



# Application of the $np+mP$ modeling approach for simulating secondary organic particulate matter formation from $\alpha$ -pinene oxidation

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## ABSTRACT

Simulations of the levels of organic particulate matter (OPM) in chemical transport models typically proceed by a two-product (2p) model approach, in which up to two lumped products are assumed to represent the condensable oxidation products of each hydrocarbon precursor. With the 2p approach, as well as with more detailed semi-explicit approaches, significant underpredictions of OPM levels are not uncommon, particularly at low OPM mass loadings in the atmosphere and in chamber studies. Here the recently developed  $np+mP$  OPM model approach was applied to evaluate OPM formation by  $\alpha$ -pinene ozonolysis using: 1) product lumping based on carbon number and an estimate of molecular polarity, and 2) explicit inclusion of a low-volatility “polymeric” (P) compound. The  $np+mP$  approach allows for consideration of more than two products of type p ( $n > 2$ ) per precursor, and consideration of further oxidation and/or reaction of those products to form  $m$  essentially non-volatile high molecular weight products of type P. Simulations were carried out for several different case types, namely 16p+0P, 8p+0P, 5p+0P, and 5p+1P in which one representative low-volatility compound was added. Predicted OPM levels were compared with levels predicted using alternative parameterizations (2p and volatility basis set) and with levels measured in chamber experiments conducted over a range of  $\alpha$ -pinene oxidation conditions. The results from the 5p+1P case provided good agreement with available data from low, atmospherically-relevant mass loading experiments. Predicted O:C and H:C ratios also were compared with measured ratios, providing insight into differences and similarities between model compounds and the products they represent. The results will inform further development of OPM models, especially as regards oxidation product lumping and inclusion of low-volatility products.

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## 1. Introduction

Organic materials often comprise a significant fraction (20–90%) of fine particulate matter (PM) in the atmosphere (Kanakidou et al., 2005). For any given sample of organic particulate matter (OPM), be it atmospheric or chamber-derived, the molecular identities of all constituent compounds are never fully known, a consequence of the essentially limitless complexities of emissions (for atmospheric samples) and of the processing to which organic compounds are subjected (e.g., time-dependent oxidation, accretion, fragmentation, etc.). Efforts to understand the formation and chemical aging of OPM

constituents and to adequately represent those processes in models thus remain subject to significant challenges. Those challenges must be overcome if improved predictions are to be achieved from air quality models regarding the relative efficacies of OPM reduction strategies, and from climate models on the effects of OPM on climate.

PM formation in chemical transport models typically proceeds based on simplified applications of gas/particle (G/P) partitioning theory as developed by Pankow (1994a,b). The partitioning of each individual (or lumped) compound  $i$  is governed by the absorptive G/P partitioning constant given by

$$K_{p,i} = \frac{F_i/M_{\text{TPM}}}{A_i} = \frac{fRT}{10^6 MW_{\zeta_i}^{\zeta_i} P_{L,i}^0} \quad (1)$$

where  $F_i$  ( $\mu\text{g m}^{-3}$ ) is the mass concentration of  $i$  associated with the particle phase;  $A_i$  ( $\mu\text{g m}^{-3}$ ) is the mass concentration of  $i$  in the gas phase;  $M_{\text{TPM}}$  ( $\mu\text{g m}^{-3}$ ) is the total mass concentration of PM;  $f$  is the

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mass fraction of the TPM into which  $i$  can condense;  $R$  is the ideal gas constant;  $T$  is temperature;  $\overline{MW}$  is the mean molecular weight of the absorbing phase;  $\zeta_i$  is the mole fraction scale activity coefficient of  $i$  in the absorbing phase; and  $p_{L,i}^o$  is the pure compound vapor pressure of  $i$ . Each  $K_{p,i}$  is controlled largely by the values of  $p_{L,i}^o$  and  $\zeta_i$ .

In this work we focus on simulating OPM formed in chamber studies in which the amount of initial OPM is essentially zero so that all of the PM is secondary organic aerosol (SOA). For the PM, the mass concentrations of organic material and water are denoted  $M_o$  and  $M_w$  ( $\mu\text{g m}^{-3}$ ). In the absence of inorganic material besides water in the TPM then  $M_{\text{TPM}} = M_o + M_w = M_t$ .

The fraction of each  $i$  that is present in the particle-phase  $f_{p,i}$  is (Liang and Pankow, 1996)

$$f_{p,i} = \frac{F_i}{F_i + A_i} = \frac{K_{p,i}M_t}{1 + K_{p,i}M_t} \quad (2)$$

The total mass concentration of OPM is (Pankow, 1994b; Pankow et al., 2001)

$$M_o = \sum_i f_{p,i}T_i \quad (3)$$

where  $T_i$  ( $\mu\text{g m}^{-3}$ ,  $= A_i + F_i$ ) is the total mass concentration of  $i$ . The ability to accurately predict OPM levels depends on the extent to which the relevant  $K_{p,i}$  and  $T_i$  values are known.

