



Development of Organic Compound Emission Inventories for Volatility Basis Set-Based Chemical Transport Models

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1. Introduction

Organic compound emissions from combustion sources such as biomass burning are major contributors to fine particulate matter (PM) mass in regional scales. Some of this organic material is directly emitted as particles, but most is emitted as vapors. At the source, combustion emissions are concentrated and hot. Upon entering the atmosphere, the emissions mix with background air, cooling and diluting the exhaust, which alters the gas-particle partitioning of condensable vapors. Therefore, PM emissions begin to be transformed immediately after leaving the source. All these organic vapors can then undergo chemical transformations (oxidation by hydroxyl radical, ozone, etc) and may be transferred to the particulate phase as secondary particulate matter (Donahue et al., 2009). To develop effective control strategies, the overall contribution of emissions from biomass burning to ambient PM—direct particle emissions and PM formed in the atmosphere—must be understood. Therefore, accounting for atmospheric transformations is essential.

In the existing emission inventories used for either regulatory or scientific applications, organic compounds are included as either non-volatile primary organic aerosol (OA) emissions or as volatile organic compounds (VOCs). If these emissions are plotted as a function of the effective saturation concentration of the compounds then the corresponding graph has an obvious gap between 0 and $10^3 \mu\text{g m}^{-3}$ (Figure 1a). Such a gap is unrealistic because there are numerous known compounds emitted to the atmosphere with saturation concentrations in that range.

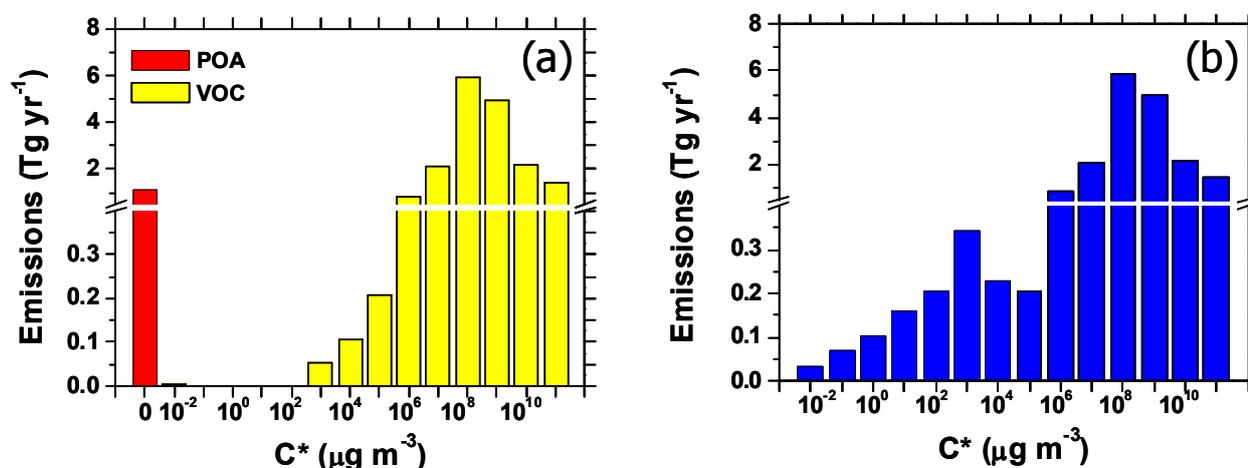


Figure 1. Annual emissions of organic compounds in the US as a function of the saturation concentration C^* of the corresponding compounds for 2002: (a) Emissions of particles and VOCs in the traditional inventory and (b) estimated emissions of low volatility, semivolatile, intermediate volatility, and volatile organic compounds.

A number of studies summarized by Robinson et al. (2009) prove that the OA emissions from combustion sources including biomass burning are semivolatile and evaporate during dilution to atmospherically relevant concentrations. The corresponding emissions can be measured using dilution samplers as a function of dilution and then the corresponding emissions can be estimated as a function of the saturation concentration of the corresponding compounds (Grieshop et al., 2009). The resulting emissions (Figure 1b) now cover the complete volatility range. Emissions in the $1-10^4 \mu\text{g m}^{-3}$ saturation range are quite important because they partition between the gas and particulate phases both during the emission measurement process and in the atmosphere, but also because they can be easily converted to secondary OA through atmospheric reactions with the hydroxyl radical (OH).

