Modeling Semivolatile Organic Aerosol Mass Emissions from Combustion Systems

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Experimental measurements of gas-particle partitioning
and organic aerosol mass in diluted diesel and wood
combustion exhaust are interpreted using a two-component
absorptive-partitioning model. The model parameters are
determined by fitting the experimental data. The changes in
partitioning with dilution of both wood smoke and diesel
exhaust can be described by two lumped compounds in
roughly equal abundance with effective saturation
concentrations of ~1600 μg m^{-3} and ~20 μg m^{-3}. The
model is used to investigate gas-particle partitioning of
emissions across a wide range of atmospheric conditions.
Under the highly dilute conditions found in the atmosphere,
the partitioning of the emissions is strongly influenced by the
ambient temperature and the background organic aerosol
concentration. The model predicts large changes in
primary organic aerosol mass with varying atmospheric
conditions, indicating that it is not possible to specify a single
value for the organic aerosol emissions. Since atmospheric
conditions vary in both space and time, air quality
models need to treat primary organic aerosol emissions
as semivolatile. Dilution samplers provide useful information
about organic aerosol emissions; however, the measure-
ments can be biased relative to atmospheric conditions and
constraining predictions of absorptive-partitioning models
requires emissions data across the entire range of
atmospherically relevant concentrations.

Introduction

Sources of organic aerosol such as diesel engines and wood
stoves emit semivolatile organic material. As high temper-
ature emissions leave the exhaust system, they rapidly mix
with background air; this mixing cools and dilutes the exhaust
which changes the gas-particle partitioning and the emitted
organic aerosol mass (*1, 2*). Gas-particle partitioning depends
on the concentration and saturation vapor pressure of the
semivolatile species and the concentration and composition
of sorptive material (*3, 4*). Cooling of the exhaust lowers
saturation vapor pressures, promoting gas-to-particle con-
version. Dilution reduces the concentrations of semivolatile
compounds and sorptive material, shifting semivolatile
material from the particle to the gas phase. At high levels of
dilution, the temperature and concentrations of semivolatile
and sorptive material approach background levels; therefore,
background conditions should strongly influence the ultimate
partitioning of the emissions.

These issues make measurement and simulation of
organic aerosol emissions from high-temperature sources a
challenge. Dilution samplers are commonly used to measure
aerosol emissions; they mix exhaust with particle- and
organic-free air in an attempt to simulate atmospheric
conditions (*2*). Although the temperature of the diluted
exhaust is often close to ambient, the concentrations of
semivolatile and sorptive material inside dilution samplers
can be much higher than atmospheric conditions, biasing
measured aerosol emission rates (*1*). An important issue is
how to extrapolate dilution sampler measurements to
atmospheric conditions with varying temperature and dif-
ferent mixtures of emissions and background pollutants. At
present, organic aerosol emissions from sources such as
vehicles and wood combustion are treated as nonvolatile in
air quality models (*5, 6*). This approach implicitly assumes
that emission factors measured using dilution samplers are
representative for the entire range of atmospheric conditions
simulated by the model.

Thermodynamic models are an important tool for un-
derstanding gas-particle partitioning of semivolatile organics.
These models have been widely applied to investigate the
phase partitioning of individual compounds and secondary
organic aerosol (*7−11*). In comparison, the effects of phase
partitioning on the overall organic aerosol mass emitted by
combustion and other high-temperature sources have re-
ceived little attention. Simple condensation theory was found
insufficient to explain the effects of varying dilution ratio
and filter temperature on gas-to-particle partitioning in diesel
exhaust (*12, 13*). A Langmuir adsorption model has also been
used to investigate the effects of dilution ratio and filter
temperature on fine particle mass; however, the analysis was
largely qualitative in nature because of uncertainties in the
kinetic adsorption constants for diesel soot (*12, 13*).

Emissions from combustion systems and other high
temperature sources are a complex mixture of hundreds of
individual compounds which makes it infeasible to predict
overall changes in organic aerosol mass based on the phase
partitioning of individual compounds. An alternative ap-
proach is to model the behavior of the complex mixture using
a reduced set of lumped species. This is routinely done to
interpret smog chamber data of secondary organic aerosol
formation (*7, 14*). The mass fractions and partitioning
coefficients of the lumped compounds are determined by
fitting the partitioning behavior of the overall mixture.