In some SOA formation models,  $K_{p,i}$  and  $T_i$  values are calculated explicitly based on predicted reaction sequences that begin with a single parent hydrocarbon (HC) (e.g., Camredon et al., 2007; Griffin et al., 2003). More commonly, a highly reduced set of  $K_{p,i}$  and  $T_i$  values are obtained as fitted (lumped) parameters from chamber experiments of SOA formed from a single parent HC, as in the applications of the two-product (2p) approach of Odum et al. (1996) described by Hoffmann et al. (1997) and Griffin et al. (1999). The 2p approach assumes that up to two lumped products (denoted here  $p_A$  and  $p_B$ ) adequately represent the condensable oxidation products formed in each HC/oxidant system. The total levels of  $p_A$  and  $p_B$  are assumed to be given by  $T_A = \alpha_A \Delta\text{HC}$  and  $T_B = \alpha_B \Delta\text{HC}$ , where  $\alpha_A$  and  $\alpha_B$  are mass yields that are derived from the fits;  $\Delta\text{HC}$  is the amount of parent hydrocarbon reacted. Expressing each  $f_{p,i}$  according to Eq.(2) and substituting for  $T_A$  and  $T_B$ , the amount of SOA for each parent HC  $j$  is (Odum et al., 1996)

$$M_{o,j} = \Delta\text{HC}_j \left[ \frac{K_{p,A,j}M_t}{1 + K_{p,A,j}M_t} \alpha_{A,j} + \frac{K_{p,B,j}M_t}{1 + K_{p,B,j}M_t} \alpha_{B,j} \right] \quad (4)$$

With  $N$  possible HCs, this  $N \cdot 2p$  approach yields

$$M_o = \sum_j^N M_{o,j} \quad (5)$$

When applied to the atmosphere, the  $N \cdot 2p$  approach assumes that the  $K_p$  and  $\alpha$  values obtained from chamber studies with individual HCs can be used to represent ambient SOA formation from mixtures of parent HCs under a wide range of  $M_o$  conditions. In particular, it has often been assumed that chamber experiments can approximate the atmosphere in terms of the: 1) identities and levels of the oxidation products that contribute to atmospheric OPM; and 2) effects of the condensed phase variables ( $\overline{MW}$  and  $\zeta_i$  values) and environmental variables (e.g.,  $T$  and RH). Making such assumptions is complicated by recent evidence that HC:NO<sub>x</sub> ratios and UV levels affect oxidation products and SOA yields ( $\Delta M_o/\Delta\text{HC}$ ) (Ng et al., 2007a,b; Presto et al., 2005a,b; Song et al., 2005). More problematically, the ability of just two

products per parent HC to adequately predict SOA formation depends on the specific  $M_o$  range for which the predictions are sought. Thus, two lumped products per HC may suffice when making predictions for a narrow  $M_o$  range ( $\sim 1$  order of magnitude) within the span of the underlying fits, but problems can be expected outside of that range where inclusion of multiple products with a broader range of volatilities becomes required. In particular: 1) at relatively low  $M_o$ , the value of  $M_o$  can be dominated by high  $K_p$  products even if those products are present at low  $T_i$  values; and 2) at relatively high  $M_o$ , the value of  $M_o$  can be dominated by low  $K_p$  products that can have relatively large  $T_i$  values and can condense to a significant degree because  $M_o$  is high. Additionally, there are important time-dependent aspects at both ends of the product volatility spectrum: with time, increasing levels of large  $K_p$  values can accumulate and so contribute increasingly to  $M_o$ , and, oxidation products with  $K_p$  values too low to initially contribute materially to  $M_o$  can be precursors for compounds with larger  $K_p$  values. The volatility basis set (VBS) approach of Donahue et al. (2006) directly addresses these deficiencies by allowing for a range of lumped products distributed in logarithmically spaced  $C^*$  ( $=1/K_p$ ,  $\mu\text{g m}^{-3}$ ) volatility bins, though chemical properties beyond simple volatility remain unaddressed in the one-dimensional VBS. (A 2D-VBS approach is under development, Donahue et al., 2010.)

In most applications of the  $N \cdot 2p$  and VBS approaches, temperature is the only non-kinetic variable for which differences between chamber and ambient conditions are accounted. Pankow and Chang (2008) have shown, however, that when  $M_o$  is low, water uptake caused by RH  $\neq 0$  can cause large changes in  $\overline{MW}$  and  $\zeta_i$  values in the absorbing phase, leading to significant effects on SOA levels. Similarly, Pun (2008) concluded that consideration of  $\zeta_i$  effects is essential when modeling atmospheric SOA formation in cases involving simultaneous condensation of polar organic compounds, non-polar organic compounds, and water. Thus, while attractive in their simplicities, neither the  $N \cdot 2p$  or VBS approaches will be adequate for general modeling of SOA formation in the ambient atmosphere. The effects of varying  $\overline{MW}$  and  $\zeta_i$  values can, however, be considered in the  $np+mP$  approach proposed by Pankow and Barsanti (2009) because it allows for: 1) formation of  $n > 2$  compounds per parent HC with volatilities greater and/or less than the conventional 2p lumped products; 2) formation of  $m$  essentially non-volatile, polymer-like P organic compounds; 3) possible time dependence in the number and characteristics of the p and P products; and 4) a 2-D chemical property consideration of  $i$ -dependent MW and polarity. Varying levels of complexity are possible, ranging from  $n+m$  products that are static in number and chemical characteristics (level I) to the time-dependent consideration of the numbers of oxidation products, subsequent breakdown products, and P-type compounds (level III).

In this work, various level I applications of the  $np+mP$  approach are examined to investigate the robustness of the approach in developing parameterizations of OPM formation from a single HC. Four cases are considered for the  $\alpha$ -pinene/O<sub>3</sub> system: 1) 16p+0P, 2) 8p+0P, 3) 5p+0P, and 4) 5p+1P in which an organic ester serves as the low-volatility product P. For chamber studies carried out over a range of SOA mass loadings (including atmospherically-relevant levels), predicted  $M_o$  values and SOA yields are compared with predicted values and yields using published 2p and VBS parameterizations, and with measured values and yields using published experimental data. In addition, because particular empirical formulas are assumed for the  $n$  p and  $m$  P species, predicted particle-phase O:C and H:C ratios are compared with O:C and H:C ratios reported by Shilling et al. (2009) and Chan et al. (2009).

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