A Revised Framework for Treating Primary Organic Aerosol Emissions in Inventories and Models

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ABSTRACT

This paper discusses a revised framework for treating primary organic aerosol emissions in inventories and models. Instead of using static aerosol emission factors, we represent the organic aerosol emissions using a volatility distribution. Conceptually, this distribution can be derived from speciated emissions data by lumping species with similar saturation vapor pressures. However, this is not possible in practice because less than 10% of the condensed and semivolatile mass has been speciated. We determine volatility distributions by fitting isothermal dilution data with absorptive partitioning theory, similar to well-established analyses of secondary organic aerosol. Representing emissions with a volatility distribution allows explicit treatment of both gas-particle partitioning and photochemical aging of primary emissions. We have implemented this approach using the chemical transport model PMCAMx, and present results from simulations conducted over the Eastern United States. The results show a dramatically altered picture of ambient organic aerosol.

INTRODUCTION

Sources of primary organic aerosols such as motor vehicles, wood combustion, and industrial processes emit thousands of organic compounds (Schauer et al., 1999a; Schauer et al., 1999b; Schauer et al., 2001; Schauer et al., 2002b; Schauer et al., 2002a). The gas-particle partitioning of these emissions change dramatically as they are rapidly cooled and diluted. In order to account for these changes, primary organic aerosol (POA) emission factors are measured using dilution samplers (Hildemann et al., 1989). Emission inventories and models currently treat POA emissions as non-reactive and non-volatile, implicitly assuming that the dilution sampler measurements represent the full range of atmospheric conditions.

This paper discusses a revised framework for treating primary organic aerosol emissions in inventories and models. The framework uses a volatility basis set to represent organic emissions and allows for explicit accounting of changes in gas-particle partitioning due to dilution, temperature changes and photochemical aging.

BODY

Gas-Particle Partitioning and Primary Organic Aerosol Emissions

Recent measurements in our laboratory reveal that POA emission factors measured from diesel engine exhaust and wood combustion decrease with increasing dilution due to evaporation of

semivolatile organic compounds (Lipsky and Robinson, 2006; Shrivastava et al., 2006). The semivolatile character of POA is illustrated in Figure 1a, which plots the fuel-based POA emission factor for wood combustion as a function of dilution (Lipsky and Robinson, 2006). The measured POA emission factor decreased as emissions were diluted to progressively higher dilution ratios at a constant temperature; this reduction is, due to the evaporation of semivolatile organics.

Gas-particle partitioning occurs via absorption into an organic solution and adsorption onto soot and mineral surfaces (Pankow, 1987; Pankow, 1994). The relative importance of these two mechanisms depends on the amount and type of each sorptive material. For ambient aerosols, absorption into an organic solution is thought to be the dominant partitioning mechanism (Liang et al., 1997; Roth et al., 2005b).

Emissions from many combustion systems such as engines contain a mixture of organic and elemental carbon (OC/EC). The relative amount of OC and EC vary widely depending on source type and combustion conditions. For example, carbonaceous emissions from wood combustion and non-catalyst-equipped gasoline-powered vehicles are dominated by organic material (Hildemann et al., 1991a; Schauer et al., 2001; Schauer et al., 2002b) while emissions from diesel engines are generally dominated by EC (Hildemann et al., 1991a; Schauer et al., 1999b). Although EC adsorbs organic material, other organic compounds can form a solution with the adsorbed organic layer (Sakurai et al., 2003). Therefore, absorptive partitioning is expected to be the dominant partitioning mechanism in emissions from gasoline vehicles, wood combustion, and other sources with OC/EC ratios greater than 2 (Roth et al., 2005a).

The changes in emission factor with dilution shown in Figure 1a follow well-established absorptive partitioning theory (Donahue et al., 2006; Shrivastava et al., 2006). We express partitioning in terms of a particle fraction (X_p), which is the ratio of the organic particulate mass to the total (gas plus particle) semi-volatile organic mass in the emissions (Shrivastava et al., 2006). Following partitioning theory, Figure 1b plots X_p as a function of mass concentration of the absorbing phase – the organic aerosol concentration (C_{OA}). As expected, X_p monotonically increases towards one with increasing C_{OA}, reflecting changes in partitioning as organic material shifts from the gas to the particle phase at higher C_{OA}.