In this paper, we use an absorptive partitioning model to
investigate changes in primary organic aerosol mass in diesel
exhaust and wood smoke that occur as the emissions are
mixed with background air. The model is applied to laboratory
data obtained using dilution samplers (*1*). The objective is
to describe the observed changes in primary organic aerosol
mass with dilution using absorptive partitioning theory and
a set of lumped species, similar to analyses of secondary
organic aerosol (*7*). The model is then used to examine the
effects of varying levels of dilution, background aerosol

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concentrations, and ambient temperature on the phase partitioning of emissions and their contribution to ambient aerosol concentrations.

Theoretical Approach

Absorptive Versus Adsorptive Partitioning. Gas-particle partitioning occurs via absorption into organic solution and adsorption onto soot and mineral surfaces (*3, 4*). 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 (*8, 15*).

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 varies widely by source type and with combustion conditions. For example, wood smoke and exhaust from noncatalyst gasoline vehicles are dominated by organic material (*11, 16, 17*) while emissions from diesel engines are generally dominated by EC (*16, 18*). Although EC adsorbs organic material, other organic compounds can form a solution with the adsorbed organic layer (*19*). 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 (*20*).

Absorptive Partitioning Model. Pankow (*4*) describes absorptive-partitioning theory; here we present this theory in the form used to fit the experimental data reported by Lipsky and Robinson (*1*). To interpret the data, we define a particle fraction (X_p) to characterize the partitioning of the semi-volatile organic emissions. X_p is the ratio of the organic particulate mass in the emissions to the total (gas plus particle) semi-volatile organic mass in the emissions. One simply multiplies the total emission rate of semivolatile organics by X_p to determine the particle phase emissions.

We assume that semi-volatile species partition into an absorbing organic phase. Following the formulation of Odum et al. (*7*), X_p can be written in terms of the partitioning of the individual species,

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

where f_i is the mass fraction of species i relative to the total (gas plus particle) semi-volatile organic material in the emissions, C_i^* is the effective saturation concentration of species i, C_{OA} is the mass concentration of the absorbing organic phase, and n is the number of components in the emissions. Note that C_i^* is the inverse of the partitioning coefficient ($K_{om,i}$) defined by Odum et al. (*7*).

Equation 1 is fit to a set of measured X_p and C_{OA} values assuming a two-component solution ($n = 2$) which requires finding three unknowns: C_1^*, C_2^* and f_1 ($f_2 = 1 - f_1$). The number of experimental measurements is significantly larger than the number of unknowns so the solution is over constrained and a nonlinear fitting algorithm is used to determine the optimum fit by minimizing sum-squared residuals between measured and predicted values of X_p.

Experimental Section

The absorptive-partitioning model is applied to experimental data from Lipsky and Robinson (*1*). They measured fine particle mass emissions from a small, single-cylinder diesel engine and a wood stove at dilution ratios ranging from 20:1 to 510:1. During a given experiment, up to three dilution samplers were operated simultaneously to obtain data at different dilution ratios. The dilution samplers were operated with particle- and organic-free dilution air.
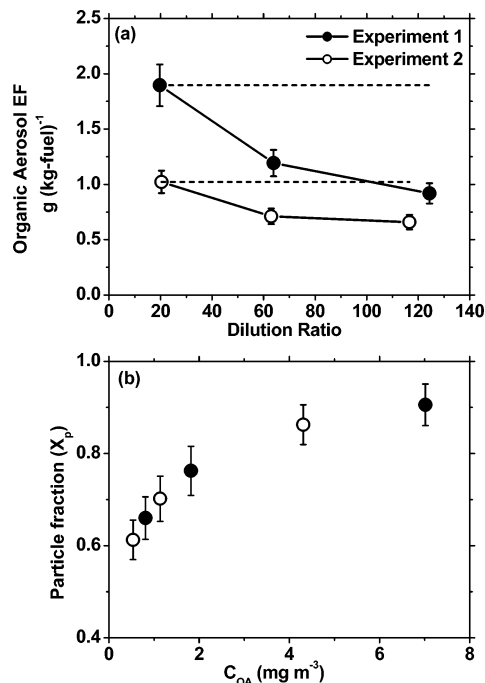
FIGURE 1. (a) Fuel-based organic aerosol mass emission factor as a function of dilution ratio and (b) particle faction (X_p) as a function of organic aerosol concentration (C_{OA}). Data are from two different wood smoke experiments (*1*). If emissions were nonvolatile, there would be no change in the fuel-based emission factor with dilution, as indicated by the dashed horizontal lines in (a). The error bars indicate measurement uncertainty and are based on data from inter-comparison experiments (*29*).