Donahue et al. (2006) proposed the discretization of the volatility distribution of atmospheric organic compounds into logarithmically spaced bins and called the corresponding framework the Volatility Basis Set (VBS). The organic compounds can thus be separated in four groups:

(i) *Low Volatility Organic Compounds* (LVOCs, with $C^* < 3.2 \times 10^{-1} \mu\text{g m}^{-3}$, volatility bins 10^{-3} , 10^{-2} and $10^{-1} \mu\text{g m}^{-3}$). These compounds are in the particulate phase in the atmosphere.

(ii) *Semi Volatile Organic Compounds* (SVOCs, with $3.2 \times 10^{-1} \mu\text{g m}^{-3} < C^* < 3.2 \times 10^2 \mu\text{g m}^{-3}$, volatility bins 1, 10 and $100 \mu\text{g m}^{-3}$). SVOCs exist in both the gas and particulate phases.

(iii) *Intermediate Volatility Organic Compounds* (IVOCs, with $3.2 \times 10^2 \mu\text{g m}^{-3} < C^* < 3.2 \times 10^6 \mu\text{g m}^{-3}$, volatility bins 10^3 , 10^4 , 10^5 and $10^6 \mu\text{g m}^{-3}$). These exist in the gas phase and can be converted to condensible compounds producing secondary OA.

(iv) *Volatile Organic Compounds* (VOCs, with $C^* > 3.2 \times 10^6 \mu\text{g m}^{-3}$). Most of the emissions of gas-phase organics fall in this group.

Emissions of all four groups are needed as input to CTMs that simulate the formation and partitioning of atmospheric OA. Extremely low volatility compounds (ELVOCs) may be important for certain chemical processes (e.g., formation and growth of new particles by nucleation).

2. Gas-Particle Partitioning of Primary OA

Thermodynamic models are commonly used to predict gas-particle partitioning of semi-volatile organics in the atmosphere. The available dilution sampler data support the use of absorptive partitioning theory for the description of the corresponding processes. The equilibrium partitioning of a constituent i between the vapor and particle phase with organic aerosol with concentration (C_{OA}) is:

$$X_{p,i} = \left(1 + \frac{C_i^*}{C_{OA}} \right)^{-1} \quad (1)$$

where $X_{p,i}$ is the fraction of the constituent in the particle or condensed phase (particle fraction) and C_i^* is the effective saturation concentration of the compound. C_i^* is a semi-empirical property that describes partitioning of a complex mixture of organics; it is related to the compound saturation vapor pressure. C_i^* depends on temperature and the composition of the system. The effects of composition on the partitioning of atmospheric organics are not well understood; currently, most models assume that organics form a pseudoideal solution in which the activity coefficients are constant.

In theory, Eq. 1 can be directly applied to predict the contribution of semi-volatile emissions to ambient PM levels. This requires knowledge of the composition and thermodynamic properties of all of the emissions. However, a complete accounting of all species is essentially impossible because the number of compounds is staggering. Existing analytical techniques are only able to identify a small fraction of the emissions on a compound-by-compound basis. In practice, Eq. 1 is used in a semi-empirical fashion with a set of surrogate or lumped species that describes the partitioning behavior of a complex mixture. The amount of each lumped species is determined by fitting gas-particle partitioning data with Eq 1. The phase partitioning of POA emissions can be described using a set of lumped species distributed across a volatility basis set (VBS) with volatility bins or surrogate species that have C^* values separated by an order of magnitude at 298 K. This set of lumped species defines the volatility distribution of the emissions; it can be expressed as a set of mass fractions (f_i) or emission factors (EF_i), one for each volatility bin i . If this distribution is known, one can use Eq 1 to calculate the phase partitioning of the emissions over the full range of atmospheric conditions using:

$$C_{OA} = \sum_i X_{p,i} f_i C_{tot} \quad (2)$$

where C_{tot} is the total (gas + particle) concentration of semi-volatile organics. Volatility distributions are defined by fitting measured gas-particle partitioning data. For example, Grieshop et al. (2009) derived volatility distributions for diesel and wood smoke POA using data collected with dilution samplers, a smog chamber, and thermodenuders. Figure 2 shows the dilution data compiled by Grieshop et al. (2009) for presented on a partitioning plot, which relates the overall particle fraction ($X_p=C_{OA}/C_{tot}$) versus C_{OA} . All of the measurements were made at sufficiently dilute conditions that the exhaust was essentially at ambient temperatures. In Figure 2a, the particle fraction has been defined as the ratio of primary OA to the mass of organics collected on a quartz filter at low dilution ratio. As expected from Eq. 1, the particle fraction decreases with decreasing C_{OA} , meaning that the primary OA evaporates as the concentration of organic aerosol in a plume decreases.

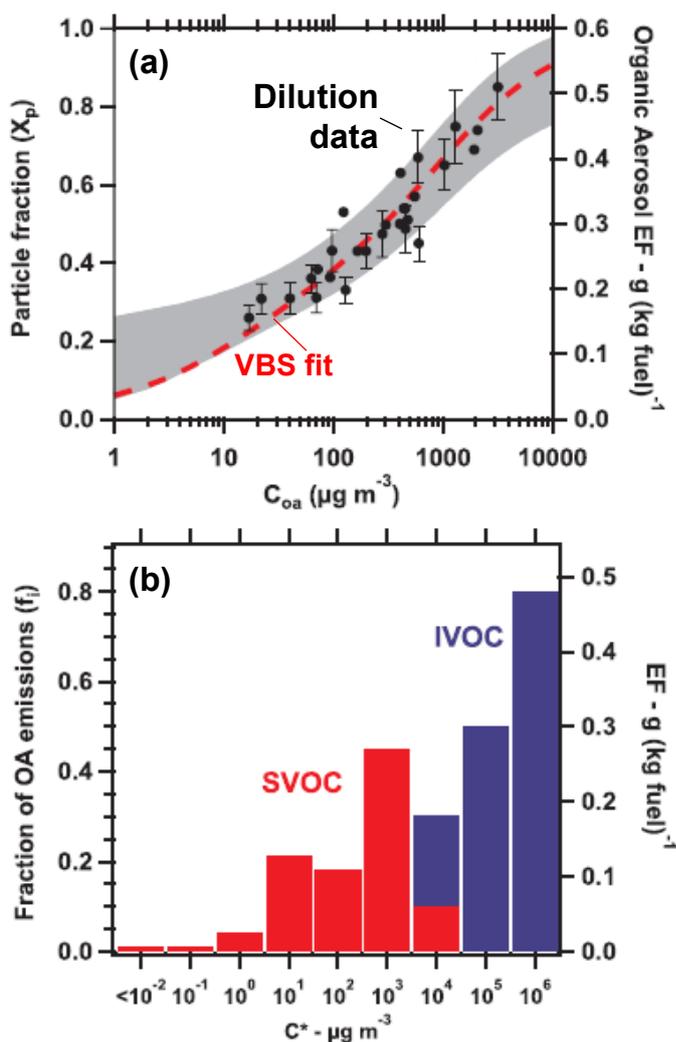


Figure 2. (a) Partitioning plot of isothermal gas-particle data of combustion POA compiled by Grieshop et al. (2009). The dashed line is the best fit of data with the VBS using partitioning theory; the gray area represents the uncertainty of the fit. (b) Volatility distribution of the corresponding POA. The volatility distribution derived by the best fit corresponds to the red bars. The blue bars in panel B are an estimate of the IVOC vapors not collected on quartz filters therefore, the sum of fractional contributions to organic aerosol (f_i) from the SVOC and IVOC bars is >1 . EF is the fuel-based emission factor.