Continuous changes in partitioning of POA with dilution (or alternately, with temperature) should not be surprising. It simply reflects the fact that primary emissions are comprised of a wide range of compounds with up to thirty-or-more carbon atoms (Schauer et al., 1999b; Schauer et al., 2001; Schauer et al., 2002b). Although speciated data are available for only a small fraction of the emissions, non-compound specific gas chromatography has achieved good mass recovery. This approach separates material on a volatility/carbon number basis and reveals that the unresolved material is spread across a wide range of volatilities (Hildemann et al., 1991b).

The semivolatile character of primary emissions creates two challenges. First, emission factors are often measured at low dilution ratios (20:1 to 200:1). This level of dilution generally reduces the temperature of the exhaust to atmospheric levels; however, the aerosol concentrations in the diluted exhaust can be orders of magnitude higher than typical atmospheric conditions (Shrivastava et al., 2006). Measurements under these conditions can create large biases in measured emission factors relative to highly diluted background atmosphere (Shrivastava et al., 2006). Second, gas-particle partitioning varies continuously with background aerosol concentration and temperature, preventing the definition of a static primary organic aerosol emission factor (Shrivastava et al., 2006).

Unfortunately, emission inventories and models currently treat primary organic aerosol emissions as non-volatile, implicitly assuming that dilution sampler measurements represent the full range of atmospheric conditions. In the atmosphere, background aerosol concentrations and temperature vary in space and time. Since these parameters strongly influence partitioning, a single value for POA emission factor cannot accurately represent the atmospheric behavior of POA emissions..

Semivolatile Emissions and Secondary Organic Aerosol

We have recently proposed that oxidation of semivolatile emissions is an important, but largely unaccounted for source of secondary organic aerosol (SOA) in the atmosphere (Robinson et al., 2007). This proposal is motivated by laboratory results showing an unexpectedly large amount of SOA formation during the photo-oxidization of diluted exhaust from a diesel engine (Robinson et al., 2007). Figure 2 plots results from a smog chamber experiment in which diluted diesel exhaust was exposed to UV light, initiating photochemistry similar to what occurs in summertime in an urban area.. After 3 hours of aging, SOA had almost doubled the initial (wall-loss corrected) aerosol mass, and more than doubled the OA concentrations. Decay of gas phase organics indicate roughly one generation of processing and ~ 3 x 10^6 molec cm^{-3} OH -- typical of a summer day (Heard and Pilling, 2003). Substantial SOA production from photo-oxidation of diesel exhaust has also been reported by Lee et al. (2004).

To assess the contribution of known SOA sources, we spiked the chamber with light aromatics and calculated traditional SOA production using measured precursor consumption and the published SOA yield curves used in the chemical transport model PMCAMx (Koo et al., 2003). Calculations with this model accounted for the contribution from 58 precursors but could explain only 15% of the SOA formed during this experiment. This gap is much too large to be closed by simply increasing the yields for existing precursors, indicating a major unaccounted-for source of SOA. Recent model evaluations (Heald et al., 2005; Johnson et al., 2006) and field studies (de Gouw et al., 2005; Volkamer et al., 2006) also suggest a large missing source of SOA.

We hypothesize that oxidation of low-volatility species explains the unpredicted SOA observed in our experiments (Robinson et al., 2007). Diesel exhaust is a complex mixture of thousands of compounds that span a wide range of volatilities (Schauer et al., 1999b). Partitioning data similar to that shown in Figure 1 (Shrivastava et al., 2006; Robinson et al., 2007) and speciation measurements (Schauer et al., 1999b; Schauer et al., 2001; Schauer et al., 2002b) indicate that a significant fraction of the emissions have saturation concentrations between 10^2 and 10^6 $\mu g\ m^{-3}$ and therefore exist primarily in the gas phase at atmospheric conditions. However, these emissions are not accounted for in current emission inventories which have largely been developed to simulate tropospheric ozone.