Lipsky and Robinson (*1*) observed large reductions in fine particle organic mass with increasing dilution during wood combustion experiments and when the diesel engine was operated at low load. For example, Figure 1a shows the changes in fuel-based organic aerosol mass emissions as a function of dilution ratio measured during two different wood smoke experiments. The emissions are plotted on a fuel basis in order to account for the changes in concentration due to dilution (*1*). If the particles were inert (nonvolatile and chemically stable), there would be no changes in the fuel-based mass emission factor with dilution. Lipsky and Robinson (*1*) attributed the changes in fuel-based emissions with dilution to changes in gas-particle partitioning. The low-load diesel emissions and wood smoke were predominantly organic carbon with OC/EC ratios greater than 2; therefore, it is appropriate to apply an absorptive partitioning model to interpret the data.

Multiple experiments were run using the wood stove and the diesel engine. Instead of fitting data from individual experiments, the partitioning model is applied to the entire set of low-load diesel data or to the entire set of wood smoke data in order to determine the lumped compounds that best represent the overall partitioning properties of the emissions from each source. Dilution ratio is a parameter commonly used to describe dilution sampler operation, but it cannot be used as the basis for combining data from the different experiments. The problem is the experiment to experiment variability in the emission rates illustrated by the data in Figure 1a. Since the same procedures were used to conduct each experiment, we attribute this variability to the poorly controlled nature of wood combustion. Much less variability was observed in the diesel experiments.

Although emission rates vary from experiment to experiment, data can be combined, on the basis of eq 1, if X_p and C_{OA} are used. This is demonstrated in Figure 1b, which shows
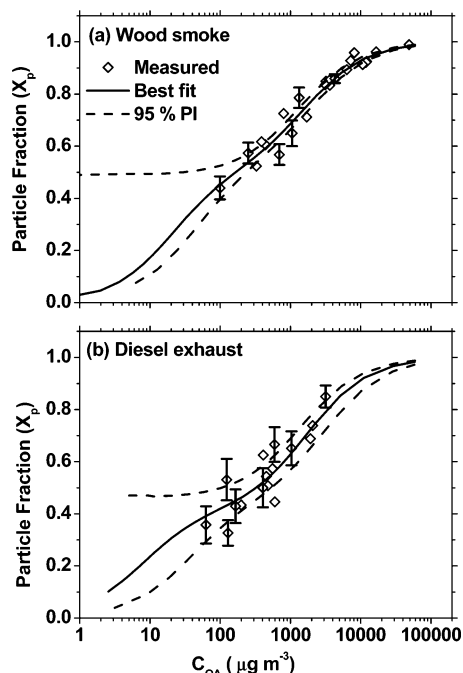
FIGURE 2. Particle fraction (X_p) versus total organic aerosol mass concentration (C_{OA}) for (a) wood smoke and (b) low-load diesel exhaust experiments. The solid lines are the best fit of the two-component absorptive partitioning model; the dashed lines are the 95% prediction intervals (PI). The parameters for the best-fit line are listed in Table 1. Error bars are shown for selected data points to illustrate typical measurement uncertainty; uncertainty of other points is similar in magnitude. Uncertainty of wood smoke data at high values of C_{OA} is of order of the size of the symbols.

that the data from the two experiments in Figure 1a collapse onto a single curve, indicating the partitioning behavior of the emissions from the two experiments is the same. The derivation of C_{OA} and X_p from the experimental data is described in the Supporting Information.

Figure 2 plots X_p as a function of C_{OA} for the entire set of wood combustion (Figure 2a) and diesel (Figure 2b) experiments. As expected from eq 1, X_p monotonically increases toward one with increasing C_{OA}, reflecting changes in partitioning as organic material shifts from the gas to the particle phase at higher organic aerosol concentrations.

Figure 2 indicates that the experiment-to-experiment variability of X_p at a given C_{OA} can be greater than the estimated measurement uncertainty. We attribute this variability to experiment-to-experiment differences in the composition of the emissions. By combining data from different experiments together we are assuming that only the emission rate and not the volatility distribution of the emissions changes between experiments. However, the scatter in Figure 2 suggests that this assumption is not strictly valid.

