Atmospheric Environment 96 (2014) 331–344

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

Insight into the numerical challenges of implementing 2-dimensional SOA models in atmospheric chemical transport models

W.J. Napier [a, 1], J.J. Ensberg [a, *, 1], J.H. Seinfeld [a, b, **]

[a] Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA, USA
[b] Division of Engineering and Applied Science, California Institute of Technology, Pasadena, CA, USA

HIGHLIGHTS

- The newest SOA box models are computationally expensive.
- We present a novel technique to overcome these computational challenges.
- The technique uses probability distributions to represent discrete 2D SOA grids.
- Examining the strengths and limitations of the technique provides valuable insight.
- Potential solutions for overcoming the limitations are discussed.

ARTICLE INFO

Article history:
Received 4 February 2014
Received in revised form
23 July 2014
Accepted 28 July 2014
Available online 30 July 2014

Keywords:
Secondary organic aerosol
2-Dimensional SOA model
Chemical transport model
Probability distribution
Computational efficiency

ABSTRACT

The new generation of secondary organic aerosol (SOA) models that represent gas- and particle-phase chemistry and thermodynamic partitioning using discrete two-dimensional grids (e.g. SOM, 2D-VBS) cannot be efficiently implemented into three-dimensional atmospheric chemical transport models (CTMs) due to the large number of bins (tracers) required. In this study, we introduce a novel mathematical framework, termed the Oxidation State/Volatility Moment Method, that is designed to address these computational burdens so as to allow the new generation of SOA models to be implemented into CTMs. This is accomplished by mapping the two-dimensional grids onto probability distributions that conserve carbon and oxygen mass. Assessment of the Moment Method strengths (speed, carbon and oxygen conservation) and weaknesses (numerical drift) provide valuable insight that can guide future development of SOA modules for atmospheric CTMs.

1. Introduction

Secondary organic aerosol (SOA) formation ensues with homogeneous gas-phase reactions between volatile organic compounds (VOCs) and oxidants (OH, O_3, NO_3), leading to products of sufficiently low volatility to condense into the particle phase. For most VOCs, the initial oxidant attack is followed by several generations of gas-phase reactions, involving functionalization or fragmentation reactions of the products (Jimenez et al., 2009). Heterogeneous and particle-phase reactions may also play a significant role in certain systems (Cappa and Wilson, 2012; Zhang and Seinfeld, 2012). Whereas it is desirable to embody within a model describing SOA formation as much basic understanding as possible of the formation and evolution process, a key goal of SOA model development is a computational module that can be included in 3-dimensional atmospheric chemical transport models (CTMs). Consequently, the challenge is to balance the desire for chemical fidelity with the need for computational feasibility.

Aerosol Mass Spectrometer (AMS) measurements of organic aerosols, now a routine component of atmospheric measurements and chamber experiments, enable derivation of the atomic O:C and H:C ratios of SOA, from which one can infer overall aerosol oxidation state (Kroll et al., 2011). The volatility of the organic mixture is related to the molecular properties of its components, as embodied, for example, in carbon number and oxidation state. The relationship between oxidation state and volatility is not unique; that is, molecular mixtures with the same overall oxidation state do not

---

* Corresponding author.
** Corresponding author. Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA, USA.
E-mail addresses: josephjamesensberg@gmail.com (J.J. Ensberg), seinfeld@caltech.edu (J.H. Seinfeld).
[1] These authors contributed equally.

http://dx.doi.org/10.1016/j.atmosenv.2014.07.048

necessarily exhibit the same overall volatility. Therefore, an essential characteristic of an SOA model is the representation of volatility and oxidation state.

The new generation of SOA models represents SOA formation and evolution in terms of the competition between functionalization and fragmentation, particle-phase chemistry, the extent of oxidation, and the change of volatility. For instance, Pankow and Barsanti (2009) introduced the "carbon number – polarity grid" (CNPG) framework, which expands the traditional "2-product" concept of Odum et al. (1996) to the "$np + mP$", in which n products with m possible types of low volatility compounds represent the lumped oxidation and accretion products. The carbon number and polarity of each product need to be evaluated according to the current understanding of gas-phase SOA formation. SOA growth is computed based on equilibrium partitioning theory (Barsanti et al., 2011; Pankow and Barsanti, 2009).

Donahue et al. (2011) developed the two-Dimensional Volatility Basis Set (2D-VBS) employing saturation mass concentration, C^*, and the mean oxidation state, $\overline{OS}$, of the aerosol to describe the coupled aging and phase partitioning of SOA. A bin in the 2D space represents a suite of molecules; an ensemble of molecules with the same C^* and $\overline{OS}$ is assumed to behave similarly in the aggregate. When chamber data are available, the volatility distribution of the products is obtained by SOA mass yield fitting. A gas-phase photooxidation mechanism for a parent VOC provides the functionalization and fragmentation channels leading to products that map onto the 2D-VBS grid. A key issue is to assign the SOA yield of each bin that potentially comprises a suite of compounds sharing similar C^* and $\overline{OS}$ (Donahue et al., 2012, 2011).