We expect that oxidation of low volatility vapors is an important source of SOA because oxidation of large saturated compounds produces acids, nitrates, and carbonyls with lower vapor pressures than the parent compounds (Lim and Ziemann, 2005). Only C-C bond cleavage typically increases the volatility of the reaction products, however this cleavage is uncommon for the relatively unsubstituted compounds typical of primary emissions (Lim and Ziemann, 2005; Reisen et al., 2005). Therefore, the first few generations of oxidation likely reduce the volatility of these species by several orders of magnitude, causing a large fraction of the organic mass to partition to the condensed phase.

Another important consideration is the low initial volatility of these vapors. Lim and Ziemann (2005) report that SOA yields more or less increase monotonically with decreasing precursor vapor pressure. The light aromatics and monoterpenes that dominate SOA production in current models have

effective saturation concentrations between 10^7 and 10^9 μg m^{-3} and therefore produce SOA with low efficiency (typical yields are <10%). In comparison, oxidation of semivolatile vapors should produce SOA with much higher efficiency.

The available data indicate that emissions of low-volatility vapors are several times those of POA emissions. Therefore, these vapors have potential to produce substantial SOA, exceeding the contribution of POA. SOA formed from oxidation of low-volatility vapors may explain the unexpectedly rapid and substantial formation of SOA observed off the coast of New England (de Gouw et al., 2005) and in Mexico City (Volkamer et al., 2006). SOA formed from oxidation of low-volatility vapors likely contributes to the persistent underprediction of OA levels, especially during photochemical episodes (Held et al., 2005; Vutukuru et al., 2006).

Although current SOA models do account for some SOA production from low-volatility vapors, such as large alkanes and cycloparaffins, oxidation products of these vapors are predicted to contribute little SOA compared to those of light aromatics and biogenic species (Koo et al., 2003; Pun et al., 2003; Vutukuru et al., 2006). A major problem is that little attention has been paid to including low-volatility vapor emissions in inventories because they only constitute a small fraction of the total VOC emissions, which are dominated by high volatility species.

Basis-Set Approach

Updating our conceptual model of primary organic aerosol emission requires a framework that efficiently represents both gas-particle partitioning and photochemical aging in regional and global chemical transport models (CTMs). We have recently developed such a framework, which we call the volatility basis set (Donahue et al., 2006). The approach lumps low volatility organics into a set of "volatility bins" that span a basis set of effective saturation concentrations (C_i*) separated by powers of 10, typically ranging from 0.01 to 10^6 μg m^{-3} at 298 K. If this volatility distribution is known, one can calculate the OA mass from partitioning theory (Pankow, 1994; Odum et al., 1996; Donahue et al., 2006). The basis-set approach uses a volatility operator to treat SOA production by photochemical aging; the operator represents how the volatility distribution evolves with aging.

The major advantages of the basis set approach include: 1) it provides a single framework for describing gas-particle partitioning of both POA and SOA; 2) it allows for multiple generations of SOA chemistry without increasing the number of tracked SOA products beyond what can be handled efficiently in a CTM; and 3) the required inputs – the volatility distribution of emissions and volatility operator – can be derived from experimental data. Fitting to a fixed basis set also minimizes an artifact of the two-product fitting procedure in which the two products tend to have volatilities on either end of the concentration range explored in the particular experiment.

We express gas-particle partitioning in terms of a particle fraction (X_p), which is the ratio of the organic particulate mass to the total (gas plus particle) semi-volatile organic mass in the emissions (Shrivastava et al., 2006),

$$X_p = \sum_{i=1}^{n} f_i \left(1 + \frac{C_i^*}{C_{OA}}\right)^{-1} \quad (1)$$

where f_i is the mass fraction in bin i relative to the total (gas plus particle) semi-volatile organic material in the emissions, C_i* is the effective saturation concentration of each volatility bin [0.01, 0.1, 1, 10, 100,

10^3, 10^4, 10^5, 10^6] μg m^{-3}, C_{OA} is the mass concentration of the absorbing organic phase, and n is the number of bins. The set of f_i represents the volatility distribution of the organic mixture, and the total OA mass is X_p times the concentration of semivolatile organics.