For example, decreasing the C_{OA} from 1 mg m^{-3} to $20 \text{ } \mu\text{g m}^{-3}$ at $25 \text{ }^\circ\text{C}$ caused approximately half of the POA to evaporate. Furthermore, the particle fraction varies gradually and continuously with C_{OA} , which means that the emissions are distributed across a wide range of volatilities. Partitioning data for wood smoke exhibit similar behavior to that shown in the above example.

3. Estimation of Volatility-Resolved Biomass Burning OA Emissions

The volatility distribution of the emissions is the key input for the estimation of volatility-resolved emissions from traditional particulate emission data. For the purposes of this project we will use the May et al. (2013) volatility distribution for biomass burning OA. Briefly, May et al. (2013) used heating and dilution to investigate the volatility of smoke particles from combustion of common North American trees/shrubs/grasses during the third Fire Lab at Missoula Experiment (FLAME-III). Fifty to eighty percent of the mass of biomass burning POA evaporated when isothermally diluted from plume ($\sim 1000 \text{ } \mu\text{g m}^{-3}$) to ambient-like concentrations ($\sim 10 \text{ } \mu\text{g m}^{-3}$), while $\sim 80\%$ of the POA evaporated upon heating to $100 \text{ }^\circ\text{C}$ for a residence time of ~ 10 seconds. Therefore the majority of the POA emissions were semivolatile. An evaporation kinetics model was used to derive volatility distributions and enthalpies of vaporization from the thermodenuder data. Thermodenuder measurements made at three different residence times indicated there were not substantial mass transfer limitations to evaporation (i.e., the mass accommodation coefficient was greater than 0.01). A single volatility distribution (Table 1) can be used to represent the measured gas-particle partitioning from the entire set of experiments, including different fuels, organic aerosol concentrations, and thermodenuder residence times. This distribution is compared to the one currently used for all sources in PMCAMx (based on Robinson et al. (2007)) in Figure 3.

This distribution, derived from the thermodenuder measurements, also predicts the dilution driven changes in gas-particle partitioning (Figure 4). The fraction of the material that will be in the particulate phase increases as the organic aerosol concentration increases. This dilution curve is used for the calculation of the volatility resolved emissions.

Table 1. Volatility Distribution for Biomass Burning OA

C_i^* ($\mu\text{g m}^{-3}$)	f_i	$\Delta H_{\text{vap},i}$ (kJ mol^{-1})
10^{-2}	0.2	93
10^{-1}	0.0	89
1	0.1	85
10	0.1	81
10^2	0.2	77
10^3	0.1	73
10^4	0.3	69