Cappa and Wilson (2012) formulated the Statistical Oxidation Model (SOM) that describes SOA formation as a statistical evolution in the space of numbers of carbon and oxygen atoms, n_C and n_O, respectively, with fitted parameters that govern the probability of fragmentation vs. functionalization, the number of oxygen atoms added per functionalization reaction, and the decrease in vapor pressure accompanying addition of an oxygen atom. An advantage of SOM is that the functionalization channel is fully represented by several free parameters so that no adjustment (e.g., molar yields for each bin of 2-D VBS, distribution of functional groups in FGOM) is required before optimal fitting of the free parameters to chamber-generated SOA. A disadvantage is that predicted products do not necessarily correspond to actual molecules (Cappa and Wilson, 2012).

Zhang and Seinfeld (2012) developed the Functional Group Oxidation Model (FGOM), which is based on explicit functional groups that result from the oxidation of a parent VOC, but also characterized by a set of parameters that are determined by fitting to chamber data. The progressive gas-phase oxidation channel leading to a distribution of different functional groups is generated according to specific VOC photooxidation mechanisms. The fragmentation channel, particle-phase oxidative and non-oxidative channels are represented by a set of adjustable parameters. The distribution and evolution of a set of functional groups that can sufficiently represent the gas-phase photochemistry of a certain hydrocarbon is required (Zhang and Seinfeld, 2012).

In short, significant progress has been made in the development of next-generation models to represent the formation and evolution of SOA. However, the gap between the new class of 2D SOA models and the computational requirements of 3D CTMs has not been bridged. Specifically, each of the SOA models described above, except the FGOM, represents the evolution of the SOA-forming chemistry via a matrix of properties. Simulating the physio-chemical evolution of such a matrix within a box-model does not present a computational problem. However, in a 3D CTM, the advection–diffusion equation requires each matrix to be defined over the entire 3D grid so that matrices can be transported between grid cells. Since a typical 3D grid may contain thousands of grid cells, this poses a severe computational burden. Consequently, the Odum 2-product model (Odum et al., 1996), although now out of date, has remained the most commonly used SOA parameterization in state-of-the-art 3D CTMs (Barsanti et al., 2013). Therefore, computational simplifications need to be devised to implement any of the 2D SOA models in a 3D model. Here we describe a new computational approach, termed the Oxidation State/Volatility Moment Method (hereafter referred to as the Moment Method). We focus on the 2D-VBS as exemplary of the new class of SOA models for demonstrating the strengths and limitations of the new approach.

2. Discrete 2D-VBS

In the 2-Dimensional Volatility Basis Set (2D-VBS) (Donahue et al., 2012, 2011), SOA formation and evolution is represented by lumping species into discrete bins according to their oxidation state and the pure component saturation concentration (C^*) of the molecule. Donahue et al. (2011) originally used O:C ratio as the 2D-VBS ordinate, whereas Donahue et al. (2012) use the mean oxidation state of carbon, $\overline{OS}$. Since O:C ratio and $\overline{OS}$ are intimately linked, we use the O:C ratio as a measure of oxidation because, as will be shown later, this allows the Moment Method to conserve oxygen mass. At any instant in time, the 2D-VBS predicts the fraction of the carbon atom concentration (i.e. the probability of finding carbon) associated with molecules that have a given discrete O:C and C^*, defined here as $F_{g,p}(\mathrm{O{:}C}, C^*)$ (g = gas, p = particle). The 2D probability distributions are such that:

$$\sum_{\mathrm{O:C}} \sum_{C^*} F_g(\mathrm{O:C}, C^*) = 1 \tag{1}$$

$$\sum_{\mathrm{O:C}} \sum_{C^*} F_p(\mathrm{O:C}, C^*) = 1 \tag{2}$$

These probability distributions are combined with the total carbon concentrations (C-atoms m^{-3}) in the gas and particle phases, denoted by $\mathrm{NC}_{\mathrm{tot},g}$ and $\mathrm{NC}_{\mathrm{tot},p}$, respectively.

$$\mathrm{NC}_g(\mathrm{O:C}, C^*) = \mathrm{NC}_{\mathrm{tot},g} F_g(\mathrm{O:C}, C^*) \quad \left[\mathrm{C-atom\ m^{-3}}\right] \tag{3}$$

$$\mathrm{NC}_p(\mathrm{O:C}, C^*) = \mathrm{NC}_{\mathrm{tot},p} F_p(\mathrm{O:C}, C^*) \quad \left[\mathrm{C-atom\ m^{-3}}\right] \tag{4}$$

$$\sum_{\mathrm{O:C}} \sum_{C^*} \mathrm{NC}_g(\mathrm{O:C}, C^*) = \mathrm{NC}_{\mathrm{tot},g} \quad \left[\mathrm{C-atom\ m^{-3}}\right] \tag{5}$$

$$\sum_{\mathrm{O:C}} \sum_{C^*} \mathrm{NC}_p(\mathrm{O:C}, C^*) = \mathrm{NC}_{\mathrm{tot},p} \quad \left[\mathrm{C-atom\ m^{-3}}\right] \tag{6}$$

where, for example, C^* may range from 10^{-5}–10^{9} $\mu\mathrm{g\ m^{-3}}$, separated by powers of 10, and O:C may range from 0 to 1, in increments of 0.1. $\mathrm{NC}_g(\mathrm{O:C}, C^*)$ and $\mathrm{NC}_p(\mathrm{O:C}, C^*)$ are the portions of the carbon atom concentration associated with molecules that have the specified values of O:C and C^* in the gas and the particle phases, respectively. As will be shown later, the average number of carbon atoms per molecule can be determined from the total carbon atom concentration, C^*, and the O:C ratio in each grid cell.