In order to employ the basis set approach, one must know the volatility distribution of the emissions (the set of f_i's in eq. 1) for each source. A volatility distribution can be constructed from speciated emissions data by lumping species with similar saturation vapor pressures. In practice, this is not possible because less than 10% of the condensed and semivolatile mass has been identified on a compound-by-compound basis (Schauer et al., 1999b; Schauer et al., 2001; Schauer et al., 2002b). Our approach has been to experimentally measure gas-particle partitioning (X_p and C_{OA}) and then fit the data using eqn (1) to determine the volatility distribution. The amount of each lumped compound is determined by fitting partitioning theory to the experimental data. These lumped compounds then provide an empirical representation of the volatility distribution of the emissions. This approach has been recently applied to emissions data (Shrivastava et al., 2006) and is essentially the same as that commonly used to describe the partitioning of SOA formed in smog chambers (Odum et al., 1996).

We have measured partitioning data for diesel exhaust and wood smoke using multiple dilution samplers. The procedures are described in detail in Lipsky and Robinson (2006). The derivation of X_p and C_{OA} values from the experimental measurements is explained in Shrivastava et al. (2006).

To illustrate the approach, we have fit the wood smoke measurements shown in Figure 1b using partitioning theory. Since the number of experimental measurements significantly exceeds the number of unknowns, the solution is over-constrained and a non-linear fitting algorithm is used to determine the optimum fit by minimizing sum-squared residuals between measured and predicted values of X_p. Additional details on fitting partitioning data with a volatility basis set are provided by Presto and Donahue (2006).

The best fit is indicated by the solid line in Figure 1b. The volatility distribution determined by this fit expressed as fuel-based emission factors is shown in Figure 3 (details of the fitting procedure are described below). The key point is that the fitting distributes the emissions into volatility bins to reproduce the observed partitioning behavior. Furthermore, the distribution shown in Figure 3 represents the volatility distribution of the material measured as POA on a quartz filter at low dilution ratios. Therefore, these lumped compounds represent volatility profiles that can be applied to existing primary organic aerosol emission factors.

Effects of gas-particle partitioning and aging on organic aerosol concentrations

To illustrate the effects of gas-particle partitioning and semivolatile aging of primary emissions on organic aerosol concentrations, the three-dimensional chemical transport model PMCAMx was used to simulate pollutant concentrations across the eastern half of the United States (Robinson et al., 2007). The simulations employ the basis-set approach and provide a qualitative picture of how these conceptual updates change our picture of atmospheric OA. The modeling domain covered a 3492 x 3240 km region in the eastern United States with 36 x 36 km grid resolution with 14 different levels up to 6 km (Gaydos et al., 2006). The calculations were performed for a 16-day period in July 2001, but we only present averages for the last eight simulation days to allow time for model spin-up.

Details on PMCAMx and its basic application are described elsewhere (ENVIRON, 2005; Gaydos et al., 2006). Here we provide a few details on the standard version of PMCAMx and then discuss how the model was modified to account for gas-particle partitioning of primary emissions and SOA production

from low volatility organic vapors.

Like all chemical transport models, PMCAMx assumes that POA is non-volatile and non-reactive; therefore POA concentrations only decrease due to dispersion and deposition. The emission inventories used here are the LADCO BaseE inventory generated using EMS-2003 (LADCO, 2003). This inventory is derived primarily from the U.S. EPA's National Emission Inventory (NEI) 1999 Version 2.0 (EPA, 2002a) with the following changes: on-road transportation sources are from U.S. EPA's MOBILE6 (EPA, 2002c); non-road sources are from U.S. EPA's NONROAD (EPA, 2002b). The temporal profiles for electric power utility point sources are from an analysis of Continuous Emission Monitor data (EPA, 2003; Janssen, 2003). Ammonia emissions are from the Carnegie Mellon University Ammonia Emission Inventory (Goebes et al., 2003; Pinder et al., 2004). Biogenic emissions are from BIOME3 (Wilkinson and Janssen, 2001). A different emission inventory is used for weekdays, Saturdays, and Sundays.

The standard version of PMCAMx accounts for SOA production from the oxidation products of aromatics, paraffins, anthropogenic olefins, cresols and biogenic olefins using the Secondary Organic Aerosol Model (SOAM) II as implemented by Koo et al. (2003). The chemical mechanism is based on the Carbon Bond 4 Mechanism. Equilibrium is assumed between the gas and aerosol phase.

