as the OAY defined by the Odum Equation. This simplifying assumption, while different from that used by Jiang, is also not generally valid.

Aerosol yield approaches are appropriate for describing a smog chamber experiment where temperature and relative humidity are constant, semivolatile concentrations never decrease, and there are no other sources of organic aerosol. Clearly those conditions do not hold in the atmosphere. In the ambient atmosphere, the mass concentration of condensable material available for partitioning may increase (due to chemical reaction and transport) or decrease (due to dilution and deposition), and the equilibrium constant, $K_{om,i}$, can change due to fluctuations in temperature and other atmospheric conditions. The use of the algebraic yield Eq. (1) does not account for the evaporation of condensables from the particle phase to the gas phase, which, together with condensation, establishes the thermodynamic equilibrium between the gas and particle phases. This phase equilibrium is a key assumption used in the derivation of the experimental yield and should be preserved in three-dimensional models.

Pun et al. (2003) and Zhang et al. (2004) describe several SOA algorithms that are inherently superior to any aerosol-yield-based algorithm. In these algorithms, a number of parent hydrocarbons are oxidized within the gas-phase chemistry mechanism to form less volatile products. Stoichiometric coefficients determined empirically from application of Odum's equation in prior laboratory studies determine the extent to which these semi-volatile or low-volatility products are formed during the oxidation of each ROG. Stoichiometric coefficients may also be determined by simulation of the gas-phase chemistry leading from parent hydrocarbon to semi-volatile product (Griffin et al., 2002). Existing SOA may also evaporate back to the gas phase. Finally, the partitioning of all of the available condensable products between the gas phase and the particle phase is determined by solving a matrix equation representing the multicomponent gas/particle distribution where each partitioned compound satisfies its own gas–particle equilibrium as determined by its partitioning coefficient, $K_{om,i}$ (Pankow, 1994). At any time and location, equilibrium is established between the gas and particle phases based on the total amount of condensable material available and the local atmospheric conditions.

There are several benefits to a direct partitioning-based SOA algorithm, with the most notable advantage being that of reversible mass transfer. An aerosol yield-based approach, cannot account for desorption—essentially, once aerosol mass is formed, it is treated as if it were nonvolatile. Additionally, the semi-volatile organic mass remaining in the gas phase essentially becomes volatile and cannot partition to the condensed phase when conditions shift. This would occur, for example, if M_o increases due to primary emissions or organic aerosol production from other ROGs, or if temperature decreases. Such approaches also allow for the simulation of new SOA phases, a feature that the yield approach does not allow. A direct partitioning-based SOA computational framework can be expanded also to treat the formation of multiple phases, such as a purely organic aerosol phase and an aqueous phase (Pun et al., 2002; Griffin et al., 2003), and the interactions among the organic and inorganic components of the particle. Other partitioning-based approaches use partitioning coefficients in conjunction with kinetic parameters to define condensation and evaporation rate constants that can be used to simulate SOA formation (Kamens and Jaoui, 2001). This approach has also been applied in three-dimensional modeling efforts (Andersson-Skold and Simpson, 2001).

The usefulness of Odum's equation in analyzing chamber data has been firmly established. However, using the IAY as derived by Jiang in order to improve SOA algorithms used in ambient models overlooks the general inadequacy of aerosol-yield-based approaches and is fundamentally flawed since it is assumed that $\Delta M_o = M_o$. One may consult Pun et al. (2002, 2003) and Griffin et al. (2003) for rigorous, direct-partitioning modules. Moreover, in consideration of the burgeoning evidence suggesting a potentially significant role for heterogeneous and particle-phase chemistry in SOA particle formation (Jang et al., 2002), direct-partitioning-based SOA algorithms represent the only viable approach for atmospheric models.

References

Andersson-Skold, Y., Simpson, D., 2001. Secondary organic aerosol formation in northern Europe: a model study. Journal of Geophysical Research 106, 7357–7374.

Binkowski, F.S., Roselle, S.J., 2003. Models-3 Community Multiscale Air Quality (CMAQ) model aerosol component, 1, Model description. Journal of Geophysical Research 108, 4183 doi:10.1029/2001JD001409.

Griffin, R.J., Dabdub, D., Seinfeld, J.H., 2002. Secondary organic aerosol: I. Atmospheric chemical mechanism for production of molecular constituents. Journal of Geophysical Research 107, 4332 doi:10.1029/2001JD000541.

Griffin, R.J., Nguyen, K., Dabdub, D., Seinfeld, J.H., 2003. A combined hydrophobic-hydrophilic module for predicting secondary organic aerosol formation. Journal of Atmospheric Chemistry 44, 171–190.

Jang, M.S., Czoschke, N.M., Lee, S., Kamens, R.M., 2002. Heterogeneous atmospheric aerosol production by acid-catalyzed particle-phase reactions. Science 298, 814–817.

Jiang, W., 2003. Instantaneous secondary organic aerosol yields and their comparison with overall aerosol yields for aromatic and biogenic hydrocarbons. Atmospheric Environment 37, 5439–5444.

Kamens, R.M., Jaoui, M., 2001. Modeling aerosol formation from alpha-pinene plus NO_x in the presence of natural sunlight using gas-phase kinetics and gas–particle partitioning theory. Environmental Science and Technology 35, 1394–1405.

Odum, J.R., Hoffmann, T., Bowman, F., Collins, D., Flagan, R.C., Seinfeld, J.H., 1996. Gas/particle partitioning and secondary organic aerosol yields. Environmental Science and Technology 30, 2580–2585.

Pankow, J.F., 1994. An absorption model of the gas/aerosol partitioning involved in the formation of secondary organic aerosol. Atmospheric Environment 28, 189–193.

Pun, B.K., Griffin, R.J., Seigneur, C., Seinfeld, J.H., 2002. Secondary organic aerosol 2. Thermodynamic model for gas/particle partitioning of molecular constituents. Journal of Geophysical Research 107, 4333 doi:10.1029/2001JD000542.

Pun, B.K., Wu, S.-Y., Seigneur, C., Seinfeld, J.H., Griffin, R.J., Pandis, S.N., 2003. Uncertainties in modeling secondary organic aerosols: three-dimensional modeling studies in Nashville/Western Tennessee. Environmental Science and Technology 37, 3647–3661.

Schell, B., Ackermann, I.J., Hass, H., Binkowski, F.S., Ebel, A., 2001. Modeling the formation of secondary organic aerosol within a comprehensive air quality model system. Journal of Geophysical Research 106, 28275–28293.

Zhang, Y., Pun, B., Vijayaraghavan, K., Wu, S.-Y., Seigneur, C., Pandis, S., Jacobson, M., Nenes, A., Seinfeld, J.H., 2004. Development and application of the Model of Aerosol Dynamics, Reaction, Ionization and Dissolution (MADRID). Journal of Geophysical Research 109, D01202 doi:10.1029/2003JD003501.