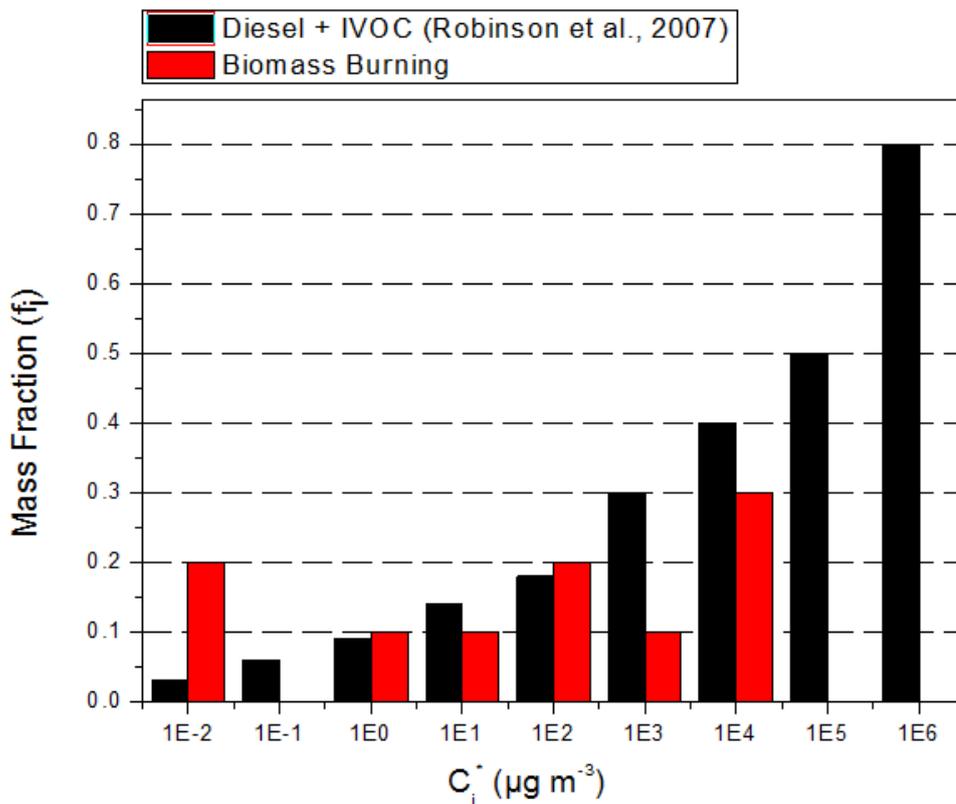


Figure 3. Volatility distribution for biomass burning OA of May et al. (2013). Also shown for comparison the Robinson et al. (2007) distribution currently used in PMCAMx.

According to the May et al. (2013) volatility distribution the low-volatility, semivolatile and intermediate volatility cover a range of volatilities from 10^{-2} to $10^4 \mu\text{g m}^{-3}$. While this range can be extended to even higher volatilities, we will discuss the calculation of the emissions using this specific distribution. If we define as E_{OM} the emissions of total organic mass by biomass burning independent of its phase with

volatility less or equal to $10^4 \mu\text{g m}^{-3}$ then the emissions for each volatility bin i , E_i are given simply by:

$$E_i = f_i E_{OM} \quad (3)$$

where the f_i are the fractions in Table 1. Therefore, the problem of the calculation of the volatility distributions of the emissions becomes equivalent to the calculation of EOM if the emissions E have been measured for at a concentration level C_E .