In order to treat gas-particle partitioning of the primary emissions, we modified both the PMCAMx model and the POA emission inventories. For the simulations shown in Figs. 4b, 4c, and 4d, the POA was represented using nine condensable species, for which the model tracks both gas and particle phase concentrations. The effective saturation concentrations (C_i*), molecular weights, and enthalpies of vaporization of these nine species are listed in Table 1, which are based on fits of diesel partitioning data (Robinson et al., 2007). The gridded emissions of each condensable species were calculated by applying this volatility distribution to all of the POA emissions in the BaseE inventory; the existing POA emissions were multiplied by the mass fractions listed in Table 1. The gas-particle partitioning of the nine condensable species was calculated in the same way as for the traditional SOA, using the existing PMCAMx partitioning module (Koo et al., 2003). We assume that the bulk gas and particle phases are in equilibrium and that all condensable organics form an ideal solution. The Clausius-Clapeyron equation is used to account for changes in C_i* with temperature.

The volatility distribution listed in Table 1 was applied to all POA emissions (fossil and modern). The limited available data suggest that emissions from most important sources have similar volatility distributions. For example, diesel exhaust and wood smoke exhibit similar partitioning behavior (Shrivastava et al., 2006). Also, non-specific carbon-number-based gas chromatography indicates that many different sources have similar carbon-number distributions (Hildemann et al., 1991b). Intermediate volatility organic compounds (IVOC), with effective saturation concentrations between 10^3 and 10^6 $\mu g\ m^{-3}$, also contribute a significant fraction of emissions from all high-temperature sources (Schauer et al., 1999b; Schauer et al., 2001; Schauer et al., 2002b).

The effects of explicitly treating gas-particle partitioning and aging of primary emissions are illustrated in Figure 4, which presents maps of ground-level OA concentrations from four simulations. The "traditional" model with nonvolatile POA (Figure 4a) and "traditional SOA" predicts high POA concentrations (> 3 $\mu g\ m^{-3}$) in heavily urbanized areas and substantial urban-to-regional concentration gradients. Allowing primary emissions to partition but not react (Figure 4b) dramatically reduces OA levels throughout the modeling domain, suggesting that the majority of the traditional POA emissions actually evaporate at ambient OA levels. Photochemical aging of low-volatility vapors creates significant regional SOA (Figs. 4c and 4d). If one accounts only for aging of the existing primary

emissions (Figure 4c), predicted OA levels are lower than the traditional model. The most comprehensive simulation (Figure 4d) adds additional emissions of low volatility organics to the model, producing large amounts of regional SOA. The net result is that regional OA levels exceed the traditional model, the urban-rural OA concentration gradient is greatly reduced, and resulting OA field is dominated by SOA, even in urban areas (Robinson et al., 2007). Figure 5 indicates that the spatial distribution of OA in the revised model is in much better agreement with observations than the traditional model.

CONCLUSIONS

The semivolatile character of primary organic aerosol has important implications for measuring and simulating emissions. Dilution sampler measurements have traditionally been made at low levels of dilution, sufficient to reduce exhaust temperature to ambient levels. However, C_{OA} inside the sampler can be orders of magnitude higher than atmospheric levels. Under high C_{OA} conditions, Figure 1 indicates a larger fraction of emissions partitioning to the condensed phase relative to cleaner atmospheric conditions (Shrivastava et al., 2006). Therefore, some emissions are misclassified as primary organic aerosol, causing models and inventories to overestimate the primary emissions' contributions to organic aerosol concentrations. For key sources such as smoking gasoline vehicle or wood combustion, this bias may be as large as a factor of five (Shrivastava et al., 2006). In reality, much of these emissions evaporate as the exhaust is diluted to background levels. Unfortunately, most primary emissions measurements conducted until now have not considered semivolatile partitioning, and so reported data lack key values such as C_{OA}.

Semivolatile vapors may be an important source of secondary organic aerosol. Currently emissions of semivolatile organics are poorly represented in emission inventory and models.

Chemical transport modeling reveals that gas-particle partitioning and photochemical aging dramatically alter the predicted organic aerosol concentrations. The net effect of these two revisions is to replace the current static representation of POA emissions with a far more dynamic picture in which low-volatility organics evaporate, oxidize and recondense over time.