A final issue is the temperature of the diluted exhaust. Under the conditions of these experiments, the temperature of the diluted exhaust was constant (27 °C) at all dilution ratios (1). Therefore, the trends shown in Figures 1 and 2 are due to changes in concentrations of sorbent (C_{OA}) and semivolatile material inside the dilution sampler, not the temperature of the diluted exhaust.

Results

This section describes the results from fitting the absorptive-partitioning model to the low-load diesel and wood smoke data. The best-fit lines using a two-component model are plotted in Figure 2; these lines follow the observed data as a function of C_{OA}. The R^2 values of the fits are 0.68 for the diesel exhaust data and 0.94 for the wood smoke data. The
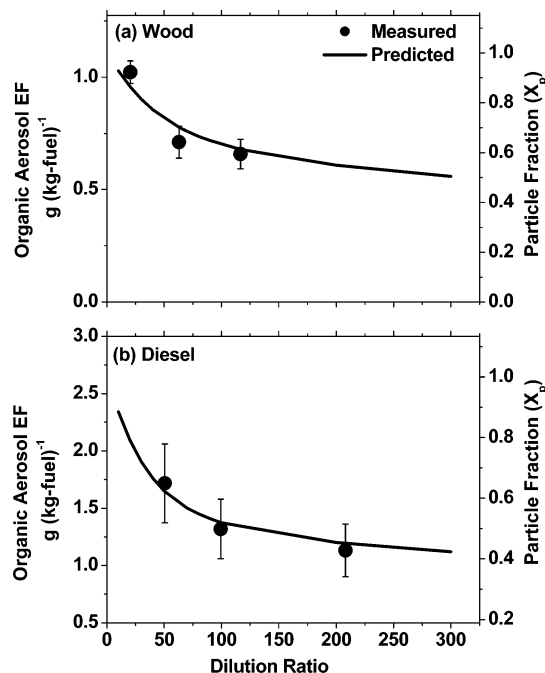

FIGURE 3. Measured and calculated fuel-based organic aerosol emission factor as a function of dilution ratio for individual (a) wood combustion and (b) low-load diesel experiments. Vertical bars indicate experimental uncertainty.

TABLE 1. Effective Saturation Concentrations (C^*) and Compound Mass Fractions (f_i) of Lumped Compounds Determined from Fits of Experimental Data

source	C^* ($\mu g\ m^{-3}$)	mass fractions (f_i)
diesel exhaust	1724	0.58
	8	0.42
wood smoke	1646	0.49
	20	0.51

much higher R^2 value for the wood smoke fit is due to the wood smoke dataset containing a number of measurements at high C_{OA} with X_p values close to 1. Removing these points from the dataset reduces the R^2 value of the wood smoke fit to 0.74, but does not change the abundances and saturation concentrations of the lumped compounds.

We also examined fitting the data with one- and three-component models. A one-component model cannot reproduce the curvature of the data shown in Figure 2 and, therefore, yields much lower R^2 values. Within the range of the experimental data, a three-component model yields essentially the same best-fit line and R^2 value as the two-component model. As one extrapolates beyond the data to lower C_{OA} values, the predictions of the three- and two-component model diverge, but in this region neither fit is based on experimental data so there is no basis for using the more complicated model. Therefore, a two-component model adequately describes the experimental data and the R^2 values of the fits are limited by the scatter in the data.

Figure 3 shows that the model reproduces the changes in fuel-based organic aerosol mass emissions with dilution measured during individual diesel and wood smoke experiments. The calculations are based on the measured emission rate of total semivolatile organics from the specific experiment and the global fits listed in Table 1. Additional details on these calculations are provided in the Supporting Information. The good agreement is not unexpected given that the data shown in Figure 3 are part of the larger dataset used to determine the lumped compounds. Figure 3 only presents

data from a single experiment because of the previously discussed experiment-to-experiment variability in the emission rate; the overall quality of the fits with respect to the entire dataset is shown in Figure 2.

Table 1 lists the lumped compounds determined by fitting the two-component model to the diesel exhaust and to the wood smoke data. The overall changes in partitioning of the emissions from each source is described by a low volatility compound with an effective saturation concentration (C^*) around 20 μg m^{-3} and a more volatile compound with a C^* around 1600 μg m^{-3}, in roughly equal abundances. Given the differences in the composition of wood smoke and diesel exhaust (*11*, *18*), one might consider the similarity in the two sets of lumped parameters to be somewhat surprising. However, these parameters represent the average partitioning properties of the hundreds of semivolatile organic compounds in diesel exhaust or wood smoke. The similarity in the two sets of lumped parameters indicates that, in contrast to the differences in chemical composition, the overall volatility distribution of emissions from these two sources are similar.