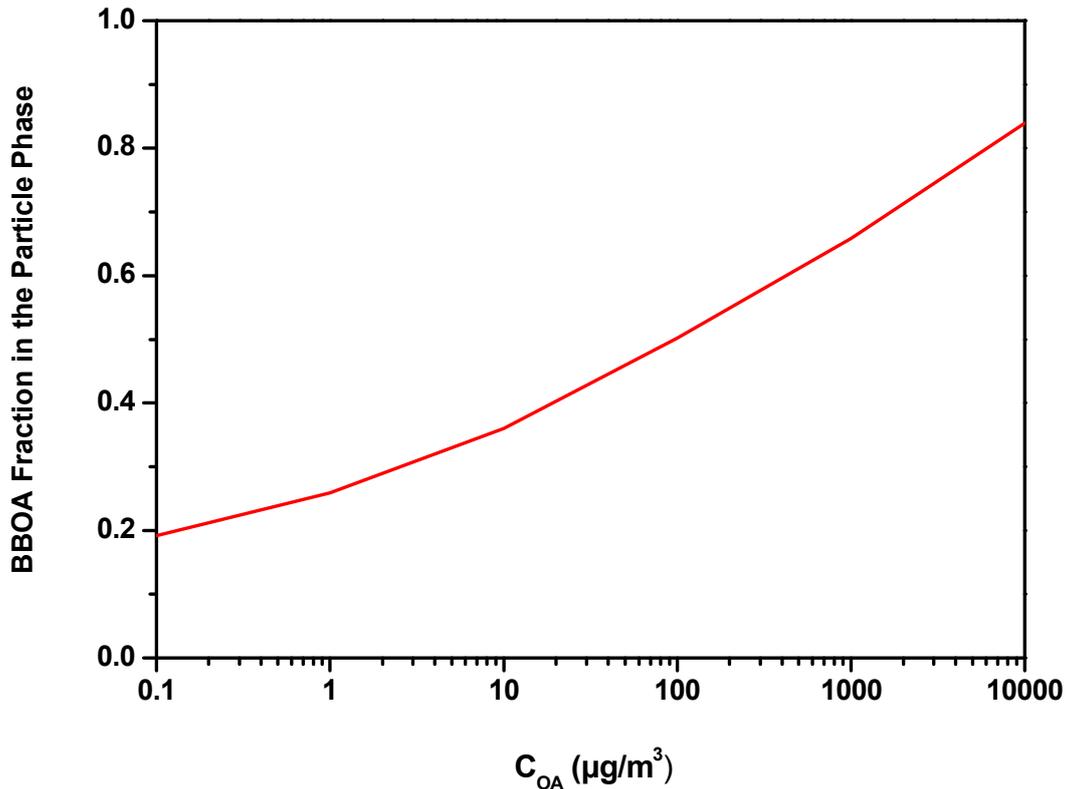


Figure 4. *Fraction of the biomass burning organic emissions in the particulate phase as a function of the organic aerosol concentration.*

As an example, we can assume that the organic particulate matter concentration for a particulate emission measurement was $C_E=1,000 \mu\text{g m}^{-3}$ and the emission rate was $E=1 \text{ g kg}^{-1}$ of fuel. According to Figure 4, the fraction of the organic material in the particulate phase for this emission rate measurement was 0.64, therefore the measurement did not capture 36% of the material that was in the gas phase during the measurement. In this example, the total organic material emission rate is given by:

$$E_{OM} = E/0.64 = 1.56 E = 1.56 \text{ g Kg}^{-1} \quad (4)$$

This process can be generalized for any available measurement from woodburning. The fraction of the OA mass that has been measured can be calculated from Figure 4 using the OA concentration for the measurement, and then it can be used to “correct” the measurement for the missing vapor material calculating E_{OM} . Then the corresponding volatility distributed emissions are calculated using Eq. 3.

This process can be extended to account for temperature effects on the partitioning if the emission measurement took place at a different temperature than 25°C. The partitioning diagram of Figure 4 in this case needs to be recalculated at the temperature of the measurements. This is done by recalculating the volatilities (C^*) of each volatility bin using the Clausius-Clapeyron equation

$$C_i^* = C_{i,0}^* \frac{T_0}{T} \exp\left(\frac{\Delta H_i}{R} \left(\frac{1}{T_0} - \frac{1}{T}\right)\right) \quad (5)$$

where C_i^* and $C_{i,0}^*$ are the saturation concentrations at T and T_0 , respectively, R is the gas constant, and ΔH_i is the enthalpy of vaporization and the enthalpies of vaporization estimated by May et al. (2013) shown in Table 1.

References

- Donahue, N. M., A. L. Robinson, C. O. Stanier, and S. N. Pandis (2006) Coupled partitioning, dilution, and chemical aging of semivolatile organics, *Environ. Sci. Technol.*, 40, 2635–2643.
- Donahue N. M., A. L. Robinson, and S. N. Pandis (2009) Atmospheric organic particulate matter: From smoke to secondary organic aerosol, *Atmos. Environ.*, 43, 97-109.
- Grieshop A. P., M. A. Miracolo, N. M. Donahue, and A. L. Robinson (2009) Constraining the volatility distribution and gas-particle partitioning of combustion aerosols using isothermal dilution and thermodenuder measurements, *Environ. Sci. Tech.*, 43, 4750-4756.
- May A. A., E. T. Levin, C. J. Hennigan, I. Riipinen, T. Lee, S. M. Kreidenweis, and A. L. Robinson (2013) Gas-particle partitioning of primary organic aerosol emissions: 3. Biomass burning, *J. Geophys. Res.*, 118, 11327-11338.
- Robinson, A. L., Donahue, N. M., Shrivastava, M. K., Weitkamp, E. A., Sage, A. M., Grieshop, A. P., Lane, T. E., Pierce, J. R., and Pandis, S. N. (2007). Rethinking organic aerosols: Semivolatile emissions and photochemical aging. *Science*, 315:1259– 1262.
- Robinson, A. L., A. P. Grieshop, N. M. Donahue, and S. W. Hunt (2009) Updating the conceptual model for fine particle mass emissions from combustion systems, *J. Air Waste Manag. Assoc.*, 60, 1204-1222.