The basis set approach provides a more physically realistic framework for accounting for primary organic aerosol emissions in emission inventories. This framework also enables regional and global chemical transport models to explicitly represent gas-particle partitioning and aging of primary emissions. Implementing this framework requires updating the way we measure emissions. Instead of measuring a fixed organic aerosol emission factor, we need to measure the volatility distribution of the emissions. We have done this by measuring the changes in partitioning of emissions using dilution samplers operating at different levels of dilution. Using this approach we have measured the volatility distribution of emissions from a diesel engine and a woodstove. Clearly data are needed for a larger number of sources.

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Semivolatile Emissions
Gas-Particle Partitioning

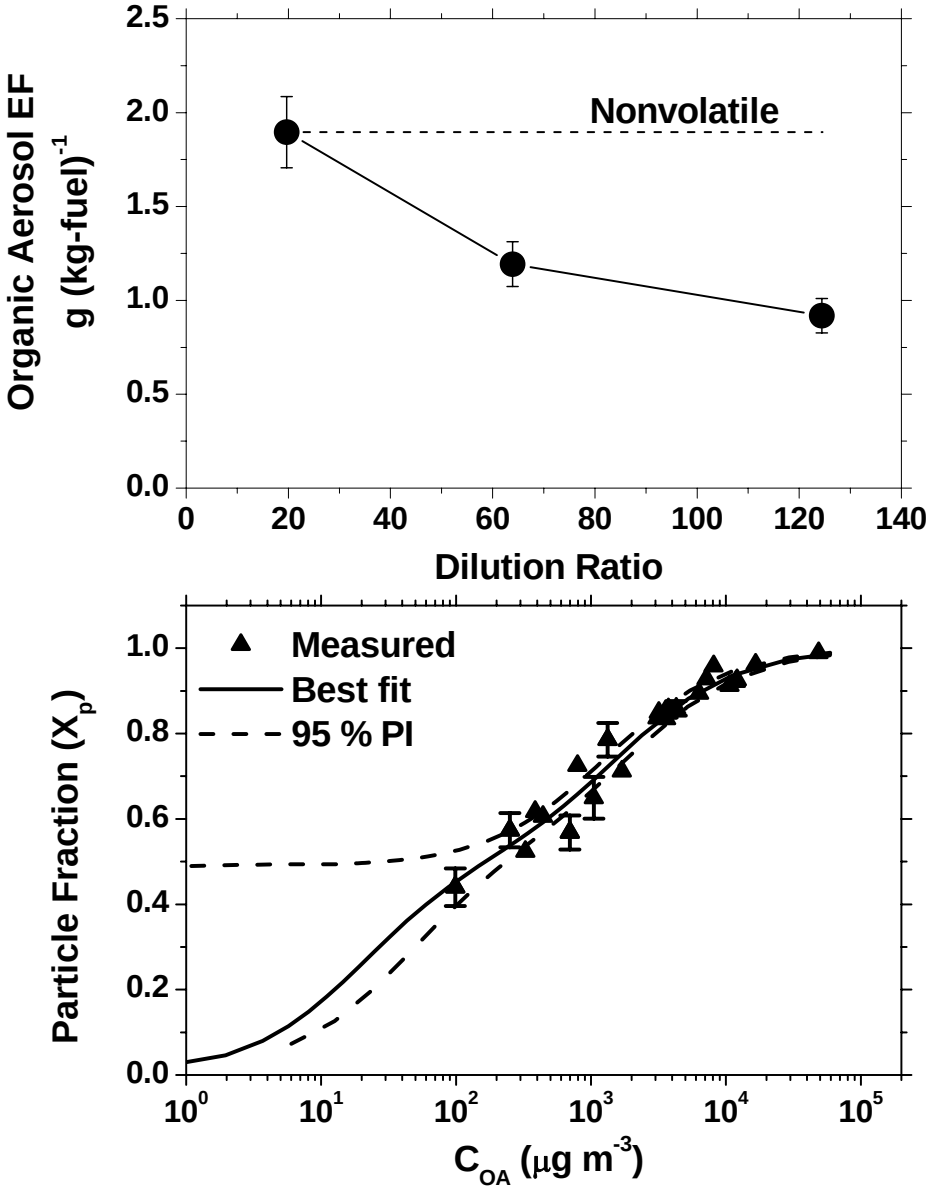

Figure 1. Measured gas-particle partitioning of POA in wood smoke. (a) Fuel-based POA emission factor as a function of dilution (Lipsky and Robinson, 2006). (b) Data from multiple experiments plotted according to partitioning theory (Shrivastava et al., 2006).