The prediction intervals for the two fits are plotted in Figure 2. These intervals are relatively tight within the range of the data but diverge as one extrapolates beyond the data to very low values of C_{OA}. Therefore, the two-compound fits accurately represent the changes in partitioning across the range of experimental conditions. These conditions correspond to the higher pollutant levels commonly encountered near sources such as roadways, highly polluted urban environments, inside dilution samplers, and concentrated aerosol streams used for toxicity studies. Typical atmospheric levels of C_{OA} are between 1 and 50 μg m^{-3}. The model predictions are poorly constrained at the lower end of this range.

The prediction intervals diverge at low values of C_{OA} because of uncertainty in the C^* of the less-volatile lumped compound. The values listed in Table 1 are for the best fit (maximum R^2 value); however, varying the C^* of the less-volatile compound between 0 and 50 μg m^{-3} negligibly changes the quality of the fit for either dataset. This large uncertainty exists because the experiments only diluted the exhaust enough to achieve C_{OA} values of ~50 μg m^{-3}. Equation 1 indicates that, under these conditions, species with a C^* less than 50 μg m^{-3} are predominantly in the particle phase across the entire set of experiments. Therefore, the data provide little information on the changes of partitioning of this component of the emissions. To better resolve changes in partitioning of less-volatile species, experimental data are needed at lower C_{OA} (higher levels of dilution). Although measurements at low values of C_{OA} are experimentally challenging, they are essential for constraining the predictions of the model under the highly dilute conditions commonly encountered in the atmosphere.

Effects of Varying Atmospheric Conditions on Partitioning. In this section, the two-component model is used to examine the effects of background aerosol and ambient temperature on the phase partitioning of primary organic aerosol emissions. The goal is to investigate partitioning across a wide range of conditions in order to better understand measurements made with dilution samplers, assumptions commonly made by air quality models, and conditions inside exposure chambers operated using concentrated aerosol streams.

The analysis considers a hypothetical plume formed from emissions mixed with polluted background air at different temperatures. The volatility distribution of the emissions is defined by the wood smoke fits listed in Table 1. Background organic aerosol concentrations are included in the model as an additional nonvolatile species that forms an ideal solution with the emissions. Therefore, the background aerosol
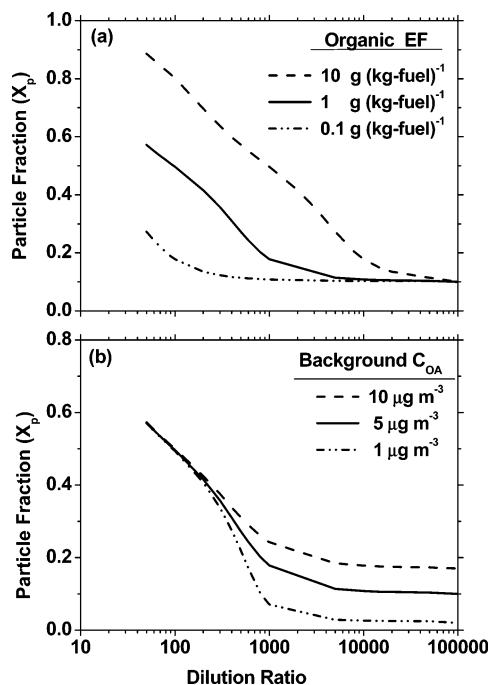

FIGURE 4. Predicted particle fraction (X_p) as a function of dilution ratio for (a) three different gas plus particle phase semivolatile organic emission rates assuming a background organic aerosol concentration of 5 μg m^{-3} and (b) three different background organic aerosol concentrations assuming a medium emitter, 1 g kg-fuel^{-1}. Calculations are based on the wood smoke fits listed in Table 1.

contributes to the mass of the absorbing organic phase, C_{OA} in eq 1. This analysis only considers partitioning at ambient temperatures and not the large changes in partitioning that occur immediately downstream of the exhaust system as the emissions are rapidly cooled. Ambient temperatures are reached at relatively low levels of dilution (20:1 to 100:1, depending on initial temperature of the exhaust).