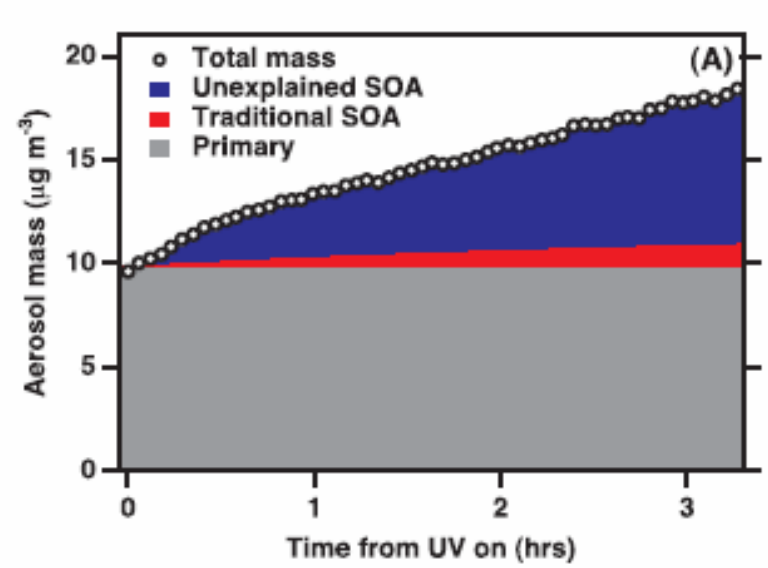

Figure 2. Wall-loss corrected aerosol mass measured during photochemical oxidation of diluted diesel exhaust in a smog chamber (Robinson et al., 2007).

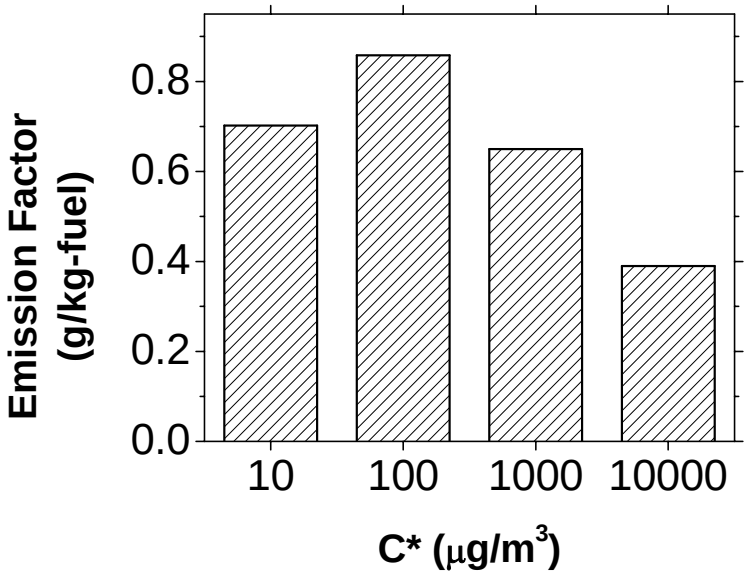

Figure 3. Volatility distribution for wood smoke derived by fitting the emissions data shown in Figure 1b.