Figure 4 considers the effects of dilution on emissions from the perspective of an individual source, plotting the predicted particle fraction (X_p) as a function of dilution ratio. Figure 4 only shows predictions at dilution ratios greater than 50:1 at which point the emissions are assumed to have reached 27 °C, the temperature of the experimental data. Additional details on the calculations can be found in the Supporting Information.

Figure 4a shows model predictions for three different fuel-based emission factors of total (gas plus particle) semivolatile organics, 0.1, 1, and 10 g kg-fuel^{-1}, assuming a constant background organic aerosol concentration of 5 μg m^{-3}. The low end of this range corresponds to a properly operating catalyst-equipped gasoline powered car (*17*), while the high end corresponds to a smoking gasoline vehicle or wood combustion (*11*, *21*). Figure 4b shows model predictions for a source emitting at 1 g kg-fuel^{-1} and three different background organic aerosol concentrations: 1, 5, and 10 μg m^{-3}.

At low levels of dilution, Figure 4 shows that X_p decreases as the exhaust concentrations in the plume are reduced by mixing with background air. At high levels of dilution, the particle fraction of the emissions reaches a minimum value that is independent of dilution ratio. This occurs when concentrations inside the plume are dominated by the background. The partitioning under these well-mixed conditions is defined by eq 1 with C_{OA} set at the background level. Figure 4a shows that the amount of dilution required to reach this ultimate partitioning depends strongly on the emission rate of semivolatile material. Little dilution is required for low emitting sources, while substantial dilution is required
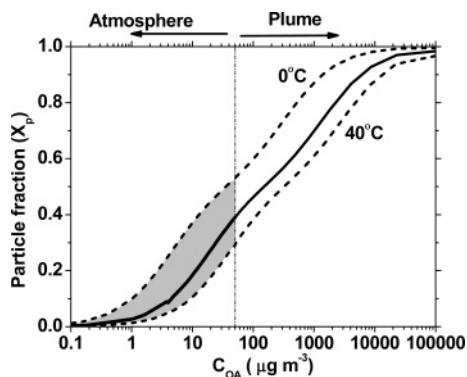
FIGURE 5. Predicted particle fraction (X_p) as a function of organic aerosol concentration (C_{OA}) for three different temperatures. The predictions are based on the wood smoke fits listed in Table 1. The solid line is calculated directly using the values listed in the table (note that the experimental data were measured at 27 °C). The dashed line indicates model predictions at 0 and 40 °C, as described in the text. The vertical line at 50 μg m^{-3} provides a rough separation between plume-like and well-mixed atmospheric conditions; the gray-area indicates partitioning across a range of atmospheric conditions from a heavily polluted city to the remote atmosphere in both cold and hot weather.

for sources with high emission rates. This underscores the problems with using dilution ratio as the core parameter to evaluate partitioning.

At very low dilution ratios, Figure 4b shows that the background aerosol does not influence partitioning because the emissions dominate concentrations inside the plume. As the level of dilution increases, the model predictions for different background levels diverge as the background begins to contribute appreciably to C_{OA} in the plume. Under well-mixed conditions, a larger fraction of the emissions partition to the particle phase when background levels are high (higher background C_{OA}).

Although Figure 4 indicates a strong dilution-ratio dependence on the partitioning at low dilution ratios, atmospheric mixing eventually disperses the emissions such that the pollutant concentrations are dominated by the background. For many sources, these well-mixed conditions are achieved within seconds of the emissions leaving the exhaust system (22). Therefore, except in the near-source region where concentrations of emissions are elevated, the partitioning under well-mixed, background-dominated conditions defines the contribution of the source to ambient particulate mass. Figure 4 demonstrates that this ultimate partitioning does not depend on emission rate, but on the background concentration. Another key parameter is the volatility distribution of the emissions.

A more useful way to examine the changes in partitioning is to plot X_p as a function of C_{OA} as is done Figure 5. In this framework, all of the predictions presented in Figure 4 collapse onto a single curve (the heavy, solid line in Figure 5). The upper-right-hand portion of this curve corresponds to high-concentration, plume-like conditions. Mixing with background air shifts the emissions toward the left along the curve as partitioning changes from the particle to the gas phase. This continues until the plume is well mixed with the background at which point the ultimate partitioning is defined by the background C_{OA}. The shape of the curve is determined by the volatility distribution of the emissions.

Ambient temperature also influences partitioning. The temperature dependence of C^* can be described using the Clausius–Clapeyron equation,

$$C_i^*(T) = C_i^*(300K) \exp\left[\frac{\Delta H_v}{R}\left(\frac{1}{300K} - \frac{1}{T}\right)\right]\frac{300}{T} \qquad (2)$$

where C_i^*(300 K) is the effective saturation concentration at the reference temperature (300 K, the temperature at which the experimental measurements were made), T is temperature in Kelvins, ΔH_v is the enthalpy of vaporization, and R is the ideal gas constant. An ΔH_v value of 42 kJ mol^{-1} is used to estimate the temperature dependence of both lumped compounds. This value is based on fits of smog chamber data of complex aerosol mixtures using a lumped component partitioning model (23, 24).

Model predictions of partitioning as a function of C_{OA} at 0 and 40 °C are shown by the dashed lines in Figure 5. Increasing the ambient temperature reduces the fraction of the emissions in the particle phase.

In the atmosphere, background aerosol concentrations and temperature vary in space and time. Since these parameters strongly influence partitioning, one cannot define primary organic aerosol emissions using a single value. The gray-shaded region shown in Figure 5 indicates the model predictions across a range of atmospheric conditions from a heavily polluted city to the remote atmosphere in both the cold and warm weather. Large changes in partitioning are predicted across this range of conditions; for example, the model predicts that eight times more emitted semivolatile organic mass exists in the particle phase in the atmosphere if background levels of C_{OA} are increased from 1 to 10 μg m^{-3} at 27 °C.

The magnitude of the changes in partitioning with varying atmospheric conditions depends on the volatility distribution of the emissions; specifically, the fraction of the emissions that exists in both phases at ambient conditions (material with a C^* between 0.1 and 100 μg m^{-3}). Given the previously discussed uncertainty in C^* of the less-volatile fraction of the exhaust, this means that the size of the gray-shaded region in Figure 5 is not well constrained. The region is so large because the fits of the experimental data assign roughly half of the emissions to the less-volatile, lumped compound that has a C^* of roughly 20 μg m^{-3}. This lumped species undergoes significant changes in partitioning with varying atmospheric conditions. For example, under clean conditions ($C_{OA} = 1$ μg m^{-3}), eq 1 indicates that only 5% of a compound with a C^* of 20 μg m^{-3} partitions to the particle phase, while 71% of it partitions to the particle phase in polluted conditions ($C_{OA} = 50$ μg m^{-3}).

We expect that the actual changes in partitioning at C_{OA} levels less than 50 μg m^{-3} will be smaller than those shown in Figure 5. Published composition data indicates that some fraction of the emissions have a C* less than 20 μg m^{-3} (11, 18); for example, levoglucosan, an important constituent of wood smoke, is essentially nonvolatile. However, the two component model lumps this material into the less-volatile compound that has a C^* of 20 μg m^{-3} because of the lack of data at low values of C_{OA}. This, in turn, will cause the model to overpredict the changes in partitioning. Unfortunately, only a small fraction of the emissions have been identified on a compound-by-compound basis (11, 18), so the available composition data cannot be used to quantify the contribution of low volatility material to the overall emissions. Additional data at lower C_{OA} would likely split the less-volatile components listed in Table 1 into two or more lumped compounds with C^* values less than 50 μg m^{-3}. Describing this larger dataset will likely require adding a third, low volatility component ($C^* < 1$ μg m^{-3}) to the model.

Discussion

Primary organic aerosol emissions from sources such as diesel engines and wood stoves are semivolatile. The partitioning of these emissions varies significantly with dilution and the ultimate contribution of the emissions to ambient organic aerosol loadings depends strongly on background organic

aerosol concentrations and ambient temperature. These findings have important implications for measuring emissions using dilution samplers, investigating the health effects of aerosols, and simulating emissions using air quality models.