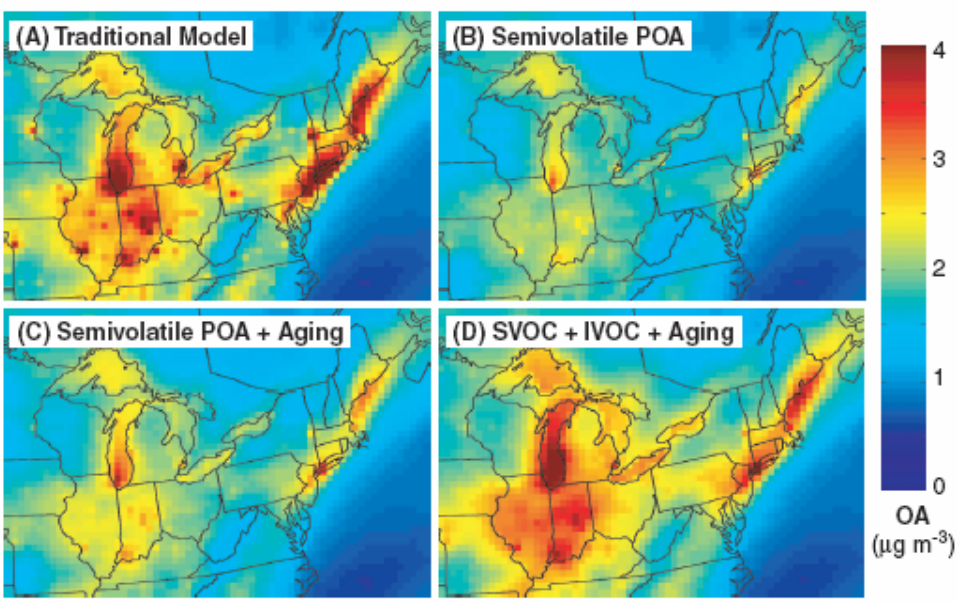

Figure 4. Maps of predicted ground-level organic aerosol (OA) concentrations for four PMCAMx simulations: a "traditional" model with nonvolatile POA emissions (A) and three simulations that account for partitioning of primary emissions - one assuming non-reactive emissions (B) and two considering photochemical aging (C & D).

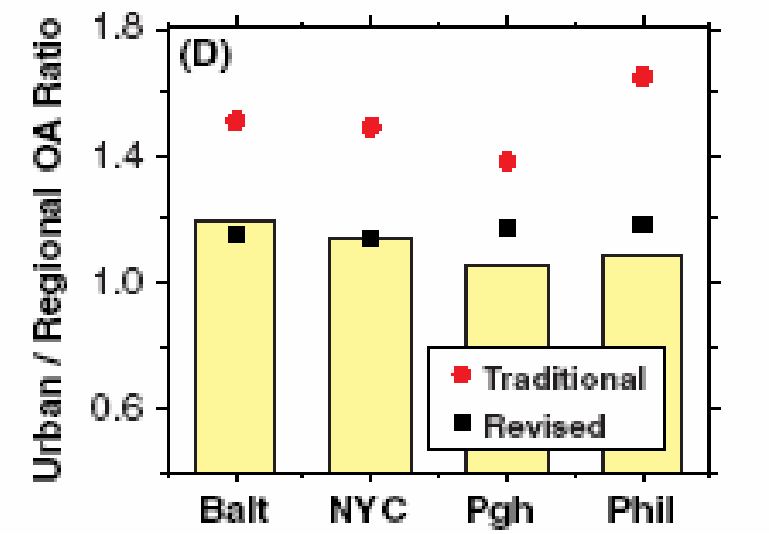

Figure 5. Comparison of average measured urban-to-regional OA ratios indicated by the bars to model predictions for four large cities.

Table 1: Parameters used to treat partitioning of POA emissions

Parameter	Lumped Species								
C* ($\mu g\ m^{-3}$)	0.01	0.1	1	10	100	1000	10000	100000	1000000
f_{SVOC}	0.03	0.06	0.09	0.14	0.18	0.30	0.20	0.00	0.00
$f_{SVOC+IVOC}$	0.03	0.06	0.09	0.14	0.18	0.30	0.40	0.50	0.80
MW ($g\ mol^{-1}$)	250	250	250	250	250	250	250	250	250
ΔH ($kJ\ mol^{-1}$)	112	106	100	94	88	82	76	70	64

- C*: Effective saturation concentration at 300K (basis set)
- f_{SVOC}: mass fractions of the POA emissions in each volatility bins used for the simulations shown in Figs. 4b and 4c
- $f_{SVOC+IVOC}$: mass fractions of POA emissions in each volatility bins used for the simulation shown in Figure 4d
- MW: molecular weight
- ΔH: Enthalpy of vaporization