Dilution sampling is a widely accepted method for measuring primary organic aerosol emissions. The results of this paper raise a number of important issues regarding the operation of dilution samplers. First, dilution samplers are typically operated at relatively low dilution ratios (20:1 to 200:1) with particle- and organics-free dilution air. This level of dilution generally reduces the temperature of the exhaust to atmospheric levels; however, the concentrations of the diluted exhaust inside the dilution sampler can be very different than typical atmospheric conditions. For high emitting sources, such as a smoking vehicle or biomass combustion, C_{OA} inside the sampler may be much greater than typical atmospheric levels, which can cause a systematic overestimate (positive bias) of the organic aerosol emissions. For low emitting sources, such as natural gas combustion, C_{OA} inside the sampler can be lower than typical atmospheric levels, which may bias measurements low relative to atmospheric conditions; note that eq 1 indicates that X_p approaches zero in the limit of infinite dilution with particle-free air. To avoid these sorts of biases, dilution sampler measurements should be made at aerosol concentrations and temperatures that are as close as possible to atmospheric concentrations or conditions of interest. In order for users to correctly interpret emissions data, the temperature and concentrations of the diluted exhaust should be routinely reported.

A second issue is that dilution samplers are typically operated at a single dilution ratio which corresponds to a single point in Figure 4 or 5, while the partitioning of the emissions varies with temperature and background pollution levels. It is not clear how existing dilution sampler data can be used to account for this variability. This paper illustrates how dilution sampler measurements can be interpreted using an absorptive-partitioning model in order to predict the contribution of emissions across a range of atmospheric conditions. Implementing this approach requires measuring C_{OA} and X_p of the emissions at varying levels of dilution. Measurements at low concentrations are particularly important for constraining the predictions of the model at the highly dilute conditions common in the atmosphere.

Changes in partitioning of primary organic aerosol emissions may also be an important consideration for health-effect studies. For example, recent research has focused on the health effects near roadways where higher pollutant concentrations may affect partitioning compared to more dilute conditions. Changes in partitioning may also influence toxicity studies performed with concentrated aerosol streams, such as emissions sampled from an individual source. Note that changes in partitioning alter both the mass and composition of the aerosol.

Air quality models can be used to account for the effects of spatial and temporal variation of atmospheric conditions on partitioning of emissions, but most models currently treat primary organic aerosol emissions as nonvolatile (5, 6). In addition, emission inventories are based on emission factors measured using dilution samplers operated at low dilution ratios. Figures 4 and 5 suggest that these assumptions may introduce significant errors in predicted concentrations of primary organic aerosol. Existing chemical-transport models, such as PMCAMx and CMAQ, that are commonly used to simulate regional air quality already contain absorptive-partitioning modules implemented to calculate partitioning of secondary organic aerosols. Therefore, in principle, these models can be easily adapted to treat primary organic aerosol as semivolatile. However, a major obstacle is emission inventories. To treat primary organic aerosol as semivolatile, inventories must be updated with both the total emission

rate of semivolatile organics and the volatility distribution of the emissions.

The central hypothesis advanced by this paper is that changes in gas-particle partitioning of semi-volatile organics can substantially alter the contribution of emissions to ambient organic aerosol concentrations. This paper presents evidence supporting this hypothesis based on experimental data from two sources, a single-cylinder diesel engine and a wood stove. However, ambient pollution is a mix of emissions from millions of individual sources; therefore, the significance of the effects illustrated in Figures 4 and 5 on the overall ambient organic aerosol budget are uncertain.

The literature provides evidence that supports our hypothesis. It is well established that many combustion systems emit semivolatile organic compounds (11, 17, 18). However, only a small fraction of the emissions have been identified on a compound-by-compound basis (11, 18), so the available composition data cannot be used to quantify the effects of partitioning on overall organic aerosol mass emissions. Carbon-number based chromatography has achieved relatively high mass recovery (25); these data indicate that organic emissions for many different sources are distributed relatively uniformly over a wide range of volatilities. Such a distribution will cause partitioning to vary continuously with atmospheric conditions. Zhang and Wexler (26) report that changes in gas-particle partitioning strongly influence the evolution of the size distribution of aerosol downwind of a highway. Similarly, data from Grieshop et al. (27) and Kuhn et al. (28) suggest that atmospherically relevant changes in temperature may strongly influence the gas-particle partitioning of motor vehicle emissions.

The key uncertainty is the relative contribution of semi-volatile species to the overall organic emissions. If their contribution is large, as it is for the two sources considered here, the issues illustrated in Figures 4 and 5 are significant. Reducing this uncertainty requires emissions data from a variety of sources measured over the entire range of atmospheric conditions.

Supporting Information Available

Derivation of X_p and C_{OA} from the experimental data and prediction of emission rates as a function of dilution. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

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